(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
03 October 2019 (03.10.2019)

WIPO | PCT

(10) International Publication Number
WO 2019/185578 A1

(51) International Patent Classification:
H01L 51/46 (2006.01)

(21) International Application Number:
PCT/EP2019/057499

(22) International Filing Date:
26 March 2019 (26.03.2019)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
18164638.1 28 March 2018 (28.03.2018) EP

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

(54) Title: ORGANIC SEMICONDUCTING COMPOUNDS

(57) Abstract: The invention relates to novel organic semiconducting compounds containing apolycyclic unit, to methods for their preparation and educts or intermediates used therein, to compositions, polymer blends and formulations containing them, to the use of the compounds, compositions and polymer blends as organic semiconductors in, or for the preparation of, organic electronic (OE) devices, especially organic photovoltaic (OPV) devices, perovskite-based solar cell (PSC) devices, organic photodetectors (OPD), organic field effect transistors (OFET) and organic light emitting diodes (OLED), and to OE, OPV, PSC, OPD,OFET and OLED devices comprising these compounds, compositions or polymer blends.

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Organic Semiconducting Compounds

Technical Field

The invention relates to novel organic semiconducting compounds containing a polycyclic unit, to methods for their preparation and educts or intermediates used therein, to compositions, polymer blends and formulations containing them, to the use of the compounds, compositions and polymer blends as organic semiconductors in, or for the preparation of, organic electronic (OE) devices, especially organic photovoltaic (OPV) devices, perovskite-based solar cell (PSC) devices, organic photodetectors (OPD), organic field effect transistors (OFET) and organic light emitting diodes (OLED), and to OE, OPV, PSC, OPD, OFET and OLED devices comprising these compounds, compositions or polymer blends.

Background

In recent years, there has been development of organic semiconducting (OSC) materials in order to produce more versatile, lower cost electronic devices. Such materials find application in a wide range of devices or apparatus, including organic field effect transistors (OFETs), organic light emitting diodes (OLEDs), organic photodetectors (OPDs), organic photovoltaic (OPV) cells, perovskite-based solar cell (PSC) devices, sensors, memory elements and logic circuits to name just a few. The organic semiconducting materials are typically present in the electronic device in the form of a thin layer, for example of between 50 and 300 nm thickness.

One particular area of importance is organic photovoltaics (OPV). Conjugated polymers have found use in OPVs as they allow devices to be manufactured by solution-processing techniques such as spin casting, dip coating or ink jet printing. Solution processing can be carried out cheaper and on a larger scale compared to the evaporative techniques used to make inorganic thin film devices. Currently, polymer based photovoltaic devices are achieving efficiencies above 10%.

Another particular area of importance is OFETs. The performance of OFET devices is principally based upon the charge carrier mobility of the semiconducting material and the current on/off ratio, so the ideal semiconductor should have a low conductivity in the off state, combined with high charge carrier mobility (> 1 x 10^{-3} cm^2 V^{-1} s^{-1}). In addition, it is important that the semiconducting material is stable to oxidation *i.e.* it has a high ionisation potential, as oxidation leads to reduced device performance. Further requirements for the semiconducting material are good processibility, especially for large-scale production of thin layers and desired patterns, and high stability, film uniformity and integrity of the organic semiconductor layer.

Organic photodetectors (OPDs) are a further particular area of importance, for which conjugated light-absorbing polymers offer the hope of allowing efficient devices to be produced by solution-processing technologies, such as spin casting, dip coating or ink jet printing, to name a few only.

The photosensitive layer in an OPV or OPD device is usually composed of at least two materials, a p-type semiconductor, which is typically a conjugated polymer, an oligomer or a defined molecular unit, and an n-type semiconductor, which is typically a fullerene or substituted fullerene, graphene, a metal oxide, or quantum dots.

However, the OSC materials disclosed in prior art for use in OE devices have several drawbacks. For example, the fullerenes or fullerene derivatives which have hitherto been used as electron acceptors in OPV or OPD devices are often difficult to synthesize or purify, and/or do not absorb light strongly in the visible and near IR spectrum >700nm, do not allow easy modification of theiri HOMO and LUMO energy levels, or do often not form a favourable morphology and/or miscibility with the donor material.

Therefore, there is still a need for OSC materials for use in OE devices like OPVs, PSCs, OPDs and OFETs, which have advantageous properties, in particular good processability, a high solubility in organic solvents, good structural organization and film-forming properties. In addition, the OSC

materials should be easy to synthesize, especially by methods suitable for mass production. For use in OPV cells, the OSC materials should especially have a low bandgap, which enables improved light harvesting by the photoactive layer and can lead to higher cell efficiencies, high stability and long lifetime. For use in OFETs the OSC materials should especially have high charge-carrier mobility, high on/off ratio in transistor devices, high oxidative stability and long lifetime.

It was an aim of the present invention to provide new OSC compounds, especially n-type OSCs, which can overcome the drawbacks of the OSCs from prior art, and which provide one or more of the above-mentioned advantageous properties, especially easy synthesis by methods suitable for mass production, good processability, high stability, long lifetime in OE devices, good solubility in organic solvents, high charge carrier mobility, and a low bandgap. Another aim of the invention was to extend the pool of OSC materials and n-type OSCs available to the expert. Other aims of the present invention are immediately evident to the expert from the following detailed description.

The inventors of the present invention have found that one or more of the above aims can be achieved by providing compounds as disclosed and claimed hereinafter.

These compounds represent a novel, alternative type of n-type organic semiconductors, which do not include a fullerene moiety, and which are hereinafter also referred to as "non-fullerene acceptor(s)" or "NFA(s)".

These NFA compounds comprise a polycyclic core as shown in formula I, and further comprise one or two terminal groups which are electron withdrawing relative to the central polycyclic core, and do optionally further comprise one or more aromatic or heteroaromatic spacer groups which are located between the polycyclic core and the terminal groups and which can be electron withdrawing or electron donating relative to the polycyclic core.

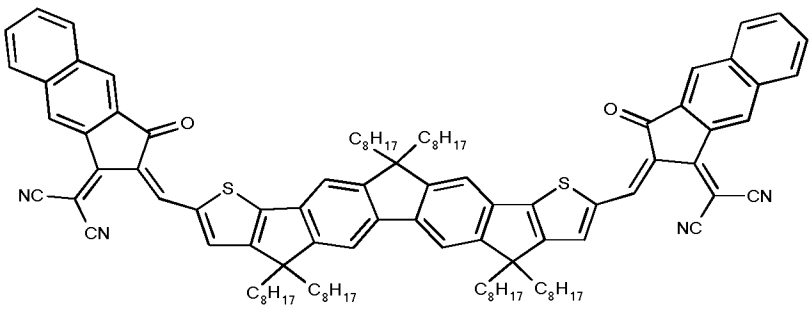
As a result, these compounds have an acceptor-donor-acceptor (A-D-A) or

A-D structure, wherein the polycyclic core acts as donor and the terminal groups, optionally together with the spacer groups, act as acceptor.

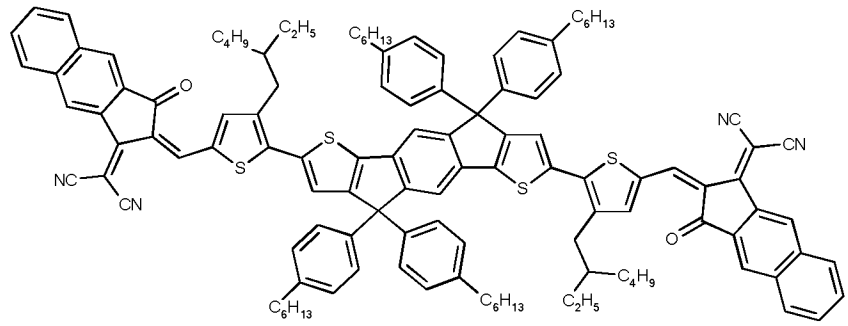
It has been found that compounds comprising the aforementioned structural features can be used as n-type OSCs which show advantageous properties as described above.

In prior aret A-D-A type NFA compounds have been reported comprising an IDT core that is flanked by two terminal 2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile withdrawing groups, as disclosed for example in Y. Lin et al., *Adv. Mater.*, **2015**, *27*, 1170; H. Lin et al., *Adv. Mater.*, **2015**, *27*, 7299; N. Qiu et al., *Adv. Mater.*, **2017**, *29*, 1604964; CN104557968 A and CN105315298 A.

H. Feng et al., Chem. Mater. 2017, 29, 7908 disclose A-D-A type NFA compounds with a fluorenedicylco-pentadithiophene core and two terminal acceptor groups, and their use as acceptor for polymer solar cells



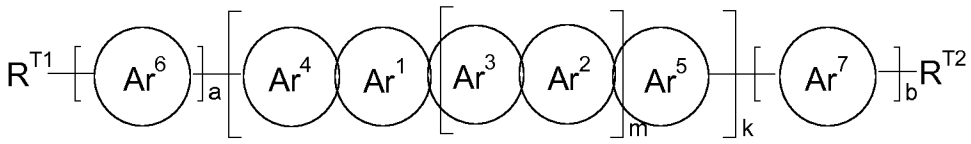
R. Li et al., J. Mater. Chem. 2017, 5, 23926 disclose A-D-A type NFA with an indacenodithiophene core and two terminal acceptor groups, and their use as acceptor for polymer solar cells.



However, compounds as disclosed and claimed hereinafter have hitherto not been disclosed in prior art for use as n-type semiconductors.

Summary

The invention relates to a compound of formula I



I

wherein the individual radicals, independently of each other and on each occurrence identically or differently, have the following meanings

Ar^1, Ar^2 a group selected from the following formulae

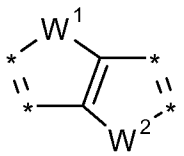


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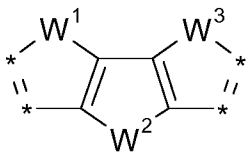


A2

Ar^3 a group selected from the following formulae and their mirror images



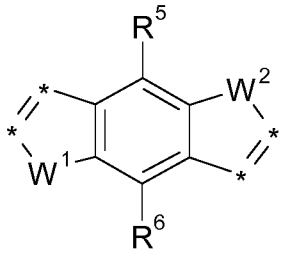
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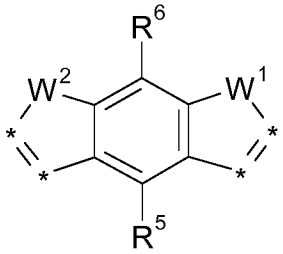
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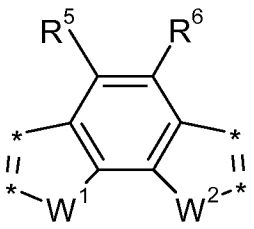
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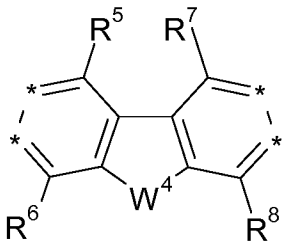
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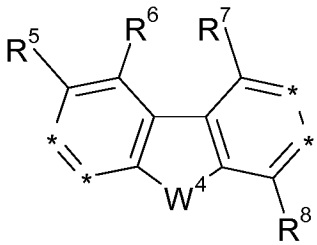
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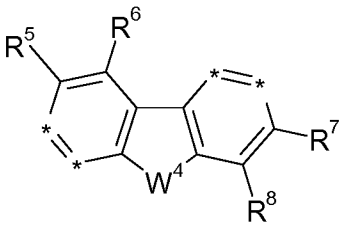
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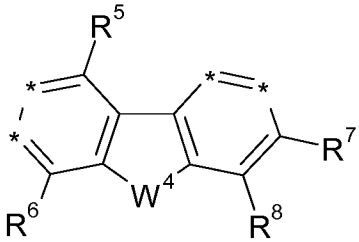
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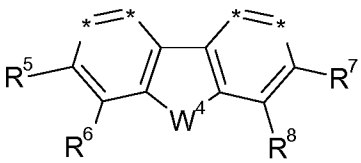
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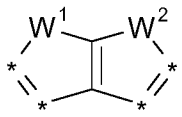
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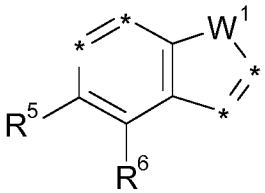
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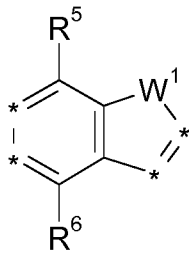
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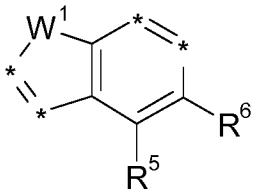
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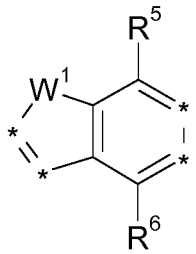
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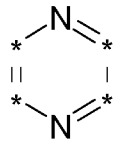
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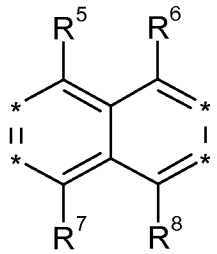
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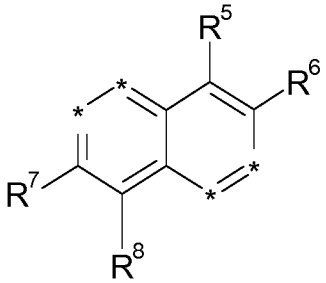
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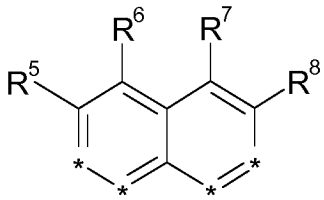
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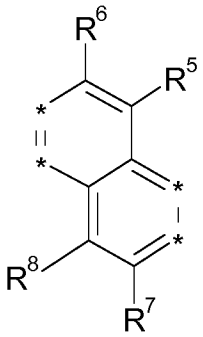
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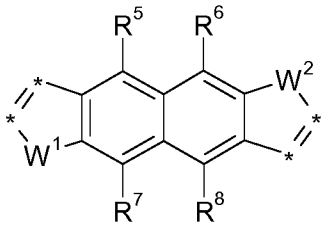
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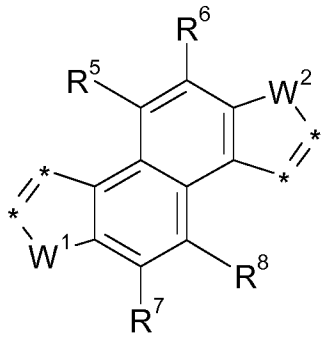
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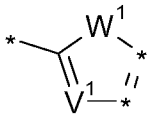


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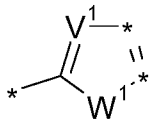


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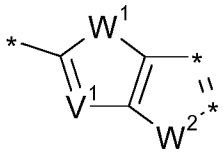
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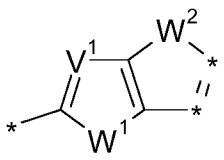
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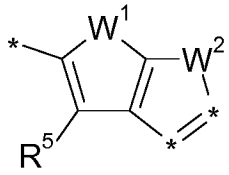
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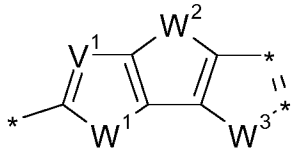
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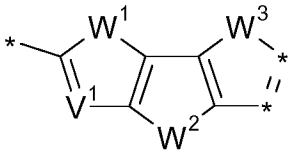
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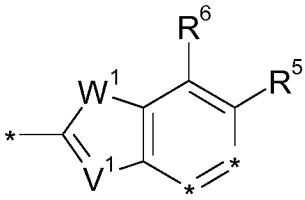
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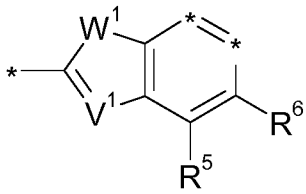
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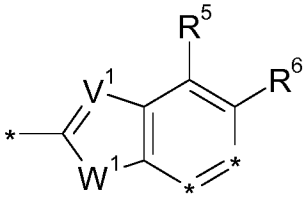
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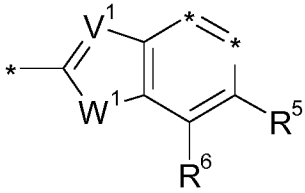
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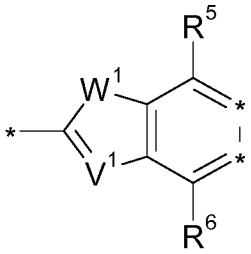
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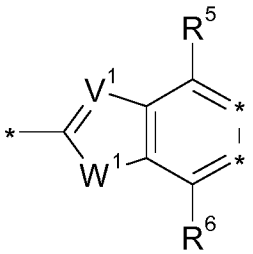
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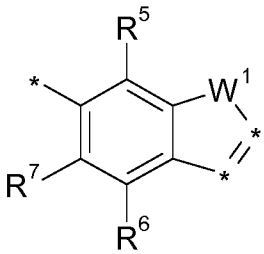
A4k



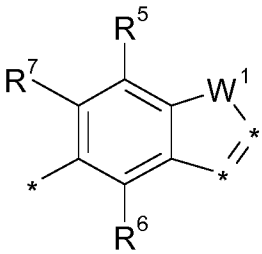
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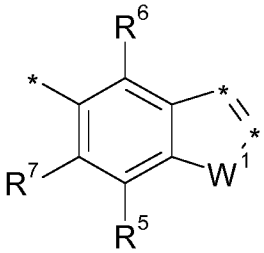
A4m



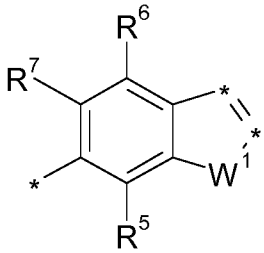
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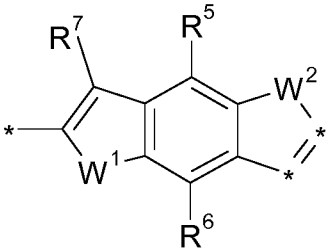
A4o



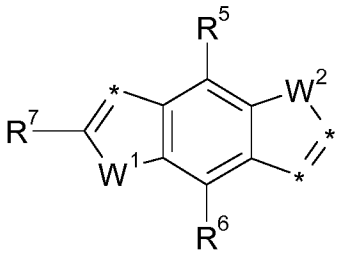
A4p



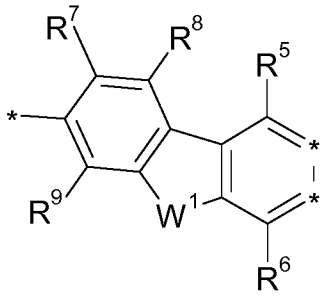
A4q



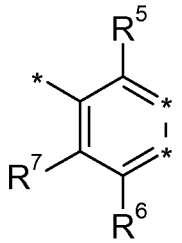
A4r



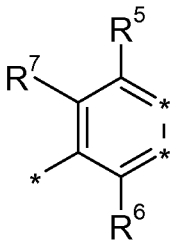
A4s



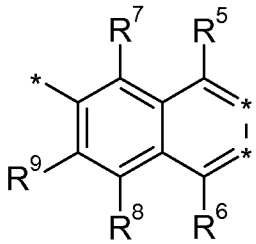
A4t



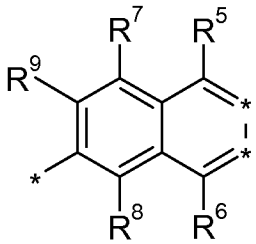
A4u



A4v

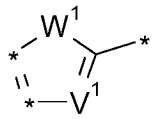


A4w

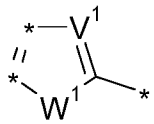


A4x

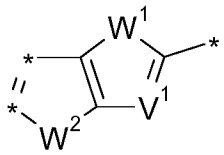
Ar^5 a group selected from the following formulae and their mirror images



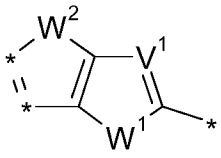
A5a



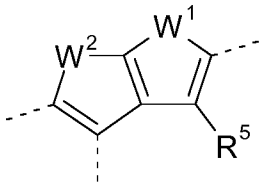
A5b



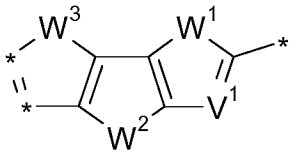
A5c



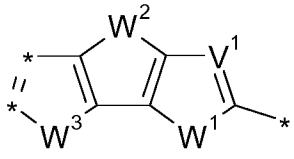
A5d



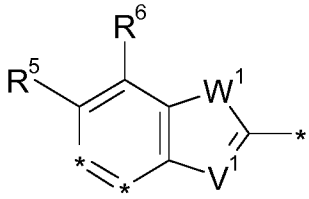
A5e



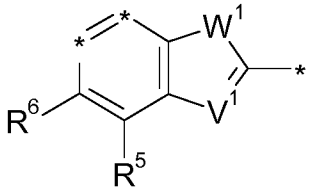
A5f



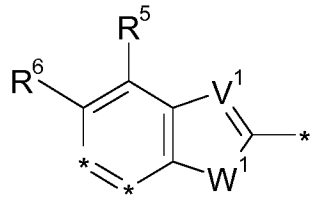
A5g



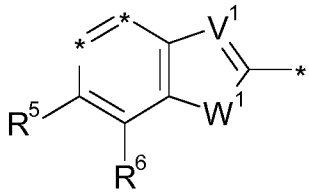
A5h



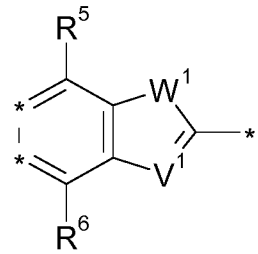
A5i



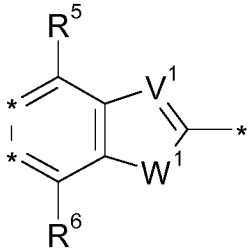
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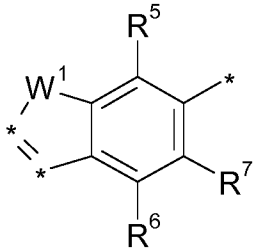
A5k



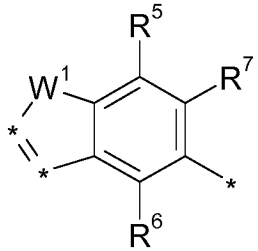
A5l



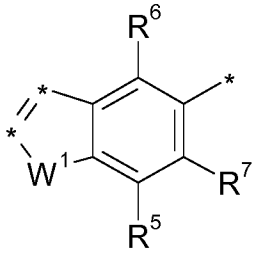
A5m



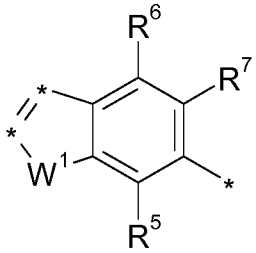
A5n



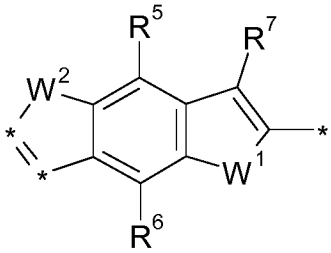
A5o



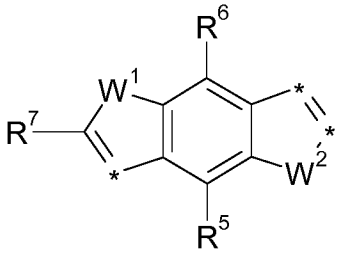
A5p



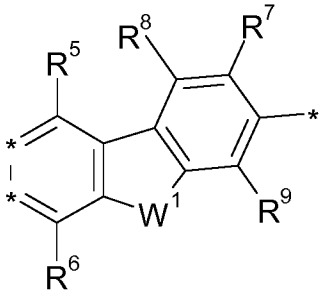
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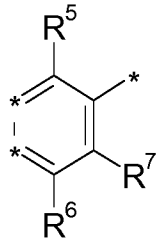
A5r



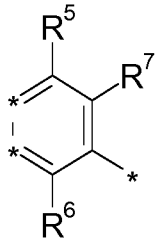
A5s

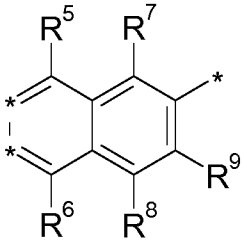


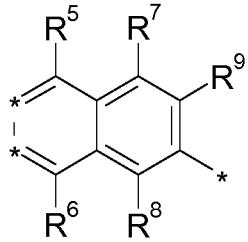
A5t



A5u



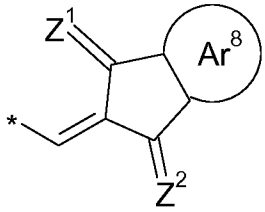




A5v	A5w	A5x
$Ar^{6,7}$	arylene or heteroarylene that has from 5 to 20 ring atoms, is mono- or polycyclic, optionally contains fused rings, and is unsubstituted or substituted by one or more identical or different groups R^1 or L^S, or $CY^1=CY^2$ or -C≡C-,	
U^1, U^2	CR^1R^2, SiR^1R^2, GeR^1R^2, $C=CR^1R^2$, NR^1 or C=O, preferably CR^1R^2,	
V^1	CR^3 or N,	
W^1, W^2, W^3	S, O, Se or C=O, preferably S,	
W^4	S, O, Se, C=O or NR^1,	
R^{1-9}	H, F, Cl, CN, or straight-chain, branched or cyclic alkyl with 1 to 30, preferably 1 to 20, C atoms, in which one or more CH_2 groups are optionally replaced by -O-, -S-, -C(=O)-, -C(=S)-, -C(=O)-O-, -O-C(=O)-, $-NR^0-$, $-SiR^0R^{00}-$, $-CF_2-$, $-CR^0=CR^{00}-$, $-CY^1=CY^2-$ or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, and in which one or more H atoms are optionally replaced by F, Cl, Br, I or CN, and in which one or more CH_2 or CH_3 groups are optionally replaced by a cationic or anionic group, or aryl, heteroaryl, arylalkyl, heteroarylalkyl, aryloxy or heteroaryloxy, wherein each of the aforementioned cyclic groups has 5 to 20 ring atoms, is mono- or polycyclic, does optionally contain fused rings, and is unsubstituted or substituted by one or more identical or different groups L^S,	
	and the pair of R^1 and R^2, together with the C, Si or Ge atom to which they are attached, may also form a spiro group with 5 to 20 ring atoms which is mono- or polycyclic, does optionally contain fused rings, and is unsubstituted or substituted by one or more identical or different groups L^S,	

R^{T1}, R^{T2}	an electron withdrawing group,
Y^1, Y^2	H, F, Cl or CN,
L^S	F, Cl, $-NO_2$, -CN, -NC, -NCO, -NCS, -OCN, -SCN, R^0, OR^0, SR^0, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)-OR^0$, $-O-C(=O)-R^0$, $-NH_2$, $-NHR^0$, $-NR^0R^{00}$, $-C(=O)NHR^0$, $-C(=O)NR^0R^{00}$, $-SO_3R^0$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-SF_5$, or optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 30, preferably 1 to 20 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, preferably F, -CN, R^0, $-OR^0$, $-SR^0$, $-C(=O)-R^0$, $-C(=O)-OR^0$, $-O-C(=O)-R^0$, $-O-C(=O)-OR^0$, $-C(=O)-NHR^0$, or $-C(=O)-NR^0R^{00}$,
R^0, R^{00}	H or straight-chain or branched alkyl with 1 to 20, preferably 1 to 12, C atoms that is optionally fluorinated,
X^0	halogen, preferably F or Cl,
a, b	0 or an integer from 1 to 10, preferably 0, 1, 2, 3, 4 or 5, very preferably 0, 1, 2 or 3,
k	an integer from 1 to 10, preferably 1, 2, 3, 4, 5, 6 or 7, very preferably 1, 2 or 3, most preferably 1,
m	0 or an integer from 1 to 10, preferably 0, 1, 2, 3, 4, 5, 6 or 7, very preferably 0, 1, 2 or 3,

wherein at least one of R^{T1} and R^{T2} is an electron withdrawing group of formula TG



TG

Ar^8		bi- or polycyclic arylene or heteroarylene having from 8 to 20 ring atoms which is optionally substituted with one or more groups L,
L		F, Cl, $-NO_2$, -CN, -NC, -NCO, -NCS, -OCN, -SCN, R^0, OR^0, SR^0, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)-OR^0$, $-O-C(=O)-R^0$, $-NH_2$, $-NHR^0$, $-NR^0R^{00}$, $-C(=O)NHR^0$, $-C(=O)NR^0R^{00}$, $-SO_3R^0$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-SF_5$, preferably F, -CN, R^0, $-OR^0$, $-SR^0$, $-C(=O)-R^0$, $-C(=O)-OR^0$, $-O-C(=O)-R^0$, $-O-C(=O)-OR^0$, $-C(=O)-NHR^0$, $-C(=O)-NR^0R^{00}$,
Z^1, Z^2		O or $C(CN)_2$ or C(CN)(C(=O)R, preferably one of Z^1 and Z^2 is O and the other is $C(CN)_2$,

and wherein at least one group Ar^3 denotes thieno[3,2-b]thiophene and/or at least one of the groups Ar^4 and Ar^5 denotes thieno[3,2-b]thiophene that is optionally substituted with R^3.

The invention further relates to novel synthesis methods for preparing compounds of formula I, and novel intermediates used therein.

The invention further relates to the use of compounds of formula I as semiconductor, preferably as electron acceptor or n-type semiconductor, preferably in a semiconducting material, an electronic or optoelectronic device, or a component of an electronic or optoelectronic device.

The invention further relates to the use of compounds of formula I as dyes or pigments.

The invention further relates to a composition comprising one or more

compounds of formula I, and further comprising one or more compounds having one or more of a semiconducting, hole or electron transport, hole or electron blocking, insulating, binding, electrically conducting, photoconducting, photoactive or light emitting property.

The invention further relates to a composition comprising one or more compounds of formula I, and further comprising a binder, preferably an electrically inert binder, very preferably an electrically inert polymeric binder.

The invention further relates to a composition comprising a compound of formula I, and further comprising one or more electron donors or p-type semiconductors, preferably selected from conjugated polymers.

The invention further relates to a composition comprising one or more n-type semiconductors, at least one of which is a compound of formula I, and further comprising one or more p-type semiconductors.

The invention further relates to a composition comprising one or more n-type semiconductors, at least one of which is a compound of formula I, and at least one other of which is a fullerene or fullerene derivative, and further comprising one or more p-type semiconductors, preferably selected from conjugated polymers.

The invention further relates to a bulk heterojunction (BHJ) formed from a composition comprising a compound of formula I as electron acceptor or n-type semiconductor, and one or more compounds which are electron donor or p-type semiconductors, and are preferably selected from conjugated polymers.

The invention further relates to the use of a compound of formula I or a composition as described above and below, as semiconducting, charge transporting, electrically conducting, photoconducting, photoactive or light emitting material.

The invention further relates to the use of a compound of formula I or a

composition as described above and below, in an electronic or optoelectronic device, or in a component of such a device or in an assembly comprising such a device.

The invention further relates to a semiconducting, charge transporting, electrically conducting, photoconducting, photoactive or light emitting material, comprising a compound of formula I or a composition as described above and below.

The invention further relates to an electronic or optoelectronic device, or a component thereof, or an assembly comprising it, which comprises a compound of formula I or a composition as described above and below.

The invention further relates to an electronic or optoelectronic device, or a component thereof, or an assembly comprising it, which comprises a semiconducting, charge transporting, electrically conducting, photoconducting or light emitting material as described above and below.

The invention further relates to a formulation comprising one or more compounds of formula I, or comprising a composition or semiconducting material as described above and below, and further comprising one or more solvents, preferably selected from organic solvents.

The invention further relates to the use of a formulation as described above and below for the preparation of an electronic or optoelectronic device or a component thereof.

The invention further relates to an electronic or optoelectronic device or a component thereof, which is obtained through the use of a formulation as described above and below.

The electronic or optoelectronic device includes, without limitation, organic field effect transistors (OFET), organic thin film transistors (OTFT), organic light emitting diodes (OLED), organic light emitting transistors (OLET), organic light emitting electrochemical cell (OLEC), organic photovoltaic devices (OPV), organic photodetectors (OPD), organic solar cells, dye-

sensitized solar cells (DSSC), organic photoelectrochemical cells (OPEC), perovskite-based solar cells (PSC), laser diodes, Schottky diodes, photoconductors, photodetectors, thermoelectric devices.

Preferred devices are OFETs, OTFTs, OPVs, PSCs, OPDs and OLEDs, in particular OPDs and BHJ OPVs or inverted BHJ OPVs.

The component of the electronic or optoelectronic device includes, without limitation, charge injection layers, charge transport layers, interlayers, planarizing layers, antistatic films, polymer electrolyte membranes (PEM), conducting substrates and conducting patterns.

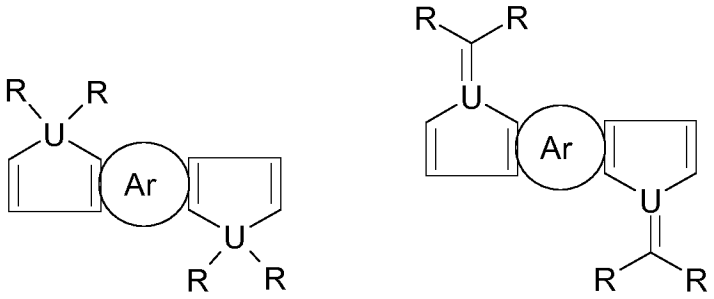
The assembly comprising an electronic or optoelectronic device includes, without limitation, integrated circuits (IC), radio frequency identification (RFID) tags, security markings, security devices, flat panel displays, LC windows, backlights of flat panel displays, electrophotographic devices, electrophotographic recording devices, organic memory devices, sensor devices, biosensors and biochips.

In addition the compounds of formula I and compositions as described above and below can be used as dichroitic dyes, especially in smart windows such as LC windows, as electrode materials in batteries, or in components or devices for detecting and discriminating DNA sequences.

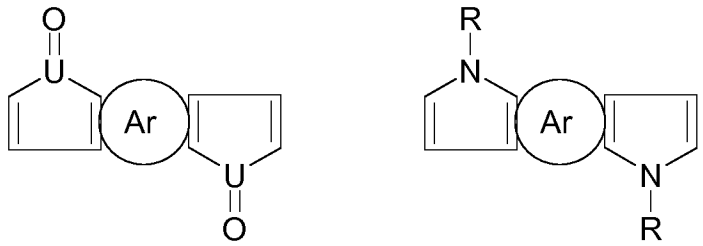
Terms and Definitions

Unless stated otherwise, in the units, polymers and compounds according to the present invention the electron withdrawing groups R^{T1} and R^{T2} are understood to be electron withdrawing relative to the polycyclic core.

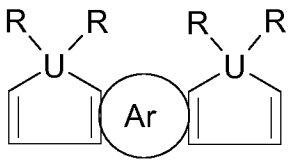
As used herein, the terms "indaceno group" and "indaceno-type group" will be understood to mean a group comprising two cyclopentadiene rings, or heterocyclic, vinylidene or ketone derivatives thereof, that are fused to a central aromatic or heteroaromatic aromatic ring Ar, and which can have cis- or trans-configuration, as exemplarily shown below



(trans-configuration)



(trans-configuration)



(cis-configuration)

wherein U is e.g. C, Si or Ge and R is a carbyl or hydrocarbyl group.

Unless stated otherwise, in a polymer according to the present invention the units of formula I have electron acceptor property ("acceptor units").

As used herein, the terms “donor” or "donating" and “acceptor” or "accepting" will be understood to mean an electron donor or electron acceptor, respectively. “Electron donor” will be understood to mean a chemical entity that donates electrons to another compound or another group of atoms of a compound. “Electron acceptor” will be understood to mean a chemical entity that accepts electrons transferred to it from another compound or another group of atoms of a compound. See also International Union of Pure and Applied Chemistry, Compendium of Chemical Technology, Gold Book, Version 2.3.2, 19. August 2012, pages 477 and 480.

As used herein, the term "donor unit" will be understood to mean a unit, preferably a conjugated arylene or heteroarylene unit, which has an electron donating or electron pushing property towards a neighboured conjugated unit. The term "acceptor unit" will be understood to mean a unit, preferably a conjugated arylene or heteroarylene unit, which has an electron accepting or electron withdrawing property towards a neighboured conjugated unit. The term "spacer unit" will be understood to mean a unit which can be conjugated or non-conjugated and is located between the polycyclic donor core and the terminal group R^{T1} or R^{T2}.

As used herein, the term "n-type" or "n-type semiconductor" will be understood to mean an extrinsic semiconductor in which the conduction electron density is in excess of the mobile hole density, and the term "p-type" or "p-type semiconductor" will be understood to mean an extrinsic semiconductor in which mobile hole density is in excess of the conduction electron density (see also, J. Thewlis, *Concise Dictionary of Physics*, Pergamon Press, Oxford, 1973).

As used herein, the term "conjugated" will be understood to mean a compound (for example a polymer) that contains mainly C atoms with sp^2-hybridization (or optionally also sp-hybridization), and wherein these C atoms may also be replaced by hetero atoms. In the simplest case this is for example a compound with alternating C-C single and double (or triple) bonds, but is also inclusive of compounds with aromatic units like for example 1,4-phenylene. The term "mainly" in this connection will be understood to mean that a compound with naturally (spontaneously) occurring defects, or with defects included by design, which may lead to interruption of the conjugation, is still regarded as a conjugated compound.

As used herein, the term "small molecule" will be understood to mean a monomeric compound which typically does not contain a reactive group by which it can be reacted to form a polymer, and which is designated to be used in monomeric form. In contrast thereto, the term "monomer" unless stated otherwise will be understood to mean a monomeric compound that

carries one or more reactive functional groups by which it can be reacted to form a polymer.

As used herein, the term "polymer" will be understood to mean a molecule of high relative molecular mass, the structure of which essentially comprises multiple repetitions of units derived, actually or conceptually, from molecules of low relative molecular mass (*Pure Appl. Chem.*, **1996**, *68*, 2291). The term "oligomer" will be understood to mean a molecule of intermediate relative molecular mass, the structure of which essentially comprises a small plurality of units derived, actually or conceptually, from molecules of lower relative molecular mass (*Pure Appl. Chem.*, **1996**, *68*, 2291). In a preferred meaning as used herein present invention a polymer will be understood to mean a compound having > 1, i.e. at least 2 repeat units, preferably ≥ 5, very preferably ≥10, repeat units, and an oligomer will be understood to mean a compound with > 1 and < 10, preferably < 5, repeat units.

Further, as used herein, the term "polymer" will be understood to mean a molecule that encompasses a backbone (also referred to as "main chain") of one or more distinct types of repeat units (the smallest constitutional unit of the molecule) and is inclusive of the commonly known terms “oligomer”, “copolymer”, “homopolymer”, “random polymer” and the like. Further, it will be understood that the term polymer is inclusive of, in addition to the polymer itself, residues from initiators, catalysts and other elements attendant to the synthesis of such a polymer, where such residues are understood as not being covalently incorporated thereto. Further, such residues and other elements, while normally removed during post polymerization purification processes, are typically mixed or co-mingled with the polymer such that they generally remain with the polymer when it is transferred between vessels or between solvents or dispersion media.

As used herein, in a formula showing a polymer or a repeat unit an asterisk (*) will be understood to mean a chemical linkage, usually a single bond, to an adjacent unit or to a terminal group in the polymer backbone. In a ring, like for example a benzene or thiophene ring, an asterisk (*) will be understood to mean a C atom that is fused to an adjacent ring.

As used herein, in a formula showing a ring, a polymer or a repeat unit a dashed line (-----) will be understood to mean a single bond.

As used herein, the terms "repeat unit", "repeating unit" and "monomeric unit" are used interchangeably and will be understood to mean the constitutional repeating unit (CRU), which is the smallest constitutional unit the repetition of which constitutes a regular macromolecule, a regular oligomer molecule, a regular block or a regular chain (*Pure Appl. Chem.*, **1996**, *68*, 2291). As further used herein, the term "unit" will be understood to mean a structural unit which can be a repeating unit on its own, or can together with other units form a constitutional repeating unit.

As used herein, a "terminal group" will be understood to mean a group that terminates a polymer backbone. The expression "in terminal position in the backbone" will be understood to mean a divalent unit or repeat unit that is linked at one side to such a terminal group and at the other side to another repeat unit. Such terminal groups include endcap groups, or reactive groups that are attached to a monomer forming the polymer backbone which did not participate in the polymerization reaction, like for example a group having the meaning of R^{31} or R^{32} as defined below.

As used herein, the term "endcap group" will be understood to mean a group that is attached to, or replacing, a terminal group of the polymer backbone. The endcap group can be introduced into the polymer by an endcapping process. Endcapping can be carried out for example by reacting the terminal groups of the polymer backbone with a monofunctional compound ("endcapper") like for example an alkyl- or arylhalide, an alkyl- or arylstannane or an alkyl- or arylboronate. The endcapper can be added for example after the polymerization reaction. Alternatively the endcapper can be added in situ to the reaction mixture before or during the polymerization reaction. In situ addition of an endcapper can also be used to terminate the polymerization reaction and thus control the molecular weight of the forming polymer. Typical endcap groups are for example H, phenyl and lower alkyl.

As used herein, unless stated otherwise the molecular weight is given as the number average molecular weight M_n or weight average molecular weight M_W, which is determined by gel permeation chromatography (GPC) against polystyrene standards in eluent solvents such as tetrahydrofuran, trichloromethane (TCM, chloroform), chlorobenzene or 1,2,4-trichlorobenzene. Unless stated otherwise, chlorobenzene is used as solvent. The degree of polymerization, also referred to as total number of repeat units, n, will be understood to mean the number average degree of polymerization given as $n = M_n/M_U$, wherein M_n is the number average molecular weight and M_U is the molecular weight of the single repeat unit, see J. M. G. Cowie, *Polymers: Chemistry & Physics of Modern Materials*, Blackie, Glasgow, 1991.

As used herein, the term "carbyl group" will be understood to mean any monovalent or multivalent organic moiety which comprises at least one carbon atom either without any non-carbon atoms (like for example -C≡C-), or optionally combined with at least one non-carbon atom such as B, N, O, S, P, Si, Se, As, Te or Ge (for example carbonyl etc.).

As used herein, the term "hydrocarbyl group" will be understood to mean a carbyl group that does additionally contain one or more H atoms and optionally contains one or more hetero atoms like for example B, N, O, S, P, Si, Se, As, Te or Ge.

As used herein, the term “hetero atom” will be understood to mean an atom in an organic compound that is not a H- or C-atom, and preferably will be understood to mean B, N, O, S, P, Si, Se, Sn, As, Te or Ge.

A carbyl or hydrocarbyl group comprising a chain of 3 or more C atoms may be straight-chain, branched and/or cyclic, and may include spiro-connected and/or fused rings.

Preferred carbyl and hydrocarbyl groups include alkyl, alkoxy, thioalkyl, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy and alkoxycarbonyloxy, each of which is optionally substituted and has up to 40, preferably up to 25, very preferably up to 18 C atoms, furthermore optionally substituted

aryl or aryloxy having 6 to 40, preferably 6 to 25 C atoms, furthermore alkylaryloxy, arylcarbonyl, aryloxycarbonyl, arylcarbonyloxy and aryloxycarbonyloxy, each of which is optionally substituted and has 1 to 40, preferably 6 to 40 C atoms, wherein each of these groups optionally contains one or more hetero atoms, preferably selected from B, N, O, S, P, Si, Se, As, Te and Ge.

Further preferred carbyl and hydrocarbyl group include for example: a C_1-C_{40} alkyl group, a C_1-C_{40} fluoroalkyl group, a C_1-C_{40} alkoxy or oxaalkyl group, a C_2-C_{40} alkenyl group, a C_2-C_{40} alkynyl group, a C_3-C_{40} allyl group, a C_4-C_{40} alkyldienyl group, a C_4-C_{40} polyenyl group, a C_2-C_{40} ketone group, a C_2-C_{40} ester group, a C_6-C_{18} aryl group, a C_6-C_{40} alkylaryl group, a C_6-C_{40} arylalkyl group, a C_4-C_{40} cycloalkyl group, a C_4-C_{40} cycloalkenyl group, and the like. Preferred among the foregoing groups are a C_1-C_{20} alkyl group, a C_1-C_{20} fluoroalkyl group, a C_2-C_{20} alkenyl group, a C_2 –C_{20} alkynyl group, a C_3-C_{20} allyl group, a C_4-C_{20} alkyldienyl group, a C_2-C_{20} ketone group, a C_2-C_{20} ester group, a C_6-C_{12} aryl group, and a C_4-C_{20} polyenyl group, respectively.

Also included are combinations of groups having carbon atoms and groups having hetero atoms, like e.g. an alkynyl group, preferably ethynyl, that is substituted with a silyl group, preferably a trialkylsilyl group.

The carbyl or hydrocarbyl group may be an acyclic group or a cyclic group. Where the carbyl or hydrocarbyl group is an acyclic group, it may be straight-chain or branched. Where the carbyl or hydrocarbyl group is a cyclic group, it may be a non-aromatic carbocyclic or heterocyclic group, or an aryl or heteroaryl group.

A non-aromatic carbocyclic group as referred to above and below is saturated or unsaturated and preferably has 4 to 30 ring C atoms. A non-aromatic heterocyclic group as referred to above and below preferably has 4 to 30 ring C atoms, wherein one or more of the C ring atoms are each optionally replaced by a hetero atom, preferably selected from N, O, P, S, Si and Se, or by a -S(O)- or -$S(O)_2$- group. The non-aromatic carbo- and heterocyclic groups are mono- or polycyclic, may also contain fused rings,

preferably contain 1, 2, 3 or 4 fused or unfused rings, and are optionally substituted with one or more groups L^S.

L^S is selected from F, Cl, -CN, $-NO_2$, -NC, -NCO, -NCS, -OCN, -SCN, $-R^0$, $-OR^0$, $-SR^0$, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)-OR^0$, $-O-C(=O)-R^0$, $-NH_2$, $-NHR^0$, $-NR^0R^{00}$, $-C(=O)NHR^0$, $-C(=O)NR^0R^{00}$, $-SO_3R^0$, $-SO_2R^0$, -OH, $-CF_3$, $-SF_5$, or optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 30, preferably 1 to 20 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, wherein X^0 is halogen, preferably F or Cl, and R^0, R^{00} each independently denote H or straight-chain or branched alkyl with 1 to 20, preferably 1 to 12 C atoms that is optionally fluorinated.

Preferably L^S is selected from F, -CN, R^0, $-OR^0$, $-SR^0$, $-C(=O)-R^0$, $-C(=O)-OR^0$, $-O-C(=O)-R^0$, $-O-C(=O)-OR^0$, $-C(=O)-NHR^0$ and $-C(=O)-NR^0R^{00}$.

Further preferably L^S is selected from F or alkyl, alkoxy, oxaalkyl, thioalkyl, fluoroalkyl, fluoroalkoxy, alkylcarbonyl, alkoxycarbonyl, with 1 to 16 C atoms, or alkenyl or alkynyl with 2 to 16 C atoms.

Preferred non-aromatic carbocyclic or heterocyclic groups are tetrahydrofuran, indane, pyran, pyrrolidine, piperidine, cyclopentane, cyclohexane, cycloheptane, cyclopentanone, cyclohexanone, dihydro-furan-2-one, tetrahydro-pyran-2-one and oxepan-2-one.

An aryl group as referred to above and below preferably has 4 to 30, very preferably 5 to 20, ring C atoms, is mono- or polycyclic and may also contain fused rings, preferably contains 1, 2, 3 or 4 fused or unfused rings, and is optionally substituted with one or more groups L^S as defined above.

A heteroaryl group as referred to above and below preferably has 4 to 30, very preferably 5 to 20, ring C atoms, wherein one or more of the ring C atoms are replaced by a hetero atom, preferably selected from N, O, S, Si and Se, is mono- or polycyclic and may also contain fused rings, preferably contains 1, 2, 3 or 4 fused or unfused rings, and is optionally substituted with one or more groups L^S as defined above.

An arylalkyl or heteroarylalkyl group as referred to above and below preferably denotes -$(CH_2)_a$-aryl or -$(CH_2)_a$-heteroaryl, wherein a is an integer from 1 to 6, preferably 1, and "aryl" and "heteroaryl" have the meanings given above and below. A preferred arylalkyl group is benzyl which is optionally substituted by L^S.

As used herein, "arylene" will be understood to mean a divalent aryl group, and "heteroarylene" will be understood to mean a divalent heteroaryl group, including all preferred meanings of aryl and heteroaryl as given above and below.

Preferred aryl and heteroaryl groups are phenyl in which, in addition, one or more CH groups may each be replaced by N, naphthalene, thiophene, selenophene, thienothiophene, dithienothiophene, fluorene and oxazole, all of which can be unsubstituted, mono- or polysubstituted with L^S as defined above. Very preferred aryl and heteroaryl groups are selected from phenyl, pyrrole, preferably N-pyrrole, furan, pyridine, preferably 2- or 3-pyridine, pyrimidine, pyridazine, pyrazine, triazole, tetrazole, pyrazole, imidazole, isothiazole, thiazole, thiadiazole, isoxazole, oxazole, oxadiazole, thiophene, preferably 2-thiophene, selenophene, preferably 2-selenophene, 2,5-dithiophene-2',5'-diyl, thieno[3,2-b]thiophene, thieno[2,3-b]thiophene, furo[3,2-b]furan, furo[2,3-b]furan, seleno[3,2-b]selenophene, seleno[2,3-b]selenophene, thieno[3,2-b]selenophene, thieno[3,2-b]furan, indole, isoindole, benzo[b]furan, benzo[b]thiophene, benzo[1,2-b;4,5-b']dithiophene, benzo[2,1-b;3,4-b']dithiophene, quinole, 2- methylquinole, isoquinole, quinoxaline, quinazoline, benzotriazole, benzimidazole, benzothiazole, benzisothiazole, benzisoxazole, benzoxadiazole, benzoxazole, benzothiadiazole, 4H-cyclopenta[2,1-b;3,4-b']dithiophene, 7H-3,4-dithia-7-sila-cyclopenta[a]pentalene, all of which can be unsubstituted, mono- or polysubstituted with L^S as defined above. Further examples of aryl and heteroaryl groups are those selected from the groups shown hereinafter.

An alkyl group or an alkoxy group, *i.e.*, where the terminal CH_2 group is replaced by -O-, can be straight-chain or branched. Particularly preferred

straight-chains have 2, 3, 4, 5, 6, 7, 8, 12 or 16 carbon atoms and accordingly denote preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, dodecyl or hexadecyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, octoxy, dodecoxy or hexadecoxy, furthermore methyl, nonyl, decyl, undecyl, tridecyl, tetradecyl, pentadecyl, nonoxy, decoxy, undecoxy, tridecoxy or tetradecoxy, for example.

An alkenyl group, *i.e.*, wherein one or more CH_2 groups are each replaced by -CH=CH- can be straight-chain or branched. It is preferably straight-chain, has 2 to 10 C atoms and accordingly is preferably vinyl, prop-1-, or prop-2-enyl, but-1-, 2- or but-3-enyl, pent-1-, 2-, 3- or pent-4-enyl, hex-1-, 2-, 3-, 4- or hex-5-enyl, hept-1-, 2-, 3-, 4-, 5- or hept-6-enyl, oct-1-, 2-, 3-, 4-, 5-, 6- or oct-7-enyl, non-1-, 2-, 3-, 4-, 5-, 6-, 7- or non-8-enyl, dec-1-, 2-, 3-, 4-, 5-, 6-, 7-, 8- or dec-9-enyl.

Especially preferred alkenyl groups are C_2-C_7-1E-alkenyl, C_4-C_7-3E-alkenyl, C_5-C_7-4-alkenyl, C_6-C_7-5-alkenyl and C_7-6-alkenyl, in particular C_2-C_7-1E-alkenyl, C_4-C_7-3E-alkenyl and C_5-C_7-4-alkenyl. Examples for particularly preferred alkenyl groups are vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 1E-heptenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-heptenyl, 4-pentenyl, 4Z-hexenyl, 4E-hexenyl, 4Z-heptenyl, 5-hexenyl, 6-heptenyl and the like. Groups having up to 5 C atoms are generally preferred.

An oxaalkyl group, *i.e.*, where one CH_2 group is replaced by -O-, can be straight-chain. Particularly preferred straight-chains are 2-oxapropyl (=methoxymethyl), 2- (=ethoxymethyl) or 3-oxabutyl (=2-methoxyethyl), 2-, 3-, or 4-oxapentyl, 2-, 3-, 4-, or 5-oxahexyl, 2-, 3-, 4-, 5-, or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-,7-, 8- or 9-oxadecyl, for example.

In an alkyl group wherein one CH_2 group is replaced by -O- and one CH_2 group is replaced by -C(O)-, these radicals are preferably neighboured. Accordingly these radicals together form a carbonyloxy group -C(O)-O- or an oxycarbonyl group -O-C(O)-. Preferably this group is straight-chain and has 2 to 6 C atoms. It is accordingly preferably acetyloxy, propionyloxy,

butyryloxy, pentanoyloxy, hexanoyloxy, acetyloxymethyl, propionyloxymethyl, butyryloxymethyl, pentanoyloxymethyl, 2-acetyloxyethyl, 2-propionyloxyethyl, 2-butyryloxyethyl, 3-acetyloxypropyl, 3-propionyloxypropyl, 4-acetyloxybutyl, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, butoxycarbonyl, pentoxycarbonyl, methoxycarbonylmethyl, ethoxycarbonylmethyl, propoxycarbonylmethyl, butoxycarbonylmethyl, 2-(methoxycarbonyl)ethyl, 2-(ethoxycarbonyl)ethyl, 2-(propoxycarbonyl)ethyl, 3-(methoxycarbonyl)propyl, 3-(ethoxycarbonyl)propyl or 4-(methoxycarbonyl)-butyl.

An alkyl group wherein two or more CH_2 groups are replaced by -O- and/or -C(O)O- can be straight-chain or branched. It is preferably straight-chain and has 3 to 12 C atoms. Accordingly, it is preferably bis-carboxy-methyl, 2,2-bis-carboxy-ethyl, 3,3-bis-carboxy-propyl, 4,4-bis-carboxy-butyl, 5,5-bis-carboxy-pentyl, 6,6-bis-carboxy-hexyl, 7,7-bis-carboxy-heptyl, 8,8-bis-carboxy-octyl, 9,9-bis-carboxy-nonyl, 10,10-bis-carboxy-decyl, bis-(methoxycarbonyl)-methyl, 2,2-bis-(methoxycarbonyl)-ethyl, 3,3-bis-(methoxycarbonyl)-propyl, 4,4-bis-(methoxycarbonyl)-butyl, 5,5-bis-(methoxycarbonyl)-pentyl, 6,6-bis-(methoxycarbonyl)-hexyl, 7,7-bis-(methoxycarbonyl)-heptyl, 8,8-bis-(methoxycarbonyl)-octyl, bis-(ethoxycarbonyl)-methyl, 2,2-bis-(ethoxycarbonyl)-ethyl, 3,3-bis-(ethoxycarbonyl)-propyl, 4,4-bis-(ethoxycarbonyl)-butyl or 5,5-bis-(ethoxycarbonyl)-hexyl.

A thioalkyl group, *i.e.*, where one CH_2 group is replaced by -S-, is preferably straight-chain thiomethyl (-SCH_3), 1-thioethyl (-SCH_2CH_3), 1-thiopropyl (= -$SCH_2CH_2CH_3$), 1- (thiobutyl), 1-(thiopentyl), 1-(thiohexyl), 1-(thioheptyl), 1-(thiooctyl), 1-(thiononyl), 1-(thiodecyl), 1-(thioundecyl) or 1-(thiododecyl), wherein preferably the CH_2 group adjacent to the sp^2 hybridized vinyl carbon atom is replaced.

A fluoroalkyl group can be perfluoroalkyl C_iF_{2i+1}, wherein i is an integer from 1 to 15, in particular CF_3, C_2F_5, C_3F_7, C_4F_9, C_5F_{11}, C_6F_{13}, C_7F_{15} or C_8F_{17}, very preferably C_6F_{13}, or partially fluorinated alkyl, preferably with 1 to 15 C atoms, in particular 1,1-difluoroalkyl, all of the aforementioned being straight-chain or branched.

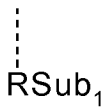
Preferably "fluoroalkyl" means a partially fluorinated (i.e. not perfluorinated) alkyl group.

Alkyl, alkoxy, alkenyl, oxaalkyl, thioalkyl, carbonyl and carbonyloxy groups can be achiral or chiral groups. Particularly preferred chiral groups are 2-butyl (=1-methylpropyl), 2-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-butyloctyl, 2-hexyldecyl, 2-octyldodecyl, 3,7-dimethyloctyl, 3,7,11-trimethyldodecyl, 2-propylpentyl, in particular 2-methylbutyl, 2-methylbutoxy, 2-methylpentoxy, 3-methyl-pentoxy, 2-ethyl-hexoxy, 2-butyloctoxyo, 2-hexyldecoxy, 2-octyldodecoxy, 3,7-dimethyloctoxy, 3,7,11-trimethyldodecoxy, 1-methylhexoxy, 2-octyloxy, 2-oxa-3-methylbutyl, 3-oxa-4-methyl-pentyl, 4-methylhexyl, 2-hexyl, 2-octyl, 2-nonyl, 2-decyl, 2-dodecyl, 6-methoxy-octoxy, 6-methyloctoxy, 6-methyloctanoyloxy, 5-methylheptyloxy-carbonyl, 2-methylbutyryloxy, 3-methylvaleroyloxy, 4-methylhexanoyloxy, 2-chloro-propionyloxy, 2-chloro-3-methylbutyryloxy, 2-chloro-4-methyl-valeryl-oxy, 2-chloro-3-methylvaleryloxy, 2-methyl-3-oxapentyl, 2-methyl-3-oxa-hexyl, 1-methoxypropyl-2-oxy, 1-ethoxypropyl-2-oxy, 1-propoxypropyl-2-oxy, 1-butoxypropyl-2-oxy, 2-fluorooctyloxy, 2-fluorodecyloxy, 1,1,1-trifluoro-2-octyloxy, 1,1,1-trifluoro-2-octyl and 2-fluoromethyloctyloxy for example. Very preferred are 2-methylbutyl, 2-ethylhexyl, 2-butyloctyl, 2-hexyldecyl, 2-octyldodecyl, 3,7-dimethyloctyl, 3,7,11-trimethyldodecyl, 2-hexyl, 2-octyl, 2-octyloxy, 1,1,1-trifluoro-2-hexyl, 1,1,1-trifluoro-2-octyl and 1,1,1-trifluoro-2-octyloxy.

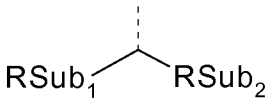
Preferred achiral branched groups are isopropyl, isobutyl (=methylpropyl), isopentyl (=3-methylbutyl), tert. butyl, isopropoxy, 2-methyl-propoxy and 3-methylbutoxy.

In a preferred embodiment, the substituents on an aryl or heteroaryl ring are independently of each other selected from primary, secondary or tertiary alkyl, alkoxy, oxaalkyl, thioalkyl, alkylcarbonyl or alkoxycarbonyl with 1 to 30 C atoms, wherein one or more H atoms are each optionally replaced by F, or aryl, aryloxy, heteroaryl or heteroaryloxy that is optionally alkylated, alkoxylated, alkylthiolated or esterified and has 4 to 30,

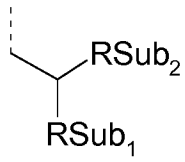
preferably 5 to 20, ring atoms. Further preferred substituents are selected from the group consisting of the following formulae



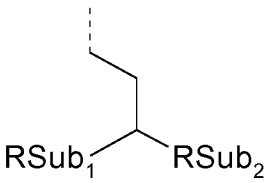
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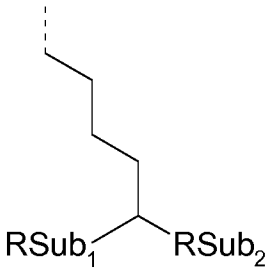
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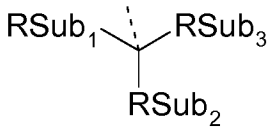
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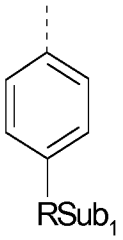
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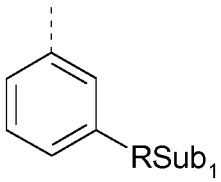
SUB5



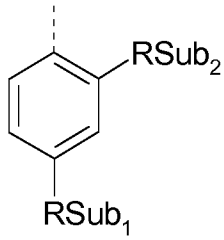
SUB6



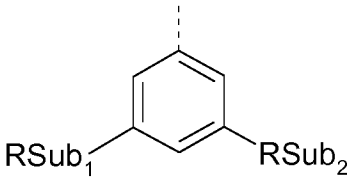
SUB7



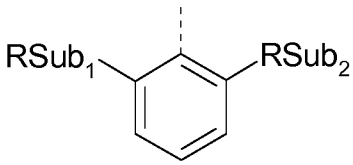
SUB8



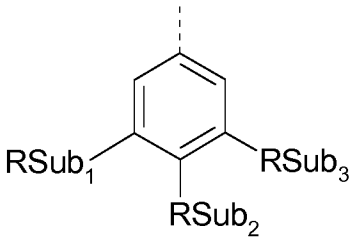
SUB9



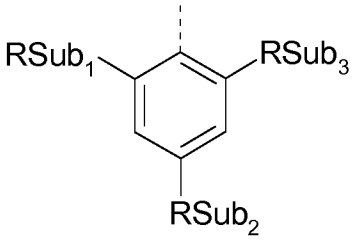
SUB10



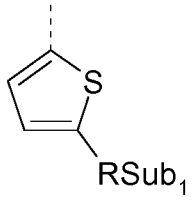
SUB11



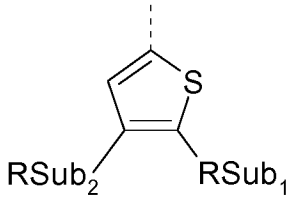
SUB12



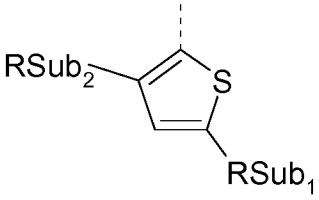
SUB13



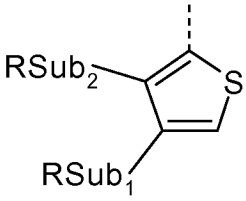
SUB14



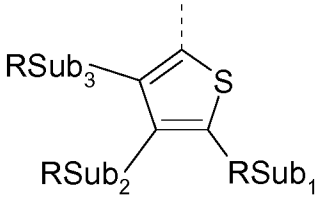
SUB15



SUB16



SUB17

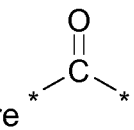


SUB18

wherein $RSub_{1-3}$ each denote L^S as defined above and below and where at least, preferably all, of $RSub_{1-3}$ is alkyl, alkoxy, oxaalkyl, thioalkyl, alkylcarbonyl or alkoxycarbonyl with up to 24 C atoms, preferably up to 20 C atoms, that is optionally fluorinated, and wherein the dashed line denotes the link to the ring to which these groups are attached. Very preferred among these substituents are those wherein all $RSub_{1-3}$ subgroups are identical.

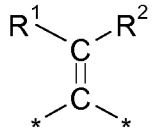
As used herein, if an aryl(oxy) or heteroaryl(oxy) group is "alkylated or alkoxylated", this means that it is substituted with one or more alkyl or alkoxy groups having from 1 to 24 C-atoms and being straight-chain or branched and wherein one or more H atoms are each optionally substituted by an F atom.

Above and below, Y^1 and Y^2 are independently of each other H, F, Cl or CN.

As used herein, -CO-, -C(=O)- and -C(O)- will be understood to mean a carbonyl group, i.e. a group having the structure 

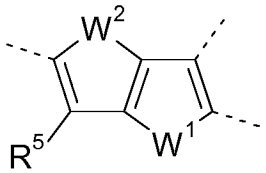
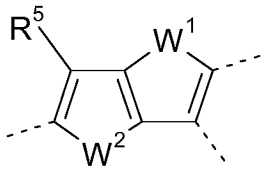
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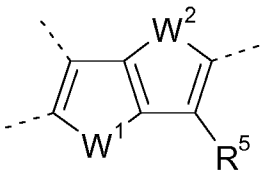
As used herein, $C=CR^1R^2$ will be understood to mean a group having the

structure  .

As used herein, "halogen" includes F, Cl, Br or I, preferably F, Cl or Br. A halogen atom that represents a substituent on a ring or chain is preferably F or Cl, very preferably F. A halogen atom that represents a reactive group in a monomer or an intermediate is preferably Br or I.

Above and below, the term "mirror image" means a moiety that can be obtained from another moiety by flipping it vertically or horizontally across an external symmetry plane or a symmetry plane extending through the moiety. For example the moiety

 also includes the mirror images 

and  .

Detailed Description

The compounds of the present invention are easy to synthesize and exhibit advantageous properties. They show good processibility for the device manufacture process, high solubility in organic solvents, and are especially suitable for large scale production using solution processing methods.

The compounds of formula I are especially suitable as (electron) acceptor or n-type semiconductor, and for the preparation of blends of n-type and p-type semiconductors which are suitable for use in OPD or BHJ OPV devices.

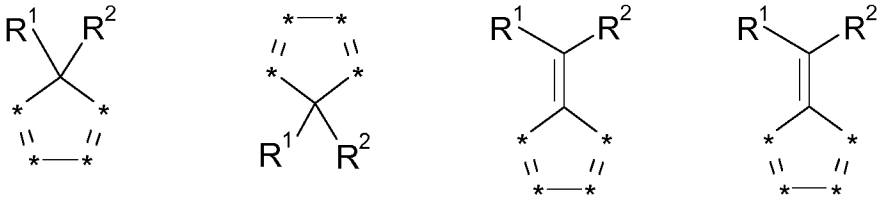
The compounds of formula I are further suitable to replace the fullerene compounds that have hitherto been used as n-type semiconductor in OPV or OPD devices.

Besides, the compounds of formula I show the following advantageous properties:

1) Introduction of an extended pi-conjugated terminal group(s) influences electronic and optical properties of the compounds thus enable higher short circuit current (Jsc)
2) Introduction of an extended pi-conjugated terminal group(s) influences solubility, thus processability of the material which is especially important for large scale manufacturing
3) Introduction of an extended pi-conjugated terminal groups influences intra- and inter-molecular packing enabling improved morphology thus higher performance.
4) When using the compounds as n-type OSC in a composition with a p-type OSC in the photoactive layer of an OPV or OPD, additional fine-tuning of the HOMO and LUMO levels of the polycyclic unit in formula I, for example through substitution and/or careful selection of the groups R^{T1} and R^{T2}, can reduce the energy loss in the electron transfer process between the n-type acceptor and the p-type donor material in the photoactive layer.
5) Further optimization of the HOMO and LUMO levels of the polycyclic unit in formula I through substitution and/or careful selection of the groups R^{T1} and R^{T2} units can increase the open circuit potential (V_{oc}).

The synthesis of the compounds of formula I can be achieved based on methods that are known to the skilled person and described in the literature, as will be further illustrated herein.

Preferred groups Ar^1 and Ar^2 in formula I are on each occurrence identically or differently selected from the following formulae and their mirror images

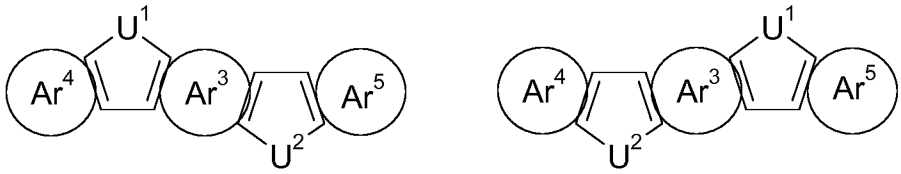


A1a A2a A1b A2b

Especially preferred groups Ar^1 and Ar^2 are selected from formulae A1a and A2a.

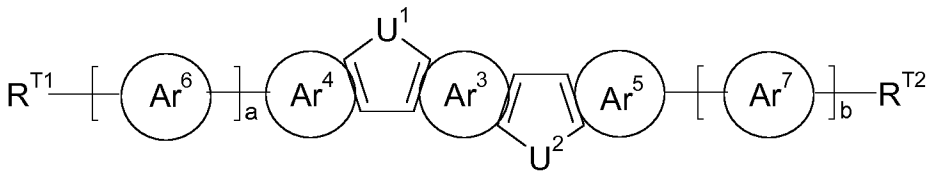
In the compounds of formula I the groups Ar^1 and Ar^2 can be selected such that the indaceno-type groups have trans- or cis-configuration.

A first preferred embodiment of the present invention relates to compounds of formula I wherein m>0 and all indaceno-type groups have trans-configuration, i.e. one of the two groups Ar^1 and Ar^2 that are fused to the same group Ar^3 is of formula A1 and the other is of formula A2, as exemplarily illustrated below.

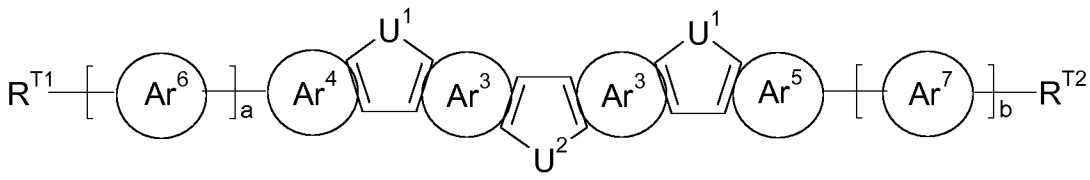


trans-configuration.

Preferred compounds units of formula I according to this first preferred embodiment are selected from the following subformulae



I1

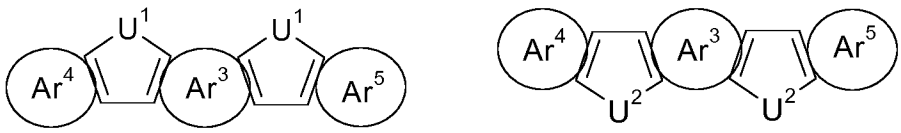


I2

wherein U^1, U^2, Ar^3, Ar^4, Ar^5, Ar^6, Ar^7, R^{T1}, R^{T2}, a and b, independently of each other and on each occurrence identically or differently, have the meanings given in formula I or one of the preferred meanings given above and below.

Preferred compounds of formula I1 and I2 are those wherein all of the groups U^1 and U^2 denote CR^1CR^2.

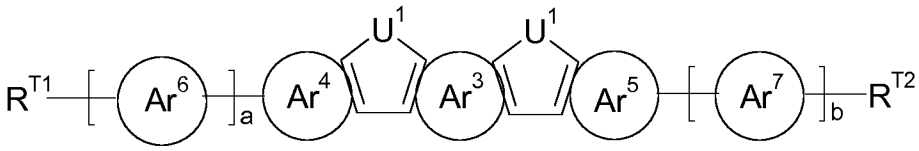
A second preferred embodiment of the present invention relates to compounds of formula I wherein m>0 and at least one, preferably all, indaceno-type groups have cis-configuration, i.e. the groups Ar^1 and Ar^2 that are fused to the same group Ar^3 are both of formula A1 or both of formula A2, as exemplarily illustrated below.



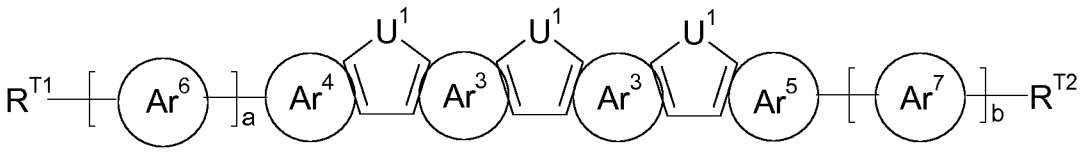
cis-configuration

This second preferred embodiment includes compounds of formula I having an "all-cis" configuration as exemplarily shown in formula I3 and I4 below, and compounds of formula I including both trans-configuration and cis-configuration, as exemplarily shown in formula I5 below.

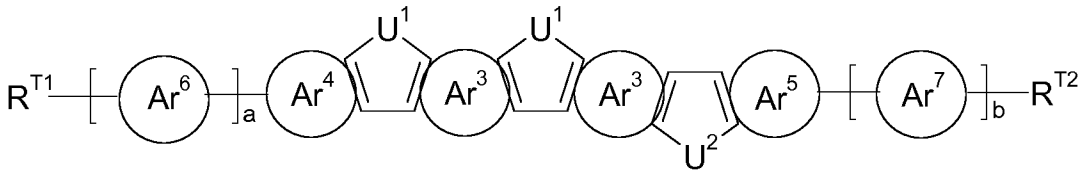
Preferred compounds of formula I according to this second preferred embodiment are selected from the following subformulae



I3



I4

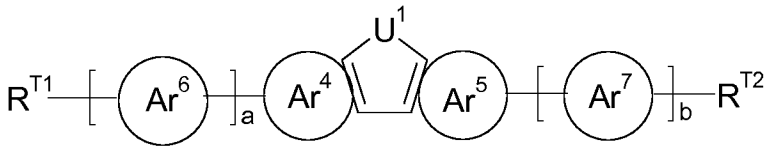


I5

wherein U^1, U^2, Ar^3, Ar^4, Ar^5, Ar^6, Ar^7, R^{T1}, R^{T2}, a and b, independently of each other and on each occurrence identically or differently, have the meanings given in formula I or one of the preferred meanings given above and below.

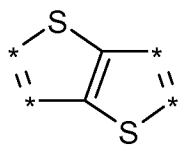
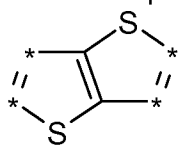
Preferred repeating units of formula I3, I4 and I5 are those wherein all groups U^1 and U^2 denote CR^1CR^2.

A third preferred embodiment of the present invention relates to compounds of formula I wherein m=0. Preferred compounds of formula I according to this third preferred embodiment are selected from the following subformulae

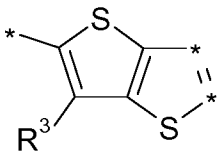
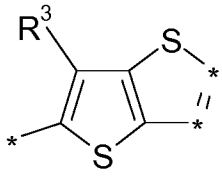


I6

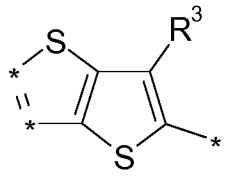
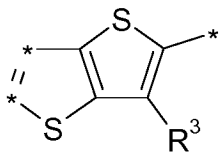
wherein U^1, U^2, Ar^3, Ar^4, Ar^5, Ar^6, Ar^7, R^{T1}, R^{T2}, a and b, independently of each other and on each occurrence identically or differently, have the meanings given in formula I or one of the preferred meanings given above and below.

In the compounds of formula I at least one of Ar^1 denotes  or ,

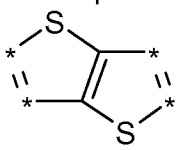
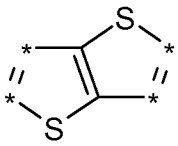
and/or

Ar^2 denotes  or ,

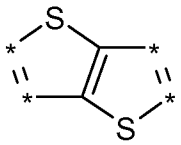
and/or

Ar^3 denotes  or .

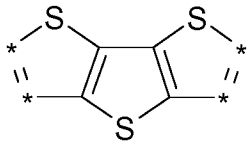
Very preferred compounds of formula I are those wherein at least one of

Ar^1 denotes  or ,

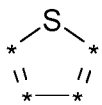
Preferred groups Ar^3 in formula I and I1-I5 and their subformulae are on each occurrence identically or differently selected from the following formulae and their mirror images



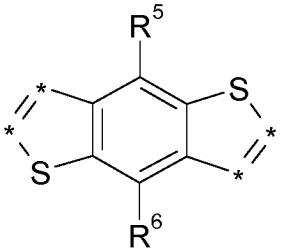
A3a1



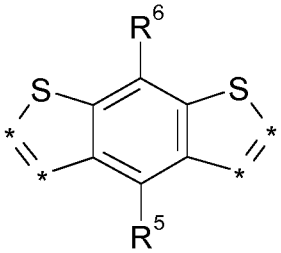
A3b1



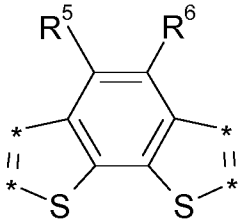
A3c1



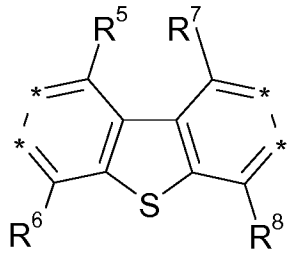
A3d1



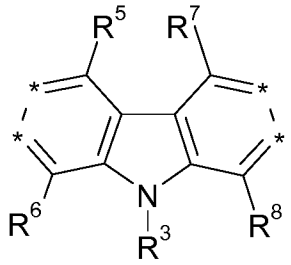
A3e1



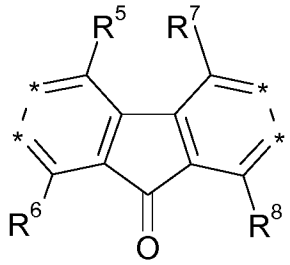
A3f1



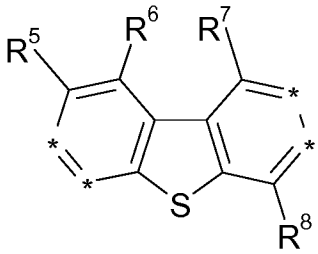
A3g1



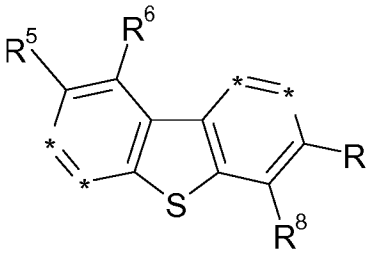
A3g2



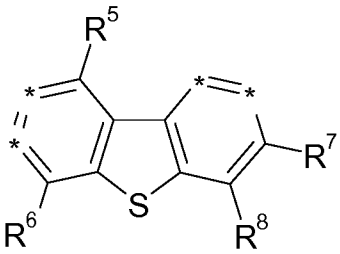
A3g3



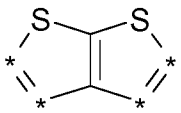
A3h1



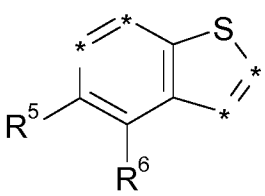
A3i1



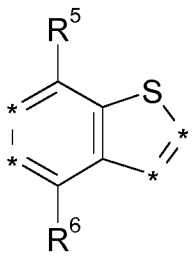
Arj1



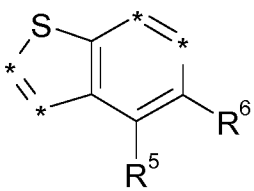
A3l1



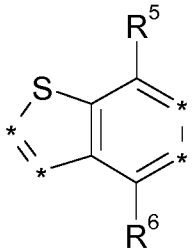
A3m1



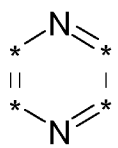
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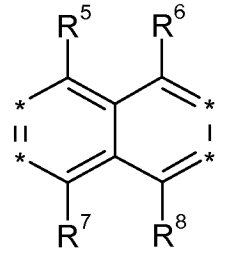
A3o1



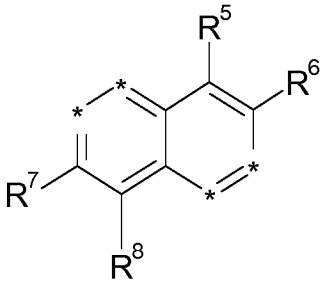
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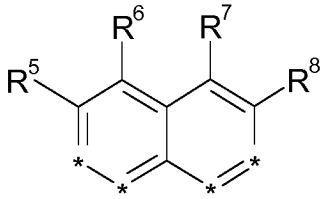
A3q1



A3r1



A3s1

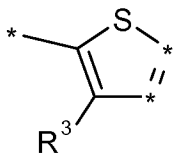


A3t1

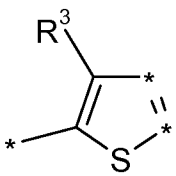
wherein R^{5-8} have the meanings given above and below.

Very preferred groups Ar^3 are those of formula A3a, most preferred those of formula A3a1.

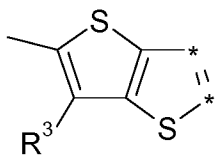
Preferred groups Ar^4 in formula I and I1-I6 and their subformulae are on each occurrence identically or differently selected from the following formulae and their mirror images



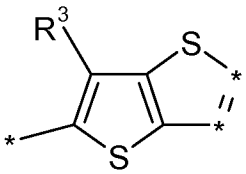
A4a1



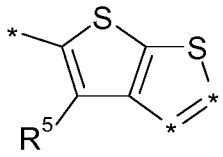
A4b1



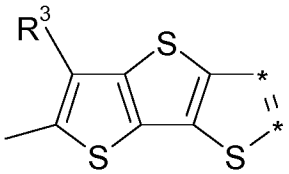
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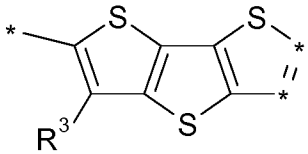
A4d1



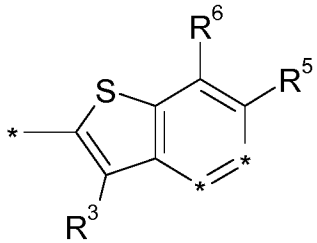
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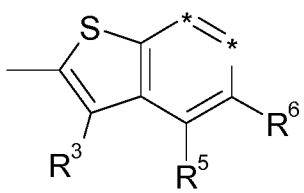
A4f1



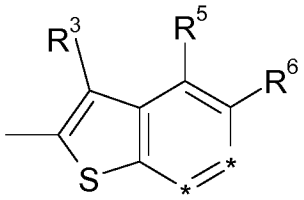
A4g1



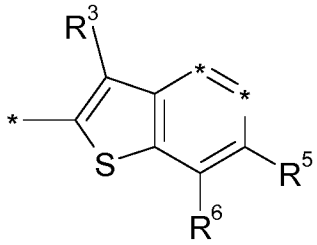
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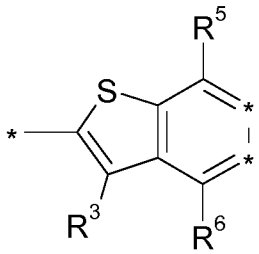
A4i1



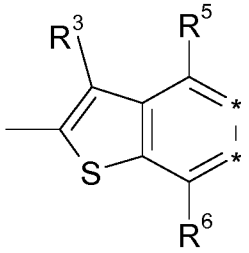
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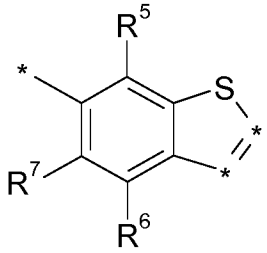
A4k1



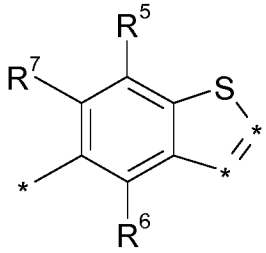
A4l1



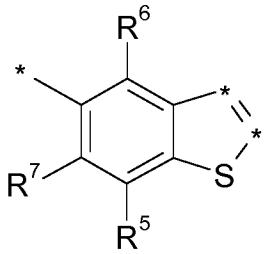
A4m1



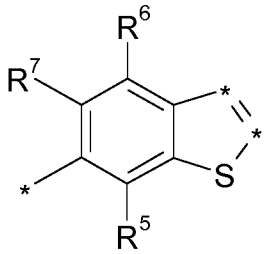
A4n1



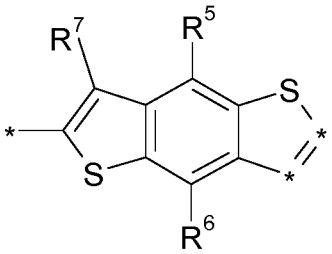
A4o1



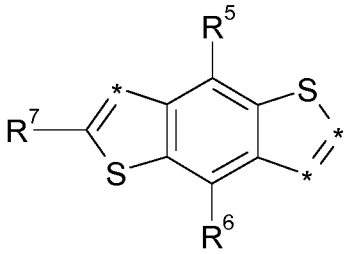
A4p1



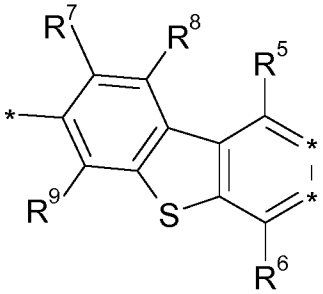
A4q1



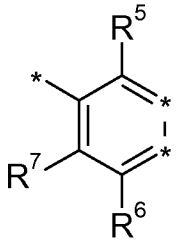
A4r1



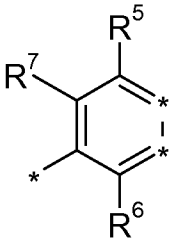
A4s1

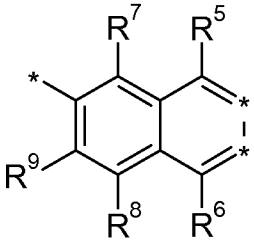


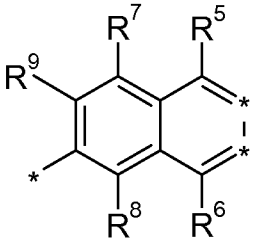
A4t1



A4u1





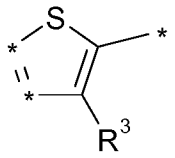


A4v1 A4w1 A4x1

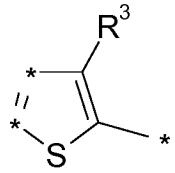
wherein R^{3-9} have the meanings given above and below.

Very preferred groups Ar^4 are those of formula A4a1, A4b1, A4c1, A4d1, A4u1, A4v1.

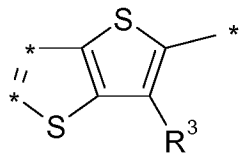
Preferred groups Ar^5 in formula I and I1-I6 and their subformulae are on each occurrence identically or differently selected from the following formulae and their mirror images



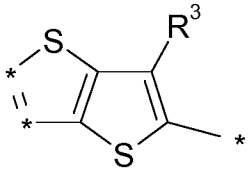
A5a1



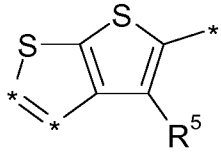
A5b1



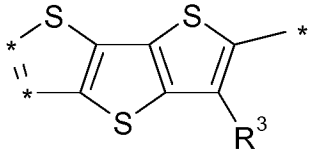
A5c1



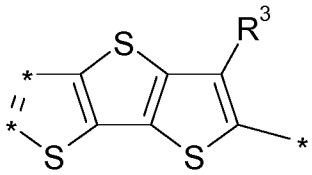
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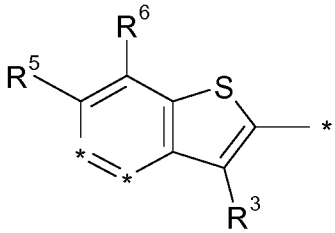
A5e1



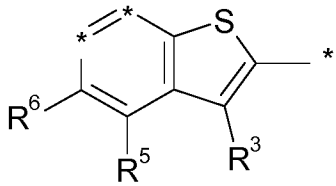
A5f1



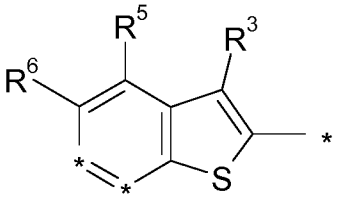
A5g1



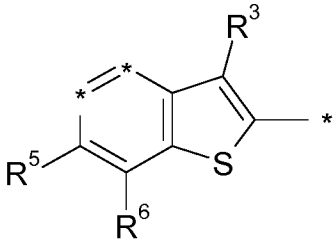
A5h1



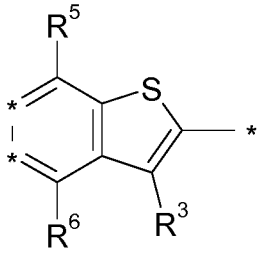
A5i1



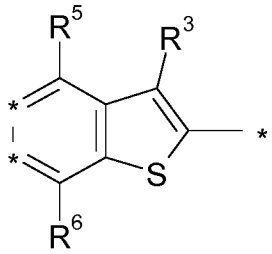
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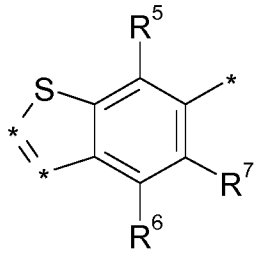
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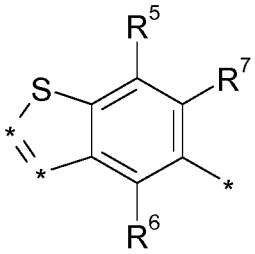
A5l1



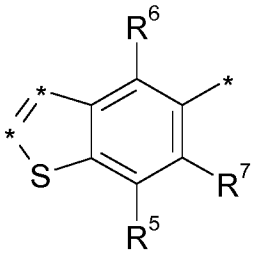
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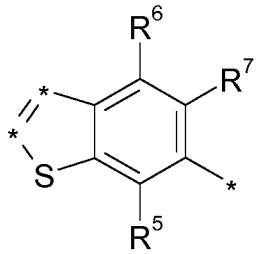
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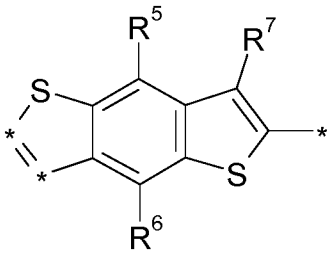
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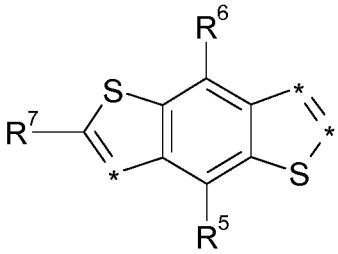
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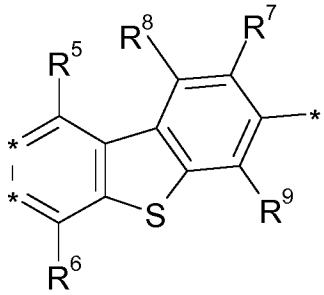
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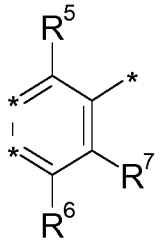
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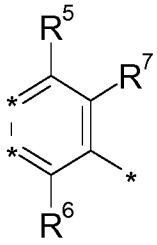
A5s1



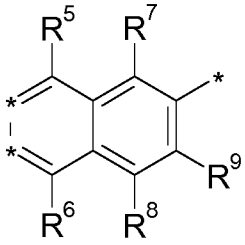
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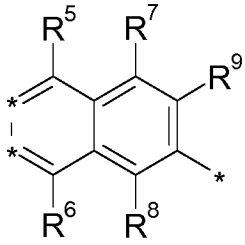
A5u1



A5v1



A5w1



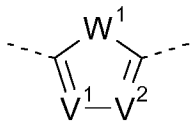
A5x1

wherein R^{3-9} have the meanings given above and below.

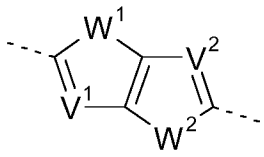
Very preferred groups Ar^5 are those of formula A5a1, A5b1, A5c1, A5d1, A5u1, A5v1.

Preferred groups Ar^6 and Ar^7 in formula I and I1-I6 and their subformulae are each independently and on each occurrence identically or differently selected from arylene or heteroarylene which has from 5 to 20 ring atoms, which is mono- or polycyclic, which optionally contains fused rings, and which is unsubstituted or substituted by one or more identical or different groups L^S, or from $-CY^1=CY^2-$.

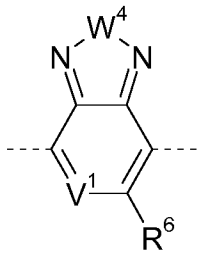
Very preferred groups Ar^6 and Ar^7 in formula I and I1-I6 and their subformulae are each independently and on each occurrence identically or differently selected from the following formulae and their mirror images:



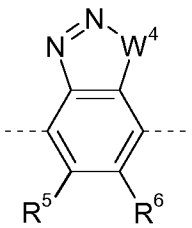
AR1



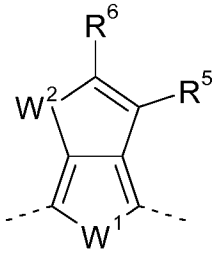
AR2



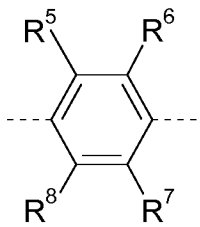
AR3



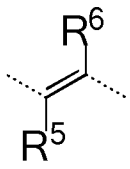
AR4



AR5



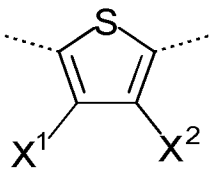
AR6



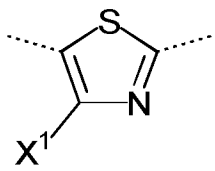
AR7

wherein, independently of each other and on each occurrence identically or differently, V^2 is CR^4 or N, R^4 has one of the meanings given for R^3, and V^1, W^1, W^2, W^4, R^{5-9} are as defined above and below.

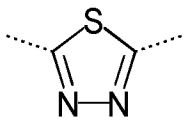
More preferred groups Ar^6 and Ar^7 in formula I and I1-I6 and their subformulae are each independently, and on each occurrence identically or differently, selected from the following formulae and their mirror images



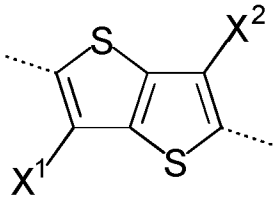
AR1-1



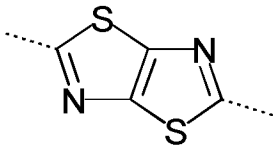
AR1-2



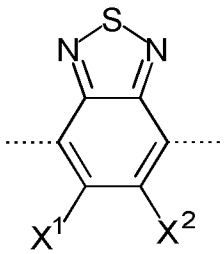
AR1-3



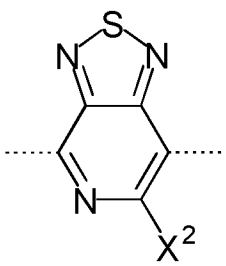
AR2-1



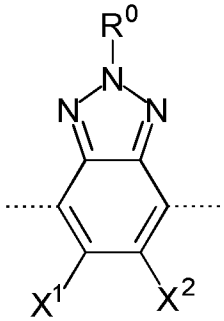
AR2-2



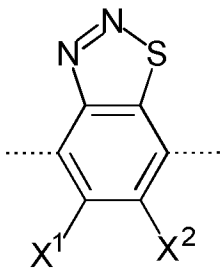
AR3-1



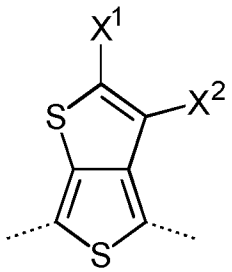
AR3-2



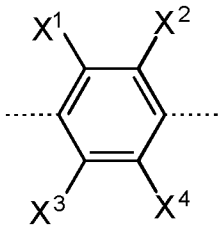
AR3-3



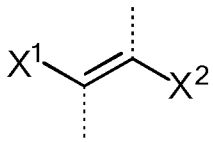
AR4-1



AR5-1



AR6-1



AR7-1

wherein X^1, X^2, X^3 and X^4 have one of the meanings given for R^1 above and below, and preferably denote H, F, Cl, -CN, R^0, OR^0 or $C(=O)OR^0$, and R^0 is as defined above and below.

Preferred formulae AR1-1 to AR6-1 are those containing at least one, preferably one, two or four substituents X^{1-4} selected from F and Cl, very preferably F.

In formula AR6-1 preferably one or two, very preferably all of X^{1-4} are F.

Preferred groups Ar^6 and Ar^7 are selected from formulae AR1, AR2, AR3, AR5 and AR7. Very preferred groups Ar^6 and Ar^7 are selected from formulae AR1-1, AR1-2, AR2-1, AR3-1, AR3-2, AR5-1 and AR7-1, most preferably from formulae AR1-1, AR1-2, AR2-1, AR2-2, AR3-1 and AR7-1.

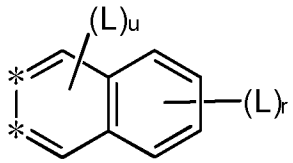
In formula I and I1-I6 and their subformulae, preferably both R^{T1} and R^{T2} are electron withdrawing groups, at least one of which is selected of formula TG.

In a preferred embodiment of the present invention both R^{T1} and R^{T2} are selected from formula TG or its preferred subformulae as described above and below.

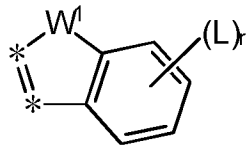
In another preferred embodiment of the present invention one of R^{T1} and R^{T2} is selected from formula TG and the other is an electron withdrawing group which is different from formula TG.

In formula TG Ar^8 is preferably bi- or polycyclic arylene or heteroarylene that consists of 2, 3 or 4 fused rings selected from benzene, thiohene and pyrazine, each of which is optionally subsituted by one or more groups L as defined above.

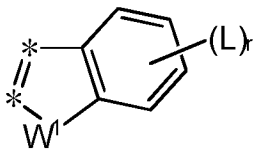
Preferably group Ar^8 in formula TG is on each occurrence identically or differently selected from the following formulae and their mirror images



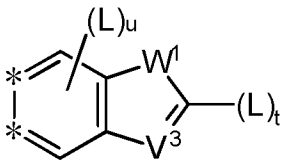
A8-1



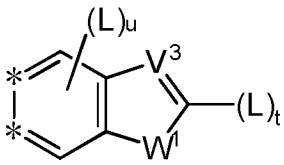
A8-2



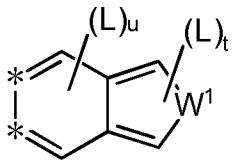
A8-3



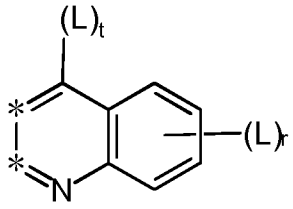
A8-4



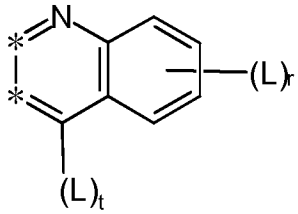
A8-5



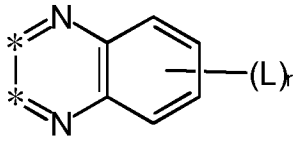
A8-6



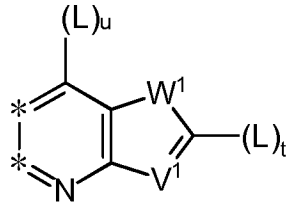
A8-7



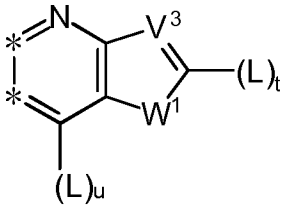
A8-8



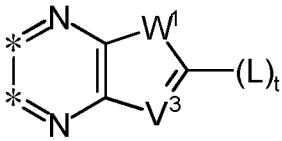
A8-9



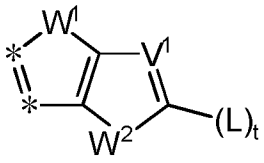
A8-10



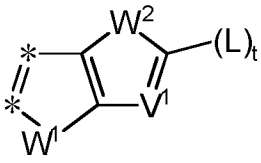
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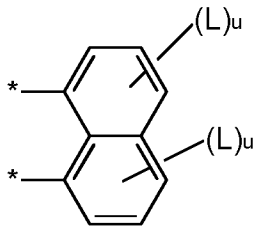
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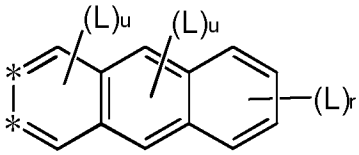
A8-13



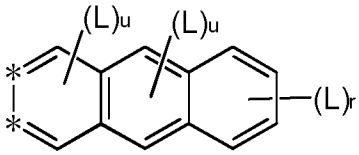
A8-14



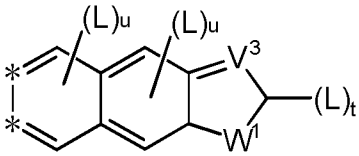
A8-15



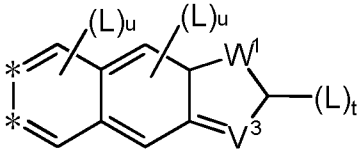
A8-16



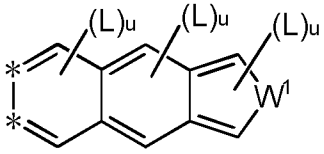
A8-17



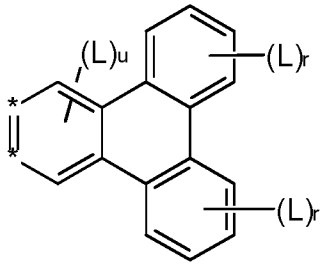
A8-18



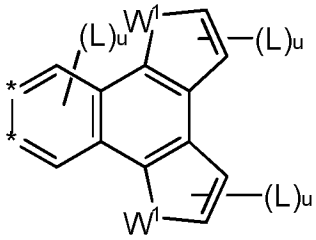
A8-19



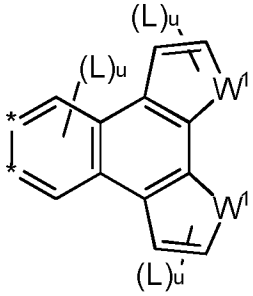
A8-20



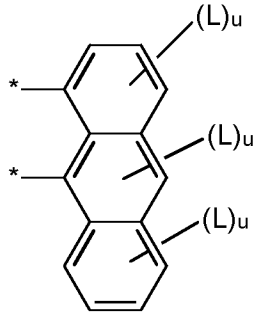
A8-21



A8-22



A8-23



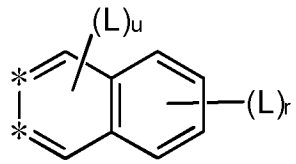
A8-24

wherein, independently of each other and on each occurrence identically or differently, W^1 and L have the meanings given above and below, V^3 is N or $C(L)_t$, r is 0, 1, 2, 3 or 4, u is 0, 1 or 2, and t is 0 or 1.

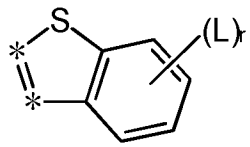
Very preferably in formulae A8-1 to A8-23 V^1 is $C(L)_t$ and W^1 is S.

Very preferred groups Ar^8 are selected from formulae A8-1, A8-2, A8-3, A8-4, A8-5 and A8-6.

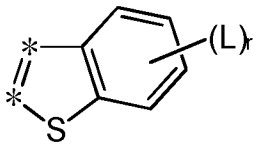
Very preferred groups Ar^8 are selected from formulae the following subformulae



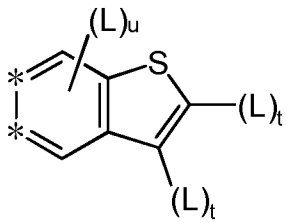
A8-1a



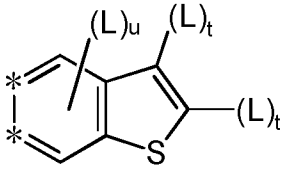
A8-2a



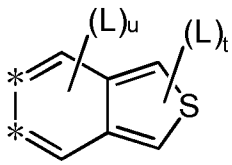
A8-3a



A8-4a



A8-5a

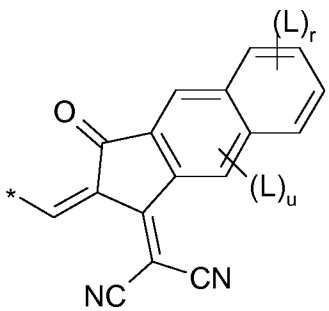


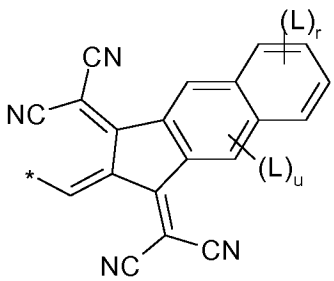
A8-6a

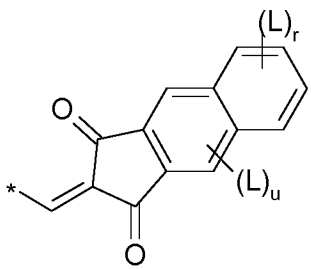
wherein L, r, t and u, independently of each other and on each occurrence identically or differently, have the meanings given above.

In formula TG preferably one of Z^1 and Z^2 is O and the other is $C(CN)_2$.

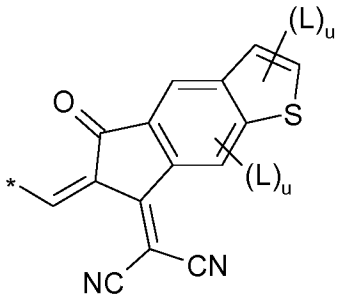
Preferred groups R^{T1} and R^{T2} in formula I are selected from the following subformulae



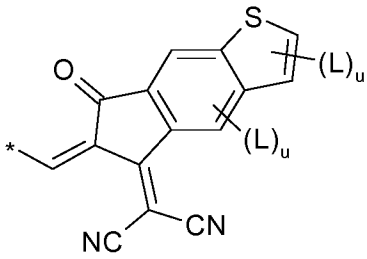




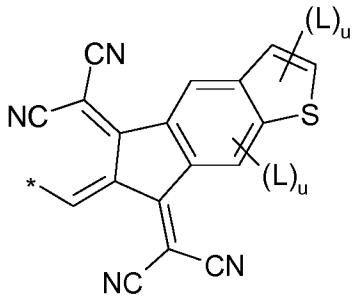
TG1



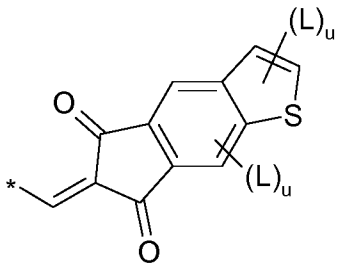
TG2



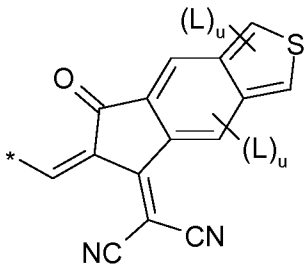
TG3



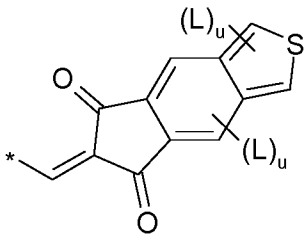
TG4



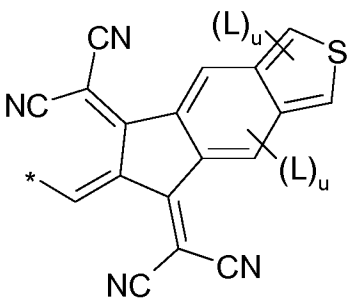
TG5



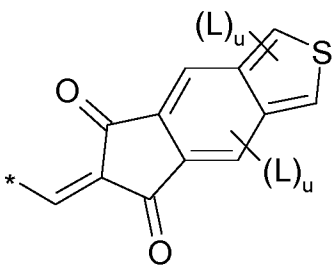
TG6



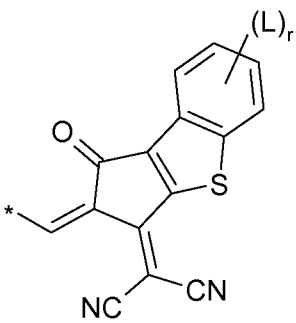
TG7



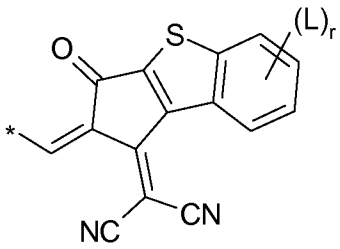
TG8



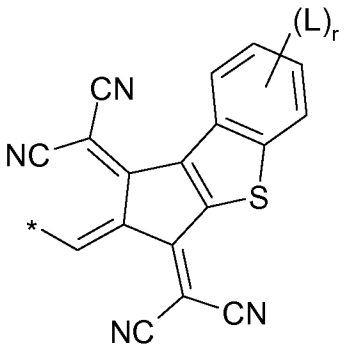
TG9



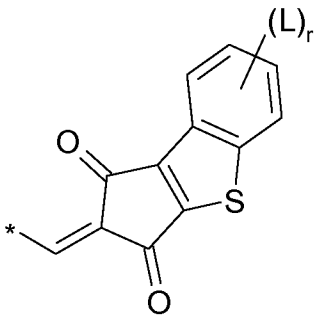
TG10



TG11



TG12



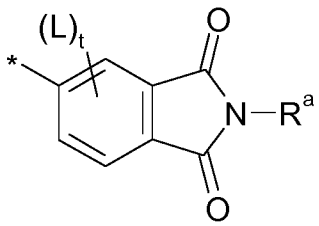
TG13 TG14 TG15

wherein L, u and r have the meanings given above.

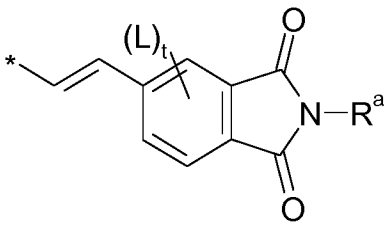
Very preferably R^{T1} and R^{T2} are selected from formulae TG1, TG4, TG5, TG8, TG9, TG12 and TG13, most preferably from formula TG1.

In another preferred embodiment of the present invention one of R^{T1} and R^{T2} is selected from formula TG, preferably wherein Ar^8, Z^1 and Z^2 have one of the preferred meanings described above, preferably selected from formulae TG1-TG15, more preferably selected from formulae TG1, TG4, TG5, TG8, TG9, TG12 and TG13, most preferably from formula TG1, and the other of R^{T1} and R^{T2} is an electron withdrawing group which is different from formula TG.

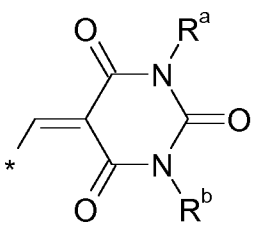
In this preferred embodiment, the group R^{T1} or R^{T2} which is different from formula TG is preferably selected from the group consisting of F, Cl, Br, -NO_2, -CN, -CF_3, -CF_2-R*, -SO_2-R*, -SO_3-R*, -C(=O)-H, -C(=O)-R*, -C(=S)-R*, -C(=O)-CF_2-R*, -C(=O)-OR*, -C(=S)-OR*, -O-C(=O)-R*, -O-C(=S)-R*, -C(=O)-SR*, -S-C(=O)-R*, -C(=O)NR*R**, -NR*-C(=O)-R*, -NHR*,-NR*R**, -CR*=CR*R**, -C≡C-R*, -C≡C-SiR*R**R***, -SiR*R**R***, -CH=CH(CN), -CH=C$(CN)_2$, -C(CN)=C$(CN)_2$, -CH=C(CN)(R^a), CH=C(CN)-C(=O)-OR*, -CH=C$(CO\text{-}OR^*)_2$, -CH=C$(CO\text{-}NR^*R^{**})_2$, and the group consisting of the following formulae



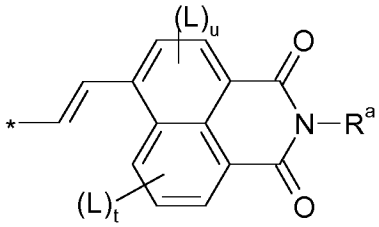
T1



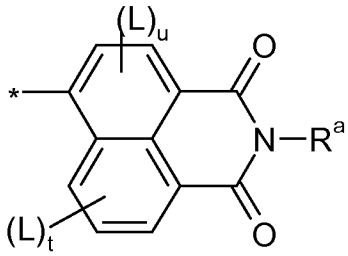
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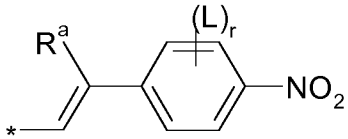
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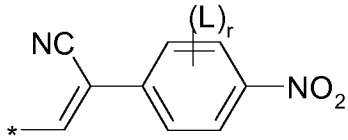
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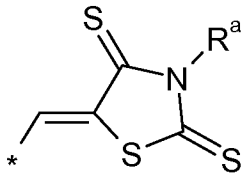
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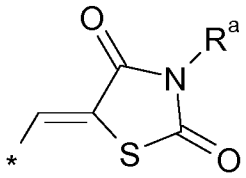
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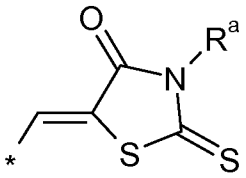
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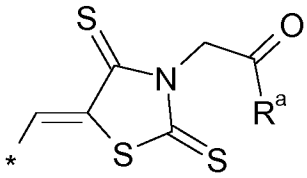
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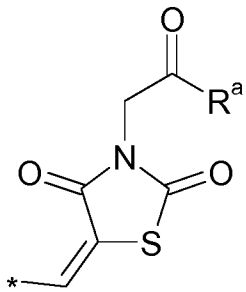
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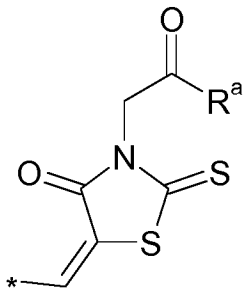
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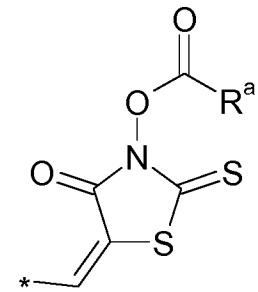
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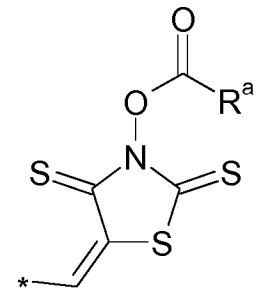
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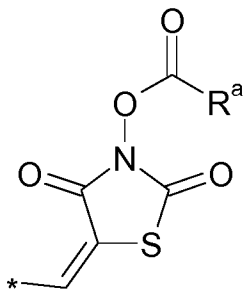
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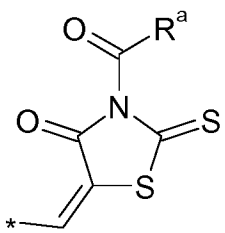
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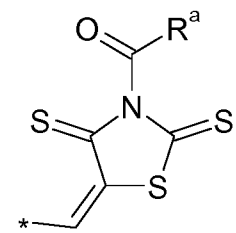
T15



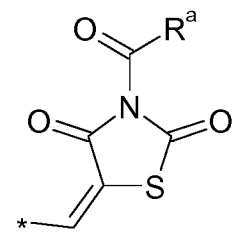
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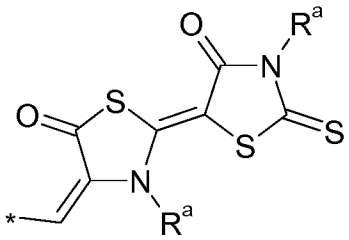
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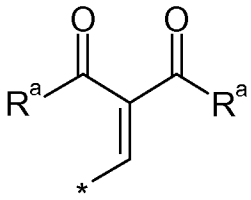
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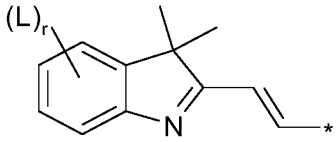
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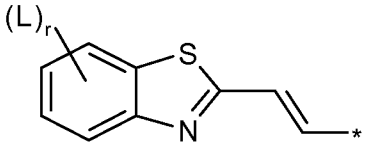
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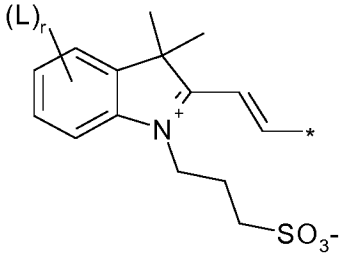
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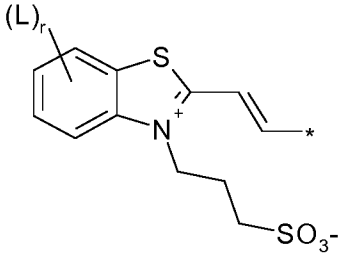
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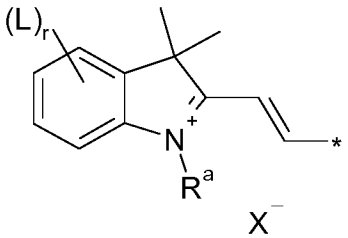
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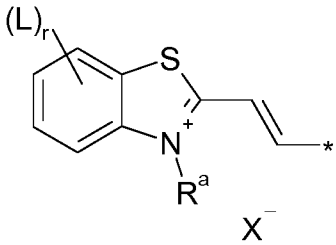
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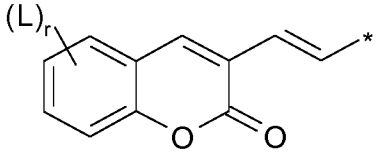
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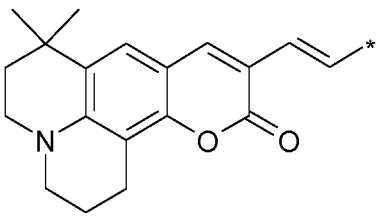
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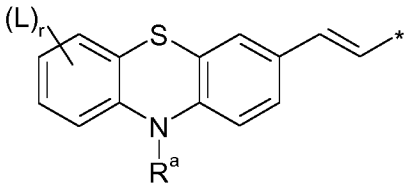
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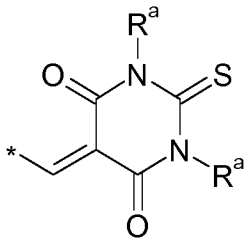
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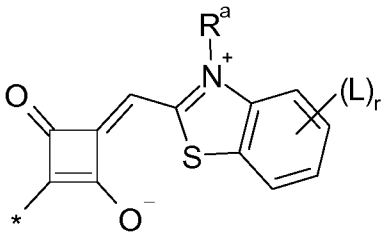
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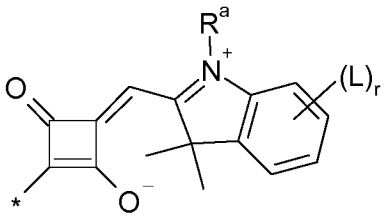
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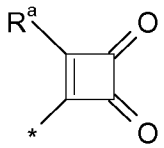
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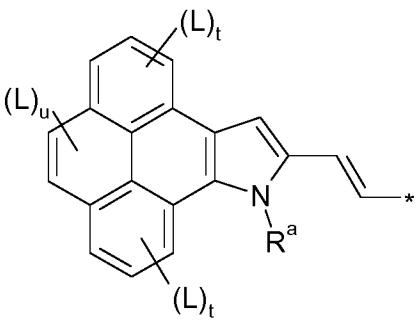
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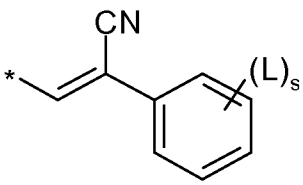
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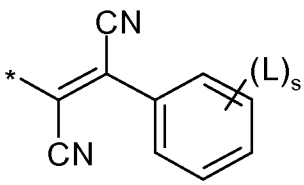
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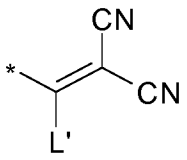
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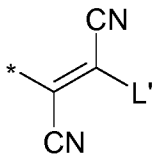
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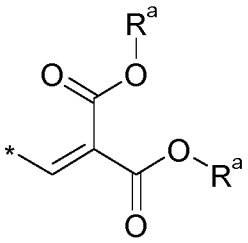
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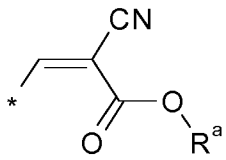
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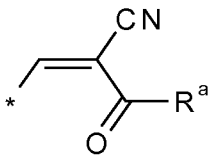
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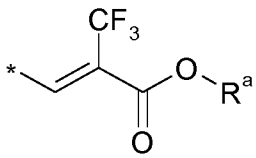
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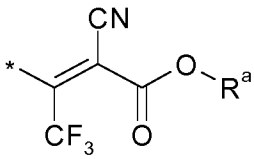
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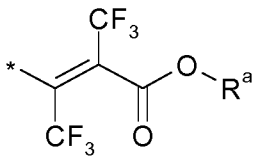
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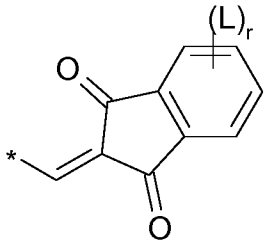
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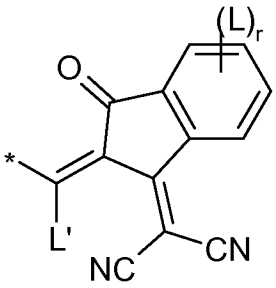
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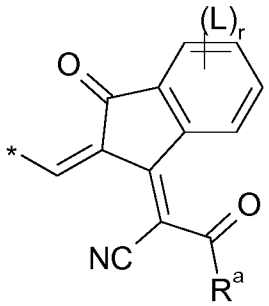
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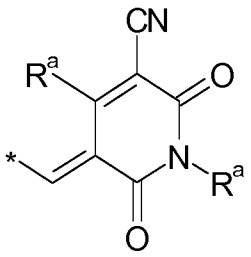
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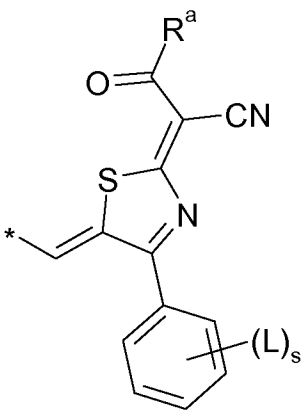
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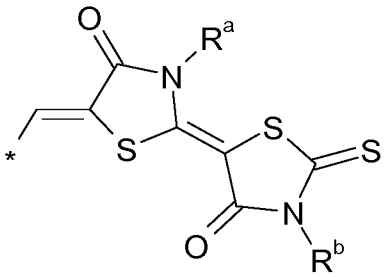
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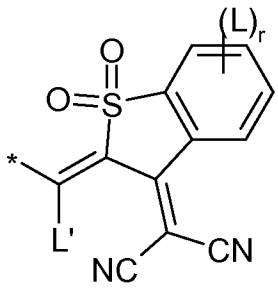
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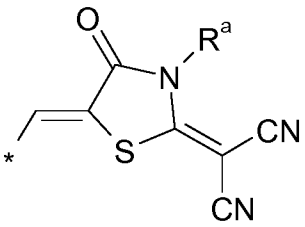
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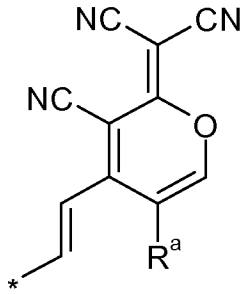
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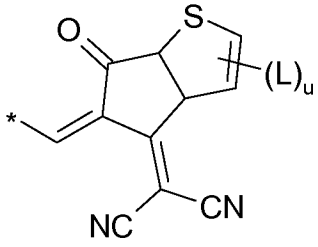
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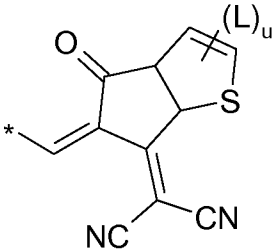
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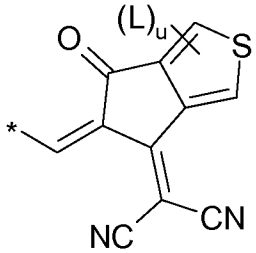
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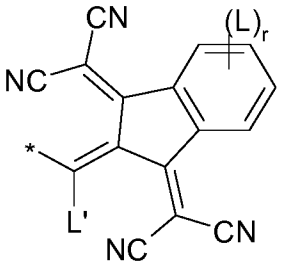
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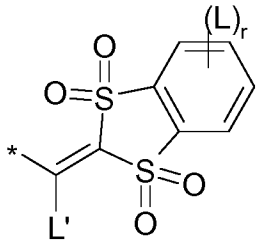
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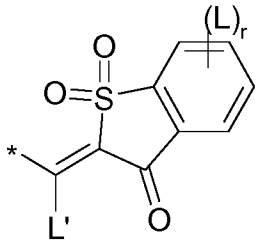
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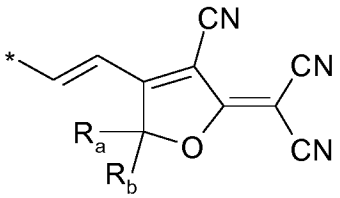
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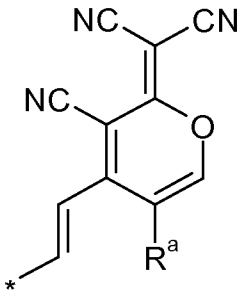
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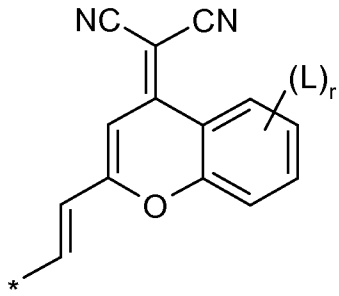
T60



T61



T62



T63

wherein the individual radicals, independently of each other and on each occurrence identically or differently, have the following meanings

R^a, R^b	aryl or heteroaryl, each having from 4 to 30, preferably from 5 to 20, ring atoms, optionally containing fused rings and being unsubstituted or substituted with one or more groups L, or one of the meanings given for L,
R*, R**, R***	alkyl with 1 to 20 C atoms which is straight-chain, branched or cyclic, and is unsubstituted, or substituted with one or more F or Cl atoms or CN groups, or perfluorinated, and in which one or more C atoms are optionally replaced by -O-, -S-, -C(=O)-, -C(=S)-, -SiR^0R^{00}-, -NR^0R^{00}-, -CHR^0=CR^{00}- or -C≡C- such that O- and/or S-atoms are not directly linked to each other,
L	F, Cl, -NO_2, -CN, -NC, -NCO, -NCS, -OCN, -SCN, R^0, OR^0, SR^0, -C(=O)X^0, -C(=O)R^0, -C(=O)-OR^0, -O-C(=O)-R^0, -NH_2, -NHR^0, -NR^0R^{00}, -C(=O)NHR^0, -C(=O)NR^0R^{00}, -SO_3R^0, -SO_2R^0, -OH, -NO_2, -CF_3, -SF_5, preferably F, -CN, R^0, -OR^0, -

	SR^0, -C(=O)-R^0, -C(=O)-OR^0, -O-C(=O)-R^0, -O-C(=O)-OR^0, -C(=O)-NHR^0, -C(=O)-NR^0R^{00},
L'	H or one of the meanings of L,
R^0, R^{00}	H or straight-chain or branched alkyl with 1 to 20, preferably 1 to 12 C atoms that is optionally fluorinated,
Y^1, Y^2	H, F, Cl or CN,
X^0	halogen, preferably F or Cl,
r	0, 1, 2, 3 or 4,
s	0, 1, 2, 3, 4 or 5,
t	0, 1, 2 or 3,
u	0, 1 or 2,

and wherein at least one of R^{T1} and R^{T2} denotes an electron withdrawing group.

Preferred groups R^{T1} and R^{T2} which are different from formula TG are each independently selected from -CN, -C(=O)-OR*, -C(=S)-OR*, -CH=CH(CN), -CH=C$(CN)_2$, -C(CN)=C$(CN)_2$, -CH=C(CN)(R^a), CH=C(CN)-C(=O)-OR*, -CH=C$(CO\text{-}OR^*)_2$, and formulae T1-T63.

Very preferred groups R^{T1} and R^{T2} which are different from formula TG are each independently selected from formulae T3, T10, T31, T36, T37, T38, T39, T47, T52, T59 and T60, wherein preferably L' is H, R^a and R^b denote H or C_1-C_{12}-alkyl, r is 0 and s is 0.

The above formulae TG1-TG15 and T1-T63 are meant to also include their respective E- or Z-stereoisomer with respect to the C=C bond in α-position to the adjacent group Ar^6 or Ar^7, thus for example the group



In the compounds of formula I, I1-I6 and their subformulae R^1 and R^2 are preferably different from H.

In a preferred embodiment of the present invention, in the compounds of formula I, I1-I6 and their subformulae R^1 and R^2 are selected from F, Cl, CN, or from straight-chain or branched alkyl, alkoxy, sulfanylalkyl, sulfonylalkyl, alkylcarbonyl, alkoxycarbonyl and alkylcarbonyloxy, each of which has 1 to 20 C atoms and is unsubstituted or substituted by one or more F atoms, most preferably from F, Cl or formulae SUB1-SUB6 above.

In another preferred embodiment of the present invention, in the compounds of formula I, I1-I6 and their subformulae R^1 and R^2 are selected from mono- or polycyclic aryl or heteroaryl, each of which is optionally substituted with one or more groups L^S as defined in formula I and has 5 to 20 ring atoms, and wherein two or more rings may be fused to each other or connected with each other by a covalent bond, very preferably phenyl that is optionally substituted, preferably in 4-position, 2,4-positions, 2,4,6-positions or 3,5-positions, or thiophene that is optionally substituted, preferably in 5-position, 4,5-positions or 3,5-positions, with alkyl, alkoxy or thioalkyl having 1 to 16 C atoms, most preferably from formulae SUB7-SUB18 above.

In the compounds of formula I, I1-I6 and their subformulae R^3 and R^4 are preferably H.

In another preferred embodiment of the present invention, in the compounds of formula I, I1-I6 and their subformulae R^3 and R^4 are different from H.

In another preferred embodiment of the present invention, in the compounds of formula I, I1-I6 and their subformulae R^3 and R^4 are selected from F, Cl, CN, or from straight-chain or branched alkyl, alkoxy, sulfanylalkyl, sulfonylalkyl, alkylcarbonyl, alkoxycarbonyl and alkylcarbonyloxy, each of which has 1 to 20 C atoms and is unsubstituted or substituted by one or more F atoms, most preferably from F, Cl or formulae SUB1-SUB6 above.

In another preferred embodiment of the present invention, in the compounds of formula I, I1-I6 and their subformulae R^3 and R^4 are selected from mono- or polycyclic aryl or heteroaryl, each of which is optionally substituted with one or more groups L^S as defined in formula I and has 5 to 20 ring atoms, and wherein two or more rings may be fused to each other or connected with each other by a covalent bond, very preferably phenyl that is optionally substituted, preferably in 4-position, 2,4-positions, 2,4,6-positions or 3,5-positions, or thiophene that is optionally substituted, preferably in 5-position, 4,5-positions or 3,5-positions, with alkyl, alkoxy or thioalkyl having 1 to 16 C atoms, more preferably from formulae SUB7-SUB18 above, most preferably from formulae SUB14-SUB18 above.

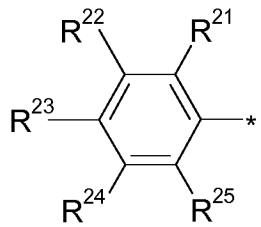
In a preferred embodiment of the present invention, in the compounds of formula I, I1-I6 and their subformulae R^{5-9} are H.

In another preferred embodiment of the present invention, in the compounds of formula I, I1-I6 and their subformulae at least one of R^{5-9} is different from H.

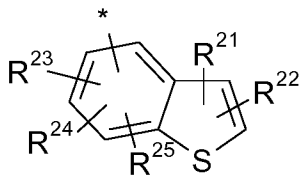
In a preferred embodiment of the present invention, in the compounds of formula I, I1-I6 and their subformulae R^{5-9}, when being different from H, are each independently selected from F, Cl, CN, or from straight-chain or branched alkyl, alkoxy, sulfanylalkyl, sulfonylalkyl, alkylcarbonyl, alkoxycarbonyl and alkylcarbonyloxy, each of which has 1 to 20 C atoms and is unsubstituted or substituted by one or more F atoms, most preferably from F, Cl or formulae SUB1-SUB6 above.

In another preferred embodiment of the present invention, in the compounds of formula I, I1-I6 and their subformulae R^{5-9}, when being different from H, are each independently selected are selected from mono- or polycyclic aryl or heteroaryl, each of which is optionally substituted with one or more groups L^S as defined in formula I and has 5 to 20 ring atoms, and wherein two or more rings may be fused to each other or connected with each other by a covalent bond, very preferably phenyl that is optionally substituted, preferably in 4-position, 2,4-positions, 2,4,6-positions or 3,5-positions, or thiophene that is optionally substituted, preferably in 5-position, 4,5-positions or 3,5-positions, with alkyl, alkoxy or thioalkyl having 1 to 16 C atoms, more preferably from formulae SUB7-SUB18 above, most preferably from formulae SUB14-SUB18 above.

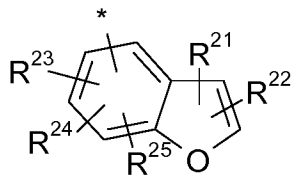
Preferred aryl and heteroaryl groups R^{1-9}, when being different from H, are each independently selected from the following formulae



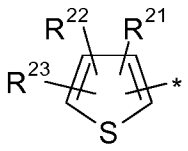
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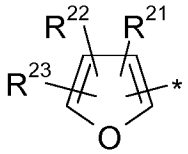
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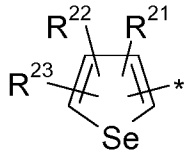
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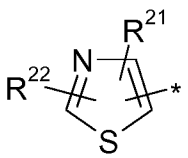
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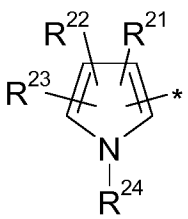
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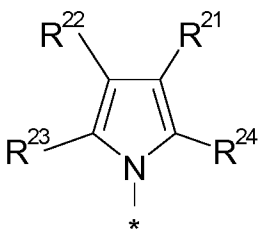
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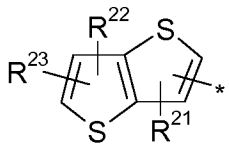
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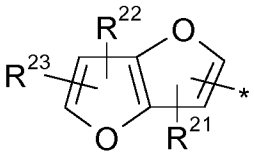
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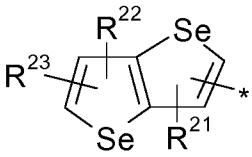
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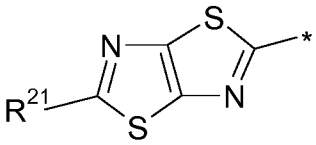
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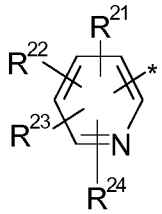
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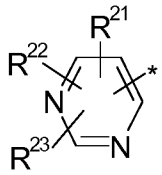
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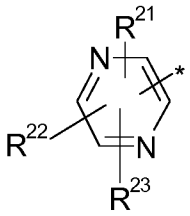
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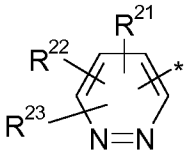
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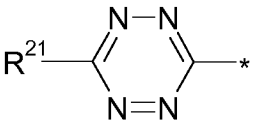
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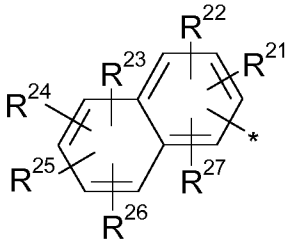
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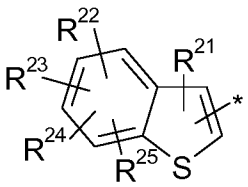
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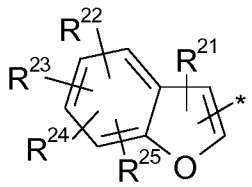
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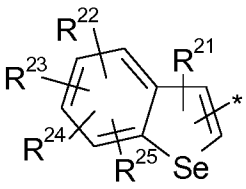
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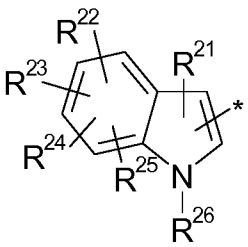


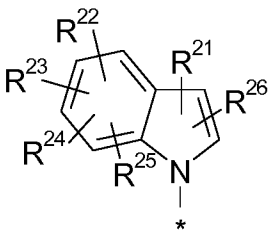
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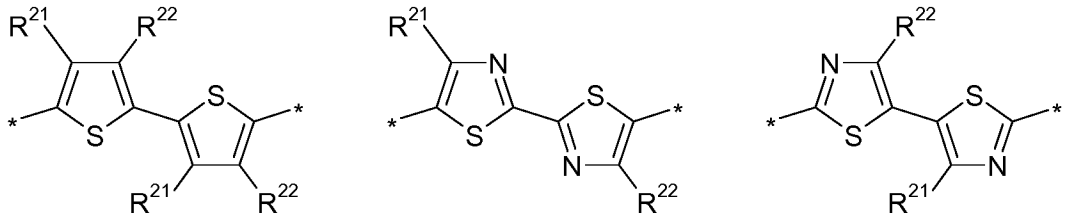
S21







S22 S23 S24



S25 S26 S27

wherein R^{21-127}, independently of each other, and on each occurrence identically or differently, denote H, F, Cl, CN, or straight-chain, branched or cyclic alkyl with 1 to 30, preferably 1 to 20, C atoms, in which one or more CH_2 groups are each optionally replaced by -O-, -S-, -C(=O)-, -C(=S)-, -C(=O)-O-, -O-C(=O)-, $-NR^0-$, $-SiR^0R^{00}-$, $-CF_2-$, $-CR^0=CR^{00}-$, $-CY^1=CY^2-$ or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, and in which one or more H atoms are each optionally replaced by F, Cl, Br, I or CN, and in which one or more CH_2 or CH_3 groups are each optionally replaced by a cationic or anionic group.

Very preferred aryl and heteroaryl groups R^{1-8}, when being different from H, are each independently selected from formulae S1, S4, S5, S7 and S10.

Most preferred aryl and heteroaryl groups R^{1-9} are each independently selected from formulae SUB7-SUB16 as defined above.

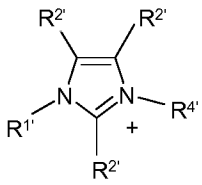
In another preferred embodiment one or more of R^{1-9} denote a straight-chain, branched or cyclic alkyl group with 1 to 50, preferably 2 to 50, very preferably 2 to 30, more preferably 2 to 24, most preferably 2 to 16 C atoms, in which one or more CH_2 or CH_3 groups are replaced by a cationic or anionic group.

The cationic group is preferably selected from the group consisting of phosphonium, sulfonium, ammonium, uronium, thiouronium, guanidinium or heterocyclic cations such as imidazolium, pyridinium, pyrrolidinium, triazolium, morpholinium or piperidinium cation.

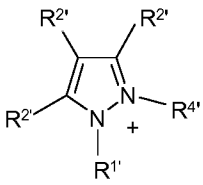
Preferred cationic groups are selected from the group consisting of tetraalkylammonium, tetraalkylphosphonium, N-alkylpyridinium, N,N-dialkylpyrrolidinium, 1,3-dialkylimidazolium, wherein "alkyl" preferably denotes a straight-chain or branched alkyl group with 1 to 12 C atoms and very preferably is selected from formulae SUB1-6 .

Further preferred cationic groups are selected from the group consisting of the following formulae

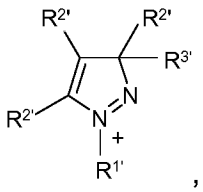
imidazolium



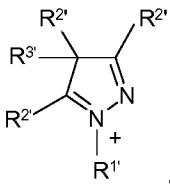
1H-pyrazolium



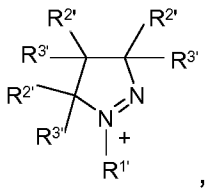
3H-pyrazolium



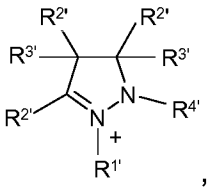
4H-pyrazolium



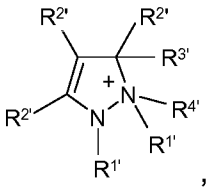
1-pyrazolinium



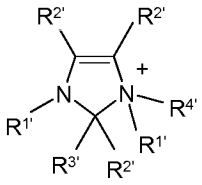
2-pyrazolinium



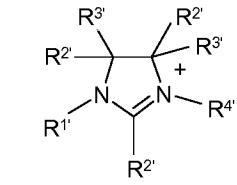
3-pyrazolinium



2,3-dihydroimidazolinium



4,5-dihydroimidazolinium



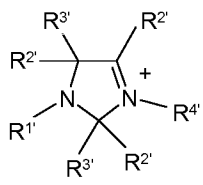
2,5-dihydroimidazolinium

pyrrolidinium

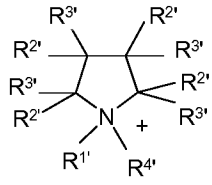
1,2,4-triazolium

1,2,4-triazolium

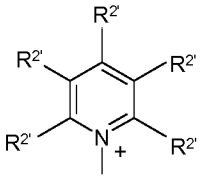
1,2,3-triazolium



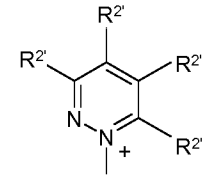
1,2,3-triazolium



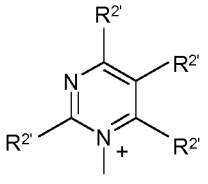
pyridinium



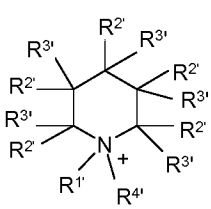
pyridazinium



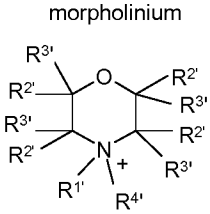
pyrimidinium



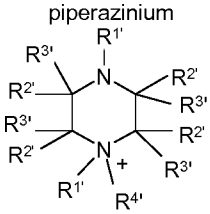
piperidinium



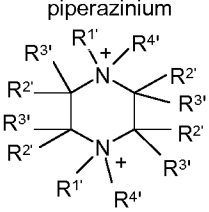
morpholinium

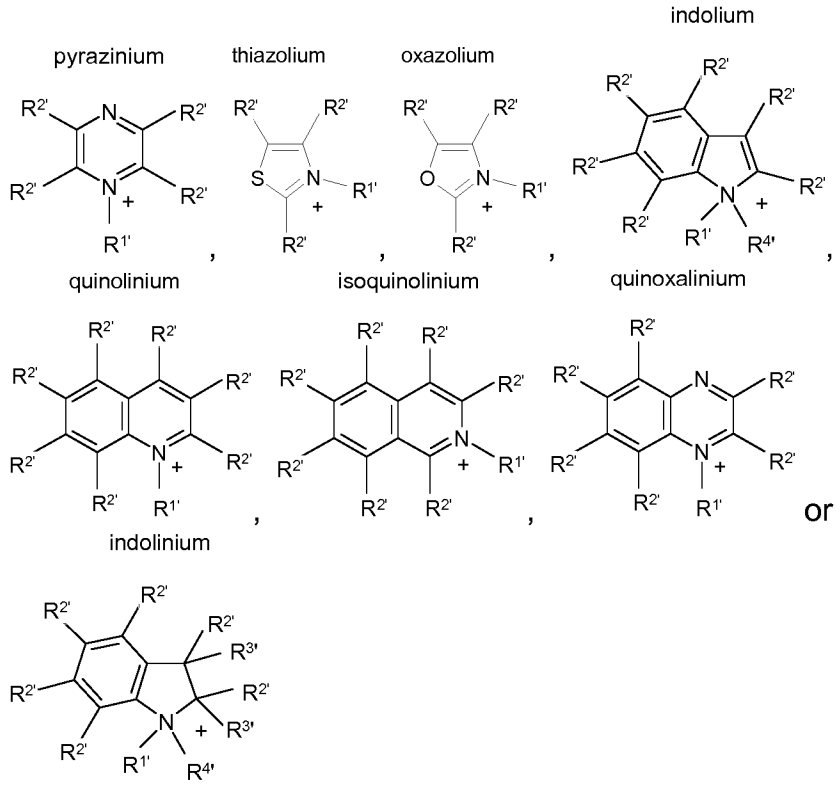


piperazinium



piperazinium





or

wherein $R^{1'}$, $R^{2'}$, $R^{3'}$ and $R^{4'}$ denote, independently of each other, H, a straight-chain or branched alkyl group with 1 to 12 C atoms or non-aromatic carbo- or heterocyclic group or an aryl or heteroaryl group, each of the aforementioned groups having 3 to 20, preferably 5 to 15, ring atoms, being mono- or polycyclic, and optionally being substituted by one or more identical or different substituents L^S as defined above, or denote a link to the respective group R^{1-9}.

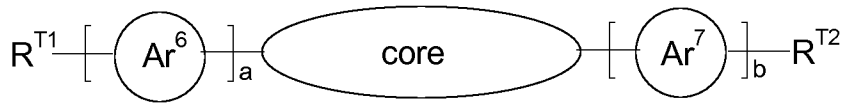
In the above cationic groups of the above-mentioned formulae any one of the groups $R^{1'}$, $R^{2'}$, $R^{3'}$ and $R^{4'}$ (if they replace a CH_3 group) can denote a link to the respective group R^{1-10}, or two neighbored groups $R^{1'}$, $R^{2'}$, $R^{3'}$ or $R^{4'}$ (if they replace a CH_2 group) can denote a link to the respective group R^1.

The anionic group is preferably selected from the group consisting of borate, imide, phosphate, sulfonate, sulfate, succinate, naphthenate or carboxylate, very preferably from phosphate, sulfonate or carboxylate.

In a preferred embodiment of the present invention Ar^1 is different from formulae A1c and A1c1 and Ar^2 is different from formulae A2c and A2c1.

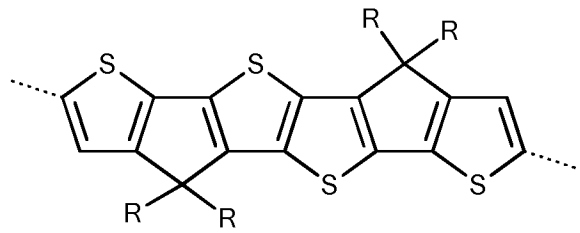
In another preferred embodiment of the present invention Ar^1 is different from Ar^2 and is not a mirror image of Ar^2.

Preferred compounds of formula I and I1-I6 are selected from formula IA

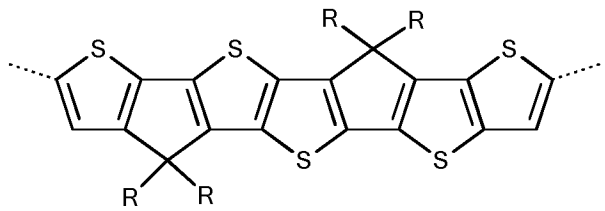


IA

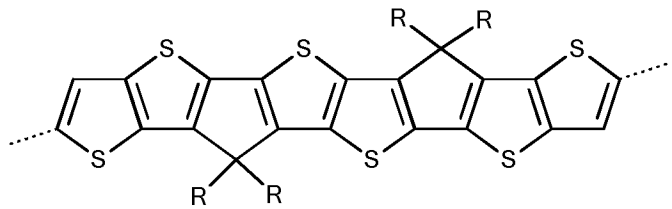
wherein Ar^6, Ar^7, R^{T1}, R^{T2}, a and b, independently of each other and on each occurrence identically or differently, have the meanings given in formula I or one of the preferred meanings given above and below, and "Core" is, on each occurrence identically or differently, a polycyclic divalent group selected from the following formulae



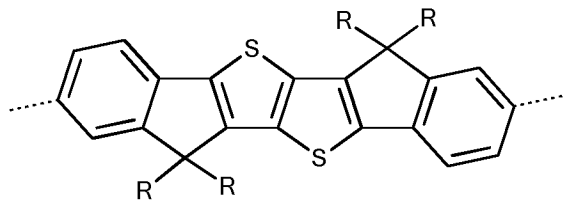
C1



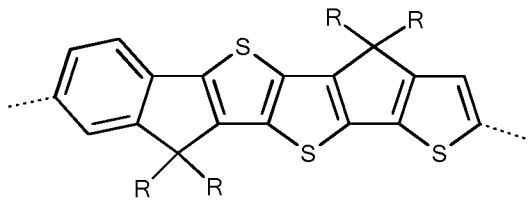
C2



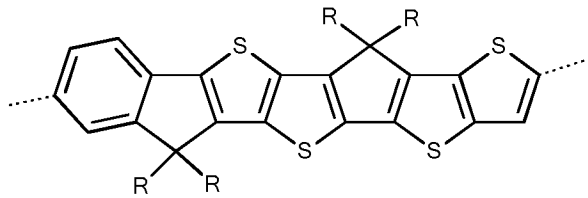
C3



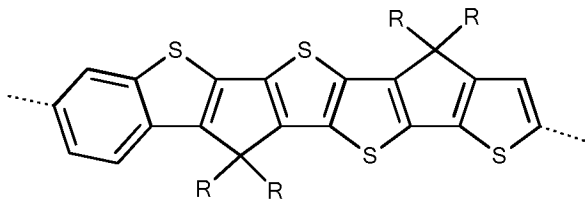
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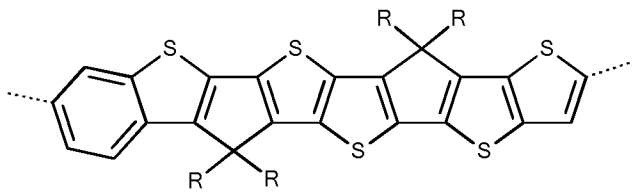
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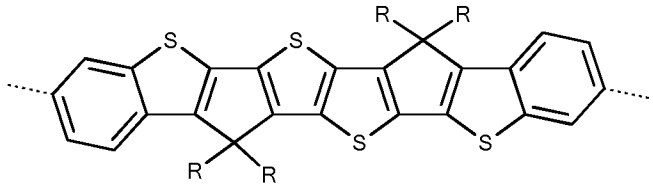
C6



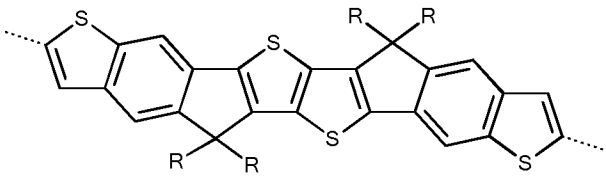
C7



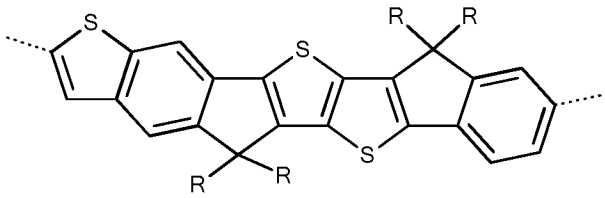
C8



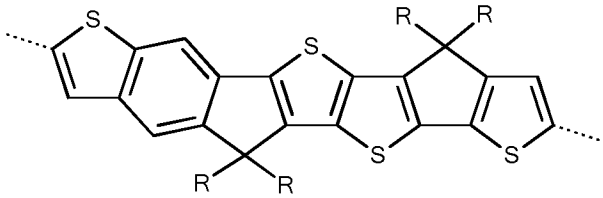
C9



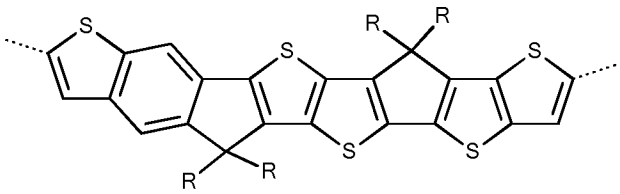
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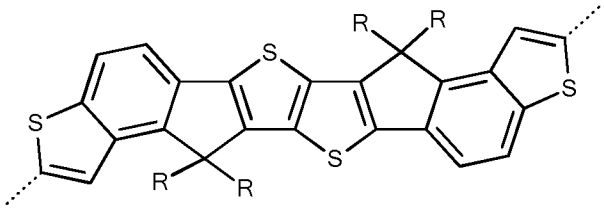
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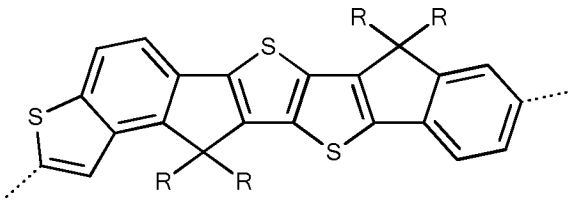
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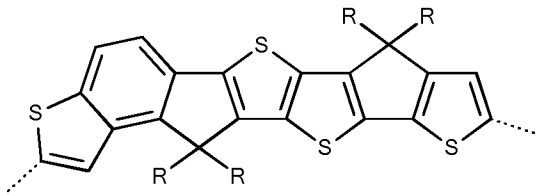
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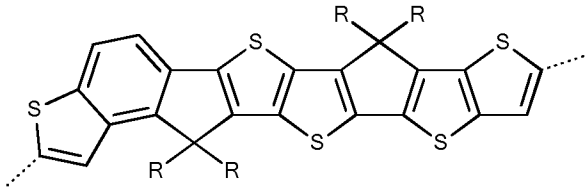
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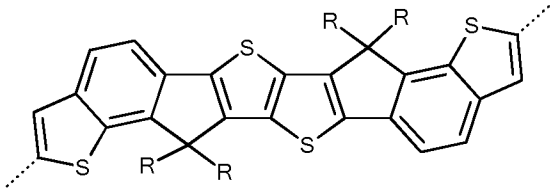
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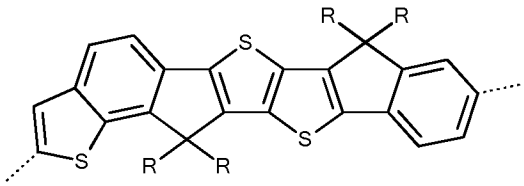
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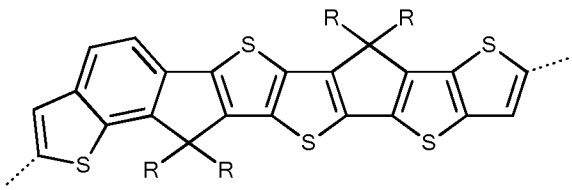
C17



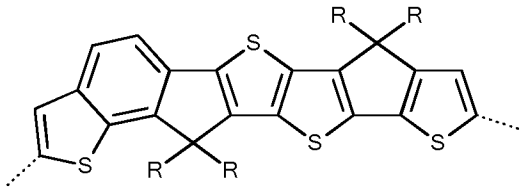
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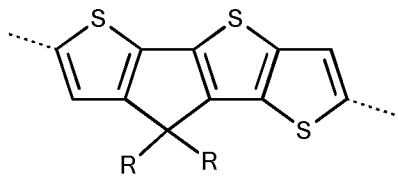
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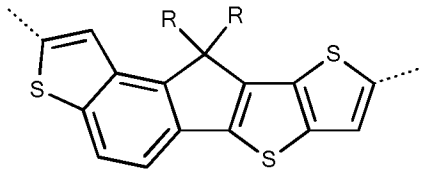
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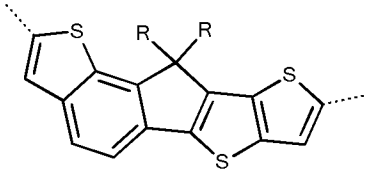
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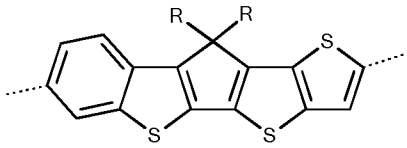
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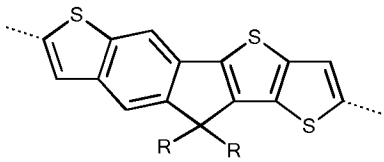
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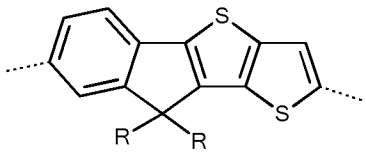
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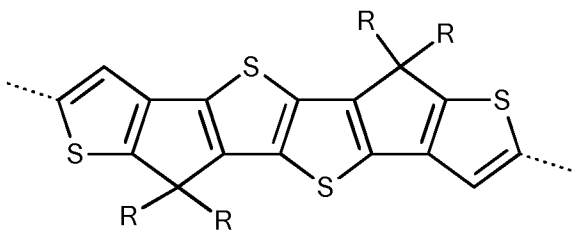
C25



C26



C27

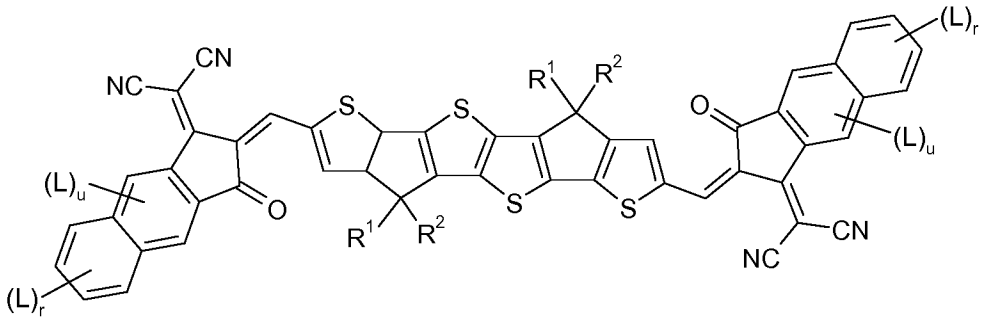


C28

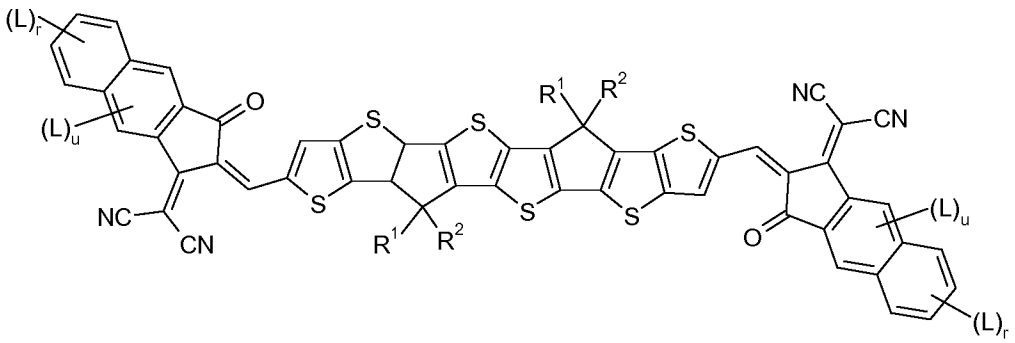
wherein R has on each occurrence identically or differently one of the meanings of R^1 as given above and below.

Very preferred are the core groups of formula C1, C2, C3, C4, C22, C28.

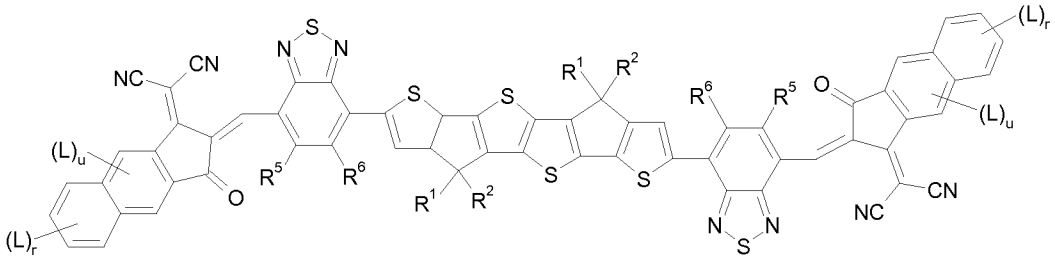
Very preferred compounds of formula I, I1-I6 and I1A are selected from the following subformulae



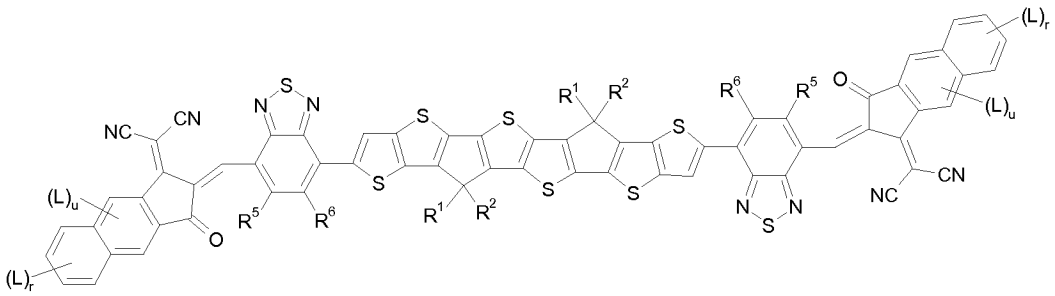
I1A



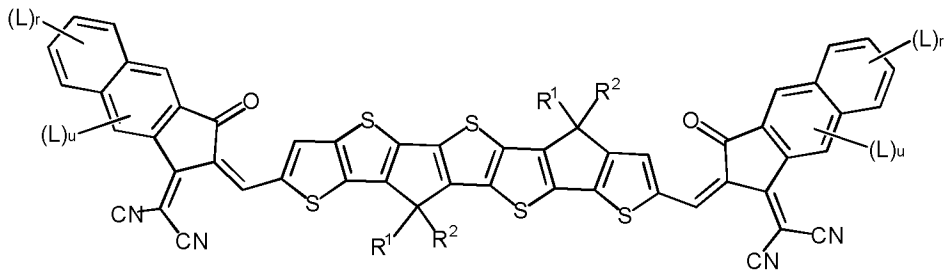
I1A



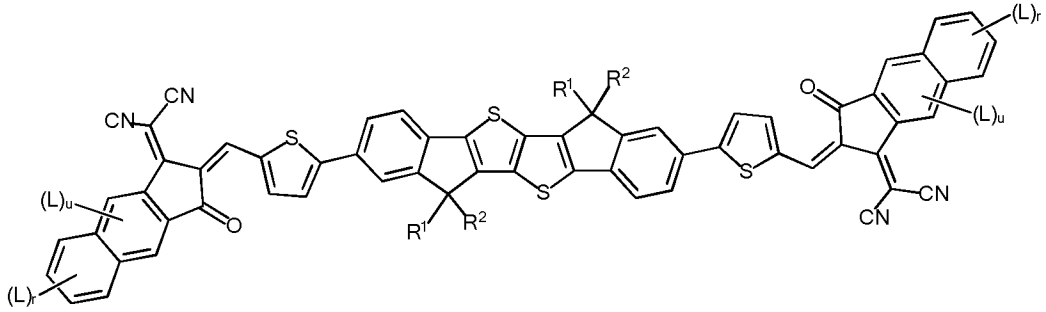
I1A



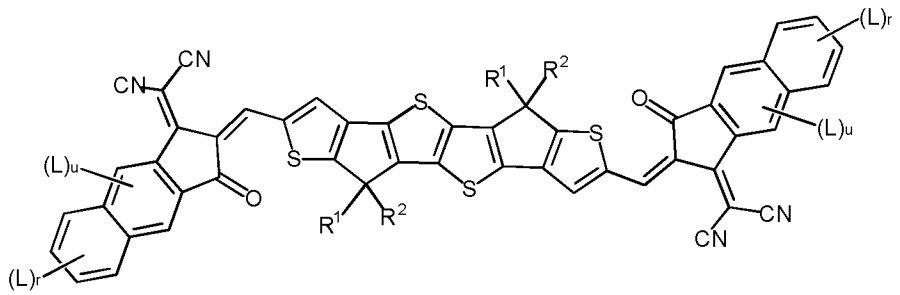
I1A



I1A



I1A



I1A

wherein R^1, R^2, R^5, R^6, L, r and u have the meanings given above and below.

Further preferred compounds of formula I, I1-I6, I1A, I1A1-I1A7 and their subformulae are selected from the following preferred embodiments or any combination thereof:

- a is 1 or 2, preferably 1,
- b is 1 or 2, preferably 1,
- a=b=0,
- a=b=1 or 2,
- m is 0,
- m is >0, preferably 1, 2 or 3,
- k is 1,
- U^1 and U^2 denote CR^1R^2,
- W^1, W^2 and W^3 are S or Se, preferably S,
- W^4 is S or NR^0, preferably S,
- V^1 is CR^3,
- V^2 is CR^4,
- V^1 is N,
- V^2 is N,
- V^1 is CR^3 and V^2 is CR^4,
- V^1 is CR^3 and V^2 is N,
- V^1 and V^2 are N,
- u is 0 and r is 1 or 2,
- L is methyl or methoxy,
- Ar^1 and Ar^2 are selected of formula A1a, A1b, A2a and A2b, preferably of formula A1a and A2a,
- Ar^3 is selected from formulae A3a-A3w, preferably from formulae A3a1-A3t1, very preferably from formulae A3a1,
- Ar^4 is selected from formulae A4a-A4x, preferably from formulae A4a1-A4x1, very preferably from formulae A4a1, A4b1, A4c1, A4d1, A4u1 and A4v1,
- Ar^5 is selected from formulae A5a-A5x, preferably from formulae A5a1-A5x1, very preferably from formulae A5a1, A5b1, A5c1, A5d1, A5u1 and A5v1,

- in Ar^3 all substituents R^{5-9} are H,
- in at least one group Ar^3 at least one, preferably one or two of R^{5-9} are different from H,
- in one or both of Ar^4 and Ar^5 all substituents R^{5-9} are H,
- in one or both of Ar^5 and Ar^5 at least one, preferably one or two of R^{5-9} are different from H,
- in one or both of Ar^6 and Ar^7 all substituents R^{5-9} are H,
- in one or both of Ar^6 and Ar^7 at least one, preferably one or two of R^{5-9} are different from H,
- Ar^6 and Ar^7 are selected from formulae AR1, AR2, AR3, AR5 and AR7,
- Ar^6 and Ar^7 are selected from formulae AR1-1, AR1-2, AR2-1, AR3-1, AR3-2, AR5-1 and AR7-1, most preferably from formulae AR1-1, AR2-1, AR3-1 and AR7-1,
- Ar^6 and Ar^7 are selected from thiophene, thiazole, thieno[3,2-b]thiophene, thiazolo[5,4-d]thiazole, benzene, 2,1,3-benzothiadiazole, 1,2,3-benzothiadiazole, thieno[3,4-b]thiophene, benzotriazole, thiadiazole[3,4-c]pyridine and vinyl, which are substituted by X^1, X^2, X^3 and X^4 as defined above,
- Ar^6 and Ar^7 are selected from thiophene, thiazole, thieno[3,2-b]thiophene, thiazolo[5,4-d]thiazole, benzene, 2,1,3-benzothiadiazole, 1,2,3-benzothiadiazole, thieno[3,4-b]thiophene, benzotriazole, thiadiazole[3,4-c]pyridine and vinyl, wherein X^1, X^2, X^3 and X^4 are H,
- Ar^6 and Ar^7 are selected from thiophene, thiazole, thieno[3,2-b]thiophene, thiazolothiazole, benzene, 2,1,3-benzothiadiazole, 1,2,3-benzothiadiazole, thieno[3,4-b]thiophene, benzotriazole, thiadiazole[3,4-c]pyridine and vinyl, wherein one or more of X^1, X^2, X^3 and X^4 are different from H,
- Ar^8 is bi- or polycyclic arylene or heteroarylene consisting of 2, 3 or 4 fused rings selected from benzene, thiophene and pyrazine, each of which is optionally subsituted by one or more groups L as defined above,

- Ar^8 is selected from formulae A8-1 to A8-23, preferably formulae A8-1 to A8-6, very preferably from formulae A8-1a to A8-6a,
- Z^1 and Z^2 are selected from O and $C(CN)_2$,
- one of Z^1 and Z^2 is O and the other is $C(CN)_2$,
- R^{T1} and R^{T2} are both of formula TG,
- R^{T1} and R^{T2} are selected from the formulae TG1-TG15, preferably from formulae TG1, TG4, TG5, TG8, TG9, TG12 and TG13, most preferably from formula TG1,
- one of R^{T1} and R^{T2} is not of formula TG,
- one of R^{T1} and R^{T2} is selected from formulae T1 to T63,
- L' is H,
- L denotes F, Cl, CN, NO_2, or alkyl or alkoxy with 1 to 16 C atoms that is optionally fluorinated,
- t is 1 and L is F, Cl, CN, NO_2, or alkyl or alkoxy with 1 to 16 C atoms that is optionally fluorinated,
- u is 1 or 2 and L is F, Cl, CN, NO_2, or alkyl or alkoxy with 1 to 16 C atoms that is optionally fluorinated,
- R^1 and R^2 are different from H,
- R^1 and R^2, when being different from H, are each independently selected from F, Cl or straight-chain or branched alkyl, alkoxy, sulfanylalkyl, sulfonylalkyl, alkylcarbonyl, alkoxycarbonyl and alkylcarbonyloxy, each having 1 to 20 C atoms and being unsubstituted or substituted by one or more F atoms, or alkyl or alkoxy having 1 to 12 C atoms that is optionally fluorinated, more preferably from formulae SUB1-SUB6 above,
- R^1 and R^2, when being different from H, and are each independently selected from phenyl that is substituted, preferably in 4-position, or in 2,4-positions, or in 2,4,6-positions or in 3,5-positions, with alkyl or alkoxy having 1 to 20 C atoms, preferably 1 to 16 C atoms, very preferably 4-alkylphenyl wherein alkyl is C1-16 alkyl, most preferably 4-methylphenyl, 4-hexylphenyl, 4-octylphenyl or 4-dodecylphenyl, or 4-alkoxyphenyl wherein alkoxy is C1-16 alkoxy, most preferably 4-

hexyloxyphenyl, 4-octyloxyphenyl or 4-dodecyloxyphenyl or 2,4-dialkylphenyl wherein alkyl is C1-16 alkyl, most preferably 2,4-dihexylphenyl or 2,4-dioctylphenyl or 2,4-dialkoxyphenyl wherein alkoxy is C1-16 alkoxy, most preferably 2,4-dihexyloxyphenyl or 2,4-dioctyloxyphenyl or 3,5-dialkylphenyl wherein alkyl is C1-16 alkyl, most preferably 3,5-dihexylphenyl or 3,5-dioctylphenyl or 3,5-dialkoxyphenyl wherein alkoxy is C1-16 alkoxy, most preferably 3,5-dihexyloxyphenyl or 3,5-dioctyloxyphenyl, or 2,4,6-trialkylphenyl wherein alkyl is C1-16 alkyl, most preferably 2,4,6-trihexylphenyl or 2,4,6-trioctylphenyl or 2,4,6-trialkoxyphenyl wherein alkoxy is C1-16 alkoxy, most preferably 2,4,6-trihexyloxyphenyl or 2,4,6-trioctyloxyphenyl or 4-thioalkylphenyl wherein thioalkyl is C1-16 thioalkyl, most preferably 4-thiohexylphenyl, 4-thiooctylphenyl or 4-thiododecylphenyl, or 2,4-dithioalkylphenyl wherein thioalkyl is C1-16 thioalkyl, most preferably 2,4-dithiohexylphenyl or 2,4-dithiooctylphenyl, or 3,5-dithioalkylphenyl wherein thioalkyl is C1-16 thioalkyl, most preferably 3,5-dithiohexylphenyl or 3,5-dithiooctylphenyl, or 2,4,6-trithioalkylphenyl wherein thioalkyl is C1-16 thioalkyl, most preferably 2,4,6-trithiohexylphenyl or 2,4,6-trithiooctylphenyl, or from thiophene that is optionally substituted, preferably in 5-position, 4,5-positions or 3,5-positions, with alkyl, alkoxy or thioalkyl having 1 to 16 C atoms, most preferably from formulae SUB7-SUB18 above,

- R^3 and R^4 are H,
- R^3 and R^4 are different from H,
- R^3 and R^4, when being different from H, are each independently selected from F, Cl or straight-chain or branched alkyl, alkoxy, sulfanylalkyl, sulfonylalkyl, alkylcarbonyl, alkoxycarbonyl and alkylcarbonyloxy, each having 1 to 20 C atoms and being unsubstituted or substituted by one or more F atoms, without being perfluorinated, or alkyl or alkoxy having 1 to 12 C atoms that is optionally fluorinated, more preferably from formulae SUB1-SUB6 above,
- R^3 and R^4 are different from H, and are each independently selected from phenyl that is substituted, preferably in 4-position, or in 2,4-positions, or in 2,4,6-positions or in 3,5-positions, with alkyl or alkoxy having 1 to 20 C atoms, preferably 1 to 16 C atoms, very preferably 4-

alkylphenyl wherein alkyl is C1-16 alkyl, most preferably 4-methylphenyl, 4-hexylphenyl, 4-octylphenyl or 4-dodecylphenyl, or 4-alkoxyphenyl wherein alkoxy is C1-16 alkoxy, most preferably 4-hexyloxyphenyl, 4-octyloxyphenyl or 4-dodecyloxyphenyl or 2,4-dialkylphenyl wherein alkyl is C1-16 alkyl, most preferably 2,4-dihexylphenyl or 2,4-dioctylphenyl or 2,4-dialkoxyphenyl wherein alkoxy is C1-16 alkoxy, most preferably 2,4-dihexyloxyphenyl or 2,4-dioctyloxyphenyl or 3,5-dialkylphenyl wherein alkyl is C1-16 alkyl, most preferably 3,5-dihexylphenyl or 3,5-dioctylphenyl or 3,5-dialkoxyphenyl wherein alkoxy is C1-16 alkoxy, most preferably 3,5-dihexyloxyphenyl or 3,5-dioctyloxyphenyl, or 2,4,6-trialkylphenyl wherein alkyl is C1-16 alkyl, most preferably 2,4,6-trihexylphenyl or 2,4,6-trioctylphenyl or 2,4,6-trialkoxyphenyl wherein alkoxy is C1-16 alkoxy, most preferably 2,4,6-trihexyloxyphenyl or 2,4,6-trioctyloxyphenyl or 4-thioalkylphenyl wherein thioalkyl is C1-16 thioalkyl, most preferably 4-thiohexylphenyl, 4-thiooctylphenyl or 4-thiododecylphenyl, or 2,4-dithioalkylphenyl wherein thioalkyl is C1-16 thioalkyl, most preferably 2,4-dithiohexylphenyl or 2,4-dithiooctylphenyl, or 3,5-dithioalkylphenyl wherein thioalkyl is C1-16 thioalkyl, most preferably 3,5-dithiohexylphenyl or 3,5-dithiooctylphenyl, or 2,4,6-trithioalkylphenyl wherein thioalkyl is C1-16 thioalkyl, most preferably 2,4,6-trithiohexylphenyl or 2,4,6-trithiooctylphenyl, or from thiophene that is optionally substituted, preferably in 5-position, 4,5-positions or 3,5-positions, with alkyl, alkoxy or thioalkyl having 1 to 16 C atoms, more preferably from formulae SUB7-SUB18 above, most preferably from subformulae SUB14-SUB18,

- R^{5-9} are H,
- at least one of R^{5-9} is different from H,
- R^{5-9}, when being different from H, are each independently selected from F, Cl, CN or straight-chain or branched alkyl, alkoxy, sulfanylalkyl, sulfonylalkyl, alkylcarbonyl, alkoxycarbonyl and alkylcarbonyloxy, each having up to 20 C atoms and being unsubstituted or substituted by one or more F atoms, preferably from F, or alkyl or alkoxy having up to 16 C atoms that is optionally fluorinated, more preferably from formulae SUB1-SUB6 above,

- R^{5-9}, when being different from H, are each independently selected from aryl or heteroaryl, preferably phenyl or thiophene, each of which is optionally substituted with one or more groups L^S as defined in formula IA and has 4 to 30 ring atoms, preferably from phenyl that is optionally substituted, preferably in 4-position, 2,4-positions, 2,4,6-positions or 3,5-positions, with alkyl or alkoxy having 1 to 20 C atoms, preferably 1 to 16 C atoms, more preferably from formulae SUB7-SUB18 above.

Another embodiment of the invention relates to a composition comprising a compound of formula I, and further comprising one or more electron donors or p-type semiconductors, preferably selected from conjugated polymers. Preferably, the conjugated polymer used in the said composition comprises at least one electron donating unit ("donor unit") and at least one electron accepting unit ("acceptor unit"), and optionally at least one spacer unit separating a donor unit from an acceptor unit, wherein each donor and acceptor units is directly connected to another donor or acceptor unit or to a spacer unit, and wherein all of the donor, acceptor and spacer units are each independently selected from arylene or heteroarylene that has from 5 to 20 ring atoms, is mono- or polycyclic, optionally contains fused rings, are is unsubstituted or substituted by one or more identical or different groups L^S as defined above.

Preferably the spacer units, if present, are located between the donor and acceptor units such that a donor unit and an acceptor unit are not directly connected to each other.

Preferred conjugated polymers comprise, very preferably consist of, one or more units selected from formula U1, U2 and U3, and/or one or more units selected from formula U4, U5, U6 and U7

-(D-Sp)- U1

-(A-Sp)- U2

-(A-D)- U3

-(D)- U4

-(Sp-D-Sp)- U5

-(A)- U6

-(Sp-A-Sp)- U7

wherein D denotes a donor unit, A denotes an acceptor unit and Sp denotes a spacer unit, all of which are selected, independently of each other and on each occurrence identically or differently, from arylene or heteroarylene that has from 5 to 20 ring atoms, is mono- or polycyclic, optionally contains fused rings, are is unsubstituted or substituted by one or more identical or different groups L as defined above.

Very preferred are polymers of formula Pi-Pviii

$-[(D\text{-}Sp)_x\text{-}(A\text{-}Sp)_y]_n-$ Pi

$-[(A\text{-}D)_x\text{-}(A\text{-}Sp)_y]_n-$ Pii

$-[(D)_x\text{-}(Sp\text{-}A\text{-}Sp)_y]_n-$ Piii

$-[D\text{-}Sp\text{-}A\text{-}Sp]_n-$ Piv

$-[D\text{-}A]_n-$ Pv

$-[D\text{-}Sp\text{-}A\text{-}Sp]_n$ Pvi

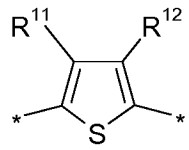
$-[D^1\text{-}A\text{-}D^2\text{-}A]_n$ Pvii

$-[D\text{-}A^1\text{-}D\text{-}A^2]_n$ Pviii

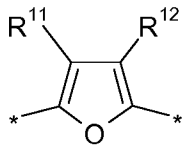
wherein A, D and Sp are as defined in formula U1-U7, A and D can each, in case of multiple occurrence, also have different meanings, D^1 and D^2 have one of the meanings given for D and are different from each other, A^1 and A^2

have one of the meanings given for A and are different from each other, x and y denote the molar fractions of the corresponding units, x and y are each, independently of one another, a non-integer >0 and <1, with x+y=1, and n is an integer >1.

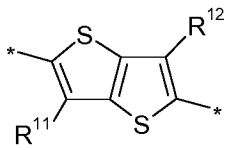
Especially preferred are repeating units and polymers of formulae U1-U7 and Pi-viii wherein D, D^1 and D^2 are selected from the group consisting of the following formulae



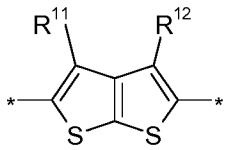
(D1)



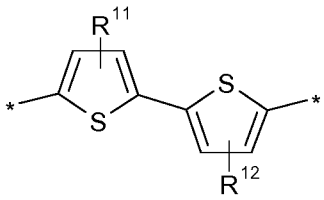
(D7)



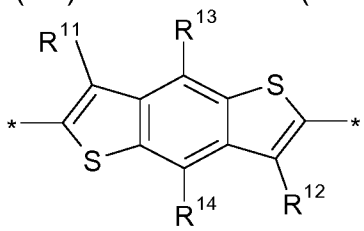
(D10)



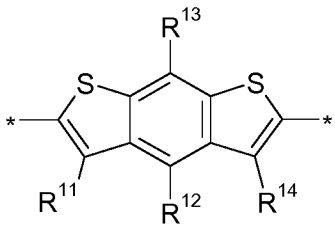
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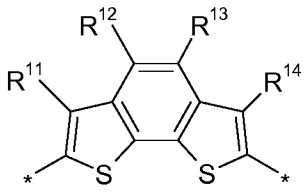
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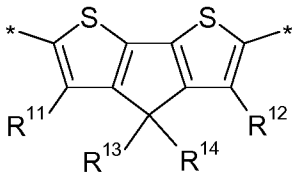
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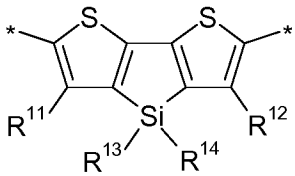
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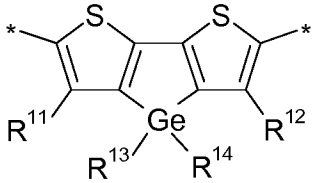
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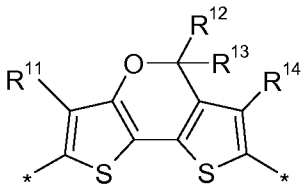
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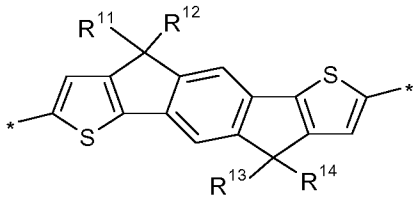


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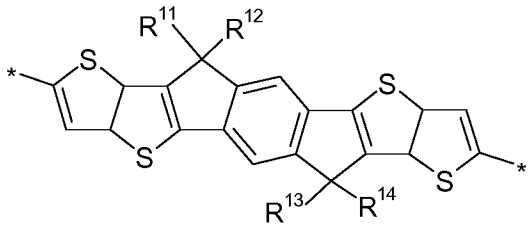


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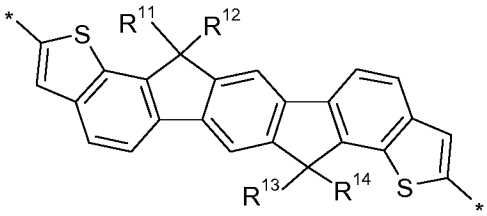




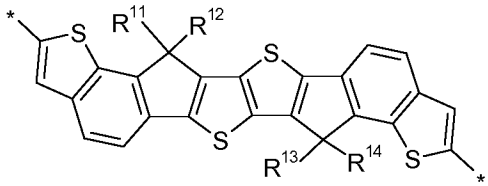
(D44) (D55)



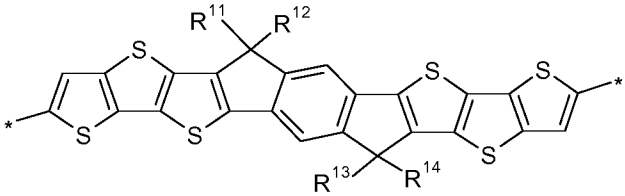
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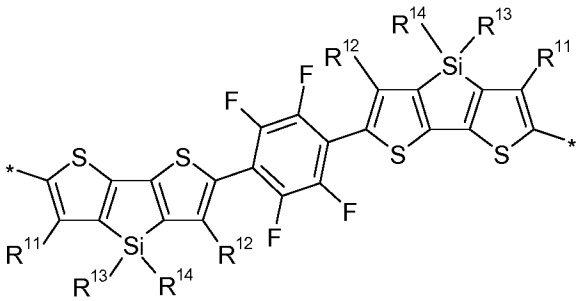
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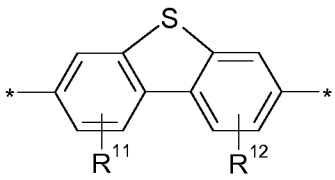
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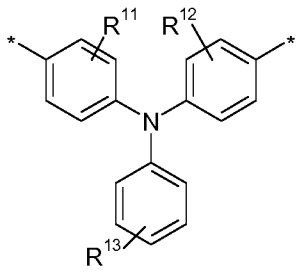
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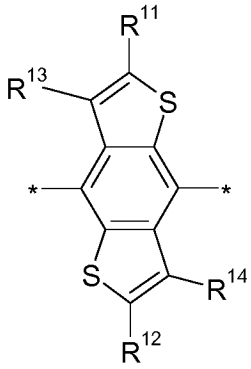
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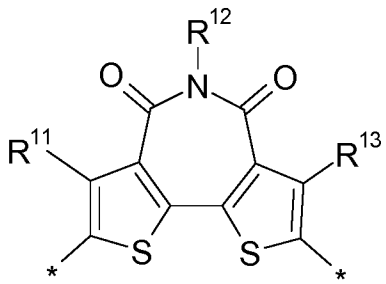
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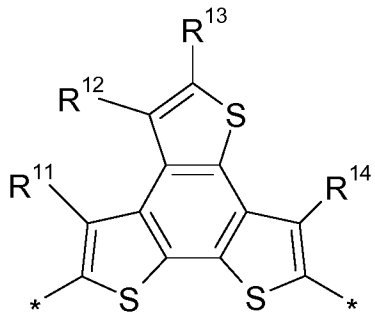
(D111)



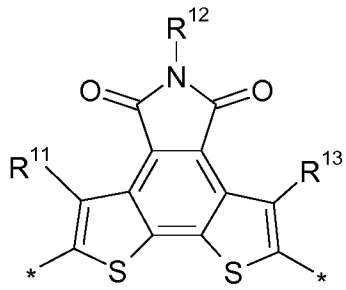
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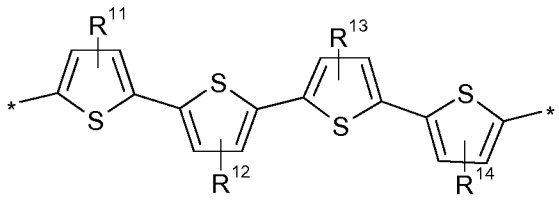
(D140



(D141)



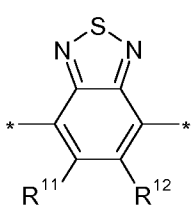
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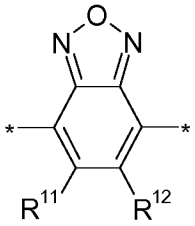
(D147)

wherein R^{11}, R^{12}, R^{13}, R^{14} independently of each other denote H or have one of the meanings of L^S, preferably of R^7, as defined above, and wherein preferably at least one of R^{11}, R^{12}, R^{13} and R^{14} is different from H and in formula D147 preferably R^{12} and R^{13} are F and R^{11} and R^{14} are H or C1-C30 alkyl.

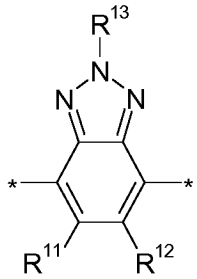
Further preferred are repeating units and polymers of formulae U1-U7 and Pi-viii wherein A, A^1 and A^2 are selected from the group consisting of the following formulae



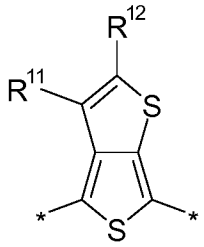
(A1)



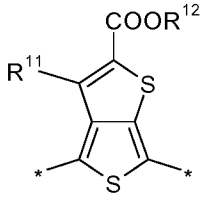
(A2)



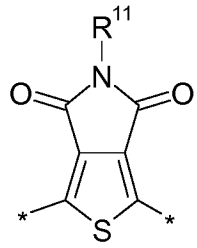
(A5)



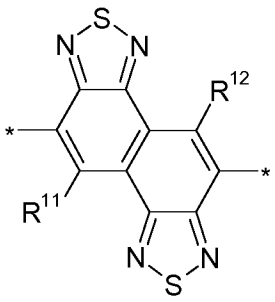
(A15)



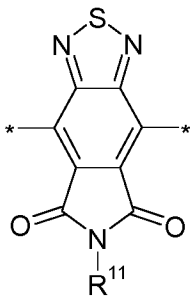
(A16)



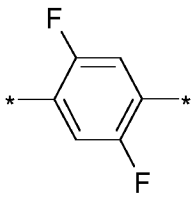
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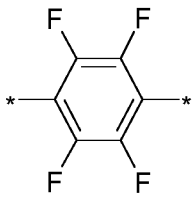
(A74)



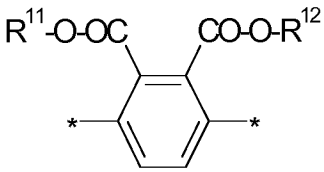
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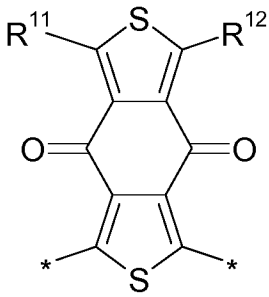
(A92)



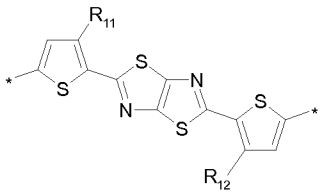
(A94)



(A98)



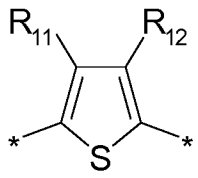
(A99)



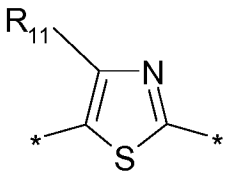
(A100)

wherein R^{11}, R^{12}, R^{13}, R^{14} independently of each other denote H or have one of the meanings of L^S, preferably of R^7, as defined above.

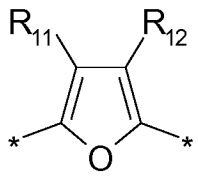
Further preferred are repeating units and polymers of formulae U1-U7 and Pi-Pviii wherein Sp is selected from the group consisting of the following formulae



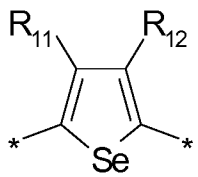
Sp1



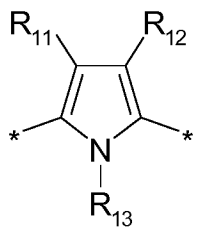
Sp2



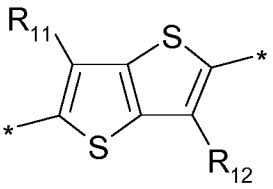
Sp3



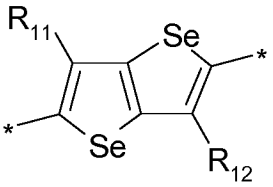
Sp4



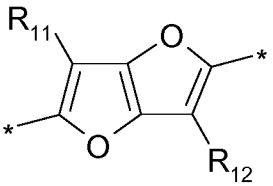
Sp5



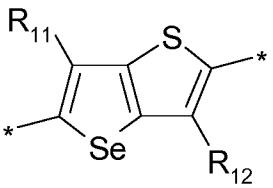
Sp6



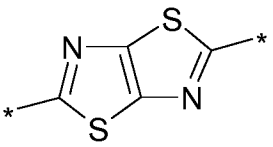
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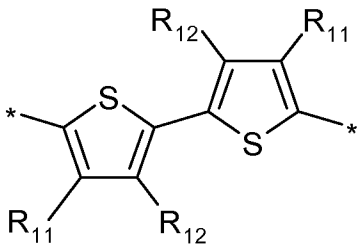
Sp8



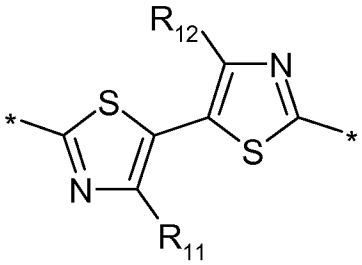
Sp9



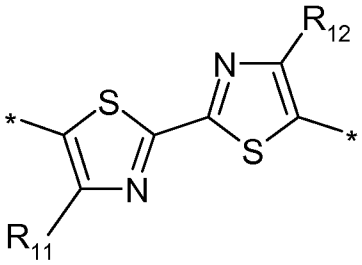
Sp10



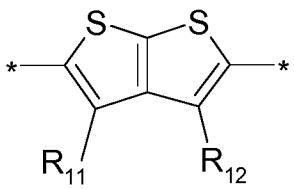
Sp11



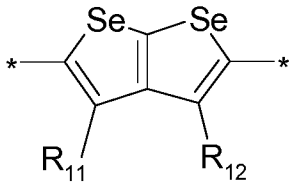
Sp12



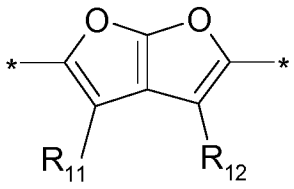
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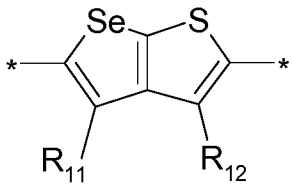
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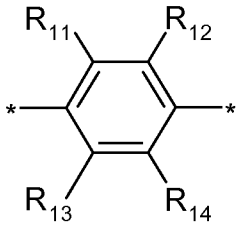
Sp15



Sp16



Sp17



Sp18

wherein R^{11}, R^{12}, R^{13}, R^{14} independently of each other denote H or have one of the meanings of L as defined above.

In the formulae Sp1 to Sp17 preferably R^{11} and R^{12} are H. In formula Sp18 preferably R^{11-14} are H or F.

Preferably the conjugated polymer contains, preferably consists of

a) one or more donor units selected from the group consisting of the formulae D1, D7, D10, D11, D19, D22, D29, D30, D35, D36, D37, D44, D55, D84, D87, D88, D89, D93, D106, D111, D119, D140, D141, D146, and D147 and/or

b) one or more acceptor units selected from the group consisting of the formulae A1, A2, A5, A15, A16, A20, A74, A88, A92, A94 and A98, A99, A100

and

c) optionally one or more spacer units selected from the group consisting of the formulae Sp1-Sp18, very preferably of the formulae Sp1, Sp6, Sp11 and Sp14,

wherein the spacer units, if present, are preferably located between the donor and acceptor units such that a donor unit and an acceptor unit are not directly connected to each other.

In a second preferred embodiment the conjugated polymer comprises, preferably consists of

one or more, preferably one, two, three or four, distinct repeating units D, and

one or more, preferably one, two or three, distinct repeating units A.

Preferably the conjugated polymer according to this second preferred embodiment contains from one to six, very preferably one, two, three or four distinct units D and from one to six, very preferably one, two, three or four distinct units A, wherein d1, d2, d3, d4, d5 and d6 denote the molar ratio of each distinct unit D, and a1, a2, a3, a4, a5 and a6 denote the molar ratio of each distinct unit A, and

each of d1, d2, d3, d4, d5 and d6 is from 0 to 0.6, and
d1+d2+d3+d4+d5+d6 is from 0.2 to 0.8, preferably from 0.3 to 0.7, and

each of a1, a2, a3, a4, a5 and a6 is from 0 to 0.6, and
a1+a2+a3+a4+a5+d6 is from 0.2 to 0.8, preferably from 0.3 to 0.7, and

d1+d2+d3+d4+d5+d6+a1+a2+a3+a4+a5+a6 is from 0.8 to 1, preferably 1.

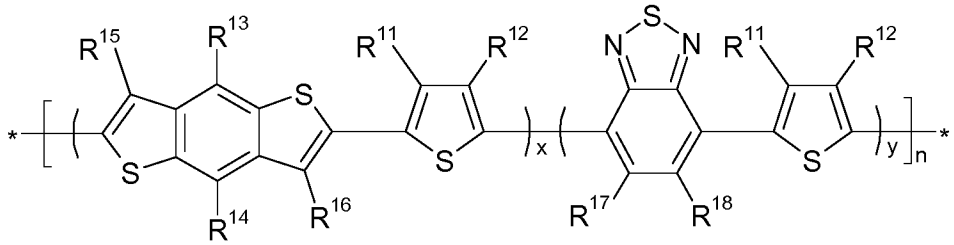
Preferably the conjugated polymer according to this second preferred embodiment contains, preferably consists of

a) one or more donor units selected from the group consisting of the formulae D1, D7, D10, D11, D19, D22, D29, D30, D35, D36, D37, D44, D55, D84, D87, D88, D89, D93, D106, D111, D119, D140, D141, D146, and D147 and/or
b) one or more acceptor units selected from the group consisting of the formulae A1, A2, A5, A15, A16, A20, A74, A88, A92, A94, A98, A99 and A100.

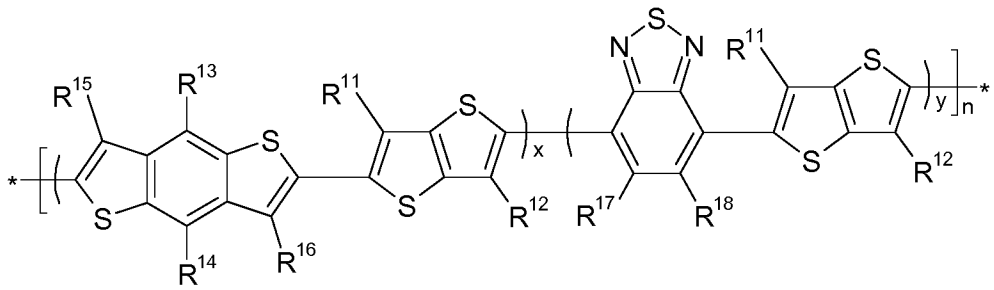
In the above conjugated polymers, like those of formula P and its subformulae, the total number of repeating units n is preferably from 2 to 10,000. The total number of repeating units n is preferably $\geq$ 5, very preferably $\geq$ 10, most preferably $\geq$ 50, and preferably $\leq$ 500, very preferably $\leq$ 1,000, most preferably $\leq$ 2,000, including any combination of the aforementioned lower and upper limits of n.

The conjugated polymers are preferably statistical or random copolymers.

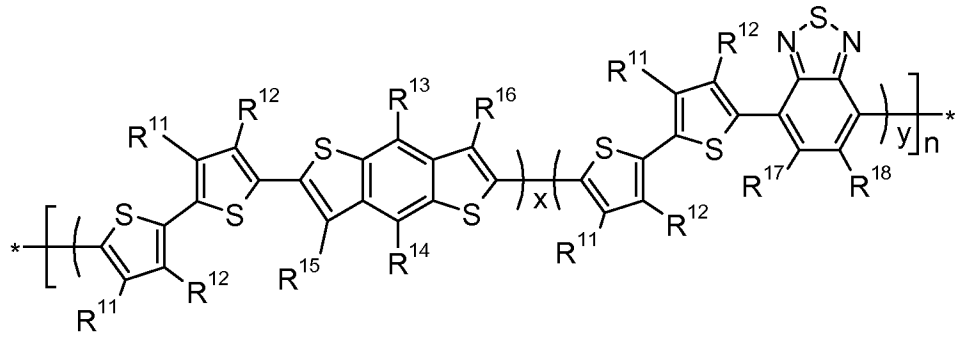
Very preferred conjugated polymers are selected from the following formulae



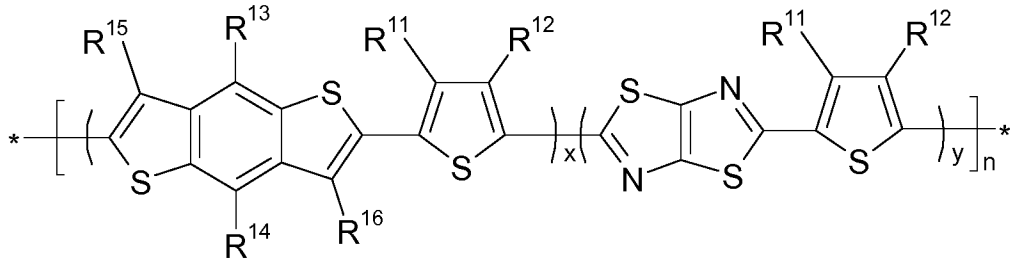
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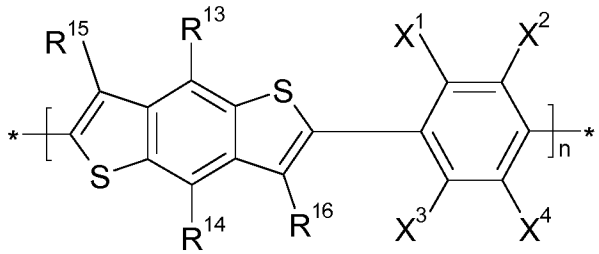
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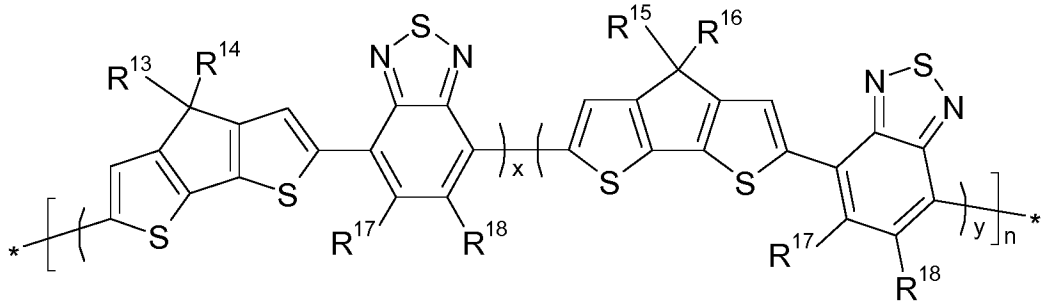
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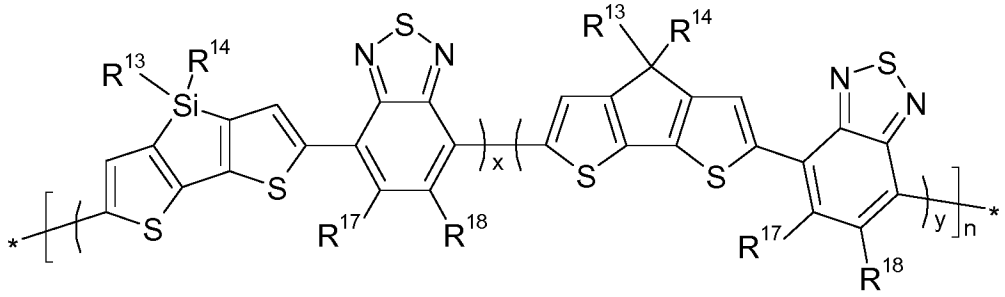
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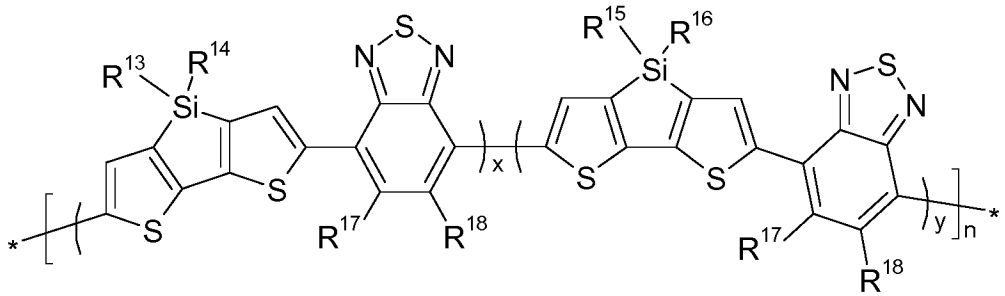
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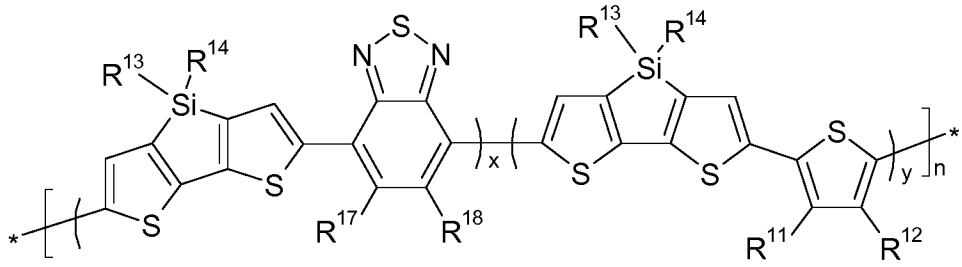
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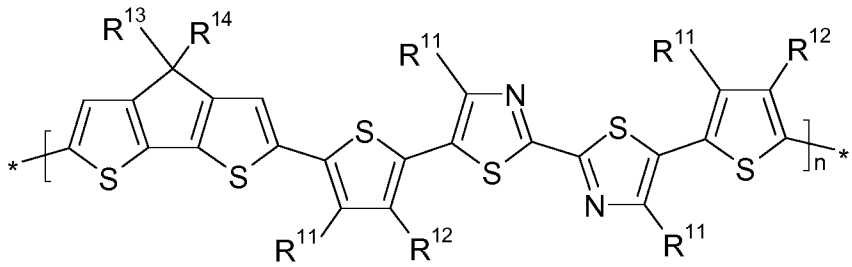
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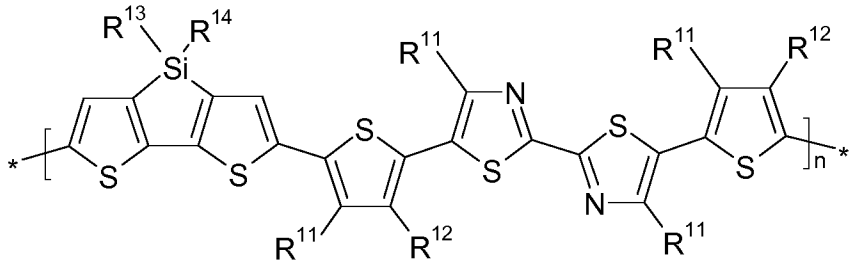
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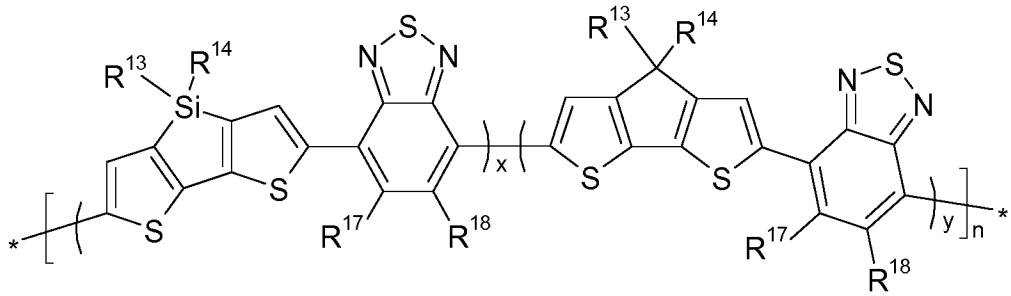
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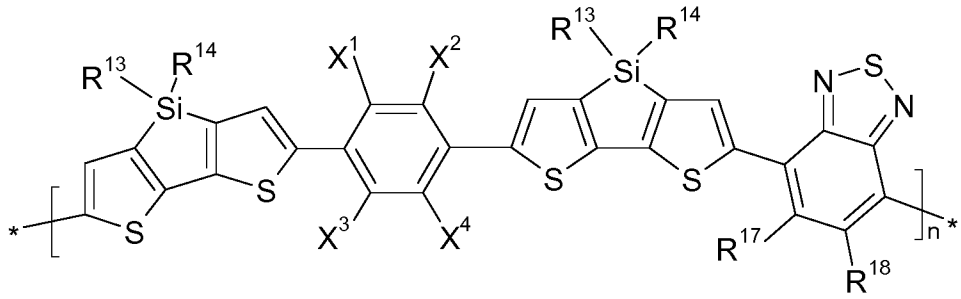
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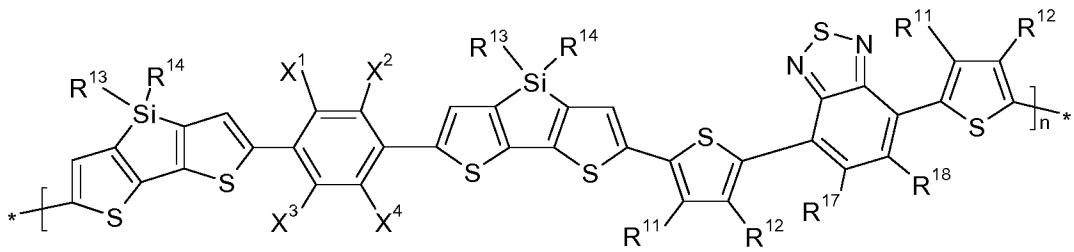
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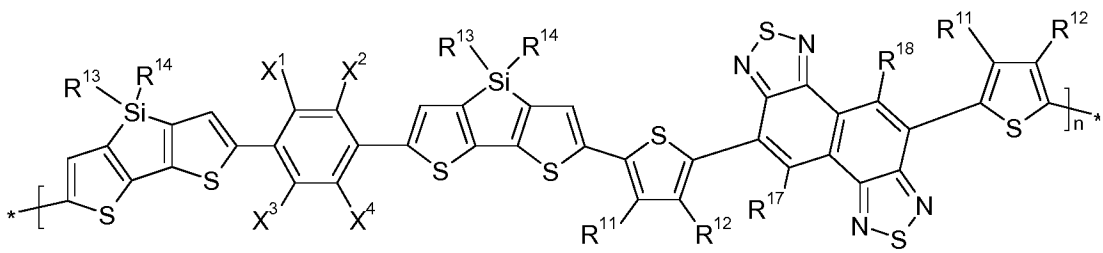
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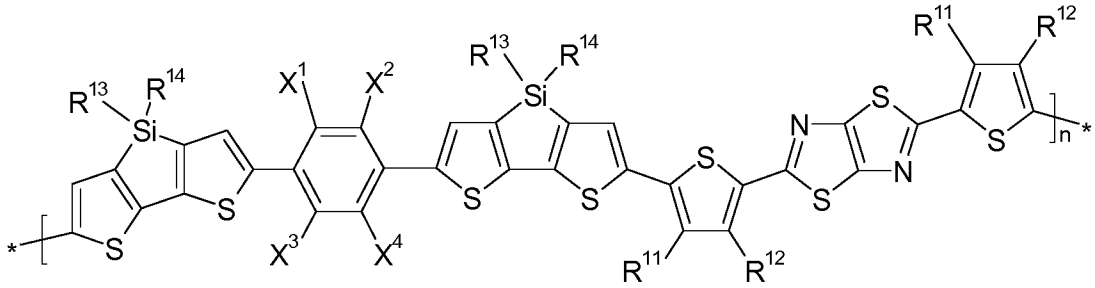
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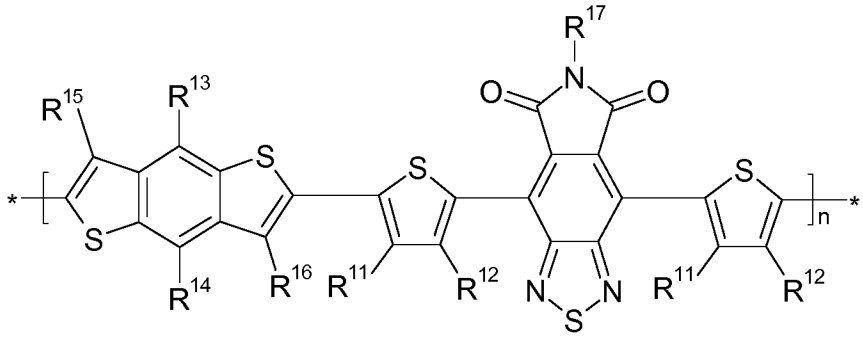
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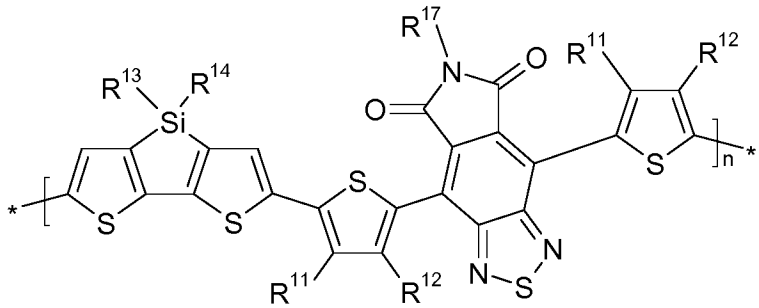
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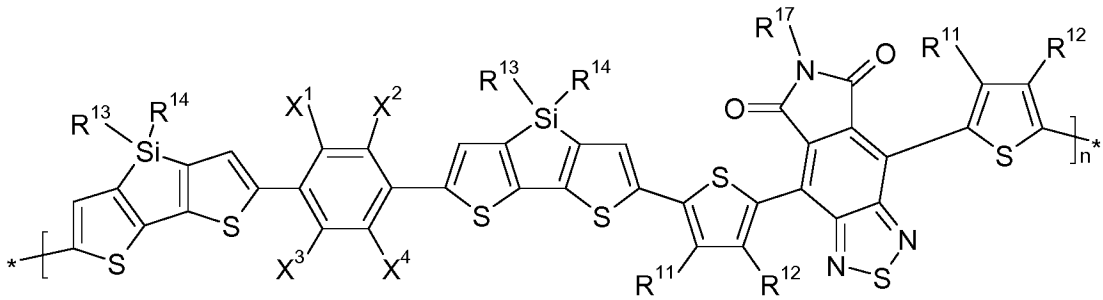
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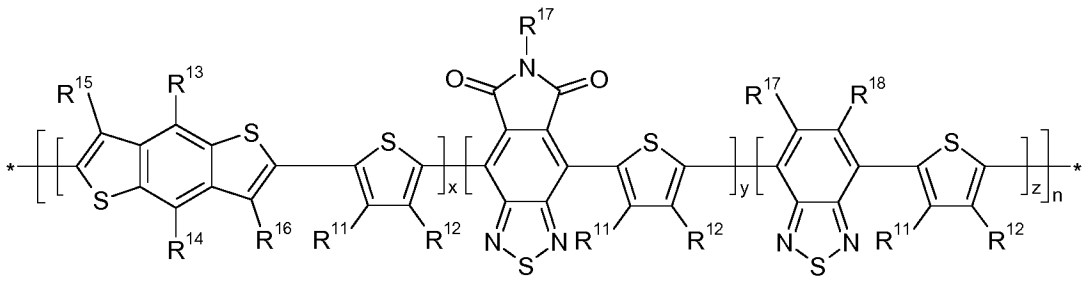
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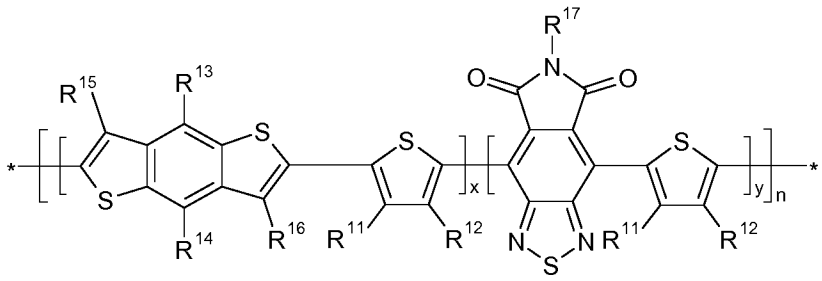
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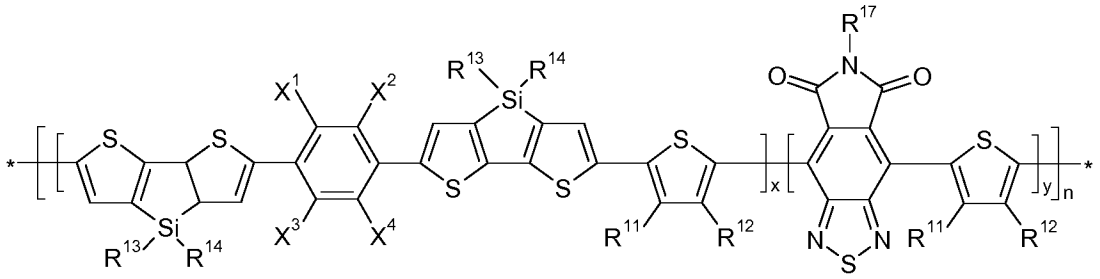
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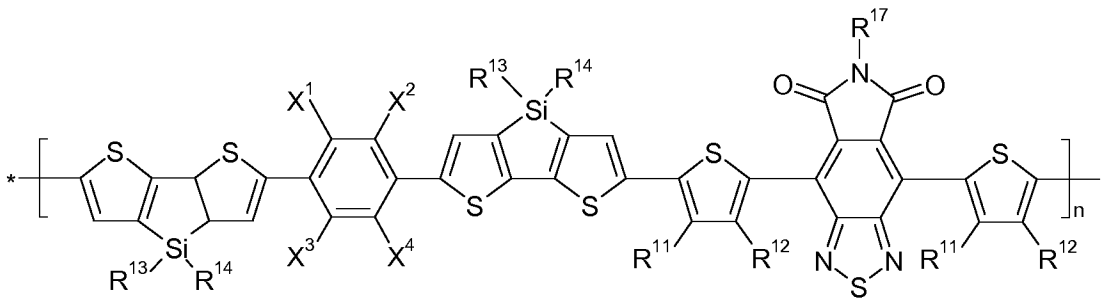
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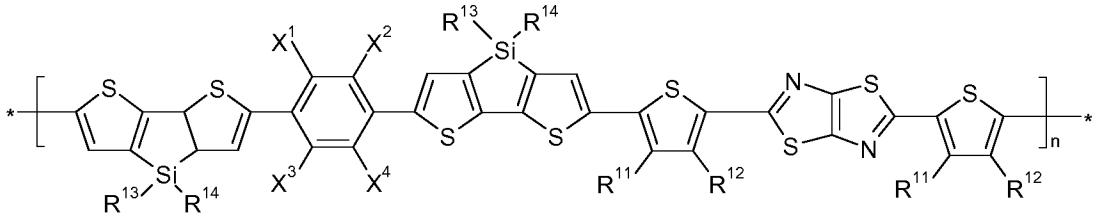
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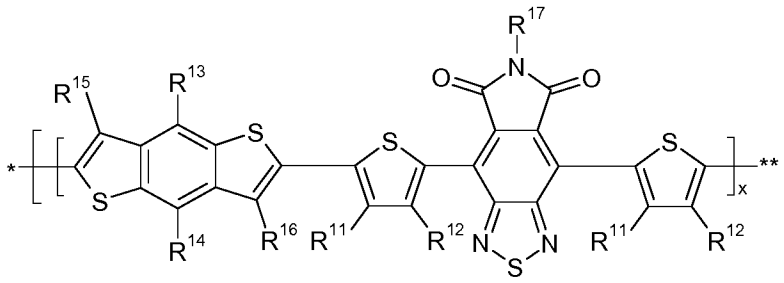
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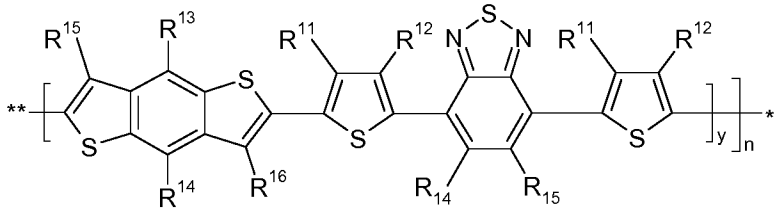
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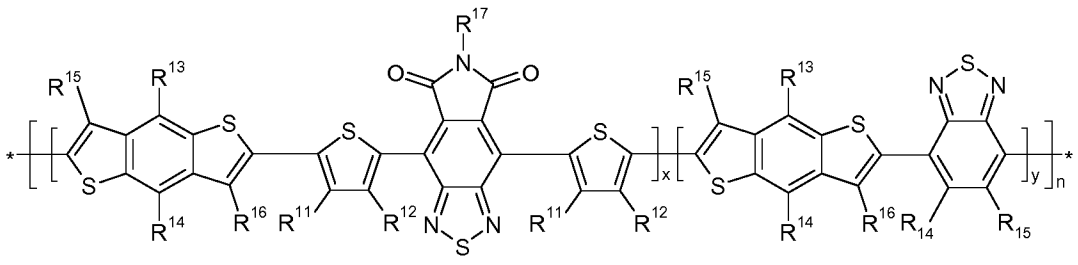


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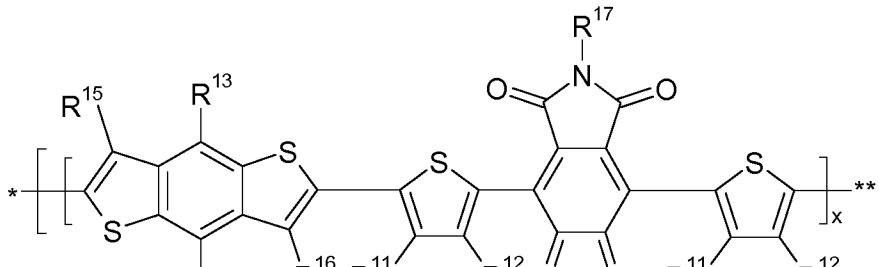


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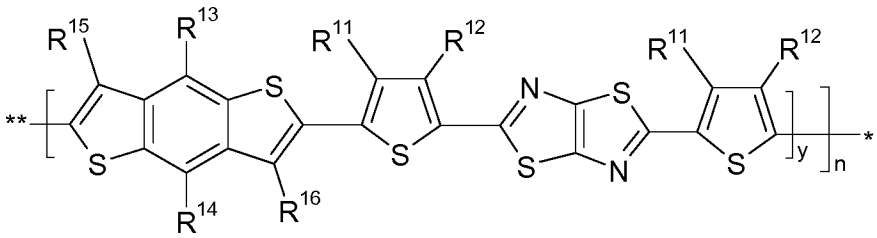


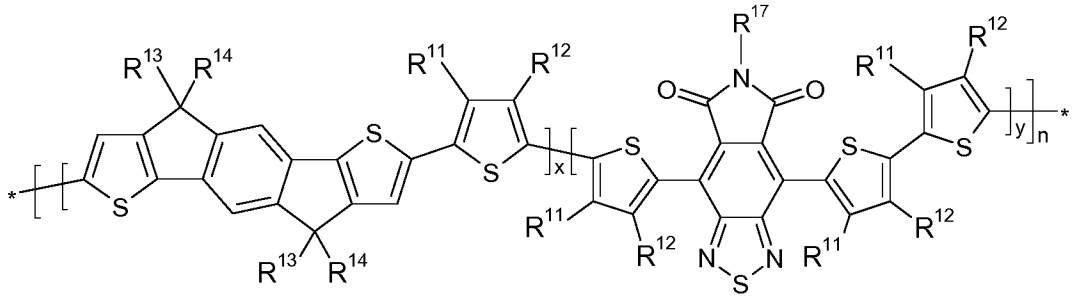


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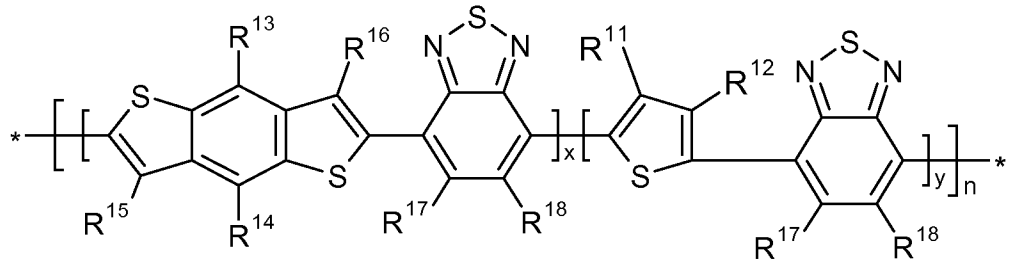


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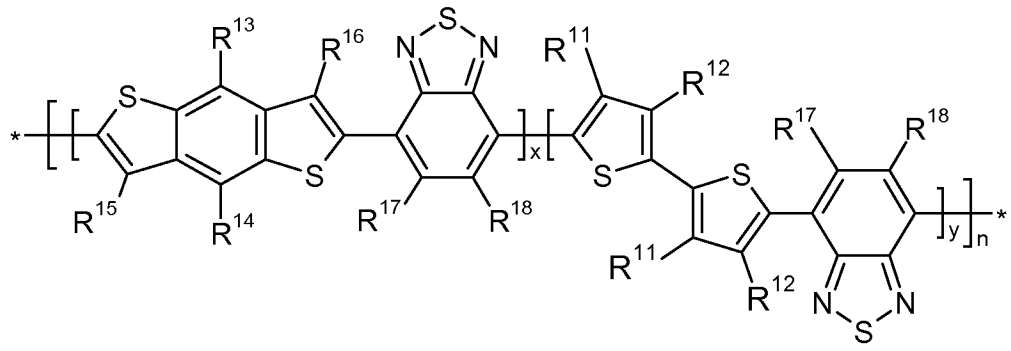




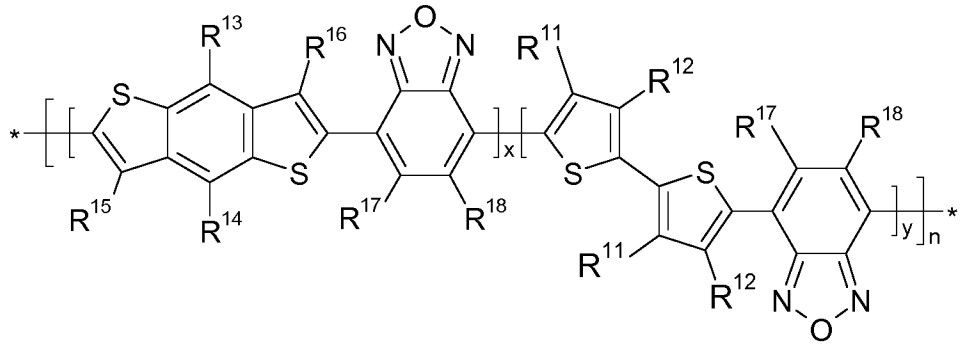
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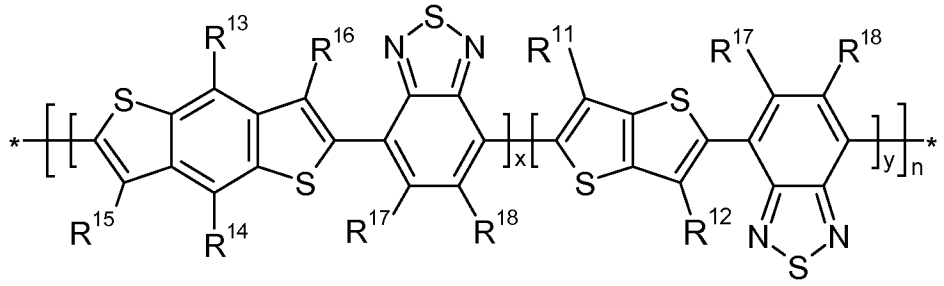
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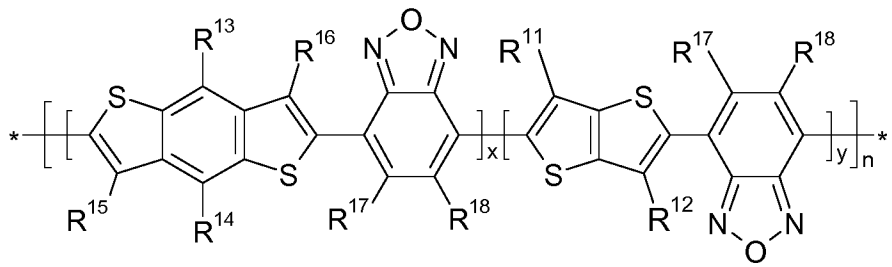
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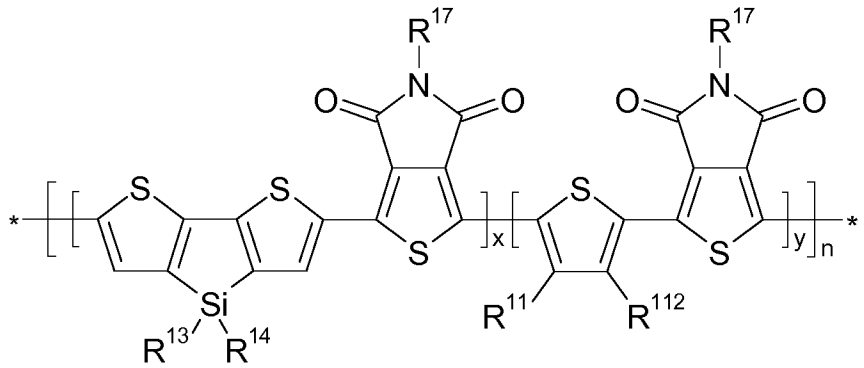
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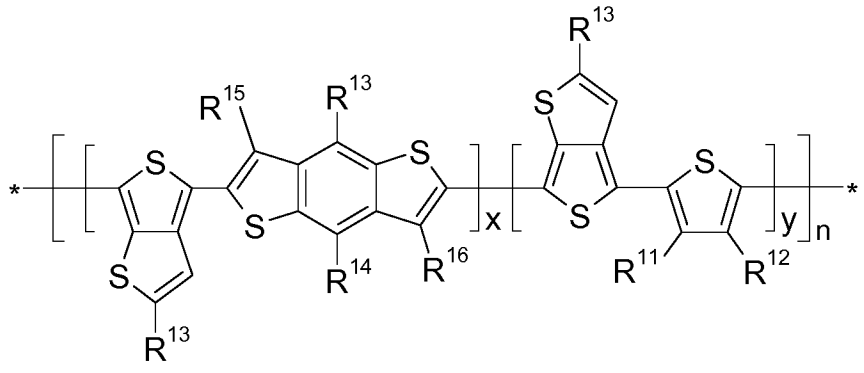
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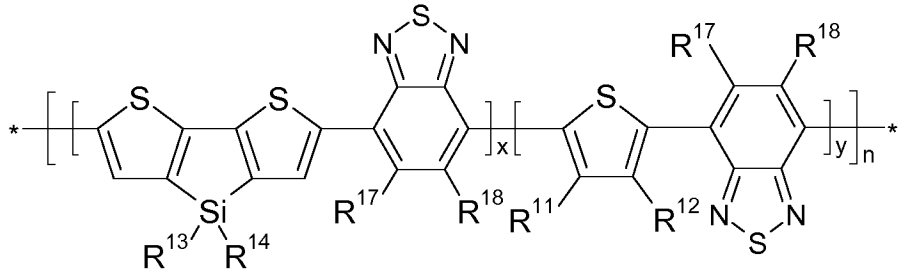
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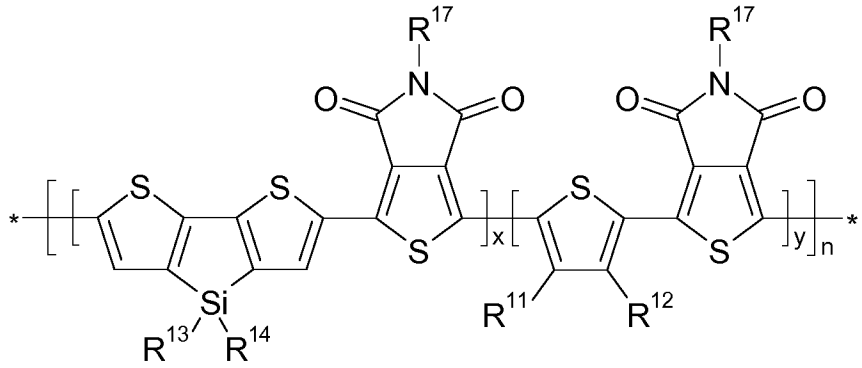
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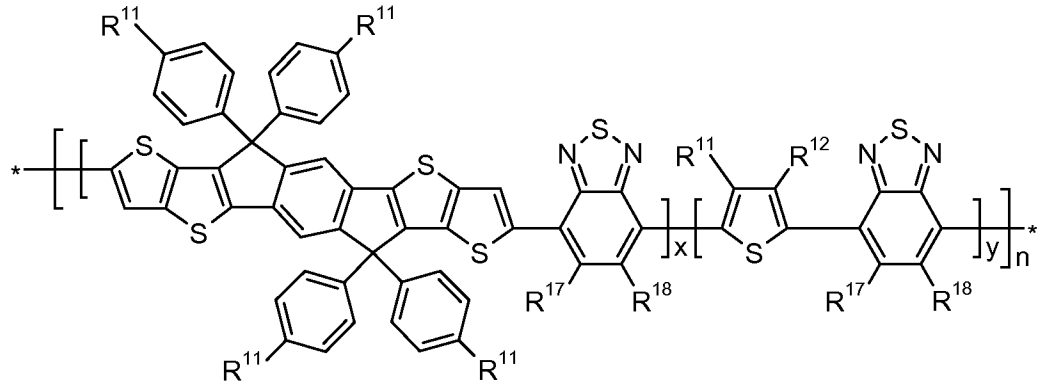
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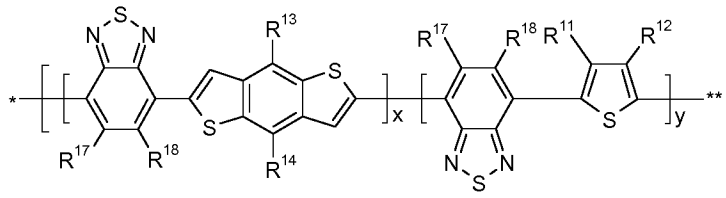
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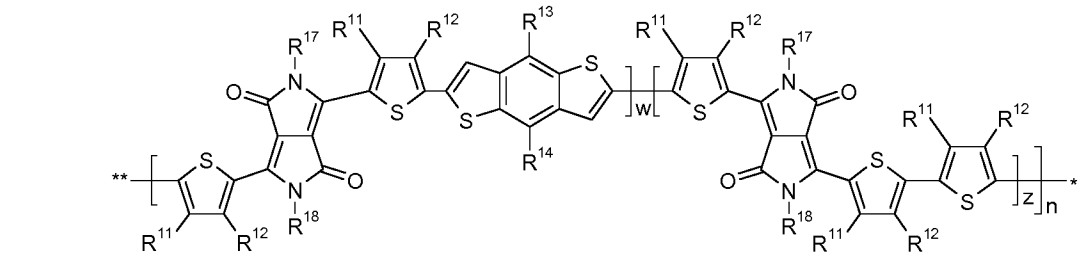
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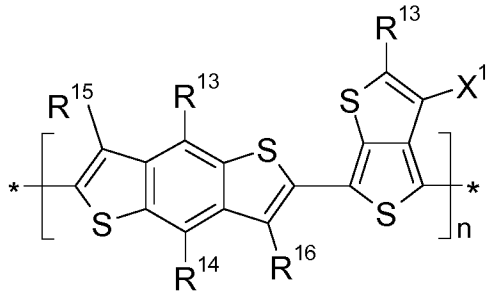
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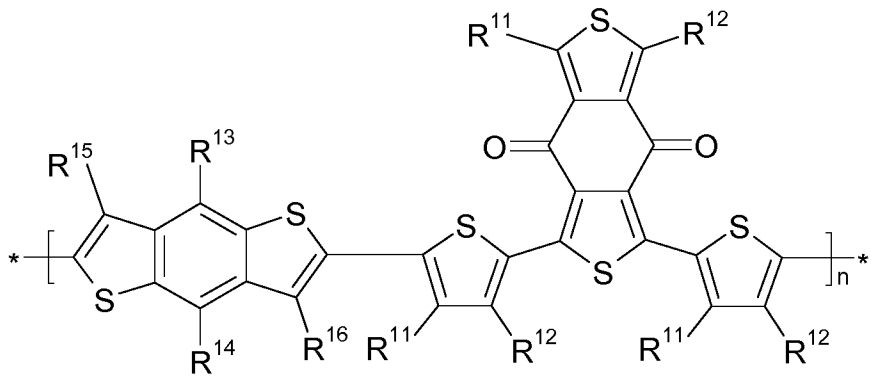
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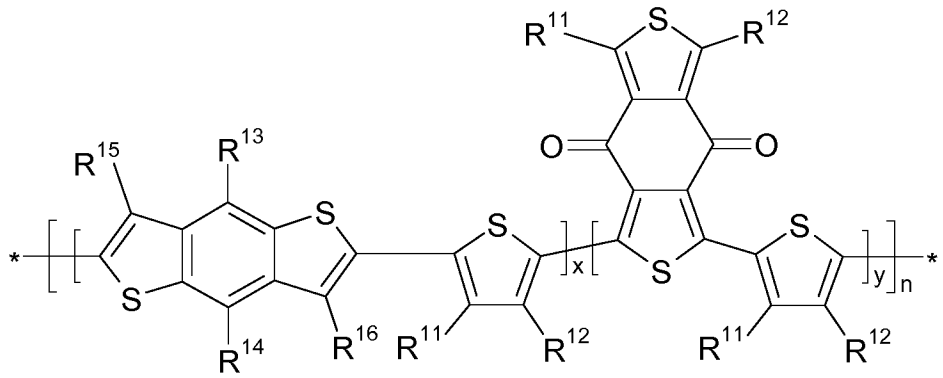
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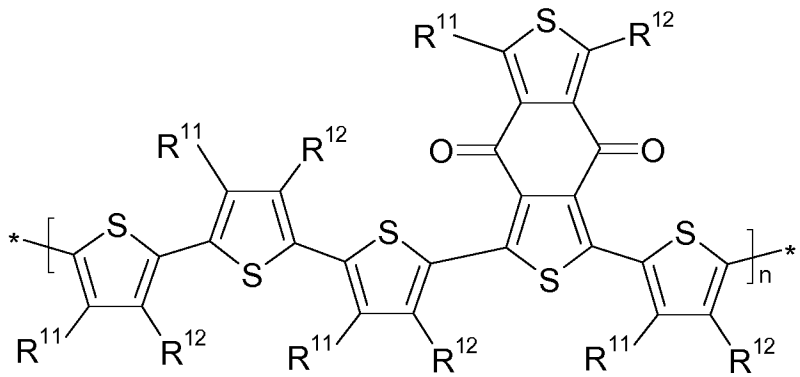
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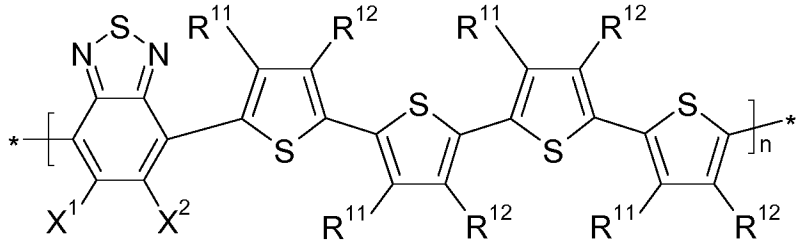


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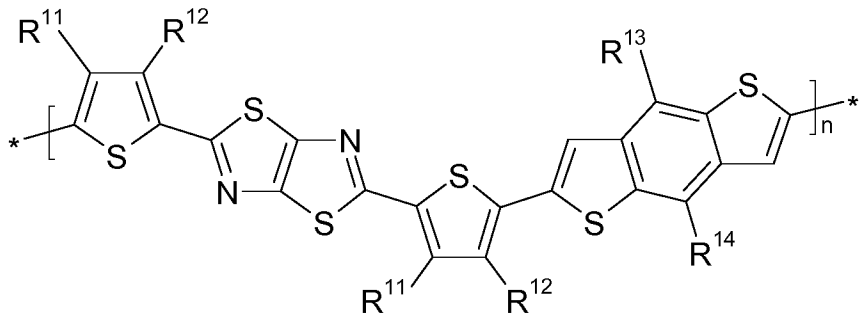


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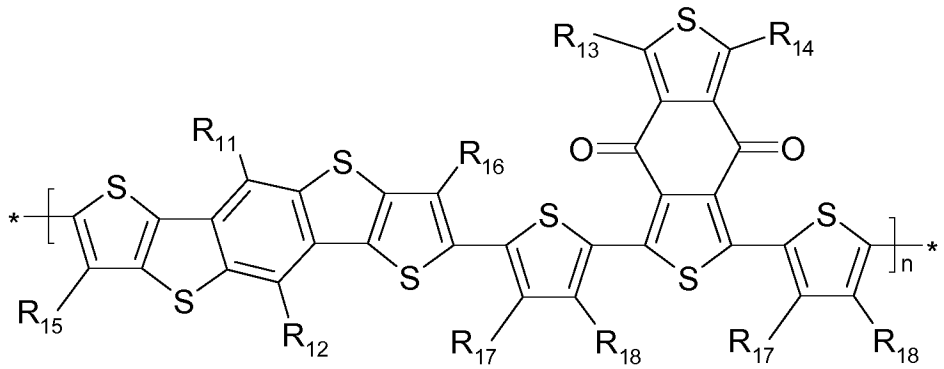




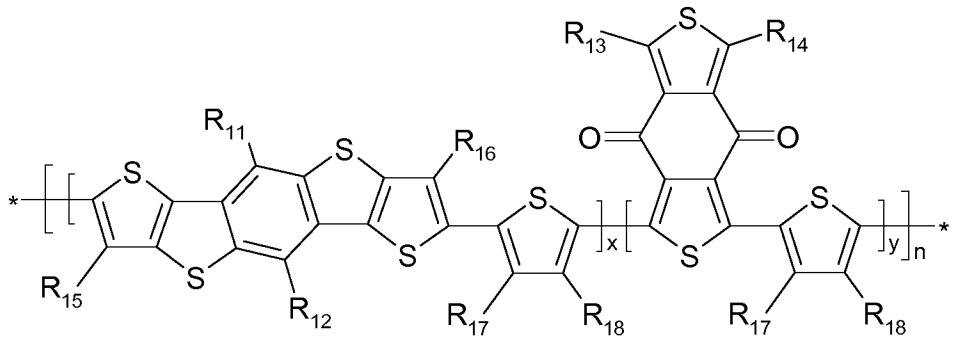
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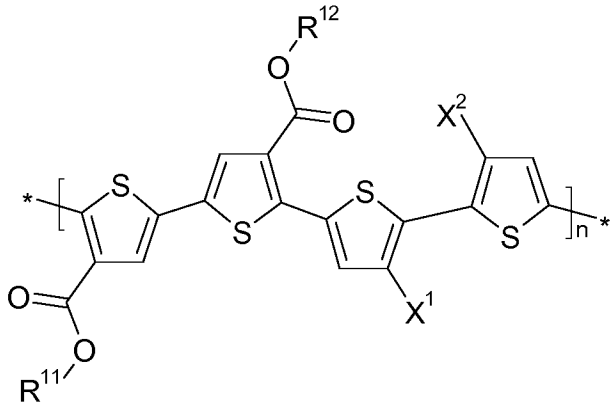
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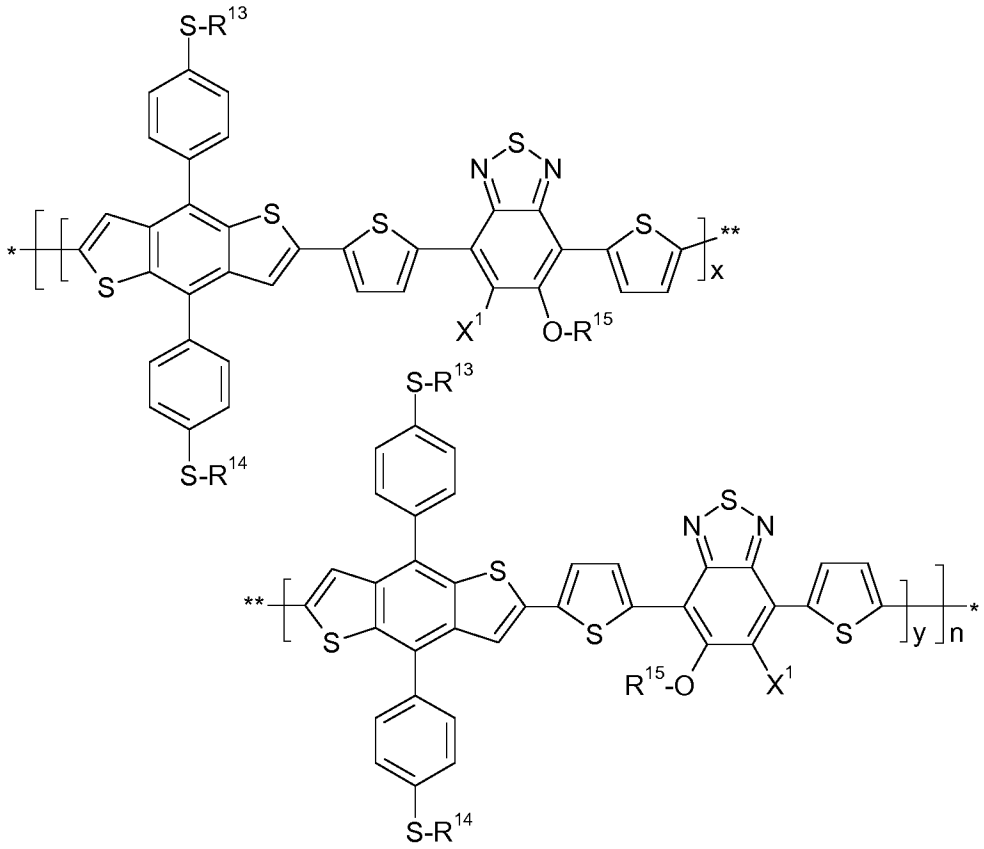
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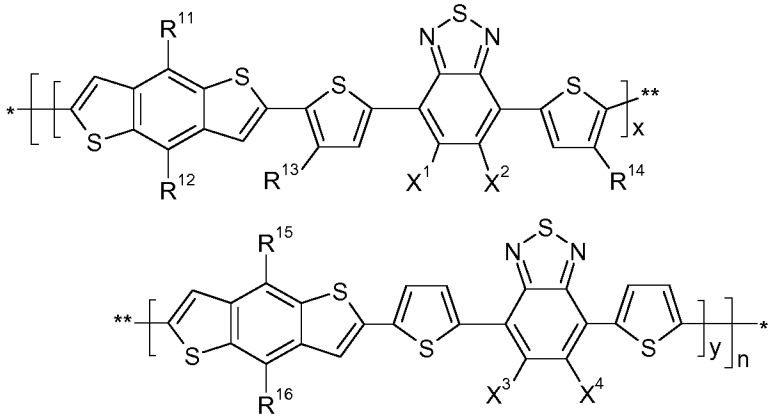


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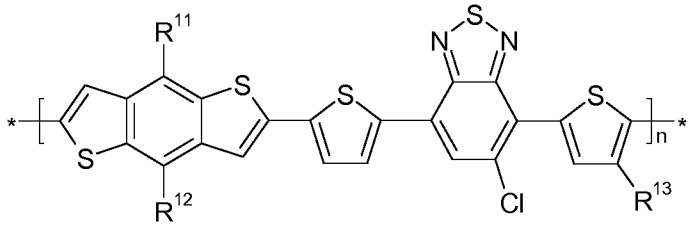


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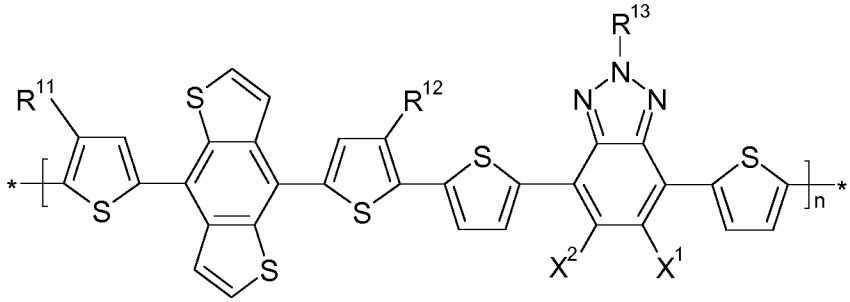
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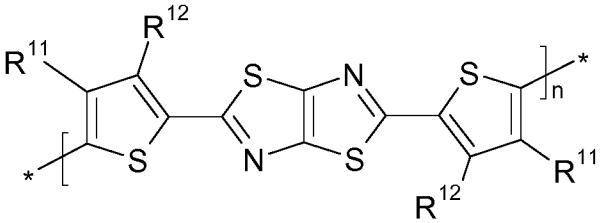
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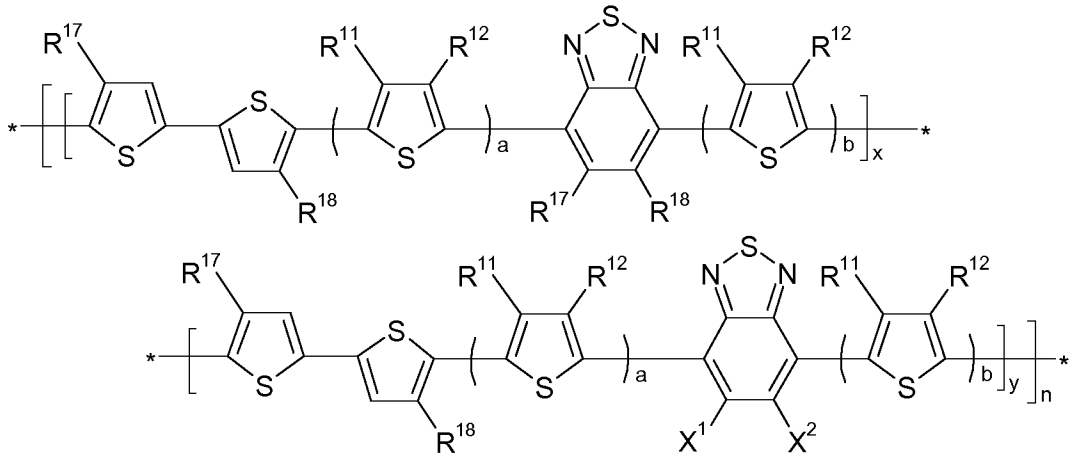


P52



P53





P54

wherein R^{11-14}, x, y and n are as defined above, w and z have one of the meanings given for y, x+y+w+z=1, R^{15}, R^{16}, R^{17} and R^{18} have one of the meanings given for R^{11}, and X^1, X^2, X^3 and X^4 denote H, F or Cl.

Further preferred are polymers comprising one of the formulae P1-P54 as one or more repeating unit.

In the polymers of formula Pi-viii and P1-P54 which are composed of two building blocks $[\ ]_x$ and $[\ ]_y$, x and y are preferably from 0.1 to 0.9, very preferably from 0.25 to 0.75, most preferably from 0.4 to 0.6.

In the polymers of formula Pi-viii which are composed of three building blocks $[\ ]_x$, $[\ ]_y$,and $[\ ]_z$, x, y and z are preferably from 0.1 to 0.8, very preferably from 0.2 to 0.6, most preferably from 0.25 to 0.4.

In the formulae P1-P54 preferably one or more of X^1, X^2, X^3 and X^4 denote F, very preferably all of X^1, X^2, X^3 and X^4 denote F or X^1 and X^2 denote H and X^3 and X^4 denote F.

In the formulae P1-P54 preferably R^{11} and R^{12} are H. Further preferably R^{11} and R^{12}, when being different from H, denote straight-chain or branched alkyl with 1 to 30, preferably 1 to 20, C atoms that is optionally fluorinated.

In the formulae P1-P54, preferably R^{15} and R^{16} are H, and R^{13} and R^{14} are different from H.

In formula P54 preferably R^{17} and R^{18} are F. Further preferably in formula P54 one or both of R^{11} and R^{12} are C1-C30 alkyl.

In the formulae P1-P54, preferably R^{13}, R^{14}, R^{15} and R^{16}, when being different from H, are each independently selected from the following groups:

- the group consisting of straight-chain or branched alkyl, alkoxy or sulfanylalkyl with 1 to 30, preferably 1 to 20, C atoms that is optionally fluorinated,
- the group consisting of straight-chain or branched alkylcarbonyl or alkylcarbonyloxy with 2 to 30, preferably 2 to 20, C atoms, that is optionally fluorinated.

In the formulae P1-P54, preferably R^{17} and R^{18}, when being different from H, are each independently selected from the following groups:

- the group consisting of straight-chain or branched alkyl, alkoxy or sulfanylalkyl with 1 to 30, preferably 1 to 20, C atoms that is optionally fluorinated,
- the group consisting of straight-chain or branched alkylcarbonyl or alkylcarbonyloxy with 2 to 30, preferably 2 to 20, C atoms, that is optionally fluorinated.
- the group consisting of F and Cl.

Further preferred are conjugated polymers selected of formula PT

R^{31}-chain-R^{32} PT

wherein “chain” denotes a polymer chain selected of formula Pi-Pviii or P1-P54, and R^{31} and R^{32} have independently of each other one of the meanings of R^{11} as defined above, or denote, independently of each other, H, F, Br, Cl, I, -CH_2Cl, -CHO, -CR'=CR"$_2$, -SiR'R"R"', -SiR'X'X", -SiR'R"X', -

$SnR'R''R'''$, -BR'R'', -B(OR')(OR''), $-B(OH)_2$, $-O-SO_2-R'$, -C≡CH, $-C\equiv C-SiR'_3$, -ZnX' or an endcap group, X' and X'' denote halogen, R', R'' and R''' have independently of each other one of the meanings of R^0 given in formula 1, and preferably denote alkyl with 1 to 12 C atoms, and two of R', R'' and R''' may also form a cyclosilyl, cyclostannyl, cycloborane or cycloboronate group with 2 to 20 C atoms together with the respective hetero atom to which they are attached.

Preferred endcap groups R^{31} and R^{32} are H, C_{1-20} alkyl, or optionally substituted C_{6-12} aryl or C_{2-10} heteroaryl, very preferably H, phenyl or thiophene.

The compounds of formula IA, IB and their subformulaeand the conjugated polymers of formula Pi-viii, P1-P54 and PT can be synthesized according to or in analogy to methods that are known to the skilled person and are described in the literature. Other methods of preparation can be taken from the examples.

For example, the compounds of the present invention can be suitably prepared by aryl-aryl coupling reactions, such as Yamamoto coupling, Suzuki coupling, Stille coupling, Sonogashira coupling, Heck coupling or Buchwald coupling. The educts can be prepared according to methods which are known to the person skilled in the art.

Preferred aryl-aryl coupling methods used in the synthesis methods as described above and below are Yamamoto coupling, Kumada coupling, Negishi coupling, Suzuki coupling, Stille coupling, Sonogashira coupling, Heck coupling, C-H activation coupling, Ullmann coupling or Buchwald coupling. Especially preferred are Suzuki coupling, Negishi coupling, Stille coupling and Yamamoto coupling. Suzuki coupling is described for example in WO 00/53656 A1. Negishi coupling is described for example in *J. Chem. Soc., Chem. Commun.*, **1977**, 683-684. Yamamoto coupling is described in for example in T. Yamamoto *et al.*, *Prog. Polym. Sci.*, **1993**, *17*, 1153-1205, or WO 2004/022626 A1. Stille coupling is described for example in Z. Bao et al., *J. Am. Chem. Soc.*, 1995, *117*, 12426–12435 and C-H activation is described for example in M. Leclerc et al, *Angew. Chem.*

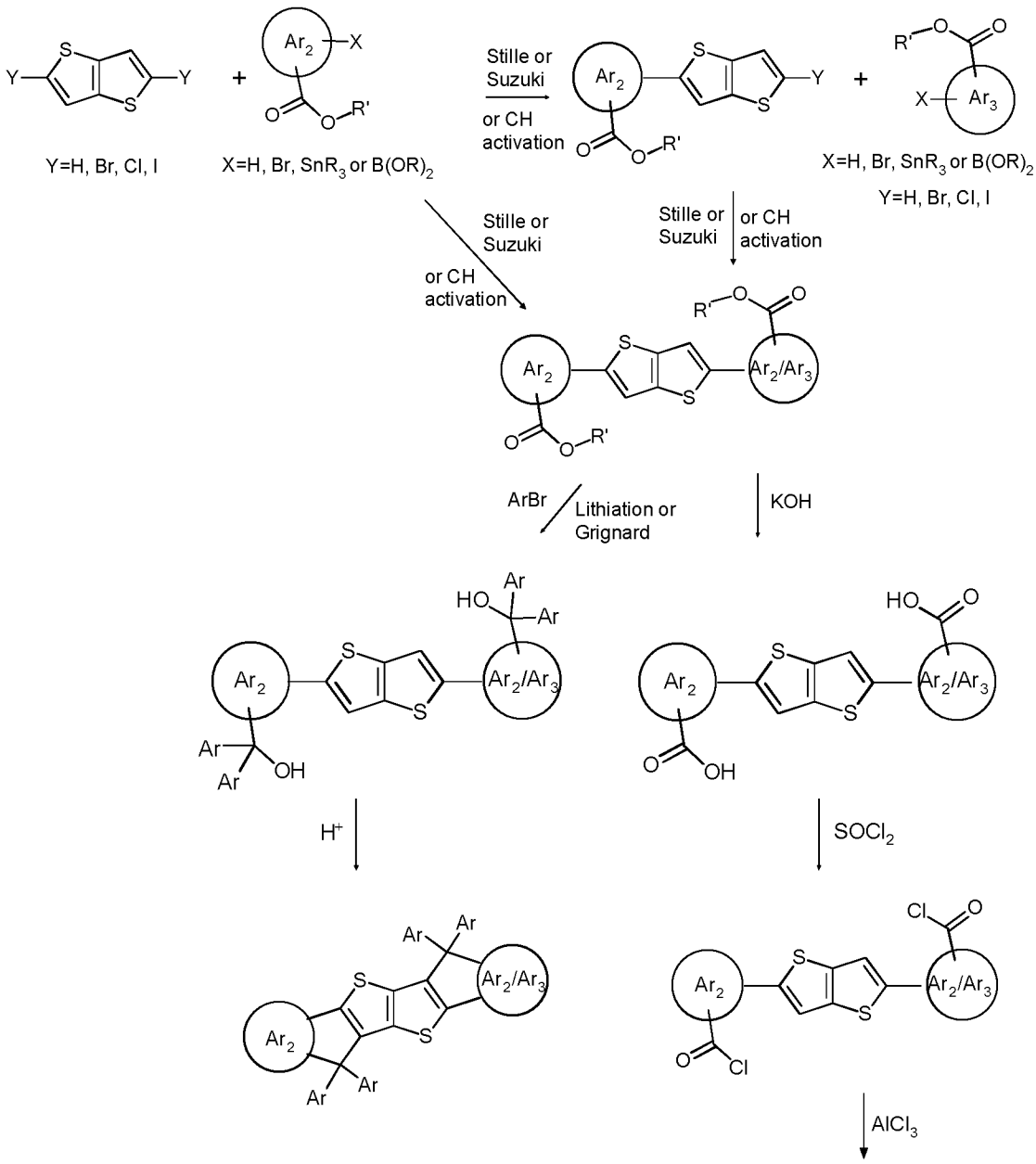
Int. Ed., 2012, 51, 2068–2071.For example, when using Yamamoto coupling, educts having two reactive halide groups are preferably used. When using Suzuki coupling, educts having two reactive boronic acid or boronic acid ester groups or two reactive halide groups are preferably used. When using Stille coupling, edcuts having two reactive stannane groups or two reactive halide groups are preferably used. When using Negishi coupling, educts having two reactive organozinc groups or two reactive halide groups are preferably used.

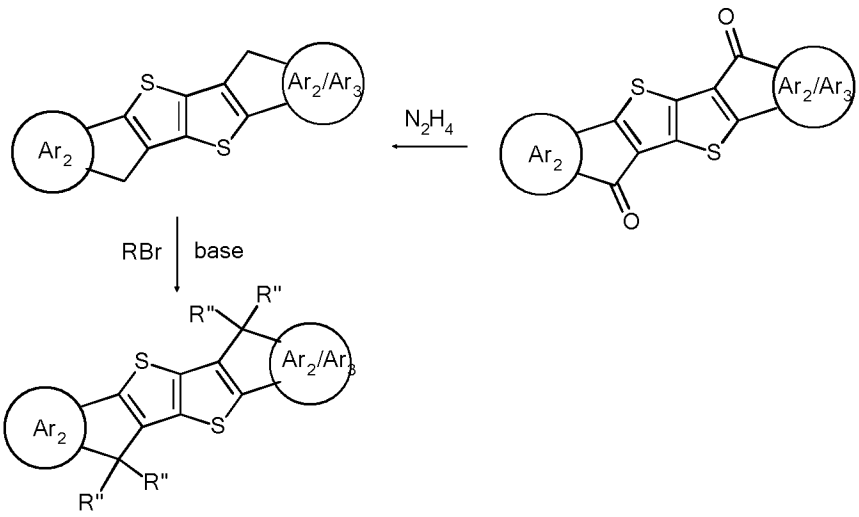
Preferred catalysts, especially for Suzuki, Negishi or Stille coupling, are selected from Pd(0) complexes or Pd(II) salts. Preferred Pd(0) complexes are those bearing at least one phosphine ligand such as $Pd(Ph_3P)_4$. Another preferred phosphine ligand is tris(*ortho*-tolyl)phosphine, i.e. $Pd(o\text{-}Tol_3P)_4$. Preferred Pd(II) salts include palladium acetate, i.e. $Pd(OAc)_2$. Alternatively the Pd(0) complex can be prepared by mixing a Pd(0) dibenzylideneacetone complex, for example tris(dibenzyl-ideneacetone)dipalladium(0), bis(dibenzylideneacetone)palladium(0), or Pd(II) salts *e.g.* palladium acetate, with a phosphine ligand, for example triphenylphosphine, tris(*ortho*-tolyl)phosphine or tri(tert-butyl)phosphine. Suzuki coupling is performed in the presence of a base, for example sodium carbonate, potassium carbonate, cesium carbonate, lithium hydroxide, potassium phosphate or an organic base such as tetraethylammonium carbonate or tetraethylammonium hydroxide. Yamamoto coupling employs a Ni(0) complex, for example bis(1,5-cyclooctadienyl) nickel(0).

As alternatives to halogens as described above, leaving groups of formula $-O\text{-}SO_2Z^0$ can be used wherein Z^0 is an alkyl or aryl group, preferably $C_{1\text{-}10}$ alkyl or $C_{6\text{-}12}$ aryl. Particular examples of such leaving groups are tosylate, mesylate and triflate.

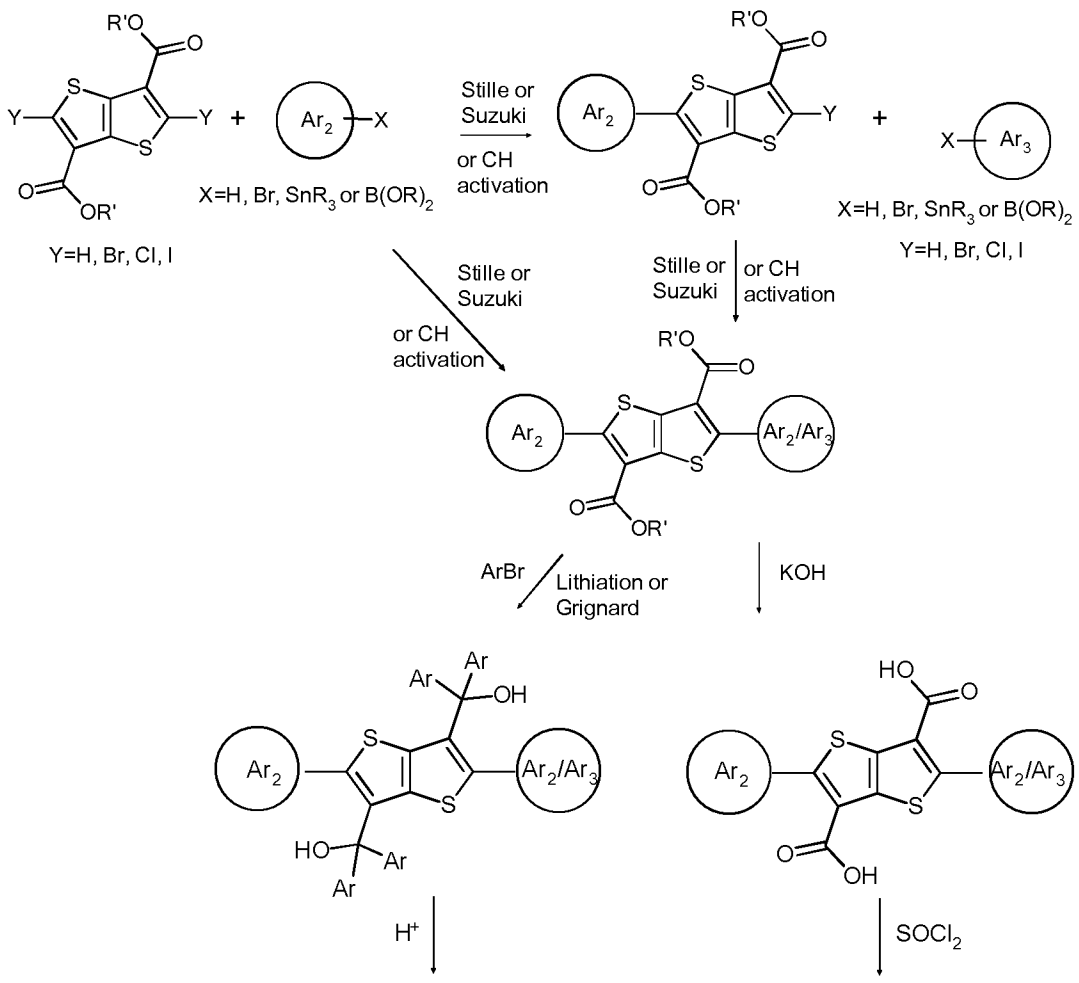
Especially suitable and preferred synthesis methods of the compounds of formula I and its subformulae are illustrated in the synthesis schemes shown hereinafter, wherein the individual radicals are as defined above and below.

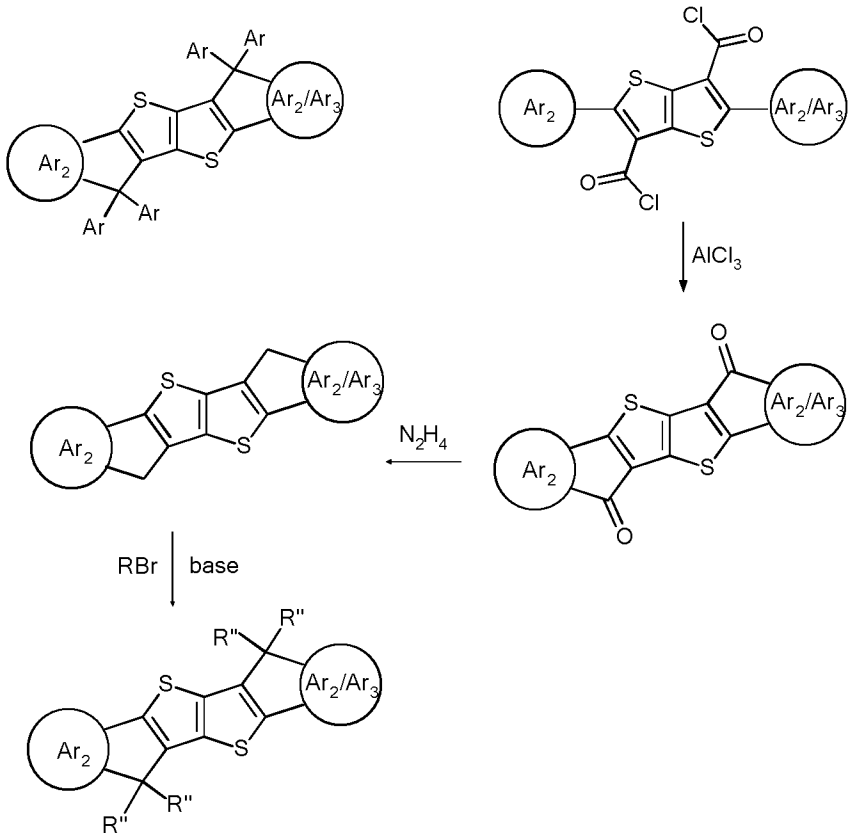
Scheme 1a


Y=H, Br, Cl, I
X=H, Br, SnR3 or B(OR)2
Stille or Suzuki
or CH activation
X=H, Br, SnR3 or B(OR)2
Y=H, Br, Cl, I
Stille or Suzuki
or CH activation
Stille or Suzuki
or CH activation
ArBr
Lithiation or Grignard
KOH
H+
SOCl2
AlCl3

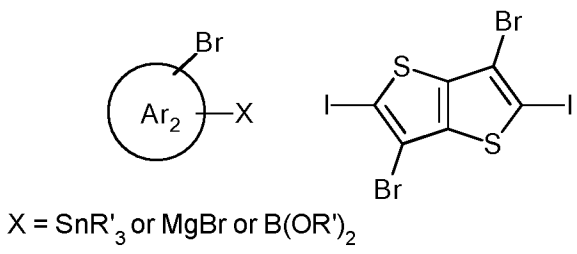

Ar2/Ar3
Ar2
S
N2H4
O
RBr
base
R''

Scheme 1b


R'O
O
Y
OR'
X=H, Br, SnR3 or B(OR)2
Y=H, Br, Cl, I
Stille or Suzuki
or CH activation
Ar2
Ar3
Ar2/Ar3
ArBr
Lithiation or Grignard
KOH
HO
Ar
OH
H+
SOCl2

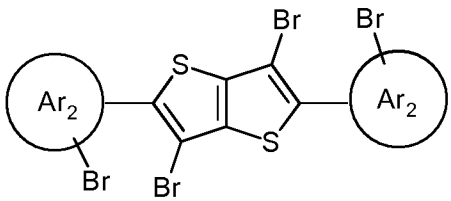


Scheme 2

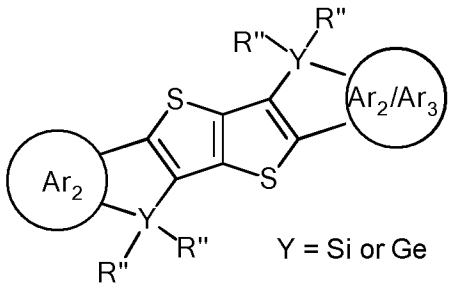


X = SnR'_3 or MgBr or $B(OR')_2$

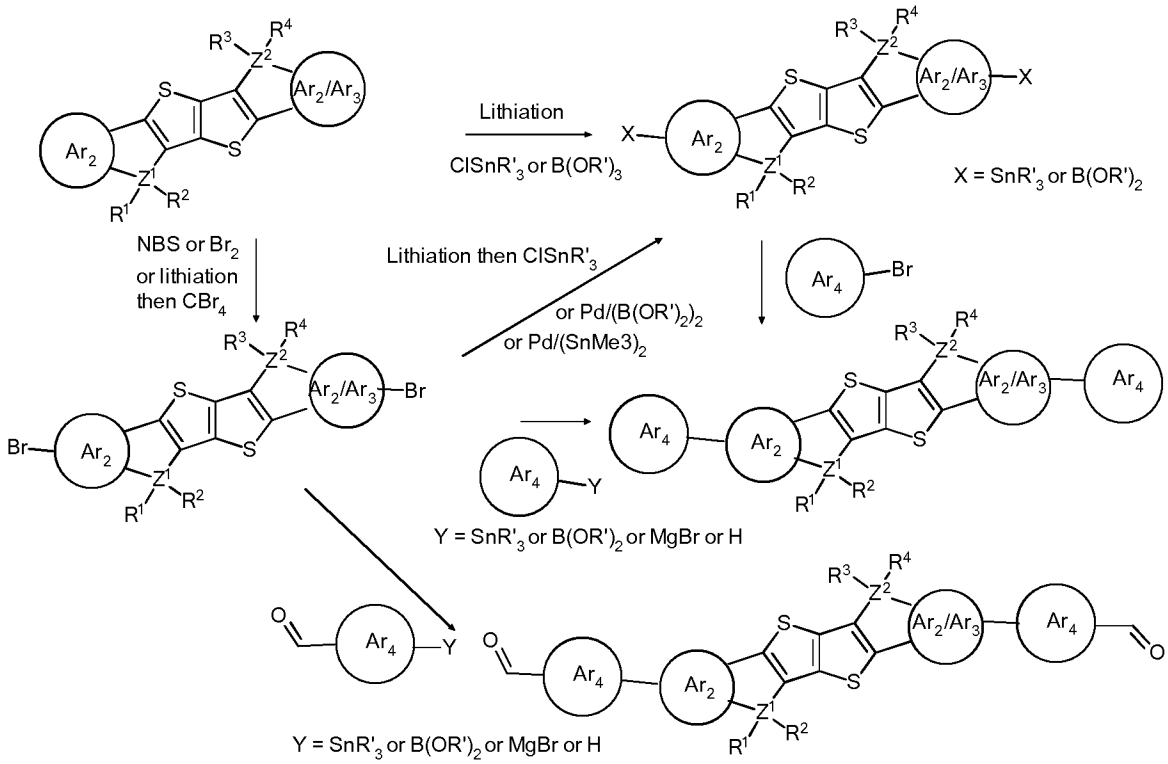
Grignard or
Stille or
Suzuki



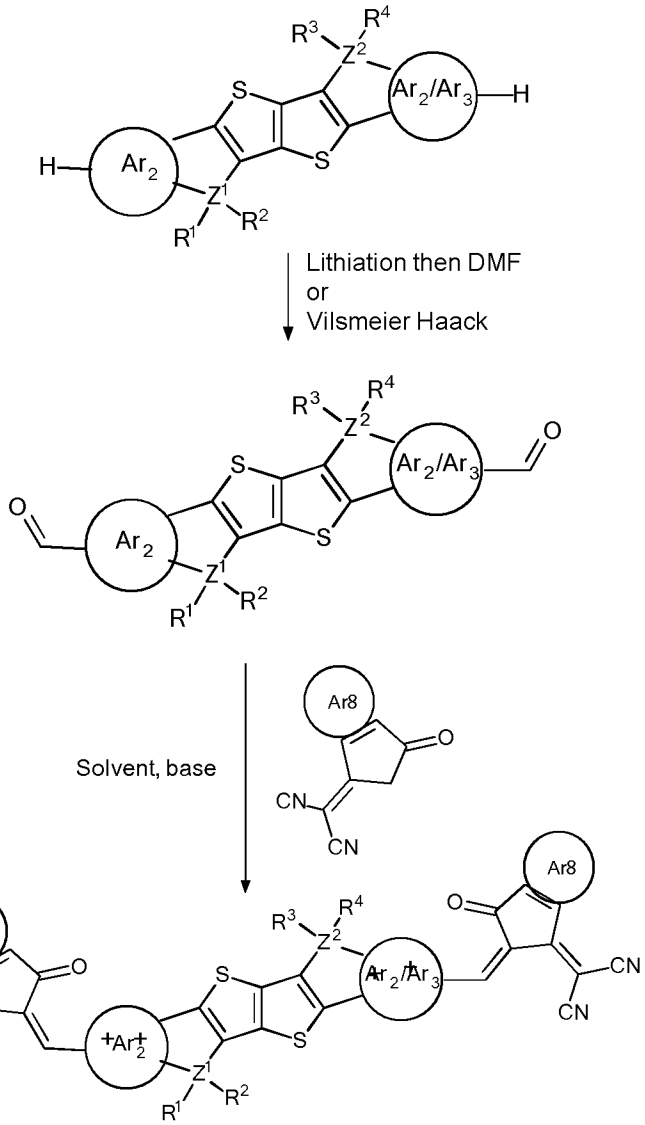
Lithiation | $Cl_2YR''_2$



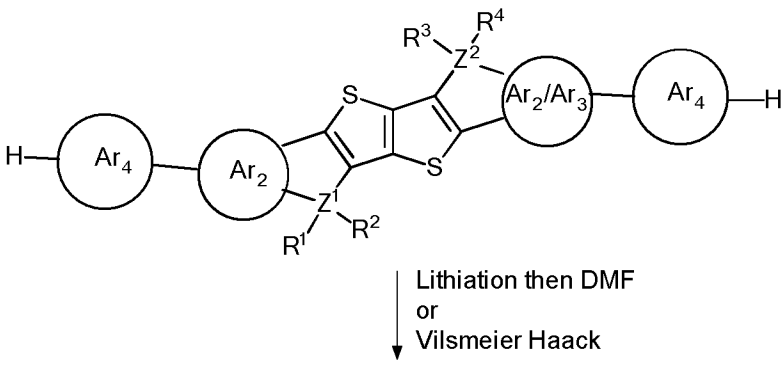
Scheme 3

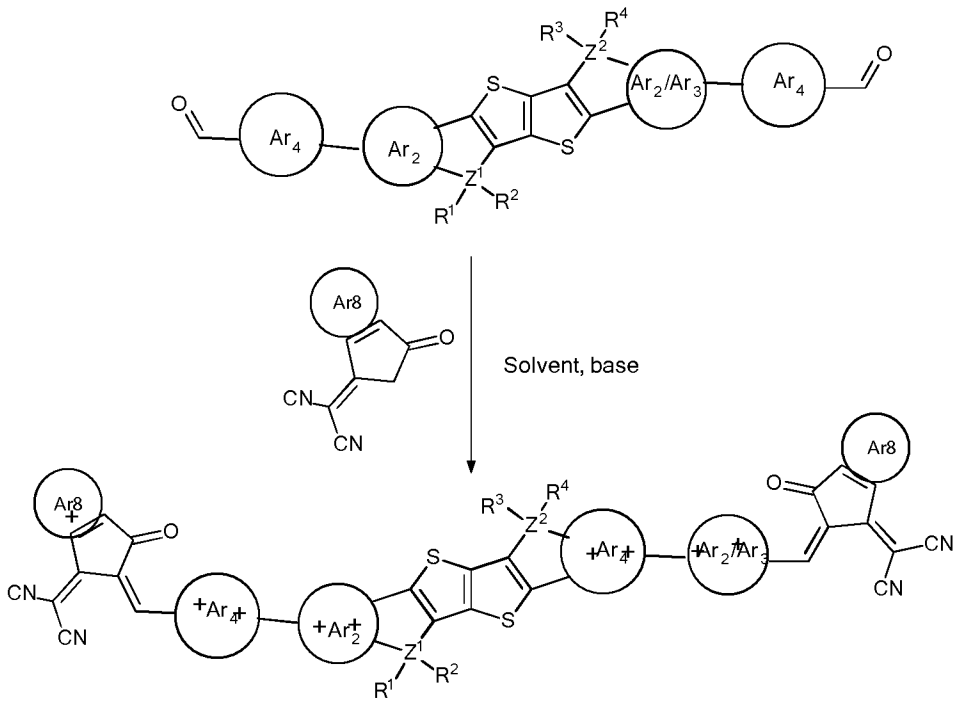


Scheme 4


Lithiation then DMF
or
Vilsmeier Haack
Solvent, base

Scheme 5


Lithiation then DMF
or
Vilsmeier Haack



Novel methods of preparing compounds of formula I are another aspect of the invention.

The compound according to the present invention can also be used in compositions, for example together with monomeric or polymeric compounds having charge-transport, semiconducting, electrically conducting, photoconducting and/or light emitting semiconducting properties, or for example with compounds having hole blocking or electron blocking properties for use as interlayers or charge blocking layers in PSCs or OLEDs.

Thus, another aspect of the invention relates to a composition comprising one or more compounds according to the present invention and one or more small molecule compounds and/or polymers having one or more of a charge-transport, semiconducting, electrically conducting, photoconducting, hole blocking and electron blocking property.

The invention further relates to a composition comprising one or more compounds according to the present invention, and further comprising one or more p-type organic semiconductors, preferably selected from

conjugated polymers.

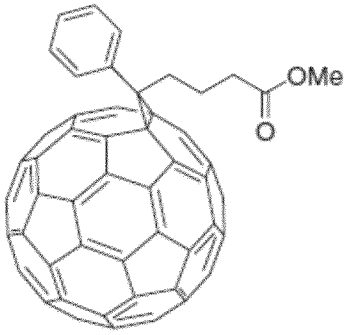
The invention further relates to a composition comprising a first n-type semiconductor which is a compound according to the present invention, a second n-type semiconductor, which is preferably a fullerene or fullerene derivative, a non-fullerene acceptor small molecule, or an n-type conjugated polymer, and a p-type semiconductor, which is preferably a conjugated polymer.

In a preferred embodiment the second n-type OSC compound is a non-fullerene acceptor (NFA) small molecule having an A-D-A structure as described above with an electron donating polycyclic core and two terminal electron withdrawing groups attached thereto.

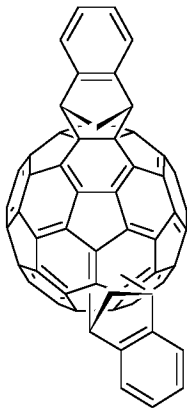
Suitable and preferred NFA small molecules for use as second n-type OSC in this preferred embodiment are for example those disclosed in Y. Lin et al., *Adv. Mater.*, **2015**, *27*, 1170; H. Lin et al., *Adv. Mater.*, **2015**, *27*, 7299; N. Qiu et al., *Adv. Mater.*, **2017**, *29*, 1604964; CN104557968 A and CN105315298 A, furthermore those disclosed in WO 2018/007479 A1.

In another preferred embodiment the second n-type OSC compound is a fullerene or substituted fullerene.

The fullerene is for example an indene-C_{60}-fullerene bisadduct like ICBA, or a (6,6)-phenyl-butyric acid methyl ester derivatized methano C_{60} fullerene, also known as "PCBM-C_{60}" or "C_{60}PCBM", as disclosed for example in G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Science 1995, Vol. 270, p. 1789 ff and having the structure shown below, or structural analogous compounds with e.g. a C_{61} fullerene group, a C_{70} fullerene group, or a C_{71} fullerene group, or an organic polymer (see for example Coakley, K. M. and McGehee, M. D. *Chem. Mater.* 2004, *16*, 4533).

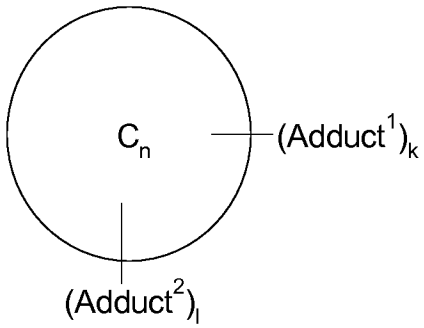


PCBM-C_{60}



ICBA-C_{60}

Preferably the compound according to the present invention is blended with an n-type semiconductor such as a fullerene or substituted fullerene of formula Full-I to form the active layer in an OPV or OPD device,



Full-I

wherein

C_n	denotes a fullerene composed of n carbon atoms, optionally with one or more atoms trapped inside,
$Adduct^1$	is a primary adduct appended to the fullerene C_n with any connectivity,
$Adduct^2$	is a secondary adduct, or a combination of secondary adducts, appended to the fullerene C_n with any connectivity,
k	is an integer ≥ 1,

and

l is 0, an integer ≥ 1, or a non-integer > 0.

In the formula Full-I and its subformulae, k preferably denotes 1, 2, 3 or, 4, very preferably 1 or 2.

The fullerene C_n in formula Full-I and its subformulae may be composed of any number n of carbon atoms Preferably, in the compounds of formula XII and its subformulae the number of carbon atoms n of which the fullerene C_n is composed is 60, 70, 76, 78, 82, 84, 90, 94 or 96, very preferably 60 or 70.

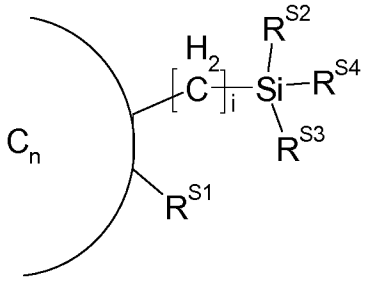
The fullerene C_n in formula Full-I and its subformulae is preferably selected from carbon based fullerenes, endohedral fullerenes, or mixtures thereof, very preferably from carbon based fullerenes.

Suitable and preferred carbon based fullerenes include, without limitation, ($C_{60\text{-}Ih}$)[5,6]fullerene, ($C_{70\text{-}D5h}$)[5,6]fullerene, ($C_{76\text{-}D2*}$)[5,6]fullerene, ($C_{84\text{-}D2*}$)[5,6]fullerene, ($C_{84\text{-}D2d}$)[5,6]fullerene, or a mixture of two or more of the aforementioned carbon based fullerenes.

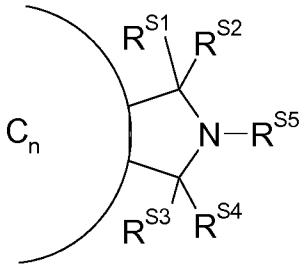
The endohedral fullerenes are preferably metallofullerenes. Suitable and preferred metallofullerenes include, without limitation, $La@C_{60}$, $La@C_{82}$, $Y@C_{82}$, $Sc_3N@C_{80}$, $Y_3N@C_{80}$, $Sc_3C_2@C_{80}$ or a mixture of two or more of the aforementioned metallofullerenes.

Preferably the fullerene C_n is substituted at a [6,6] and/or [5,6] bond, preferably substituted on at least one [6,6] bond.

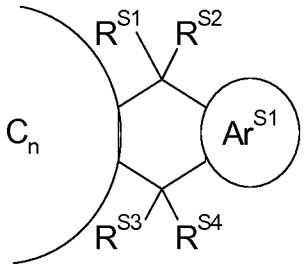
Primary and secondary adducts, named "Adduct1" and "Adduct 2" in formula Full-I and its subformulae, are each preferably selected from the following formulae



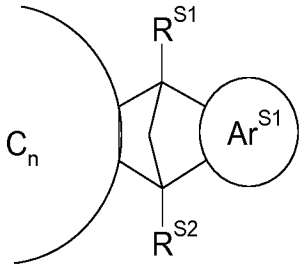
S-1



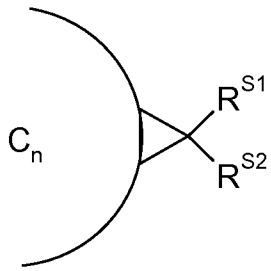
S-2



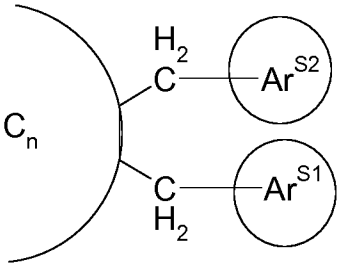
S-3



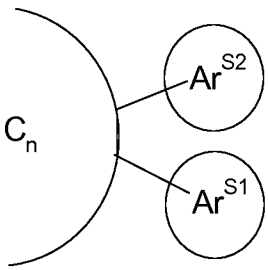
S-4



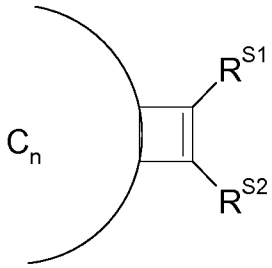
S-4



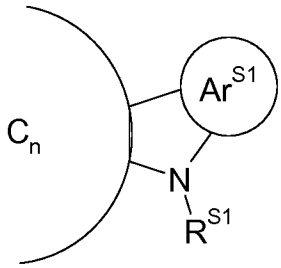
S-5



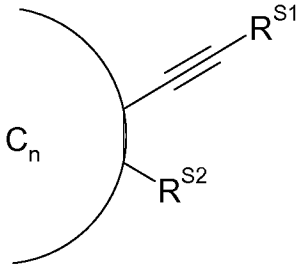
S-6



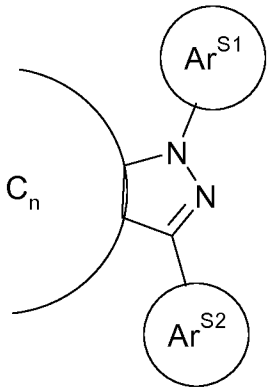
S-7



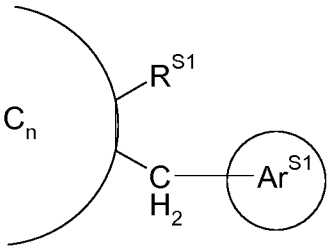
S-8



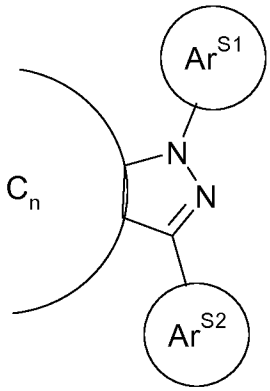
S-9



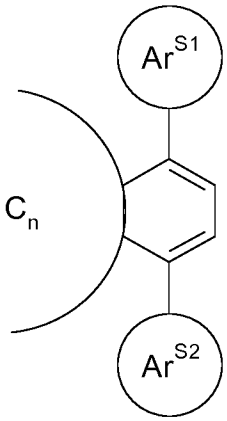
S-10



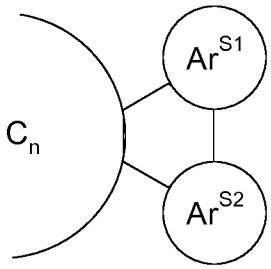
S-11



S-12



S-13



S-14

wherein

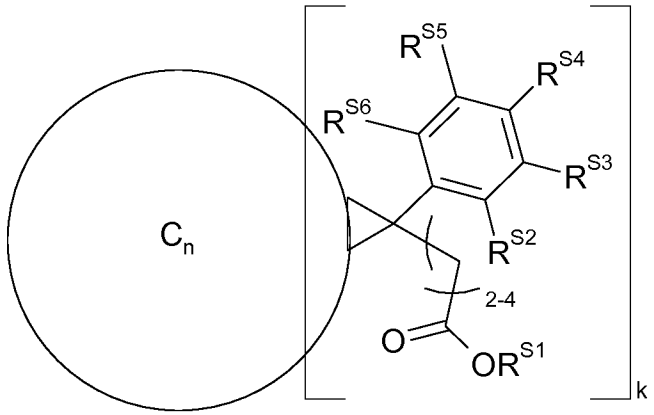
Ar^{S1}, Ar^{S2} denote, independently of each other, an aryl or heteroaryl group with 5 to 20, preferably 5 to 15, ring atoms, which is mono- or polycyclic, and which is optionally substituted by one or more identical or different substituents having one of the meanings of L as defined above and below,

R^{S1}, R^{S2}, R^{S3}, R^{S4} and R^{S5} independently of each other denote H, CN or have one of the meanings of L as defined above and below, and

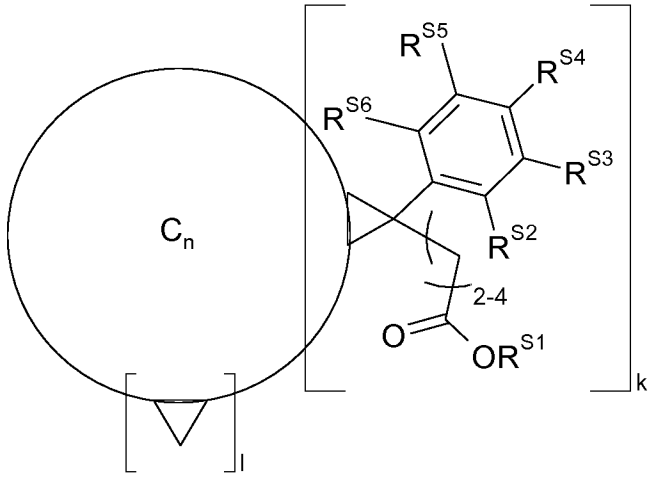
i is an integer from 1 to 20, preferably from 1 to 12.

Preferred compounds of formula Full-I are selected from the following

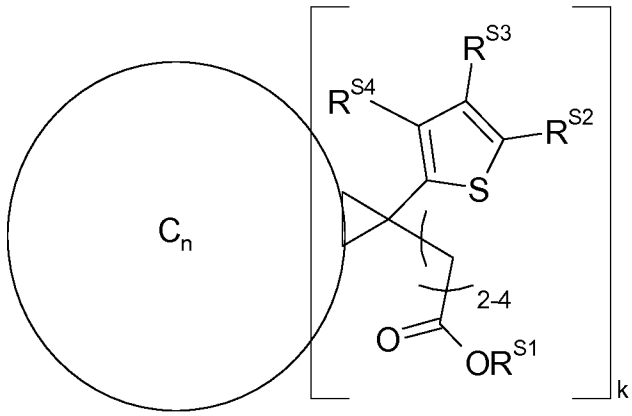
subformulae:



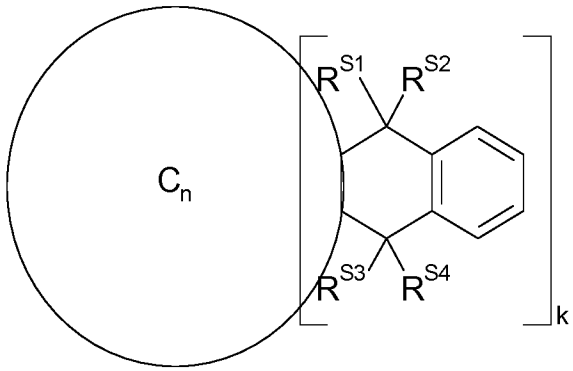
Full-Ia



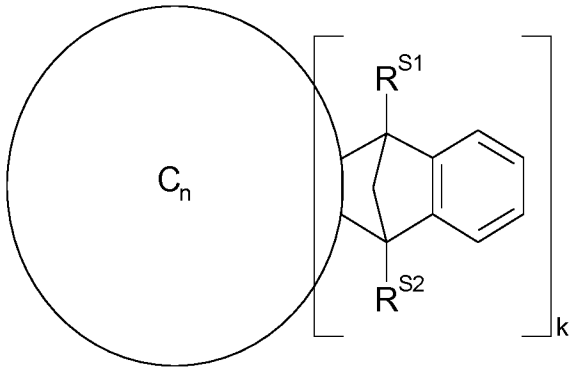
Full-Ib



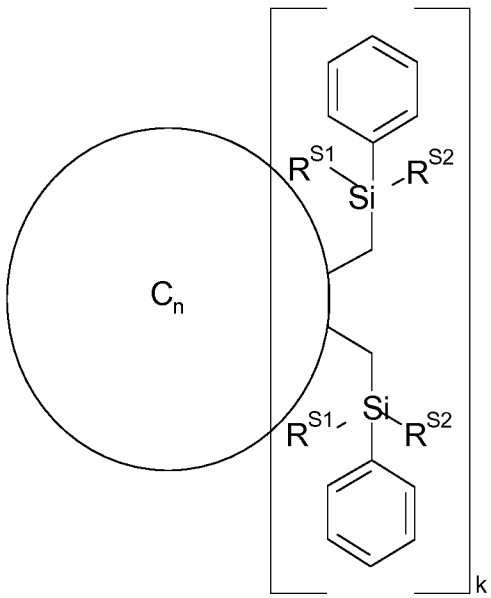
Full-Ic



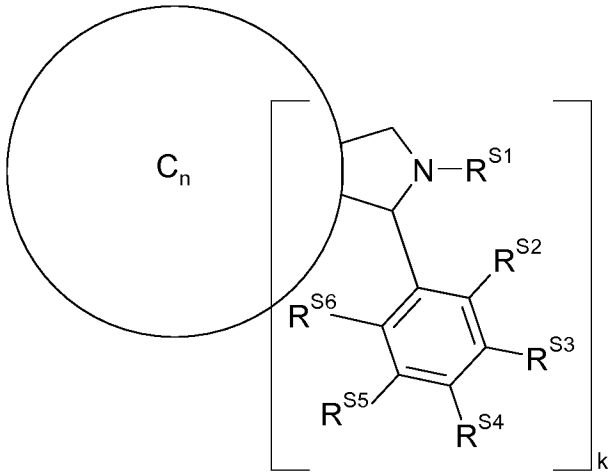
Full-Id



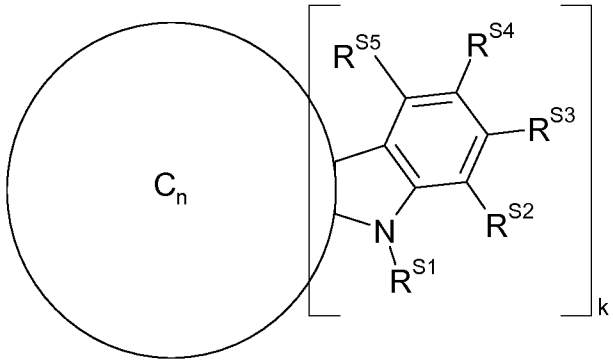
Full-Ie



Full-If



Full-Ig



Full-Ih

wherein

R^{S1}, R^{S2}, R^{S3}, R^{S4} R^{S5} and R^{S6} independently of each other denote H or have one of the meanings of R^S as defined above and below.

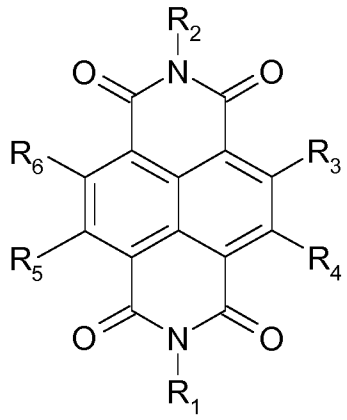
Most preferably the fullerene is PCBM-C60, PCBM-C70, bis-PCBM-C60, bis-PCBM-C70, ICMA-c60 (1′,4′-dihydro-naphtho[2′,3′:1,2][5,6]fullerene-C60), ICBA, oQDM-C60 (1',4'-dihydro-naphtho[2',3':1,9][5,6]fullerene-C60-Ih), or bis-oQDM-C60.

In another preferred embodiment the second n-type OSC compound is a small molecule which does not contain a fullerene moiety, and which is selected from naphthalene or perylene carboximide derivatives.

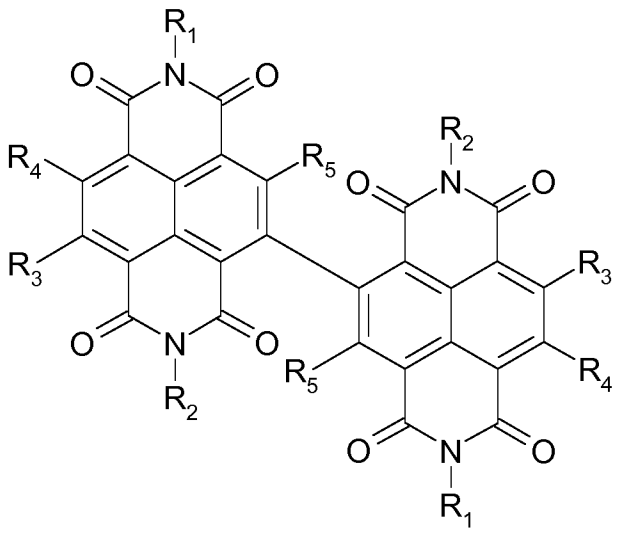
Preferred naphthalene or perylene carboximide derivatives for use as n-type OSC compounds are described for example in *Adv. Sci.* **2016**, *3*, 1600117,

Adv. Mater. **2016**, *28*, 8546–8551, *J. Am. Chem. Soc.*, **2016**, *138*, 7248–7251 and *J. Mater. Chem. A*, **2016**, *4*, 17604.

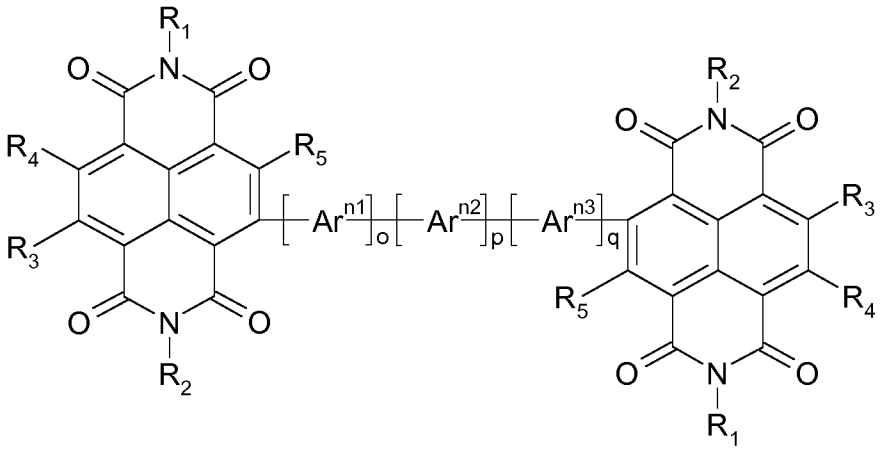
Preferred n-type OSC compounds of this preferred embodiment are selected from the following formulae



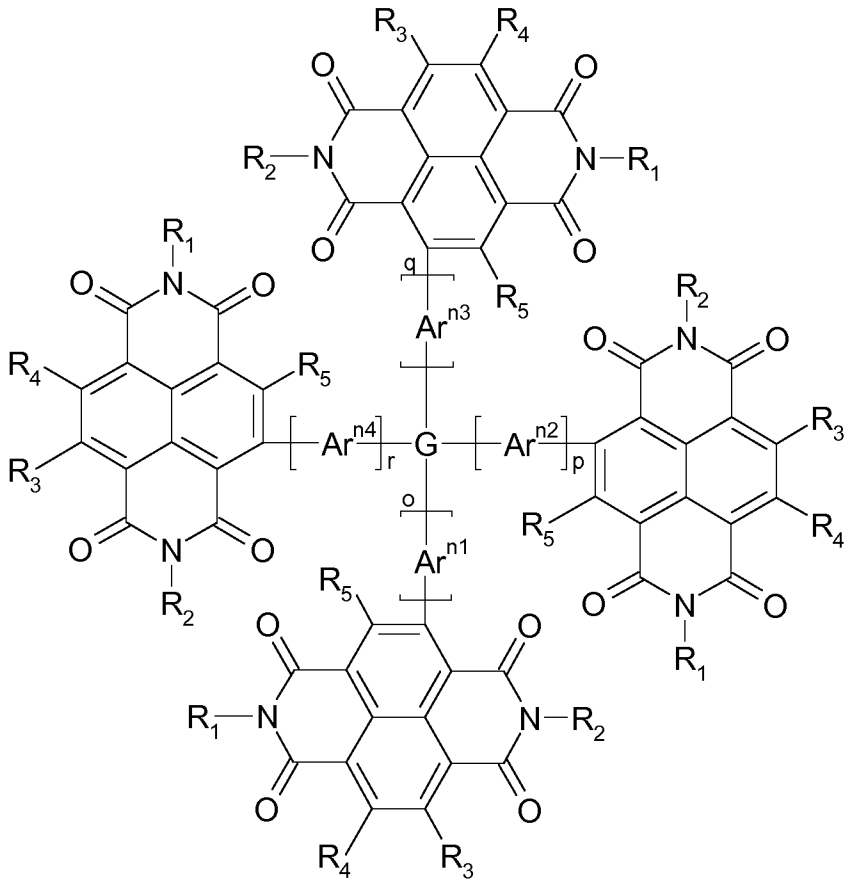
NDI1



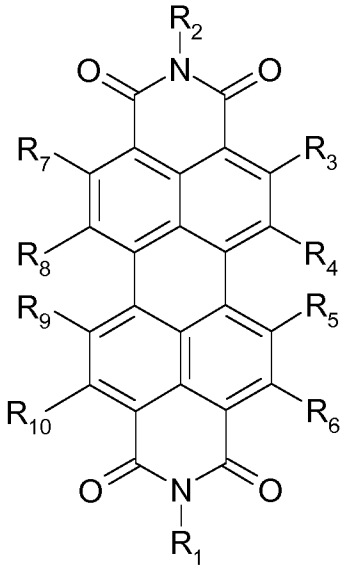
NDI2



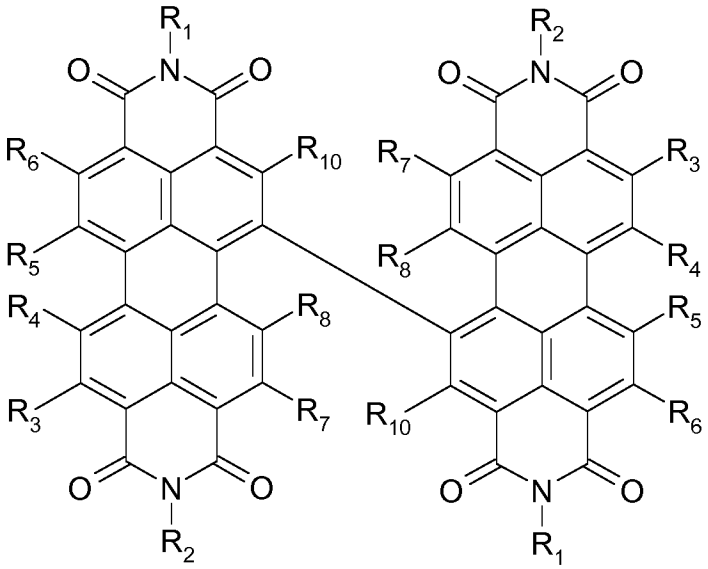
NDI3



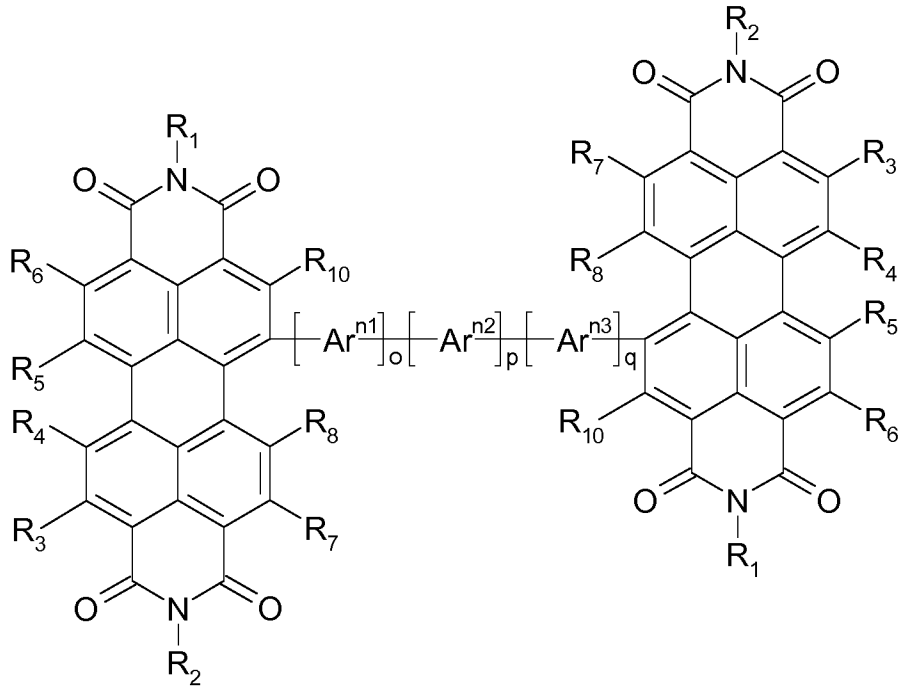
NDI4



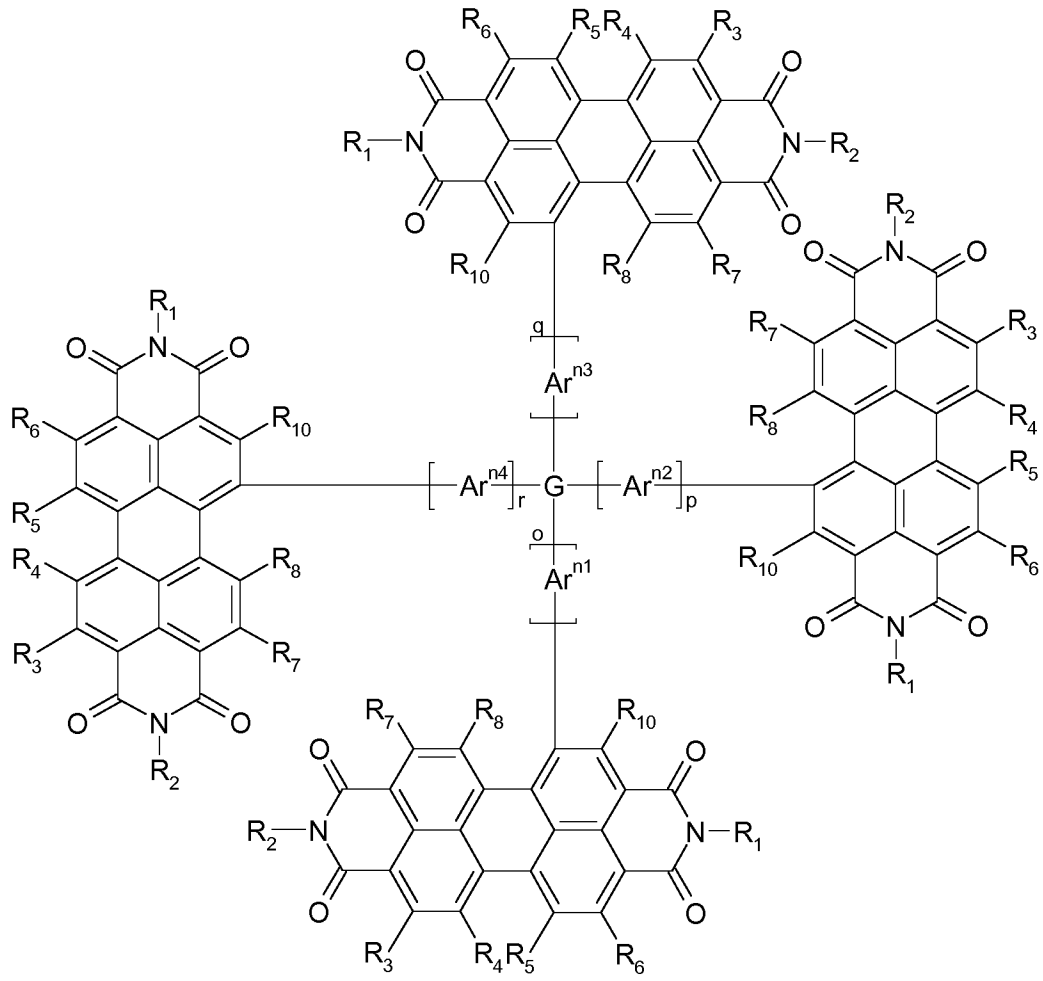
PDI



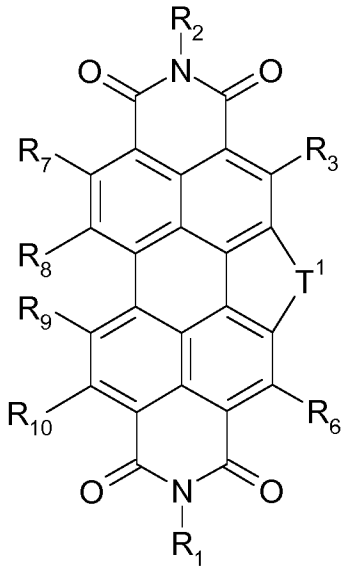
PDI



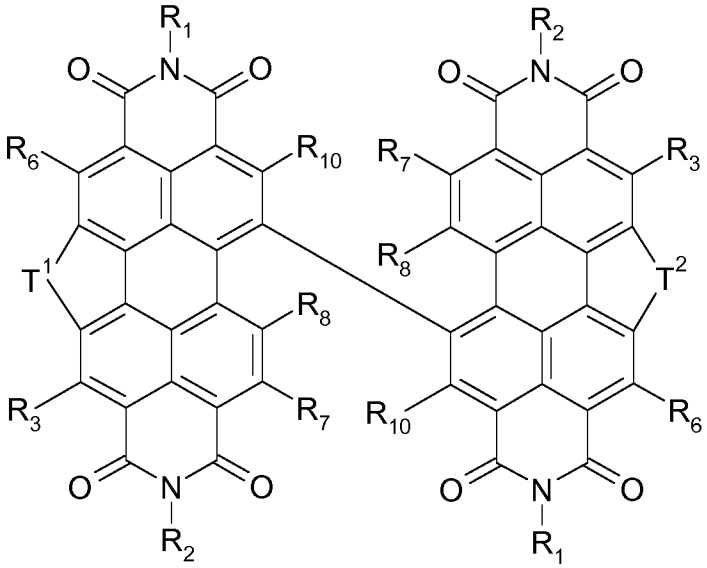
PDI



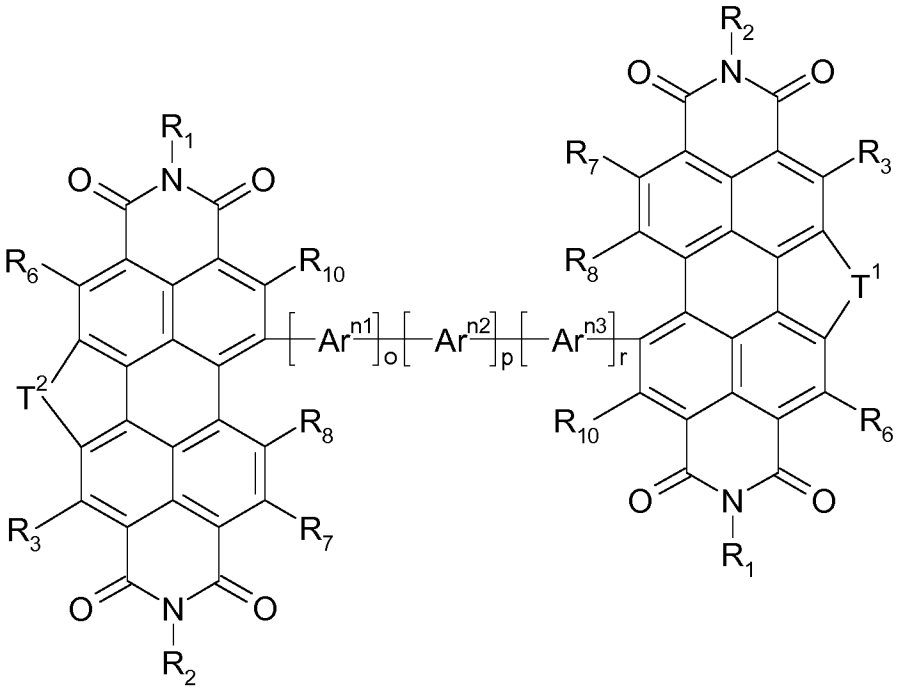
PDI



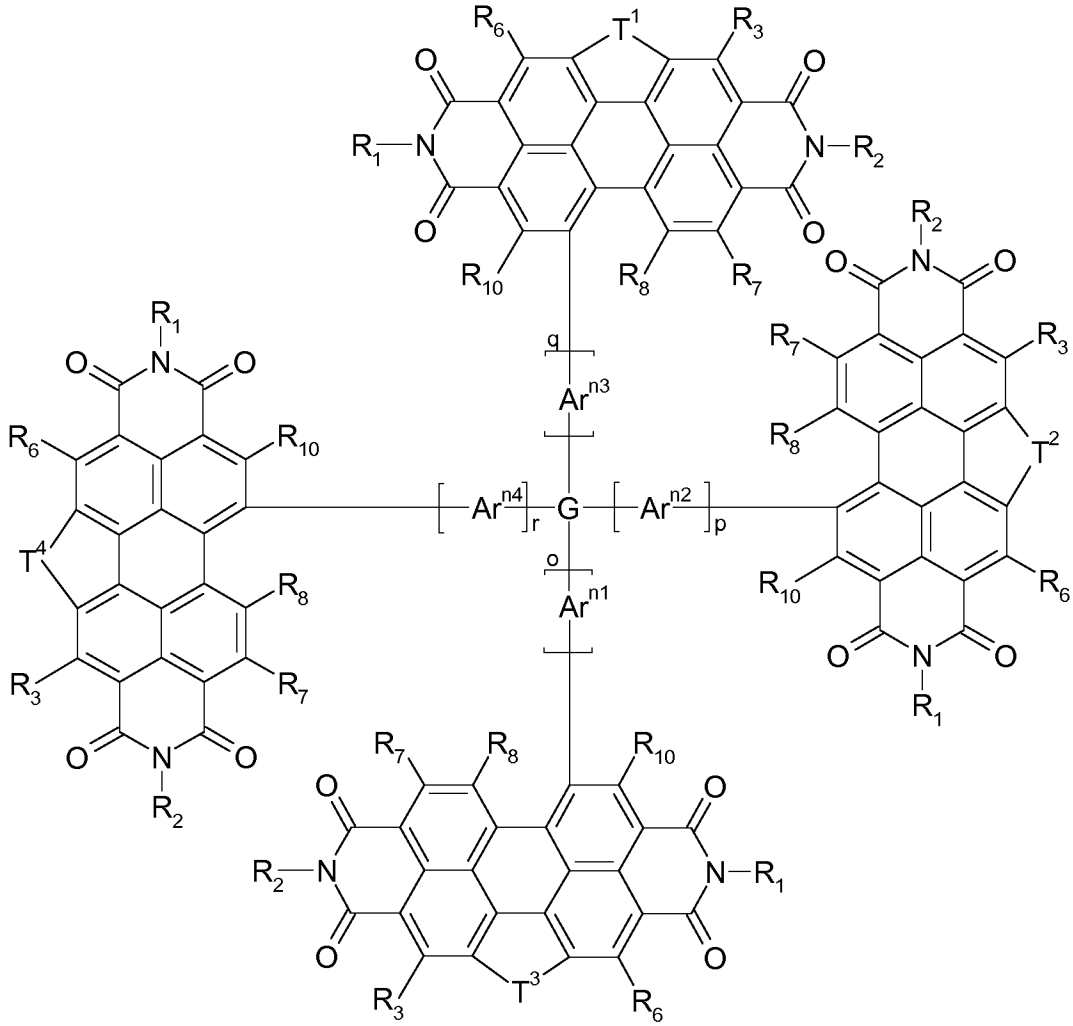
PDI



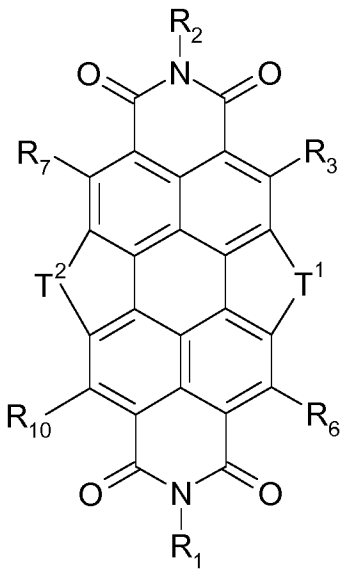
PDI



PDI



PDI



PDI

wherein the individual radicals, independently of each other and on each occurrence identically or differently, have the following meanings

R^{1-10}	R^W, H, F, Cl, or straight-chain, branched or cyclic alkyl with 1 to 30, preferably 1 to 20, C atoms, in which one or more CH_2 groups are optionally replaced by -O-, -S-, -C(=O)-, -C(=S)-, -C(=O)-O-, -O-C(=O)-, $-NR^0-$, $-SiR^0R^{00}-$, $-CF_2-$, $-CR^0=CR^{00}-$, $-CY^1=CY^2-$ or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, and in which one or more H atoms are optionally replaced by F, Cl, Br, I or CN, and in which one or more CH_2 or CH_3 groups are optionally replaced by a cationic or anionic group, or aryl, heteroaryl, arylalkyl, heteroarylalkyl, aryloxy or heteroaryloxy, wherein each of the aforementioned cyclic groups has 5 to 20 ring atoms, is mono- or polycyclic, does optionally contain fused rings, and is unsubstituted or substituted by one or more identical or different groups L^S,
R^W	an electron withdrawing group, preferably having one of the preferred meanings as given above for R^{T1}, very preferably CN,
Y^1, Y^2	H, F, Cl or CN,
L^S	F, Cl, $-NO_2$, -CN, -NC, -NCO, -NCS, -OCN, -SCN, R^0, OR^0, SR^0, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)-OR^0$, $-O-C(=O)-R^0$, $-NH_2$, $-NHR^0$, $-NR^0R^{00}$, $-C(=O)NHR^0$, $-C(=O)NR^0R^{00}$, $-SO_3R^0$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-SF_5$, or optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 30, preferably 1 to 20 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, preferably F, -CN, R^0, $-OR^0$, $-SR^0$, $-C(=O)-R^0$, $-C(=O)-OR^0$, $-O-C(=O)-R^0$, $-O-C(=O)-OR^0$, $-C(=O)-NHR^0$, or $-C(=O)-NR^0R^{00}$,
T^{1-4}	-O-, -S-, -C(=O)-, -C(=S)-, $-CR^0R^{00}-$, $-SiR^0R^{00}-$, $-NR^0-$, $-CR^0=CR^{00}-$ or -C≡C-,

G	C, Si, Ge, C=C or a four-valent aryl or heteroaryl group that has from 5 to 20 ring atoms, is mono- or polycyclic, optionally contains fused rings, and is unsubstituted or substituted by one or more identical or different groups R^1 or L^S,
Ar^{n1-n4}	independently of each other, and on each occurrence identically or differently arylene or heteroarylene that has from 5 to 20 ring atoms, is mono- or polycyclic, optionally contains fused rings, and is unsubstituted or substituted by one or more identical or different groups R^1 or L^S, or $CY^1=CY^2$ or -C≡C-,
o, p, q, r	0 or an integer from 1 to 10.

In another preferred embodiment the second n-type OSC compound is a conjugated OSC polymer. Preferred n-type OSC polymers are described, for example, in Acc. Chem. Res., 2016, 49 (11), pp 2424–2434 and WO 2013/142841 A1.

Preferred n-type conjugated OSC polymers for use as second n-type OSC compound in this preferred embodiment comprise one or more units derived from perylene or naphthalene are poly[[N,N′-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5′-(2,2′-bithiophene)], poly[[N,N′-bis(2-hexyldecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5′-thiophene].

The composition according to the present invention can be prepared by conventional methods that are described in prior art and known to the skilled person. Typically the compounds and/or polymers are mixed with each other or dissolved in suitable solvents and the solutions combined.

Another aspect of the invention relates to a formulation comprising one or more compounds according to the present invention or compositions as described above and below and one or more organic solvents.

Preferred solvents are aliphatic hydrocarbons, chlorinated hydrocarbons, aromatic hydrocarbons, ketones, ethers and mixtures thereof. Further suitable and preferred solvents used include 1,2,4-trimethylbenzene, 1,2,3,4-tetra-methyl benzene, pentylbenzene, mesitylene, cumene, cymene, cyclohexylbenzene, diethylbenzene, tetralin, indane, 1,5-dimethyltetraline, decalin, 1-methylnaphthalene, 2,6-lutidine, 2-chlorobenzotrifluoride, N,N-dimethylformamide, 2-chloro-6-fluorotoluene, 2-fluoroanisole, anisole, 2,3-dimethylpyrazine, 4-fluoroanisole, 3-fluoroanisole, 3-trifluoro-methylanisole, 2-methylanisole, phenetol, 4-methylanisole, 3-methylanisole, 4-fluoro-3-methylanisole, 2-fluorobenzonitrile, 4-fluoroveratrol, 2,6-dimethylanisole, 3-fluorobenzo-nitrile, 2,5-dimethylanisole, 2,4-dimethylanisole, benzonitrile, 3,5-dimethyl-anisole, N,N-dimethylaniline, ethyl benzoate, 1-fluoro-3,5-dimethoxy-benzene, N-methylpyrrolidinone, 3-fluorobenzo-trifluoride, benzotrifluoride, dioxane, trifluoromethoxy-benzene, 4-fluorobenzotrifluoride, 3-fluoropyridine, toluene, 2-fluoro-toluene, 2-fluorobenzotrifluoride, 3-fluorotoluene, 4-isopropylbiphenyl, phenyl ether, pyridine, 4-fluorotoluene, 2,5-difluorotoluene, 1-chloro-2,4-difluorobenzene, 2-fluoropyridine, 3-chlorofluoro-benzene, 1-chloro-2,5-difluorobenzene, 4-chlorofluorobenzene, chloro-benzene, o-dichlorobenzene, 2-chlorofluorobenzene, p-xylene, m-xylene, o-xylene, a mixture of o-, m-, and p-xylene, 2-fluoro-m-xylene, 3-fluoro-o-xylene, tetrahydrofuran, morpholine, 1,4-dioxane, 2-methylthiophene, 3-methylthiophene, chloroform, 1,2-dichloroethane, dichloromethane, carbon tetrachloride, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, acetone, methylethylketone, propiophenone, acetophenone, cyclohexanone, ethyl acetate, n-butyl acetate, ethyl benzoate, ethyl benzoate, dimethylacetamide, dimethylsulfoxide, or mixtures of the aforementioned. Solvents with relatively low polarity are generally preferred.

Examples of especially preferred solvents include, without limitation, dichloromethane, trichloromethane, chlorobenzene, o-dichlorobenzene, tetrahydrofuran, anisole, 2,4-dimethylanisole, 1-methylnaphthalene, morpholine, toluene, o-xylene, m-xylene, p-xylene, 1,4-dioxane, acetone, methylethylketone, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-

tetrachloroethane, ethyl acetate, n-butyl acetate, N,N-dimethylformamide, dimethylacetamide, dimethylsulfoxide, 1,5-dimethyltetraline, propiophenone, acetophenone, tetralin, 2-methylthiophene, 3-methylthiophene, decaline, indane, methyl benzoate, ethyl benzoate, mesitylene, or mixtures thereof.

The concentration of the compounds or polymers in the solution is preferably 0.1 to 10% by weight, more preferably 0.5 to 5% by weight. Optionally, the solution also comprises one or more binders to adjust the rheological properties, as described for example in WO 2005/055248 A1.

After the appropriate mixing and ageing, solutions are evaluated as one of the following categories: complete solution, borderline solution or insoluble. The contour line is drawn to outline the solubility parameter-hydrogen bonding limits dividing solubility and insolubility. 'Complete' solvents falling within the solubility area can be chosen from literature values such as published in "Crowley, J.D., Teague, G.S. Jr and Lowe, J.W. Jr., *Journal of Paint Technology*, **1966**, *38 (496)*, 296 ". Solvent blends may also be used and can be identified as described in "Solvents, W.H.Ellis, Federation of Societies for Coatings Technology, p9-10, 1986". Such a procedure may lead to a blend of 'non' solvents that will dissolve both the polymers and compounds of the present invention, although it is desirable to have at least one true solvent in a blend.

The compositions and formulations according to the present invention can additionally comprise one or more further components or additives selected for example from surface-active compounds, lubricating agents, wetting agents, dispersing agents, hydrophobing agents, adhesive agents, flow improvers, defoaming agents, deaerators, diluents which may be reactive or non-reactive, auxiliaries, colourants, dyes or pigments, sensitizers, stabilizers, nanoparticles or inhibitors.

In a composition according to the present invention comprising a compound according to the present invention, and a polymer, the ratio compound:polymer is preferably from 5:1 to 1:5 by weight, more preferably from 3:1 to 1:3 by weight, most preferably 2:1 to 1:2 by weight.

The composition according to the present invention may also comprise a polymeric binder, preferably from 0.001 to 95% by weight. Examples of binder include polystyrene (PS), polydimethylsilane (PDMS), polypropylene (PP) and polymethylmethacrylate (PMMA).

A binder to be used in the formulation as described before, which is preferably a polymer, may comprise either an insulating binder or a semiconducting binder, or mixtures thereof, may be referred to herein as the organic binder, the polymeric binder or simply the binder.

Preferably, the polymeric binder comprises a weight average molecular weight in the range of 1,000 to 5,000,000 g/mol, especially 1,500 to 1,000,000 g/mol and more preferable 2,000 to 500,000 g/mol. Surprising effects can be achieved with polymers having a weight average molecular weight of at least 10,000 g/mol, more preferably at least 100,000 g/mol.

In particular, the polymer can have a polydispersity index M_w/M_n in the range of 1.0 to 10.0, more preferably in the range of 1.1 to 5.0 and most preferably in the range of 1.2 to 3.

Preferably, the inert binder is a polymer having a glass transition temperature in the range of -70 to 160°C, preferably 0 to 150°C, more preferably 50 to 140°C and most preferably 70 to 130°C. The glass transition temperature can be determined by measuring the DSC of the polymer (DIN EN ISO 11357, heating rate 10°C per minute).

The weight ratio of the polymeric binder to the compound according to the present invention is preferably in the range of 30:1 to 1:30, particularly in the range of 5:1 to 1:20 and more preferably in the range of 1:2 to 1:10.

According to a preferred embodiment the binder preferably comprises repeating units derived from styrene monomers and/or olefin monomers. Preferred polymeric binders can comprise at least 80 %, preferably 90 % and more preferably 99 % by weight of repeating units derived from styrene monomers and/or olefins.

Styrene monomers are well known in the art. These monomers include styrene, substituted styrenes with an alkyl substituent in the side chain, such as α-methylstyrene and α-ethylstyrene, substituted styrenes with an alkyl substituent on the ring such as vinyltoluene and p-methylstyrene, halogenated styrenes such as monochlorostyrenes, dichlorostyrenes, tribromostyrenes and tetrabromostyrenes.

Olefin monomers consist of hydrogen and carbon atoms. These monomers include ethylene, propylene, butylenes, isoprene and 1,3-butadiene.

According to a preferred embodiment of the present invention, the polymeric binder is polystyrene having a weight average molecular weight in the range of 50,000 to 2,000,000 g/mol, preferably 100,000 to 750,000 g/mol, more preferably in the range of 150,000 to 600,000 g/mol and most preferably in the range of 200,000 to 500,000 g/mol.

Further examples of suitable binders are disclosed for example in US 2007/0102696 A1. Especially suitable and preferred binders are described in the following.

The binder should preferably be capable of forming a film, more preferably a flexible film.

Suitable polymers as binders include poly(1,3-butadiene), polyphenylene, polystyrene, poly(α-methylstyrene), poly(α-vinylnaphtalene), poly(vinyltoluene), polyethylene, cis-polybutadiene, polypropylene, polyisoprene, poly(4-methyl-1-pentene), poly (4-methylstyrene), poly(chorotrifluoroethylene), poly(2-methyl-1,3-butadiene), poly(p-xylylene), poly(α-α-α'-α' tetrafluoro-p-xylylene), poly[1,1-(2-methyl propane)bis(4-phenyl)carbonate], poly(cyclohexyl methacrylate), poly(chlorostyrene), poly(2,6-dimethyl-1,4-phenylene ether), polyisobutylene, poly(vinyl cyclohexane), poly(vinylcinnamate), poly(4-vinylbiphenyl), 1,4-polyisoprene, polynorbornene, poly(styrene-block-butadiene); 31% wt styrene, poly(styrene-block-butadiene-block-styrene);

30% wt styrene, poly(styrene-co-maleic anhydride) (and ethylene/butylene) 1 - 1.7% maleic anhydride, poly(styrene- block-ethylene/butylene-block-styrene) triblock polymer 13% styrene, poly(styrene- block-ethylene- propylene -block-styrene) triblock polymer 37% wt styrene, poly(styrene- block-ethylene/butylene-block-styrene) triblock polymer 29% wt styrene, poly(1-vinylnaphthalene), poly(1-vinylpyrrolidone-co-styrene) 64% styrene, poly(1-vinylpyrrolidone-co-vinyl acetate) 1.3:1, poly(2-chlorostyrene), poly(2-vinylnaphthalene), poly(2-vinylpyridine-co-styrene) 1:1, poly(4,5-Difluoro-2,2-bis(CF3)-1,3-dioxole-co-tetrafluoroethylene) Teflon, poly(4-chlorostyrene), poly(4-methyl-1-pentene), poly(4-methylstyrene), poly(4-vinylpyridine-co-styrene) 1:1, poly(alpha-methylstyrene), poly(butadiene-graft-poly(methyl acrylate-co-acrylonitrile)) 1:1:1, poly(butyl methacrylate-co-isobutyl methacrylate) 1:1, poly(butyl methacrylate-co-methyl methacrylate) 1:1, poly(cyclohexylmethacrylate), poly(ethylene-co-1-butene-co-1-hexene) 1:1:1, poly(ethylene-co-ethylacrylate-co-maleic anhydride); 2% anhydride, 32% ethyl acrylate, poly(ethylene-co-glycidyl methacrylate) 8% glycidyl methacrylate, poly(ethylene-co-methyl acrylate-co-glycidyl meth-acrylate) 8% glycidyl metha-crylate 25% methyl acrylate, poly(ethylene-co-octene) 1:1, poly(ethylene-co-propylene-co-5-methylene-2-norbornene) 50% ethylene, poly(ethylene-co-tetrafluoroethylene) 1:1, poly(isobutyl methacrylate), poly(isobutylene), poly(methyl methacrylate)-co-(fluorescein O-methacrylate) 80% methyl methacrylate, poly(methyl methacrylate-co-butyl methacrylate) 85% methyl methacrylate, poly(methyl methacrylate-co-ethyl acrylate) 5% ethyl acrylate, poly(propylene-co-butene) 12% 1-butene, poly(styrene-co-allyl alcohol) 40% allyl alcohol, poly(styrene-co-maleic anhydride) 7% maleic anhydride, poly(styrene-co-maleic anhydride) cumene terminated (1.3:1), poly(styrene-co-methyl methacrylate) 40% styrene, poly(vinyltoluene-co-alpha-methylstyrene) 1:1, poly-2-vinylpyridine, poly-4-vinylpyridine, poly-alpha-pinene, polymethylmethacrylate, polybenzylmethacrylate, polyethylmethacrylate, polyethylene, polyethylene terephthalate, polyethylene-co-ethylacrylate 18% ethyl acrylate, polyethylene-co-vinylacetate 12% vinyl acetate, polyethylene-graft-maleic anhydride 0.5% maleic anhydride, polypropylene, polypropylene-graft-maleic anhydride 8-10% maleic anhydride, polystyrene poly(styrene-block- ethylene/butylene-block -

styrene) graft maleic anhydride 2% maleic anhydride 1:1:1 others, poly(styrene-block-butadiene) branched 1:1, poly(styrene-block-butadiene-block-styrene), 30% styrene, poly(styrene-block-isoprene) 10% wt styrene, poly(styrene-block-isoprene-block-styrene) 17% wt styrene, poly(styrene-co-4-chloromethylstyrene-co-4-methoxymethylstyrene 2:1:1, polystyrene-co-acrylonitrile 25% acrylonitrile, polystyrene-co-alpha-methylstyrene 1:1, polystyrene-co-butadiene 4% butadiene, polystyrene-co-butadiene 45% styrene, polystyrene-co-chloromethylstyrene 1:1, polyvinylchloride, polyvinylcinnamate, polyvinylcyclohexane, polyvinylidenefluoride, polyvinylidenefluoride-co-hexafluoropropylene assume 1:1, poly(styrene-block-ethylene/propylene-block-styrene) 30% styrene, poly(styrene- block-ethylene/propylene-block-styrene) 18% styrene, poly(styrene- block-ethylene/propylene-block-styrene) 13% styrene, poly(styrene- block ethylene block-ethylene/propylene-block styrene) 32% styrene, poly(styrene- block ethylene block-ethylene/propylene-block styrene) 30% styrene, poly(styrene- block-ethylene/butylene-block-styrene) 31% styrene, poly(styrene- block-ethylene/butylene-block-styrene) 34% styrene, poly(styrene- block-ethylene/butylene-block-styrene) 30% styrene, poly(styrene- block-ethylene/butylene-block-styrene) 60%, styrene, branched or non-branched polystyrene-block-polybutadiene, polystyrene-block(polyethylene-ran-butylene)-block-polystyrene, polystyrene-block-polybutadiene-block-polystyrene, polystyrene-(ethylene-propylene)-diblock-copolymers (e.g. KRATON®-G1701E, Shell), poly(propylene-co-ethylene) and poly(styrene-co-methylmethacrylate).

Preferred insulating binders to be used in the formulations as described before are polystryrene, poly(α-methylstyrene), polyvinylcinnamate, poly(4-vinylbiphenyl), poly(4-methylstyrene), and polymethyl methacrylate. Most preferred insulating binders are polystyrene and polymethyl methacrylate.

The binder can also be selected from crosslinkable binders, like e.g. acrylates, epoxies, vinylethers, thiolenes etc. The binder can also be mesogenic or liquid crystalline.

The organic binder may itself be a semiconductor, in which case it will be referred to herein as a semiconducting binder. The semiconducting binder is still preferably a binder of low permittivity as herein defined. Semiconducting binders for use in the present invention preferably have a number average molecular weight (M_n) of at least 1500-2000, more preferably at least 3000, even more preferably at least 4000 and most preferably at least 5000. The semiconducting binder preferably has a charge carrier mobility of at least $10^{-5}cm^2V^{-1}s^{-1}$, more preferably at least $10^{-4}cm^2V^{-1}s^{-1}$.

A preferred semiconducting binder comprises a homo-polymer or copolymer (including block-copolymer) containing arylamine (preferably triarylamine).

The compounds and compositions according to the present invention are useful as charge transport, semiconducting, electrically conducting, photoconducting or light emitting materials in optical, electronic, optoelectronic, electroluminescent or photoluminescent components or devices. In these devices, the compounds and compositions of the present invention are typically applied as thin layers or films.

Thus, the present invention also provides the use of the compound or composition or layer in an electronic device. The compound or composition may be used as a high mobility semiconducting material in various devices and apparatus. The compound or composition may be used, for example, in the form of a semiconducting layer or film. Accordingly, in another aspect, the present invention provides a semiconducting layer for use in an electronic device, the layer comprising a compound or composition according to the invention. The layer or film may be less than about 30 microns. For various electronic device applications, the thickness may be less than about 1 micron thick. The layer may be deposited, for example on a part of an electronic device, by any of the aforementioned solution coating or printing techniques.

The compounds according to the present invention can also be used in patterned OSC layers in the devices as described above and below. For

applications in modern microelectronics it is generally desirable to generate small structures or patterns to reduce cost (more devices/unit area), and power consumption. Patterning of thin layers comprising a compound according to the present invention can be carried out for example by photolithography, electron beam lithography or laser patterning.

For use as thin layers in electronic or optoelectronic devices the compounds, compositions or formulations of the present invention may be deposited by any suitable method. Liquid coating of devices is more desirable than vacuum deposition techniques. Solution deposition methods are especially preferred. The formulations of the present invention enable the use of a number of liquid coating techniques. Preferred deposition techniques include, without limitation, dip coating, spin coating, ink jet printing, nozzle printing, letter-press printing, screen printing, gravure printing, doctor blade coating, roller printing, reverse-roller printing, offset lithography printing, dry offset lithography printing, flexographic printing, web printing, spray coating, curtain coating, brush coating, slot dye coating or pad printing.

For the fabrication of OPV devices and modules area printing method compatible with flexible substrates are preferred, for example slot dye coating, spray coating and the like.

Ink jet printing is particularly preferred when high resolution layers and devices needs to be prepared. Selected formulations of the present invention may be applied to prefabricated device substrates by ink jet printing or microdispensing. Preferably industrial piezoelectric print heads such as but not limited to those supplied by Aprion, Hitachi-Koki, InkJet Technology, On Target Technology, Picojet, Spectra, Trident, Xaar may be used to apply the organic semiconductor layer to a substrate. Additionally semi-industrial heads such as those manufactured by Brother, Epson, Konica, Seiko Instruments Toshiba TEC or single nozzle microdispensers such as those produced by Microdrop and Microfab may be used.

In order to be applied by ink jet printing or microdispensing, the

compounds or polymers should be first dissolved in a suitable solvent.

Suitable solvents should be selected to ensure full dissolution of all components, like p-type and n-type OSCs, and take into account the boundary conditions (for example rheological properties) introduced by the chosen printing method. For inkjet printing solvents and solvent mixtures with high boiling temperatures are preferred. For spin coating alkylated benzenes like xylene and toluene are preferred.

Apart from the requirements stated above the solvents should not have any detrimental effect on the chosen print head. Additionally, the solvents should preferably have boiling points >100°C, preferably >140°C and more preferably >150°C in order to prevent operability problems caused by the solution drying out inside the print head.

Apart from the solvents mentioned above, suitable solvents include substituted and non-substituted xylene derivatives, di-C_{1-2}-alkyl formamide, substituted and non-substituted anisoles and other phenol-ether derivatives, substituted heterocycles such as substituted pyridines, pyrazines, pyrimidines, pyrrolidinones, substituted and non-substituted *N,N*-di-C_{1-2}-alkylanilines and other fluorinated or chlorinated aromatics.

A preferred solvent for depositing a compound by ink jet printing comprises a benzene derivative which has a benzene ring substituted by one or more substituents wherein the total number of carbon atoms among the one or more substituents is at least three. For example, the benzene derivative may be substituted with a propyl group or three methyl groups, in either case there being at least three carbon atoms in total. Such a solvent enables an ink jet fluid to be formed comprising the solvent with the compound, which reduces or prevents clogging of the jets and separation of the components during spraying. The solvent(s) may include those selected from the following list of examples: dodecylbenzene, 1-methyl-4-tert-butylbenzene, terpineol, limonene, isodurene, terpinolene, cymene, and diethylbenzene. The solvent may be a solvent mixture, that is a combination of two or more solvents, each solvent preferably having a boiling point >100°C, more preferably >140°C. Such solvent(s) also

enhance film formation in the layer deposited and reduce defects in the layer.

The ink jet fluid (that is mixture of solvent, binder and semiconducting compound) preferably has a viscosity at 20°C of 1-100 mPa·s, more preferably 1-50 mPa·s and most preferably 1-30 mPa·s.

The invention additionally provides an OE device comprising a compound or composition or organic semiconducting layer according to the present invention.

Preferred OE devices are OFETs, TFTs, ICs, logic circuits, capacitors, RFID tags, OLEDs, OLETs, OPEDs, OPVs, PSCs, OPDs, solar cells, laser diodes, photoconductors, photodetectors, electrophotographic devices, electrophotographic recording devices, organic memory devices, sensor devices, charge injection layers, Schottky diodes, planarizing layers, antistatic films, conducting substrates and conducting patterns, .

Very preferred OE devices are OPV, PSC and OPD devices, OFETs, and OLEDs, in particular OPD, PSC and bulk heterojunction (BHJ) OPV devices. In an OFET, for example, the active semiconductor channel between the drain and source may comprise the compound or composition of the invention. As another example, in an OLED device, the charge (hole or electron) injection or transport layer may comprise the compound or composition of the invention.

An OPV or OPD device according to the present invention preferably further comprises a first transparent or semi-transparent electrode on a transparent or semi-transparent substrate on one side of the photoactive layer, and a second metallic or semi-transparent electrode on the other side of the photoactive layer.

Further preferably the OPV or OPD device comprises, between the photoactive layer and the first or second electrode, one or more additional buffer layers acting as hole transporting layer and/or electron blocking layer, which comprise a material such as metal oxide, like for example,

ZTO, MoO_x, NiO_x, a conjugated polymer electrolyte, like for example PEDOT:PSS, a conjugated polymer, like for example polytriarylamine (PTAA), an insulating polymer, like for example nafion, polyethyleneimine or polystyrenesulphonate, an organic compound, like for example N,N′-diphenyl-N,N′-bis(1-naphthyl)(1,1′-biphenyl)-4,4′diamine (NPB), N,N'-diphenyl-N,N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), or alternatively as hole blocking layer and/or electron transporting layer, which comprise a material such as metal oxide, like for example, ZnO_x, TiO_x, a salt, like for example LiF, NaF, CsF, a conjugated polymer electrolyte, like for example poly[3-(6-trimethylammoniumhexyl)thiophene], poly(9,9-bis(2-ethylhexyl)-fluorene]-*b*-poly[3-(6-trimethylammoniumhexyl)thiophene], or poly [(9,9-bis(3´-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9–dioctylfluorene)] or an organic compound, like for example tris(8-quinolinolato)-aluminum(III) (Alq_3), 4,7-diphenyl-1,10-phenanthroline.

The OPV device can for example be of any type known from the literature (see e.g. Waldauf *et al.*, *Appl. Phys. Lett.*, **2006**, *89*, 233517).

A first preferred OPV device according to the invention comprises the following layers (in the sequence from bottom to top):

- optionally a substrate,
- a high work function electrode, preferably comprising a metal oxide, like for example ITO, serving as anode,
- an optional conducting polymer layer or hole transport layer, preferably comprising an organic polymer or polymer blend, for example of PEDOT:PSS (poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate), or TBD (N,N'-dyphenyl-N-N'-bis(3-methylphenyl)-1,1'biphenyl-4,4'-diamine) or NBD (N,N'-dyphenyl-N-N'-bis(1-napthylphenyl)-1,1'biphenyl-4,4'-diamine),
- a layer, also referred to as "photoactive layer", comprising a p-type and an n-type organic semiconductor, which can exist for example as a p-type/n-type bilayer or as distinct p-type and n-type layers, or as blend or p-type and n-type semiconductor, forming a BHJ,
- optionally a layer having electron transport properties, for example comprising LiF or PFN,

- a low work function electrode, preferably comprising a metal like for example aluminum, serving as cathode,

wherein at least one of the electrodes, preferably the anode, is transparent to visible light, and

wherein the n-type semiconductor is a compound according to the present invention.

A second preferred OPV device according to the invention is an inverted OPV device and comprises the following layers (in the sequence from bottom to top):

- optionally a substrate,
- a high work function metal or metal oxide electrode, comprising for example ITO, serving as cathode,
- a layer having hole blocking properties, preferably comprising an organic polymer, polymer blend, metal or metal oxide like TiO_x, ZnO_x, Ca, Mg, poly(ethyleneimine), poly(ethyleneimine) ethoxylated or poly [(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9–dioctylfluorene)],
- a photoactive layer comprising a p-type and an n-type organic semiconductor, situated between the electrodes, which can exist for example as a p-type/n-type bilayer or as distinct p-type and n-type layers, or as blend or p-type and n-type semiconductor, forming a BHJ,
- an optional conducting polymer layer or hole transport layer, preferably comprising an organic polymer or polymer blend, metal or metal oxide, for example PEDOT:PSS, nafion, a substituted triaryl amine derivative like for example TBD or NBD, or WO_x, MoO_x, NiO_x, Pd or Au,
- an electrode comprising a high work function metal like for example silver, serving as anode,

wherein at least one of the electrodes, preferably the cathode, is transparent to visible light, and

wherein the n-type semiconductor is a compound according to the present invention.

In the OPV devices of the present invention the p-type and n-type semiconductor materials are preferably selected from the materials, like

the compound/polymer/fullerene systems, as described above.

When the photoactive layer is deposited on the substrate, it forms a BHJ that phase separates at nanoscale level. For discussion on nanoscale phase separation see Dennler et al, *Proceedings of the IEEE*, **2005**, *93 (8)*, 1429 or Hoppe *et al*, *Adv. Func. Mater*, **2004,** *14(10)*, 1005. An optional annealing step may be then necessary to optimize blend morpohology and consequently OPV device performance.

Another method to optimize device performance is to prepare formulations for the fabrication of OPV(BHJ) devices that may include high boiling point additives to promote phase separation in the right way. 1,8-Octanedithiol, 1,8-diiodooctane, nitrobenzene, chloronaphthalene, and other additives have been used to obtain high-efficiency solar cells. Examples are disclosed in J. Peet, *et al*, *Nat. Mater.*, **2007**, *6*, 497 or Fréchet *et al. J. Am. Chem. Soc.*, **2010**, *132*, 7595-7597.

Another preferred embodiment of the present invention relates to the use of a compound or composition according to the present invention as dye, hole transport layer, hole blocking layer, electron transport layer and/or electron blocking layer in a DSSC or a perovskite-based solar cell (PSC), and to a DSSC or PSC comprising a compound or composition according to the present invention.

DSSCs and PSCs can be manufactured as described in the literature, for example in Chem. Rev. 2010, 110, 6595–6663, Angew. Chem. Int. Ed. 2014, 53, 2–15 or in WO2013171520A1

A preferred OE device according to the invention is a solar cell, preferably a PSC, comprising a light absorber which is at least in part inorganic as described below.

In a solar cell comprising the light absorber according to the invention there are no restrictions per se with respect to the choice of the light absorber material which is at least in part inorganic.

The term “at least in part inorganic” means that the light absorber material may be selected from metalorganic complexes or materials which are substantially inorganic and possess preferably a crystalline structure where single positions in the crystalline structure may be allocated by organic ions.

Preferably, the light absorber comprised in the solar cell according to the invention has an optical band-gap ≤ 2.8 eV and ≥ 0.8 eV.

Very preferably, the light absorber in the solar cell according to the invention has an optical band-gap ≤ 2.2 eV and ≥ 1.0 eV.

The light absorber used in the solar cell according to the invention does preferably not contain a fullerene. The chemistry of fullerenes belongs to the field of organic chemistry. Therefore fullerenes do not fulfil the definition of being “at least in part inorganic” according to the invention.

Preferably, the light absorber which is at least in part inorganic is a material having perovskite structure or a material having 2D crystalline perovskite structure.

The term “perovskite” as used above and below denotes generally a material having a perovskite crystalline structure or a 2D crystalline perovskite structure.

The term perovskite solar cell (PSC) means a solar cell comprising a light absorber which is a material having perovskite structure or a material having 2D crystalline perovskite structure.

The light absorber which is at least in part inorganic is without limitation composed of a material having perovskite crystalline structure, a material having 2D crystalline perovskite structure (e.g. CrystEngComm, 2010,12, 2646-2662), Sb_2S_3 (stibnite), $Sb_2(S_xSe_{(x-1)})_3$, $PbS_xSe_{(x-1)}$, $CdS_xSe_{(x-1)}$, ZnTe, CdTe, $ZnS_xSe_{(x-1)}$, InP, FeS, FeS_2, Fe_2S_3, Fe_2SiS_4, Fe_2GeS_4, Cu_2S, CuInGa, $CuIn(Se_xS_{(1-x)})_2$, $Cu_3Sb_xBi_{(x-1)}(S_ySe_{(y-1)})_3$, Cu_2SnS_3, $SnS_xSe_{(x-1)}$, Ag_2S, $AgBiS_2$, BiSI, BiSeI, $Bi_2(S_xSe_{(x-1)})_3$, $BiS_{(1-x)}Se_xI$, WSe_2, AlSb, metal

halides (e.g. BiI_3, Cs_2SnI_6), chalcopyrite (e.g. $CuIn_xGa_{(1-x)}(S_ySe_{(1-y)})_2$), kesterite (e.g. Cu_2ZnSnS_4, $Cu_2ZnSn(Se_xS_{(1-x)})_4$, $Cu_2Zn(Sn_{1-x}Ge_x)S_4$) and metal oxide (e.g. CuO, Cu_2O) or a mixture thereof.

Preferably, the light absorber which is at least in part inorganic is a perovskite.

In the above definition for light absorber, x and y are each independently defined as follows: ($0 \leq x \leq 1$) and ($0 \leq y \leq 1$).

Very preferably, the light absorber is a special perovskite namely a metal halide perovskite as described in detail above and below. Most preferably, the light absorber is an organic-inorganic hybrid metal halide perovskite contained in the perovskite solar cell (PSC).

In one particularly preferred embodiment of the invention, the perovskite denotes a metal halide perovskite with the formula ABX_3,
where

A is a monovalent organic cation, a metal cation or a mixture of two or more of these cations

B is a divalent cation and

X is F, Cl, Br, I, BF_4 or a combination thereof.

Preferably, the monovalent organic cation of the perovskite is selected from alkylammonium, wherein the alkyl group is straight chain or branched having 1 to 6 C atoms, formamidinium or guanidinium or wherein the metal cation is selected from K^+, Cs^+ or Rb^+.

Suitable and preferred divalent cations B are Ge^{2+}, Sn^{2+} or Pb^{2+}.

Suitable and preferred perovskite materials are $CsSnI_3$, $CH_3NH_3Pb(I_{1-x}Cl_x)_3$, $CH_3NH_3PbI_3$, $CH_3NH_3Pb(I_{1-x}Br_x)_3$, $CH_3NH_3Pb(I_{1-x}(BF_4)_x)_3$, $CH_3NH_3Sn(I_{1-x}Cl_x)_3$, $CH_3NH_3SnI_3$ or $CH_3NH_3Sn(I_{1-x}Br_x)_3$ wherein x is each independently defined as follows: ($0 < x \leq 1$).

Further suitable and preferred perovskites may comprise two halides corresponding to formula $Xa_{(3-x)}Xb_{(x)}$, wherein Xa and Xb are each independently selected from Cl, Br, or I, and x is greater than 0 and less than 3.

Suitable and preferred perovskites are also disclosed in WO 2013/171517, claims 52 to 71 and claims 72 to 79, which is entirely incorporated herein by reference. The materials are defined as mixed-anion perovskites comprising two or more different anions selected from halide anions and chalcogenide anions. Preferred perovskites are disclosed on page 18, lines 5 to 17. As described, the perovskite is usually selected from $CH_3NH_3PbBrI_2$, $CH_3NH_3PbBrCl_2$, $CH_3NH_3PbIBr_2$, $CH_3NH_3PbICl_2$, $CH_3NH_3SnF_2Br$, $CH_3NH_3SnF_2I$ and $(H_2N{=}CH{-}NH_2)PbI_{3z}Br_{3(1-z)}$, wherein z is greater than 0 and less than 1.

The invention further relates to a solar cell comprising the light absorber, preferably a PSC, as described above and below, wherein the compound according to the present invention is employed as a layer between one electrode and the light absorber layer.

The invention further relates to a solar cell comprising the light absorber, preferably a PSC, as described above and below, wherein the compound according to the present invention is comprised in an electron-selective layer.

The electron selective layer is defined as a layer providing a high electron conductivity and a low hole conductivity favoring electron-charge transport.

The invention further relates to a solar cell comprising the light absorber, preferably a PSC, as described above and below, wherein the compound according to the present invention is employed as electron transport material (ETM) or as hole blocking material as part of the electron selective layer.

Preferably, the compound according to the present invention is employed as electron transport material (ETM).

In an alternative preferred embodiment, the compound according to the present invention is employed as hole blocking material.

The device architecture of a PSC device according to the invention can be of any type known from the literature.

A first preferred device architecture of a PSC device according to the invention comprises the following layers (in the sequence from bottom to top):

- optionally a substrate which, in any combination, can be flexible or rigid and transparent, semi-transparent or non-transparent and electrically conductive or non-conductive;
- a high work function electrode, preferably comprising a doped metal oxide, for example fluorine-doped tin oxide (FTO), tin-doped indium oxide (ITO), or aluminum-doped zinc oxide;
- an electron-selective layer which comprises one or more electron-transporting materials, at least one of which is a compound according to the present invention, and which, in some cases, can also be a dense layer and/or be composed of nanoparticles, and which preferably comprises a metal oxide such as TiO_2, ZnO_2, SnO_2, Y_2O_5, Ga_2O_3, $SrTiO_3$, $BaTiO_3$ or combinations thereof;
- optionally a porous scaffold which can be conducting, semi-conducting or insulating, and which preferably comprises a metal oxide such as TiO_2, ZnO_2, SnO_2, Y_2O_5, Ga_2O_3, $SrTiO_3$, $BaTiO_3$, Al_2O_3, ZrO_2, SiO_2 or combinations thereof, and which is preferably composed of nanoparticles, nanorods, nanoflakes, nanotubes or nanocolumns;
- a layer comprising a light absorber which is at least in part inorganic, particularly preferably a metal halide perovskite as described above which, in some cases, can also be a dense or porous layer and which optionally partly or fully infiltrates into the underlying layer;
- optionally a hole selective layer, which comprises one or more hole-transporting materials, and which, in some cases, can also comprise additives such as lithium salts, for example LiY, where Y is a monovalent organic anion, preferably bis(trifluoromethylsulfonyl)imide, tertiary amines such as 4-tert-butylpyridine, or any other covalent or

ionic compounds, for example tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl)imide)), which can enhance the properties of the hole selective layer, for example the electrical conductivity, and/or facilitate its processing;

and a back electrode which can be metallic, for example made of Au, Ag, Al, Cu, Ca, Ni or combinations thereof, or non-metallic and transparent, semi-transparent or non-transparent.

A second preferred device architecture of a PSC device according to the invention comprises the following layers (in the sequence from bottom to top):

- optionally a substrate which, in any combination, can be flexible or rigid and transparent, semi-transparent or non-transparent and electrically conductive or non-conductive;
- a high work function electrode, preferably comprising a doped metal oxide, for example fluorine-doped tin oxide (FTO), tin-doped indium oxide (ITO), or aluminum-doped zinc oxide;
- optionally a hole injection layer which, for example, changes the work function of the underlying electrode, and/or modifies the surface of the underlying layer and/or helps to planarize the rough surface of the underlying layer and which, in some cases, can also be a monolayer;
- optionally a hole selective layer, which comprises one or more hole-transporting materials and which, in some cases, can also comprise additives such as lithium salts, for example LiY, where Y is a monovalent organic anion, preferably bis(trifluoromethylsulfonyl)imide, tertiary amines such as 4-tert-butylpyridine, or any other covalent or ionic compounds, for example tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl)imide)), which can enhance the properties of the hole selective layer, for example the electrical conductivity, and/or facilitate its processing;
- a layer comprising a light absorber which is at least in part inorganic, particularly preferably a metal halide perovskite as described or preferably described above;
- an electron-selective layer, which comprises one or more electron-transporting materials, at least one of which is a compound according to the present invention and which, in some cases, can also be a

dense layer and/or be composed of nanoparticles, and which, for example, can comprise a metal oxide such as TiO_2, ZnO_2, SnO_2, Y_2O_5, Ga_2O_3, $SrTiO_3$, $BaTiO_3$ or combinations thereof, and/or which can comprise a substituted fullerene, for example [6,6]-phenyl C61-butyric acid methyl ester, and/or which can comprise a molecular, oligomeric or polymeric electron-transport material, for example 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline, or a mixture thereof;

and a back electrode which can be metallic, for example made of Au, Ag, Al, Cu, Ca, Ni or combinations thereof, or non-metallic and transparent, semi-transparent or non-transparent.

To produce electron selective layers in PSC devices according to the invention, the compounds according to the present invention, optionally together with other compounds or additives in the form of blends or mixtures, may be deposited by any suitable method. Liquid coating of devices is more desirable than vacuum deposition techniques. Solution deposition methods are especially preferred. Formulations comprising the compounds according to the present invention enable the use of a number of liquid coating techniques. Preferred deposition techniques include, without limitation, dip coating, spin coating, ink jet printing, nozzle printing, letter-press printing, screen printing, gravure printing, doctor blade coating, roller printing, reverse-roller printing, offset lithography printing, dry offset lithography printing, flexographic printing, web printing, spray coating, curtain coating, brush coating, slot die coating or pad printing. For the fabrication of PSC devices and modules, deposition techniques for large area coating are preferred, for example slot die coating or spray coating.

Formulations that can be used to produce electron selective layers in optoelectronic devices according to the invention, preferably in PSC devices comprise one or more compounds according to the present invention or preferred embodiments as described above in the form of blends or mixtures optionally together with one or more further electron transport materials and/or hole blocking materials and/or binders and/or other additives as described above and below, and one or more solvents.

The formulation may include or comprise, essentially consist of or consist of the said necessary or optional constituents as described above or below. All compounds or components which can be used in the formulations are either known or commercially available, or can be synthesized by known processes.

The formulation as described before may be prepared by a process which comprises:

(i) first mixing a compound according to the present invention, optionally a binder or a precursor of a binder as described before, optionally a further electron transport material, optionally one or more further additives as described above and below and a solvent or solvent mixture as described above and below and

(ii) applying such mixture to a substrate; and optionally evaporating the solvent(s) to form an electron selective layer according to the present invention.

In step (i) the solvent may be a single solvent for the compound according to the present invention and the organic binder and/or further electron transport material may each be dissolved in a separate solvent followed by mixing the resultant solutions to mix the compounds.

Alternatively, the binder may be formed *in situ* by mixing or dissolving a compound according to the present invention in a precursor of a binder, for example a liquid monomer, oligomer or crosslinkable polymer, optionally in the presence of a solvent, and depositing the mixture or solution, for example by dipping, spraying, painting or printing it, on a substrate to form a liquid layer and then curing the liquid monomer, oligomer or crosslinkable polymer, for example by exposure to radiation, heat or electron beams, to produce a solid layer. If a preformed binder is used it may be dissolved together with the compound in a suitable solvent as described before, and the solution deposited for example by dipping, spraying, painting or printing it on a substrate to form a liquid layer and then removing the solvent to leave a solid layer. It will be appreciated that solvents are chosen which are able to dissolve all ingredients of the

formulation, and which upon evaporation from the solution blend give a coherent defect free layer.

Besides the said components, the formulation as described before may comprise further additives and processing assistants. These include, inter alia, surface-active substances (surfactants), lubricants and greases, additives which modify the viscosity, additives which increase the conductivity, dispersants, hydrophobicizing agents, adhesion promoters, flow improvers, antifoams, deaerating agents, diluents, which may be reactive or unreactive, fillers, assistants, processing assistants, dyes, pigments, stabilizers, sensitizers, nanoparticles and inhibitors.

Additives can be used to enhance the properties of the electron selective layer and/or the properties of any of the neighbouring layers and/or the performance of the optoelectronic device according to the invention. Additives can also be used to facilitate the deposition, the processing or the formation of the electron selective layer and/or the deposition, the processing or the formation of any of the neighbouring layers. Preferably, one or more additives are used which enhance the electrical conductivity of the electron selective layer and/or passivate the surface of any of the neighbouring layers.

Suitable methods to incorporate one or more additives include, for example exposure to a vapor of the additive at atmospheric pressure or at reduced pressure, mixing a solution or solid containing one or more additives and a material or a formulation as described or preferably described before, bringing one or more additives into contact with a material or a formulation as described before, by thermal diffusion of one or more additives into a material or a formulation as described before, or by ion-implantation of one or more additives into a material or a formulation as described before.

Additives used for this purpose can be organic, inorganic, metallic or hybrid materials. Additives can be molecular compounds, for example organic molecules, salts, ionic liquids, coordination complexes or organometallic compounds, polymers or mixtures thereof. Additives can

also be particles, for example hybrid or inorganic particles, preferably nanoparticles, or carbon based materials such as fullerenes, carbon nanotubes or graphene flakes.

Examples for additives that can enhance the electrical conductivity are for example halogens (e.g. I_2, Cl_2, Br_2, ICl, ICl_3, IBr and IF), Lewis acids (e.g. PF_5, AsF_5, SbF_5, BF_3, BCl_3, $SbCl_5$, BBr_3 and SO_3), protonic acids, organic acids, or amino acids (e.g. HF, HCl, HNO_3, H_2SO_4, $HClO_4$, FSO_3H and $ClSO_3H$), transition metal compounds (e.g. $FeCl_3$, FeOCl, $Fe(ClO_4)_3$, $Fe(4\text{-}CH_3C_6H_4SO_3)_3$, $TiCl_4$, $ZrCl_4$, $HfCl_4$, NbF_5, $NbCl_5$, $TaCl_5$, MoF_5, $MoCl_5$, WF_5, WCl_6, UF_6 and $LnCl_3$ (wherein Ln is a lanthanoid)), anions (e.g. Cl^-, Br^-, I^-, I_3^-, HSO_4^-, SO_4^{2-}, NO_3^-, ClO_4^-, BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, $FeCl_4^-$, $Fe(CN)_6^{3-}$, and anions of various sulfonic acids, such as aryl-SO_3^-), cations (e.g. H^+, Li^+, Na^+, K^+, Rb^+, Cs^+, Co^{3+} and Fe^{3+}), O_2, redox active salts (e.g. $XeOF_4$, $(NO_2^+)(SbF_6^-)$, $(NO_2^+)(SbCl_6^-)$, $(NO_2^+)(BF_4^-)$, $NOBF_4$, $NOPF_6$, $AgClO_4$, H_2IrCl_6 and $La(NO_3)_3 \cdot 6H_2O$), strongly electron-accepting organic molecules (e.g. 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ)), transition metal oxides (e.g. WO_3, Re_2O_7 and MoO_3), metal-organic complexes of cobalt, iron, bismuth and molybdenum, $(p\text{-}BrC_6H_4)_3NSbCl_6$, bismuth(III) tris(trifluoroacetate), FSO_2OOSO_2F, acetylcholine, R_4N^+, (R is an alkyl group), R_4P^+ (R is a straight-chain or branched alkyl group 1 to 20), R_6As^+ (R is an alkyl group), R_3S^+ (R is an alkyl group) and ionic liquids (e.g. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide). Suitable cobalt complexes beside of tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl)imide)) are cobalt complex salts as described in WO 2012/114315, WO 2012/114316, WO 2014/082706, WO 2014/082704, EP 2883881 or JP 2013-131477.

Suitable lithium salts are beside of lithium bis(trifluoromethylsulfonyl)imide, lithium tris(pentafluoroethyl)trifluorophosphate, lithium dicyanamide, lithium methylsulfate, lithium trifluormethanesulfonate, lithium tetracyanoborate, lithium dicyanamide, lithium tricyanomethide, lithium thiocyanate, lithium chloride, lithium bromide, lithium iodide, lithium hexafluorophosphate, lithium tetrafluoroborate, lithium perchlorate, lithium hexafluoroantimonate,

lithium hexafluoroarsenate or a combination of two or more. A preferred lithium salt is lithium bis(trifluoromethylsulfonyl)imide.

Preferably, the formulation comprises from 0.1 mM to 50 mM, preferably from 5 to 20 mM of the lithium salt.

Suitable device structures for PSCs comprising a compound according to the present invention and a mixed halide perovskite are described in WO 2013/171517, claims 52 to 71 and claims 72 to 79, which is entirely incorporated herein by reference.

Suitable device structures for PSCs comprising a compound according to the present invention and a dielectric scaffold together with a perovskite are described in WO 2013/171518, claims 1 to 90 or WO 2013/171520, claims 1 to 94 which are entirely incorporated herein by reference.

Suitable device structures for PSCs comprising a compound according to the present invention, a semiconductor and a perovskite are described in WO 2014/020499, claims 1 and 3 to 14, which is entirely incorporated herein by reference The surface-increasing scaffold structure described therein comprises nanoparticles which are applied and/or fixed on a support layer, e.g. porous TiO_2.

Suitable device structures for PSCs comprising a compound according to the present invention and comprising a planar heterojunction are described in WO 2014/045021, claims 1 to 39, which is entirely incorporated herein by reference. Such a device is characterized in having a thin film of a light-absorbing or light-emitting perovskite disposed between n-type (electron conducting) and p-type (hole-conducting) layers. Preferably, the thin film is a compact thin film.

The invention further relates to a method of preparing a PSC as described above or below, the method comprising the steps of:

- providing a first and a second electrode;
- providing an electron selective layer comprising a compound according to the present invention.

The invention relates furthermore to a tandem device comprising at least one device according to the invention as described above and below. Preferably, the tandem device is a tandem solar cell.

The tandem device or tandem solar cell according to the invention may have two semi-cells wherein one of the semi cells comprises the compounds, oligomers or polymers in the active layer as described or preferably described above. There exists no restriction for the choice of the other type of semi cell which may be any other type of device or solar cell known in the art.

There are two different types of tandem solar cells known in the art. The so called 2-terminal or monolithic tandem solar cells have only two connections. The two subcells (or synonymously semi cells) are connected in series. Therefore, the current generated in both subcells is identical (current matching). The gain in power conversion efficiency is due to an increase in voltage as the voltages of the two subcells add up.
The other type of tandem solar cells is the so called 4-terminal or stacked tandem solar cell. In this case, both subcells are operated independently. Therefore, both subcells can be operated at different voltages and can also generate different currents. The power conversion efficiency of the tandem solar cell is the sum of the power conversion efficiencies of the two subcells.

The invention furthermore relates to a module comprising a device according to the invention as described before or preferably described before.

The compounds and compositions according to the present invention can also be used as dye or pigment in other applications, for example as an ink dye, laser dye, fluorescent marker, solvent dye, food dye, contrast dye or pigment in coloring paints, inks, plastics, fabrics, cosmetics, food and other materials.

The compounds and compositions of the present invention are also

suitable for use in the semiconducting channel of an OFET. Accordingly, the invention also provides an OFET comprising a gate electrode, an insulating (or gate insulator) layer, a source electrode, a drain electrode and an organic semiconducting channel connecting the source and drain electrodes, wherein the organic semiconducting channel comprises a compound or a composition according to the present invention. Other features of the OFET are well known to those skilled in the art.

OFETs where an OSC material is arranged as a thin film between a gate dielectric and a drain and a source electrode, are generally known, and are described for example in US 5,892,244, US 5,998,804, US 6,723,394 and in the references cited in the background section. Due to the advantages, like low cost production using the solubility properties of the compounds according to the invention and thus the processibility of large surfaces, preferred applications of these OFETs are such as integrated circuitry, TFT displays and security applications.

The gate, source and drain electrodes and the insulating and semiconducting layer in the OFET device may be arranged in any sequence, provided that the source and drain electrode are separated from the gate electrode by the insulating layer, the gate electrode and the semiconductor layer both contact the insulating layer, and the source electrode and the drain electrode both contact the semiconducting layer.

An OFET device according to the present invention preferably comprises:
- a source electrode,
- a drain electrode,
- a gate electrode,
- a semiconducting layer,
- one or more gate insulator layers,
- optionally a substrate.

wherein the semiconductor layer preferably comprises a compound according to the present invention.

The OFET device can be a top gate device or a bottom gate device.

Suitable structures and manufacturing methods of an OFET device are known to the skilled in the art and are described in the literature, for example in US 2007/0102696 A1.

The gate insulator layer preferably comprises a fluoropolymer, like e.g. the commercially available Cytop 809M® or Cytop 107M® (from Asahi Glass). Preferably the gate insulator layer is deposited, e.g. by spin-coating, doctor blading, wire bar coating, spray or dip coating or other known methods, from a formulation comprising an insulator material and one or more solvents with one or more fluoro atoms (fluorosolvents), preferably a perfluorosolvent. A suitable perfluorosolvent is e.g. FC75® (available from Acros, catalogue number 12380). Other suitable fluoropolymers and fluorosolvents are known in prior art, like for example the perfluoropolymers Teflon AF® 1600 or 2400 (from DuPont) or Fluoropel® (from Cytonix) or the perfluorosolvent FC 43® (Acros, No. 12377). Especially preferred are organic dielectric materials having a low permittivity (or dielectric constant) from 1.0 to 5.0, very preferably from 1.8 to 4.0 ("low *k* materials"), as disclosed for example in US 2007/0102696 A1 or US 7,095,044.

In security applications, OFETs and other devices with semiconducting materials according to the present invention, like transistors or diodes, can be used for RFID tags or security markings to authenticate and prevent counterfeiting of documents of value like banknotes, credit cards or ID cards, national ID documents, licenses or any product with monetary value, like stamps, tickets, shares, cheques etc.

Alternatively, the compounds and compositions (hereinafter referred to as "materials") according to the present invention can be used in OLEDs, e.g. as the active display material in a flat panel display applications, or as backlight of a flat panel display like e.g. a liquid crystal display. Common OLEDs are realized using multilayer structures. An emission layer is generally sandwiched between one or more electron-transport and/or hole-transport layers. By applying an electric voltage electrons and holes as charge carriers move towards the emission layer where their recombination leads to the excitation and hence luminescence of the

lumophor units contained in the emission layer. The materials according to the present invention may be employed in one or more of the charge transport layers and/or in the emission layer, corresponding to their electrical and/or optical properties. Furthermore their use within the emission layer is especially advantageous, if the materials according to the present invention show electroluminescent properties themselves or comprise electroluminescent groups or compounds. The selection, characterization as well as the processing of suitable monomeric, oligomeric and polymeric compounds or materials for the use in OLEDs is generally known by a person skilled in the art, see, e.g., Müller *et al, Synth. Metals*, **2000**, *111-112*, 31-34, Alcala, *J. Appl. Phys.*, **2000**, *88*, 7124-7128 and the literature cited therein.

According to another use, the materials according to the present invention, especially those showing photoluminescent properties, may be employed as materials of light sources, e.g. in display devices, as described in EP 0 889 350 A1 or by C. Weder *et al.*, *Science*, **1998**, *279*, 835-837.

A further aspect of the invention relates to both the oxidized and reduced form of the materials according to the present invention. Either loss or gain of electrons results in formation of a highly delocalized ionic form, which is of high conductivity. This can occur on exposure to common dopants. Suitable dopants and methods of doping are known to those skilled in the art, e.g. from EP 0 528 662, US 5,198,153 or WO 96/21659.

The doping process typically implies treatment of the semiconductor material with an oxidating or reducing agent in a redox reaction to form delocalized ionic centers in the material, with the corresponding counterions derived from the applied dopants. Suitable doping methods comprise for example exposure to a doping vapor in the atmospheric pressure or at a reduced pressure, electrochemical doping in a solution containing a dopant, bringing a dopant into contact with the semiconductor material to be thermally diffused, and ion-implantation of the dopant into the semiconductor material.

When electrons are used as carriers, suitable dopants are for example

halogens (e.g., I_2, Cl_2, Br_2, ICl, ICl_3, IBr and IF), Lewis acids (e.g., PF_5, AsF_5, SbF_5, BF_3, BCl_3, $SbCl_5$, BBr_3 and SO_3), protonic acids, organic acids, or amino acids (e.g., HF, HCl, HNO_3, H_2SO_4, $HClO_4$, FSO_3H and $ClSO_3H$), transition metal compounds (e.g., $FeCl_3$, FeOCl, $Fe(ClO_4)_3$, $Fe(4\text{-}CH_3C_6H_4SO_3)_3$, $TiCl_4$, $ZrCl_4$, $HfCl_4$, NbF_5, $NbCl_5$, $TaCl_5$, MoF_5, $MoCl_5$, WF_5, WCl_6, UF_6 and $LnCl_3$ (wherein Ln is a lanthanoid), anions (e.g., Cl^-, Br^-, I^-, I_3^-, HSO_4^-, SO_4^{2-}, NO_3^-, ClO_4^-, BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, $FeCl_4^-$, $Fe(CN)_6^{3-}$, and anions of various sulfonic acids, such as aryl-SO_3^-). When holes are used as carriers, examples of dopants are cations (e.g., H^+, Li^+, Na^+, K^+, Rb^+ and Cs^+), alkali metals (e.g., Li, Na, K, Rb, and Cs), alkaline-earth metals (e.g., Ca, Sr, and Ba), O_2, $XeOF_4$, (NO_2^+) (SbF_6^-), (NO_2^+) $(SbCl_6^-)$, (NO_2^+) (BF_4^-), $AgClO_4$, H_2IrCl_6, $La(NO_3)_3 \cdot 6H_2O$, FSO_2OOSO_2F, Eu, acetylcholine, R_4N^+, (R is an alkyl group), R_4P^+ (R is an alkyl group), R_6As^+ (R is an alkyl group), and R_3S^+ (R is an alkyl group).

The conducting form of the materials according to the present invention can be used as an organic "metal" in applications including, but not limited to, charge injection layers and ITO planarizing layers in OLED applications, films for flat panel displays and touch screens, antistatic films, printed conductive substrates, patterns or tracts in electronic applications such as printed circuit boards and condensers.

The materials according to the present invention may also be suitable for use in organic plasmon-emitting diodes (OPEDs), as described for example in Koller *et al.*, *Nat. Photonics*, **2008**, *2*, 684.

According to another use, the materials according to the present invention can be used alone or together with other materials in or as alignment layers in LCD or OLED devices, as described for example in US 2003/0021913. The use of charge transport compounds according to the present invention can increase the electrical conductivity of the alignment layer. When used in an LCD, this increased electrical conductivity can reduce adverse residual dc effects in the switchable LCD cell and suppress image sticking or, for example in ferroelectric LCDs, reduce the residual charge produced by the switching of the spontaneous polarization charge of the ferroelectric LCs. When used in an OLED device comprising

a light emitting material provided onto the alignment layer, this increased electrical conductivity can enhance the electroluminescence of the light emitting material.

The materials according to the present invention having mesogenic or liquid crystalline properties can form oriented anisotropic films as described above, which are especially useful as alignment layers to induce or enhance alignment in a liquid crystal medium provided onto said anisotropic film.

According to another use, the materials according to the present invention are suitable for use in liquid crystal (LC) windows, also known as smart windows, as described for example in US 2016/0108317 A1.

The materials according to the present invention may also be combined with photoisomerizable compounds and/or chromophores for use in or as photoalignment layers, as described in US 2003/0021913 A1.

According to another use, the materials according to the present invention, especially their water-soluble derivatives (for example with polar or ionic side groups) or ionically doped forms, can be employed as chemical sensors or materials for detecting and discriminating DNA sequences. Such uses are described for example in L. Chen, D. W. McBranch, H. Wang, R. Helgeson, F. Wudl and D. G. Whitten, *Proc. Natl. Acad. Sci. U.S.A.,* **1999**, *96*, 12287; D. Wang, X. Gong, P. S. Heeger, F. Rininsland, G. C. Bazan and A. J. Heeger, *Proc. Natl. Acad. Sci. U.S.A.,* **2002**, *99*, 49; N. DiCesare, M. R. Pinot, K. S. Schanze and J. R. Lakowicz, *Langmuir*, **2002**, *18*, 7785; D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.,* **2000**, *100*, 2537.

Unless the context clearly indicates otherwise, as used herein plural forms of the terms herein are to be construed as including the singular form and vice versa.

Throughout the description and claims of this specification, the words “comprise” and “contain” and variations of the words, for example “comprising” and “comprises”, mean “including but not limited to”, and are

not intended to (and do not) exclude other components.

It will be appreciated that variations to the foregoing embodiments of the invention can be made while still falling within the scope of the invention. Each feature disclosed in this specification, unless stated otherwise, may be replaced by alternative features serving the same, equivalent or similar purpose. Thus, unless stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

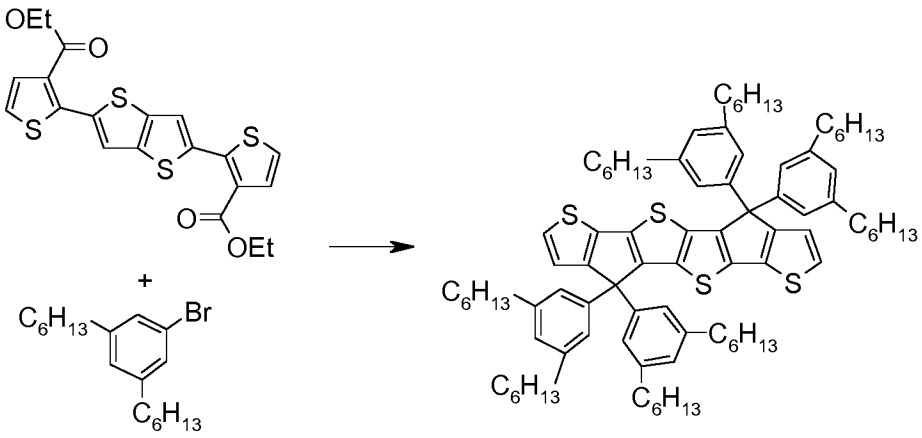
All of the features disclosed in this specification may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. In particular, the preferred features of the invention are applicable to all aspects of the invention and may be used in any combination. Likewise, features described in non-essential combinations may be used separately (not in combination).

Above and below, unless stated otherwise percentages are percent by weight and temperatures are given in degrees Celsius.

The invention will now be described in more detail by reference to the following examples, which are illustrative only and do not limit the scope of the invention.

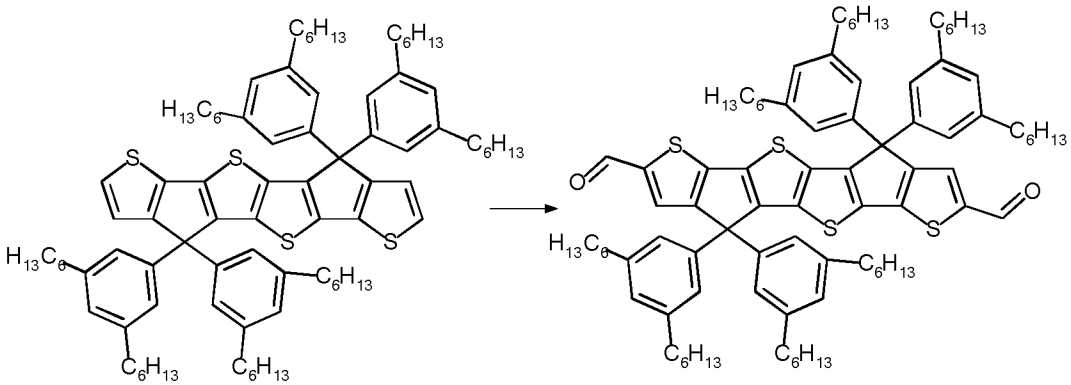
Example 1

Intermediate 1



To a solution of 1-bromo-3,5-dihexyl-benzene (14.5 g, 44.6 mmol) in anhydrous tetrahydrofuran (60 cm^3) at -78 °C is added dropwise *n*-butyllithium (17.8 cm^3, 44.6 mmol, 2.5 M in hexane) over 10 minutes. The reaction is stirred for 2 hours and ethyl 2-[5-(3-ethoxycarbonyl-2-thienyl)thieno[3,2-b]thiophen-2-yl]thiophene-3-carboxylate (4.00 g, 8.92 mmol) added. The reaction is warmed to 23 °C and stirred for 17 hours. Water (100 cm^3) is added and the product extracted with ether (100 cm^3). The organic phase is washed with water (2 x 50 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by flash chromatography (40-60 petrol then dichloromethane). The solid is suspended in toluene (40 cm^3), *p*-toluene sulphonic acid (2.0 g) added and the reaction mixture heated at 60 °C for 4 hours. The solid is collected by filtration, washed with toluene (50 cm^3) and purified by flash chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:0 to 19:1) to give intermediate 1 (2.50 g, 21%) as a pale brown oil. ^1H NMR (400 MHz, $CDCl_3$) 7.07 (2H, d, J 4.9), 6.96 (2H, d, J 4.9), 6.78 (4H, d, J 1.6), 6.74 (8H, d, J 1.5), 2.40 (16H, t, J 8.0), 1.40 - 1.48 (16H, m), 1.10 - 1.26 (48H, m), 0.69 - 0.82 (24H, m).

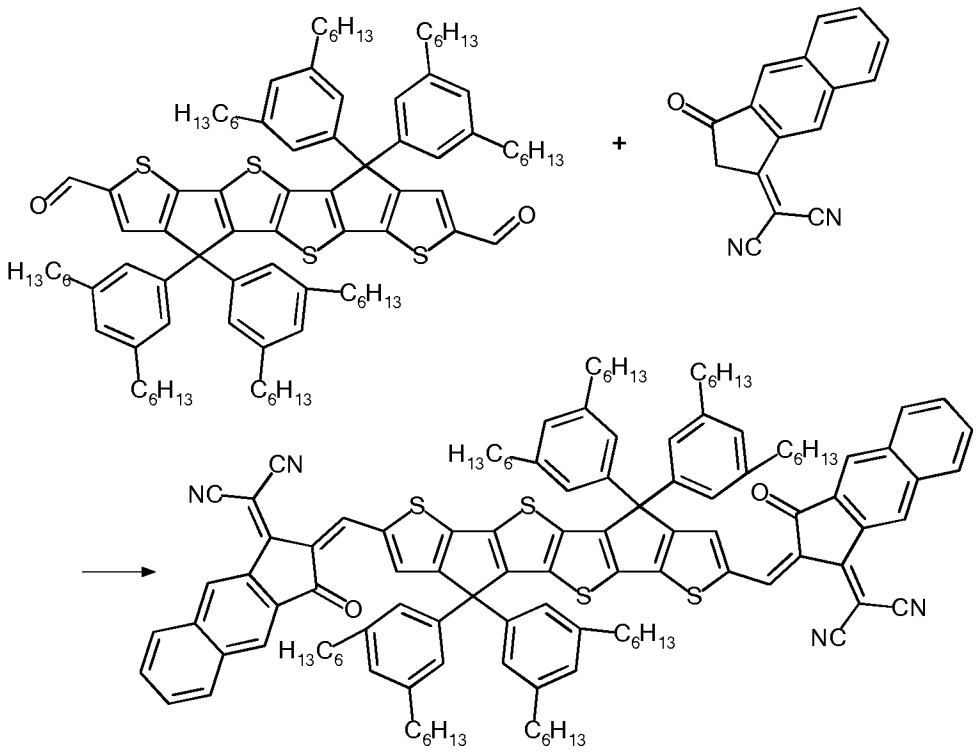
Intermediate 2



To intermediate 1 (0.50 g, 0.38 mmol), anhydrous *N,N*-dimethylformamide (0.40 cm^3, 5.2 mmol) and chloroform (20 cm^3) at 0 °C is added dropwise phosphorus oxychloride (0.47 cm^3, 5.0 mmol). The reaction is heated at 70 °C for 18 hours before cooling to 60 °C. Saturated aqueous sodium

acetate solution (7 cm^3) is added and the mixture stirred for 1 hour. The organic phase is separated and washed with water (20 cm^3), dried with anhydrous sodium sulphate, filtered and the solvent removed *in vacuo*. The solid is triturated in acetone (3 x 5 cm^3) and then collected by filtration to give intermediate 2 (400 mg, 76%) as a bright orange solid. ^1H NMR (400 MHz, CD_2Cl_2) 9.78 (2H, s), 7.64 (2H, s), 6.90 (4H, d, J 1.6), 6.78 (8H, d, J 1.6), 2.46 (16H, d, J 7.9), 1.42 - 1.51 (16H, m), 1.17 - 1.28 (48H, m), 0.76 - 0.85 (24H, m).

Compound 1

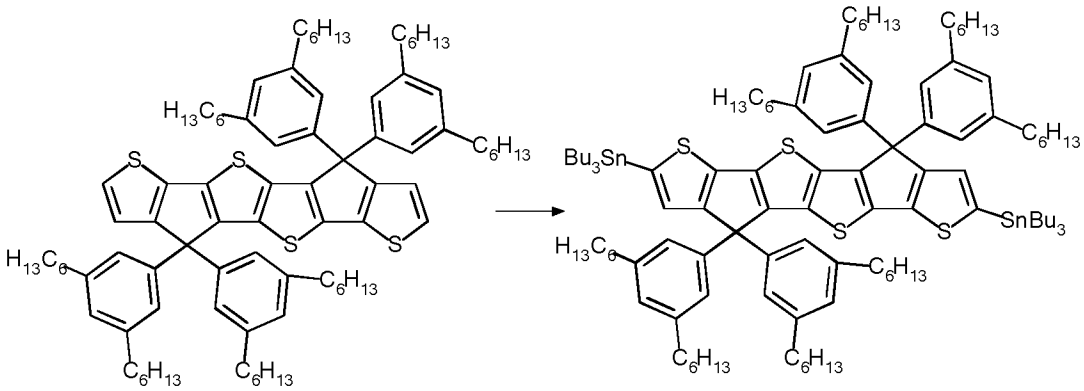


To a solution of intermediate 2 (150 mg, 0.11 mmol) in chloroform (15 cm^3) is added 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (188 mg, 0.77 mmol). The suspension is purged with nitrogen and pyridine (0.62 cm^3) is added. The resulting mixture is stirred for 3 hours. The reaction is diluted with methanol (25 cm^3), filtered and the solid washed with methanol (3 x 5 cm^3). The crude is purified using column chromatography (40-60 petrol:dichloromethane; 1:3). The solid is dissolved in chloroform (4 cm^3) at 70 °C before acetone (4 cm^3) is added, the suspension cooled to 23 °C, filtered and the solid washed with a

solution of acetone/chloroform (1:1; 2 x 3 cm^3) to afford compound 1 (60 mg, 30%) as a dark green solid. ^1H NMR (400 MHz, $CDCl_3$) 9.19 (2H, s), 8.97 (2H, s), 8.36 (2H, s), 8.03 - 8.13 (4H, m), 7.66 - 7.77 (6H, m), 6.98 (4H, t, J 1.5), 6.83 (8H, d, J 1.5), 2.54 (16H, t, J 7.9), 1.50 - 1.61 (16H, m), 1.22 - 1.38 (48H, m), 0.86 (24H, d, J 12.9).

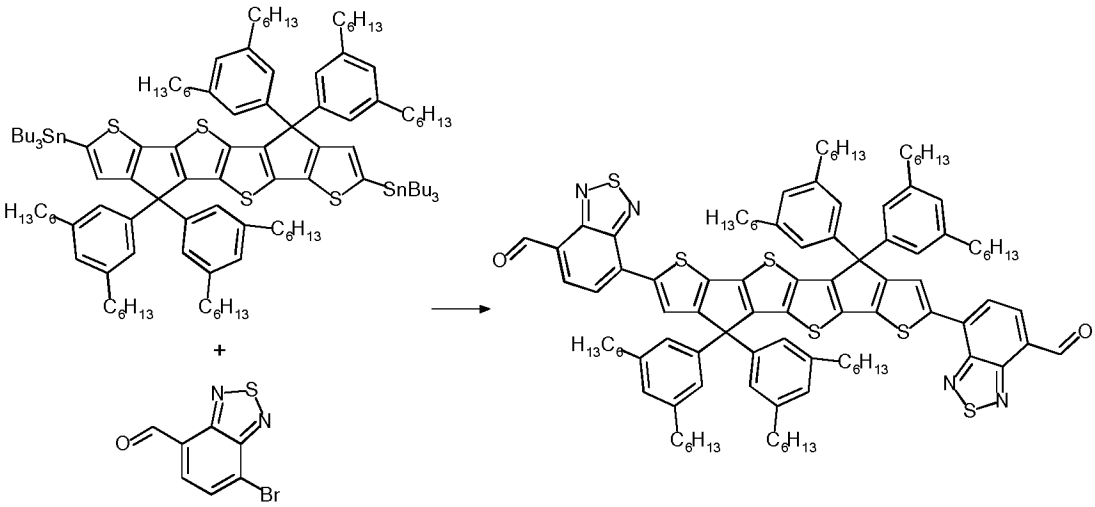
Example 2

Intermediate 3



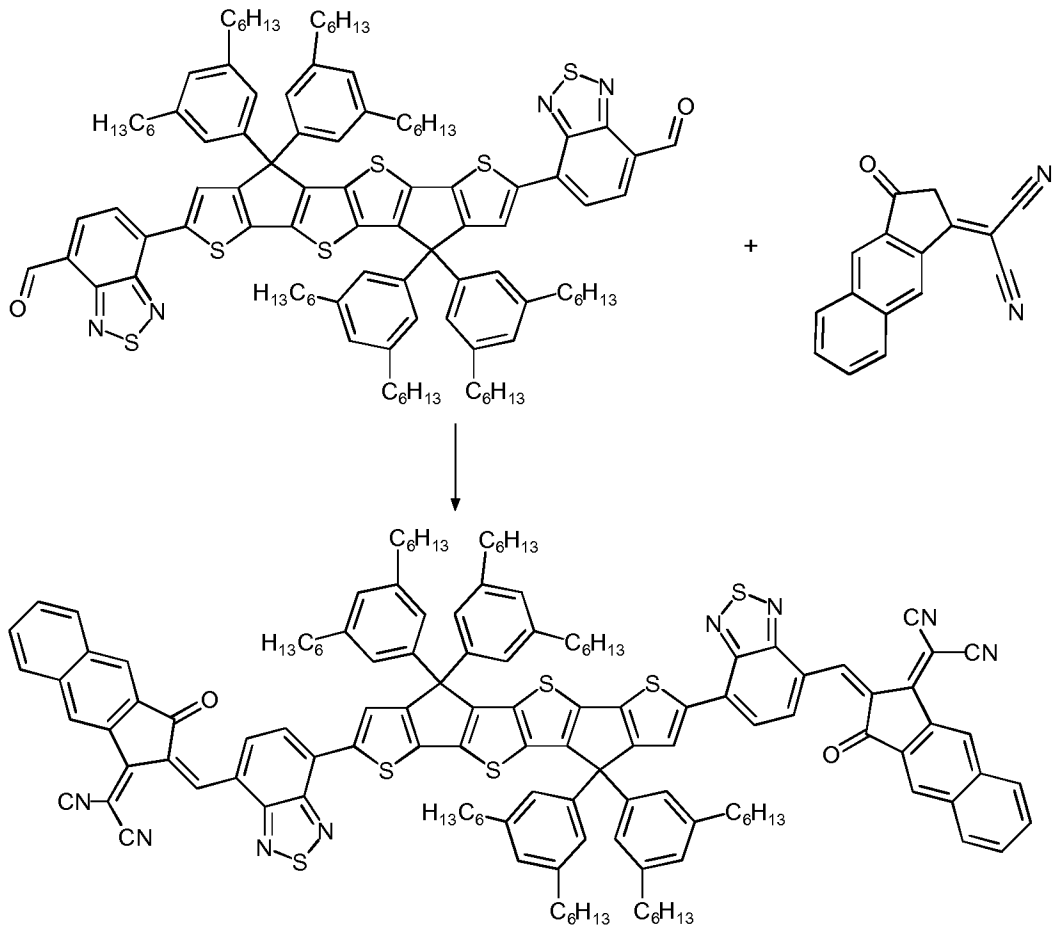
To a solution of intermediate 1 (1.60 g, 1.2 mmol) in anhydrous tetrahydrofuran (47 cm^3) at -78 °C is added dropwise *n*-butyllithium (1.96 cm^3, 4.9 mmol, 2.5 M in hexane) over 20 minutes. After addition, the reaction mixture is stirred at -78 °C for 60 minutes and then tributyltin chloride (1.5 cm^3, 5.5 mmol) is added. The mixture is then allowed to warm to 23 °C over 72 hours and the solvent removed *in vacuo*. The crude is purified by passing through a zeolite plug (40-60 petrol) followed by trituration in ethanol (2 x 100 cm^3) to give a mixture of intermediate 3 and tributyltin chloride (2.7 g) as a dark brown oil. ^1H NMR (400MHz, CD_2Cl_2) 6.99 (2H, s), 6.64 - 6.85 (12H, m), 2.38 (16H, t, J 7.7), 0.57 - 1.69 (98H, m).

Intermediate 4



A mixture of intermediate 3 (1.5 g, 0.48 mmol), 7-bromo-benzo[1,2,5]thiadiazole-4-carbaldehyde (232 mg, 0.96 mmol), tri-*o*-tolyl-phosphine (44 mg, 0.14 mmol) and anhydrous toluene (51 cm^3) is degassed by nitrogen for 10 minutes. To the mixture is added tris(dibenzylideneacetone) dipalladium(0) (35 mg, 0.04 mmol) and the mixture further degassed for 15 minutes. The mixture is stirred at 100 °C for 17 hours and, after cooling to 23 °C, the solvent removed *in vacuo*. The crude is purified using column chromatography (40-60 petrol:dichloromethane; 7:3) to give intermediate 4 (650 mg, 84%) as a dark blue solid. ^1H NMR (400 MHz, $CDCl_3$) 10.67 - 10.73 (2H, m), 8.34 (2H, s), 8.20 (2H, d, J 7.6), 7.93 (2H, d, J 7.6), 6.94 (12H, s), 2.54 (16H, t, J 7.7), 1.51 - 1.64 (16H, m), 1.20 - 1.36 (48H, m), 0.77 - 0.88 (24H, m).

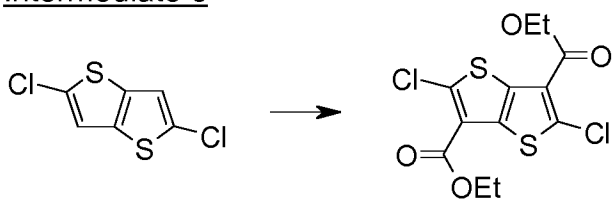
Compound 2



To a degassed solution of intermediate 4 (200 mg, 0.123 mmol), pyridine (0.69 cm^3) and anhydrous chloroform (9.7 cm^3) is added 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (89 mg, 0.37 mmol) and the mixture stirred for 30 minutes. The ice bath is then removed, and the mixture stirred for a further 60 minutes. The reaction mixture is poured into acetonitrile (250 cm^3) and stirred for 1 hour. The resulting suspension is collected by filtration and washed well with ethanol (50 cm^3) and acetone (50 cm^3). The crude product is purified by silica plug (40-60 petrol:dichloromethane; 1:1) followed by trituration with acetonitrile. The solid is collected by filtration to give compound 2 (180 mg, 71%) as a black solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.57 (2H, br s), 9.34 (2H, d, J 8.1), 9.11 - 9.20 (2H, m), 8.23 - 8.41 (4H, m), 7.86 - 8.08 (6H, m), 7.59 - 7.70 (4H, m), 6.86 (12H, br s), 2.47 (16H, t, J 7.6), 1.40 - 1.59 (16H, m), 1.09 - 1.29 (48H, m), 0.67 - 0.84 (24H, m).

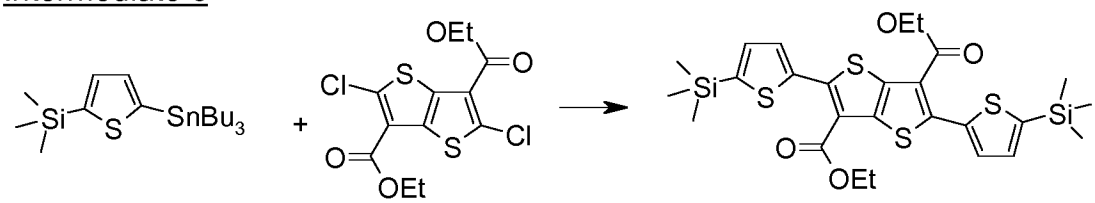
Example 3

Intermediate 5



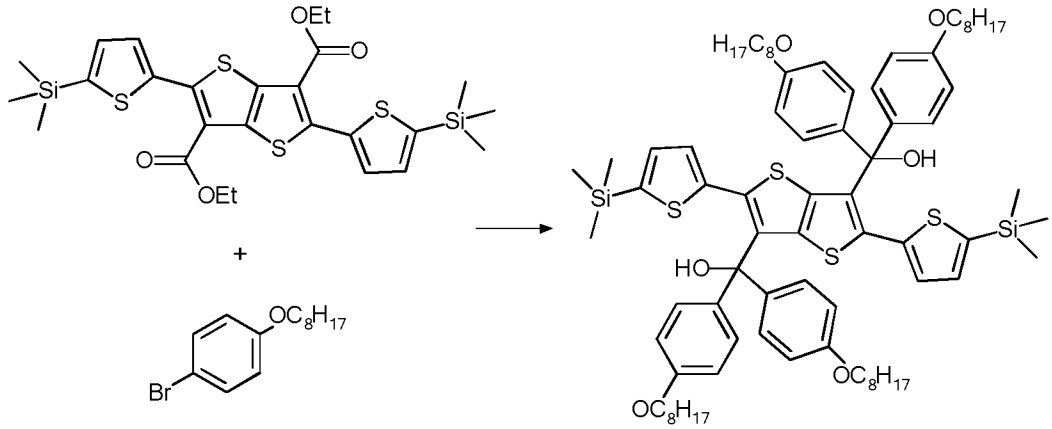
To a solution of 2,5-dichloro-thieno[3,2-b]thiophene (17.3 g, 82.7 mmol) in anhydrous tetrahydrofuran (173 cm^3) at 5 °C is added ethyl chloroformate (23.7 cm^3, 248 mmol). A solution of 2,2,6,6-tetramethylpiperidinylmagnesium chloride lithium chloride complex (207 cm^3, 207 mmol, 1.0 M in tetrahydrofuran) is then added dropwise over 1 hour. The reaction is slowly warmed to 23 °C and stirred for 42 hours. Water (200 cm^3) is added, the mixture stirred for 10 minutes, the solid collected by filtration and washed with water (2 x 100 cm^3). The solid is triturated in acetone (200 cm^3), the solid collected by filtration and washed with acetone (2 x 100 cm^3) to give intermediate 5 (26.6 g, 91%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) 4.46 (4H, q, J 7.1), 1.47 (6H, t, J 7.1).

Intermediate 6



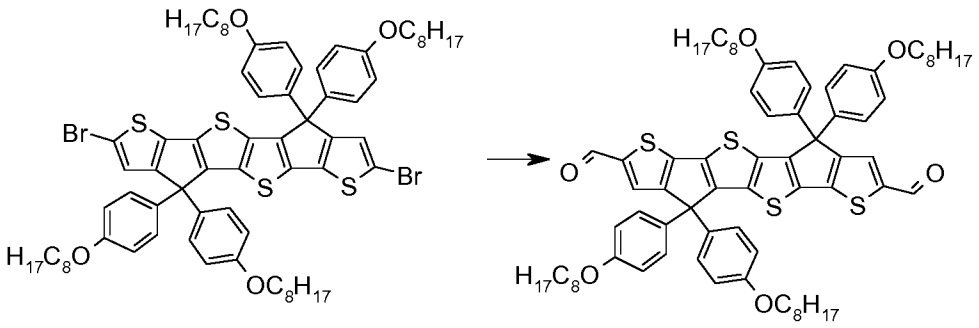
Trimethyl-(5-tributylstannanyl-thiophen-2-yl)-silane (30.5 g, 61.7 mmol), intermediate 5 (10.0 g, 28.3 mmol) and tetrakis(triphenylphosphine)palladium(0) (657 mg, 0.57 mmol) are suspended in anhydrous toluene (100 cm^3) and heated at 100 °C for 18 hours. The reaction is cooled to 23 °C and methanol (250 cm^3) added. The suspension is cooled in an ice-bath, the solid collected by filtration and washed with methanol (200 cm^3). The crude is purified by silica pad (dichloromethane) followed by column chromatography (40-60 petrol:dichloromethane; 60:40) to give intermediate 6 (7.68 g, 46%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) 7.42 (2H, d, J 3.5), 7.02 (2H, d, J 3.5), 4.19 (4H, q, J 7.1), 1.19 (6H, t, J 7.1), 0.15 (18H, s).

Intermediate 7



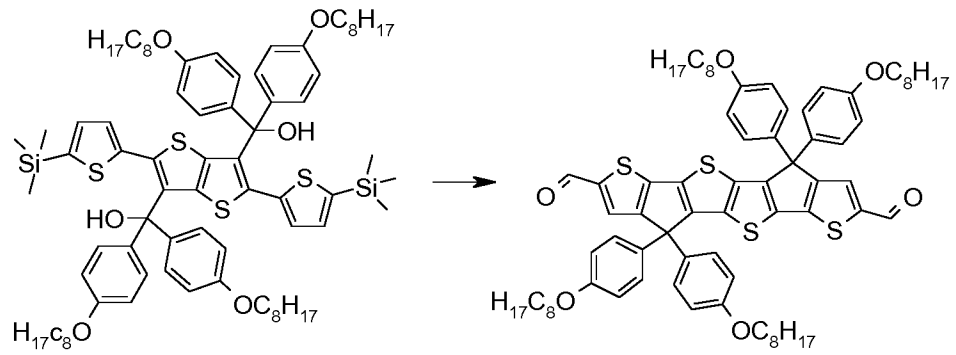
To a solution of 1-bromo-4-octyloxy-benzene (14.1 g, 49.5 mmol) in anhydrous tetrahydrofuran (73 cm^3) at -78 °C is added dropwise *t*-butyllithium (58.2 cm^3, 99.0 mmol, 1.7 M in pentane) over 20 minutes. The reaction is warmed to between -28 °C and -35 °C for 30 minutes. A second portion of 1-bromo-4-octyloxy-benzene (3.0 g, 11 mmol) is added and the reaction mixture stirred for 30 minutes. The reaction is cooled to -78 °C and a solution of intermediate 6 (4.89 g, 8.25 mmol) in anhydrous tetrahydrofuran (30 cm^3) is rapidly added. The reaction is warmed to 23 °C and stirred for 60 hours. Water (50 cm^3) is added and the organics extracted with ether (300 cm^3). The organic phase is washed with water (3 x 100 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 9:1 to 4:1) to give intermediate 7 (3.17 g, 29%) as a pale brown solid. ^1H NMR (400 MHz, $CDCl_3$) 7.16 - 7.23 (8H, m), 6.88 (2H, d, J 3.4), 6.78 - 6.85 (8H, m), 6.51 (2H, d, J 3.4), 3.97 (8H, t, J 6.6), 3.37 (2H, s), 1.75 - 1.84 (8H, m), 1.27 - 1.52 (40H, m), 0.82 - 0.95 (12H, m), 0.25 (18H, s).

Intermediate 8 – Route A



To a solution of 2,7-dibromo-4,4,9,9-tetrakis(4-(octyloxy)phenyl)-4,9-dihydro-thieno[3',2':4,5]cyclopenta[1,2-b]thieno[2",3":3',4']cyclopenta[1',2':4,5]thieno[2,3-d]thiophene (1.00 g, 0.77 mmol) in tetrahydrofuran (25 cm^3) at -78 °C is added dropwise *n*-butyllithium (0.92 cm^3, 2.30 mmol, 2.5 M in hexanes). The reaction is stirred for a further 1 hour and quenched with *N,N*-dimethylformamide (1.13 cm^3, 23.0 mmol). The reaction is warmed to 23 °C and stirred for 18 hours. Water (50 cm^3) is added and the organics extracted with dichloromethane (3 x 30 cm^3). The combined organic phase is washed with water (2 x 20 cm^3), dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 6:4 to 4:6) to give intermediate 8 (330 mg, 36%) as an orange oil. ^1H NMR (400 MHz, $CDCl_3$) 9.72 (2H, s), 7.58 (2H, s), 7.00 - 7.08 (8H, m), 6.69 - 6.82 (8H, m), 3.83 (8H, t, J 6.5), 1.61 - 1.71 (8H, m), 1.34 (8H, m), 1.11 - 1.33 (32H, m), 0.72 - 0.90 (12H, m).

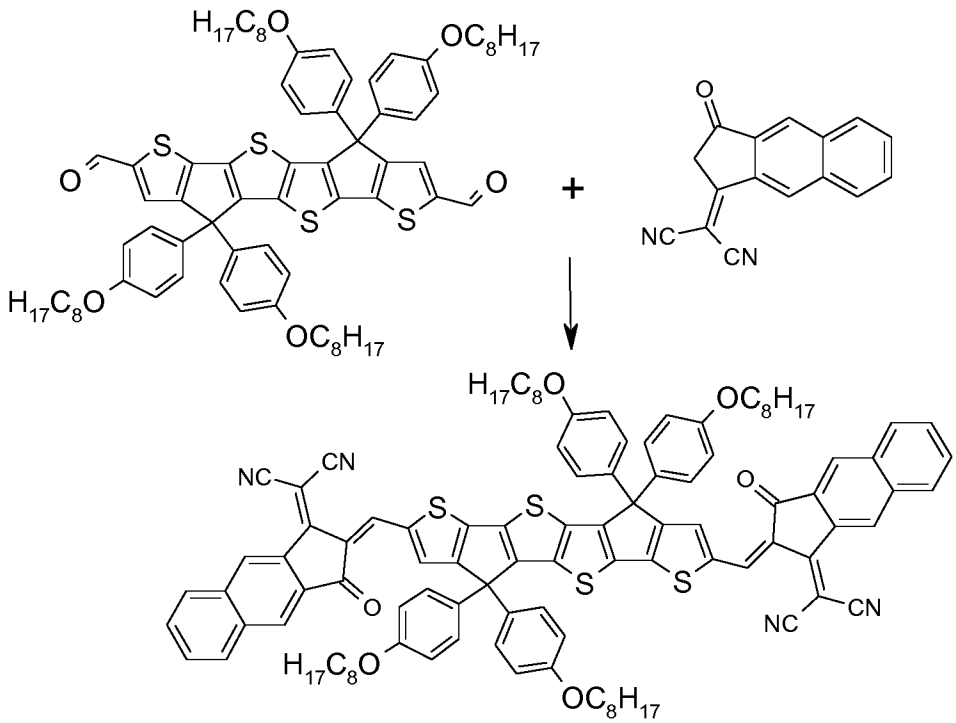
Intermediate 8 – Route B



To a degassed solution of intermediate 7 (6.00 g, 4.52 mmol) in toluene (240 cm^3) is added Amberlyst 15 strong acid (24 g), the mixture further

degassed and then heated at 75 °C for 18 hours. The solution is cooled to about 50 °C, filtered and the solid washed with toluene (200 cm^3). The filtrate is concentrated and triturated with 80-100 petrol (3 x 30 cm^3) and the solid collected by filtration. The solid is dissolved in chloroform (120 cm^3), *N,N*-dimethylformamide (5.3 g, 72 mmol) added and the solution cooled to 0 °C. Phosphorus(V) oxychloride (10.4 g, 67.9 mmol) is added over 10 minutes. The reaction mixture is then heated at 65 °C for 18 hours. Aqueous sodium acetate solution (150 cm^3, 2 M) is added at 65 °C and the reaction mixture stirred for 1 hour. Saturated aqueous sodium acetate solution is added until the mixture is pH 6 and the reaction stirred for a further 30 minutes. The aqueous phase is extracted with chloroform (2 x 25 cm^3) and the combined organic layer washed with water (50 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The solid is triturated in 80-100 petrol and the solid collected by filtration to give intermediate 8 (3.06 g, 56%) as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) 9.72 (2H, s), 7.58 (2H, s), 7.00 - 7.08 (8H, m), 6.69 - 6.82 (8H, m), 3.83 (8H, t, J 6.5), 1.61 - 1.71 (8H, m), 1.34 (8H, m), 1.11 - 1.33 (32H, m), 0.72 - 0.90 (12H, m).

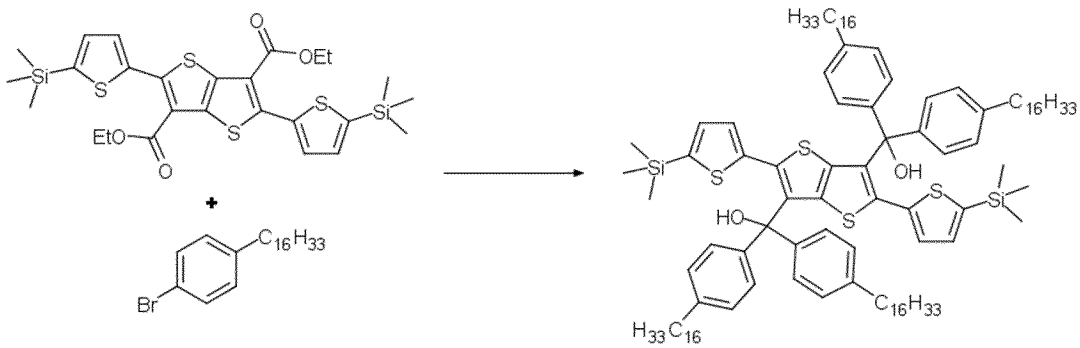
Compound 3



Intermediate 8 (120 mg, 0.10 mmol) and 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (190 mg, 0.78 mmol) are dissolved in chloroform (2.9 cm^3) at 50 °C and degassed with nitrogen for 20 minutes. Pyridine (1.1 cm^3) is added and the reaction stirred for 5 hours at 50 °C. Methanol (25 cm^3) is added, the suspension cooled to 23 °C and filtered. The solid is dissolved in chloroform (6 cm^3), acetone (18 cm^3) is added followed by methanol (24 cm^3) at 40 °C. The suspension is cooled to 23 °C and filtered. The solid is washed with chloroform:methanol (1:1; 5 cm^3). The recrystallization cycle is then repeated to afford compound 3 (32 mg, 20%) as a green solid. ^1H NMR (400 MHz, $CDCl_3$) 9.18 (2H, s), 8.94 (2H, s), 8.37 (2H, s), 8.02 - 8.11 (4H, m), 7.64 - 7.75 (6H, m), 7.15 - 7.22 (8H, m), 6.84 - 6.92 (8H, m), 5.32 (8H, s), 3.95 (8H, t, J 6.5), 1.74 - 1.82 (8H, m), 1.45 (8H, t, J 7.5), 1.25 - 1.40 (40H, m), 0.89 (12H, d, J 7.0).

Example 4

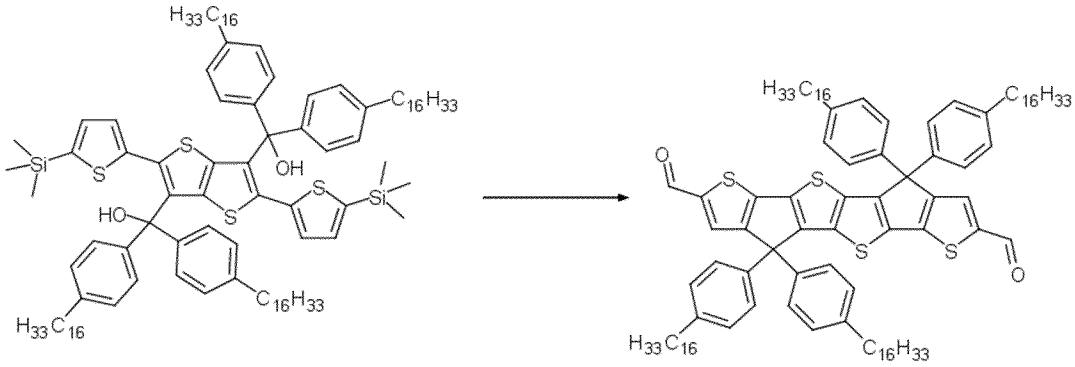
Intermediate 9



To a solution of 1-bromo-4-hexadecyl-benzene (19.3 g, 50.6 mmol) suspended in anhydrous tetrahydrofuran (400 cm^3) at -35 °C is added a solution of *t*-butyllithium (59.5 cm^3, 101 mmol, 1.7 M in pentane) over 30 minutes. The suspension is warmed to -25 °C to provide a solution which is then re-cooled to -40 °C and stirred for 1 hour before intermediate 6 (5.00 g, 8.43 mmol), dissolved in tetrahydrofuran (50 cm^3) is added dropwise. The resulting suspension is warmed to 23 °C and stirred for 16 hours. Water (20 cm^3) is added slowly to the mixture followed by another portion of water (300 cm^3). The biphasic solution is extracted with ether (300 cm^3) and the organic phase is washed with water (2 x 250 cm^3), brine

(100 cm^3), dried over magnesium sulphate, filtered and concentrated *in vacuo*. The crude product is dissolved in acetone (200 cm^3) and cooled in an ice bath. Methanol (200 cm^3) is added portion wise, the solid is collected by filtration and washed with methanol to give intermediate 9 (14 g, 97%) as an off white solid. ^{1}H NMR (400 MHz, $CDCl_3$) 6.94 - 7.01 (8H, m), 6.84 - 6.94 (8H, m), 6.61 (2H, d, J 3.4), 6.22 (2H, d, J 3.4), 3.19 (2H, s), 2.38 (8H, t, J 7.7), 1.36 - 1.43 (8H, m), 0.97 - 1.15 (104H, m), 0.67 (12H, t, J 6.8), 0.00 (18H, s).

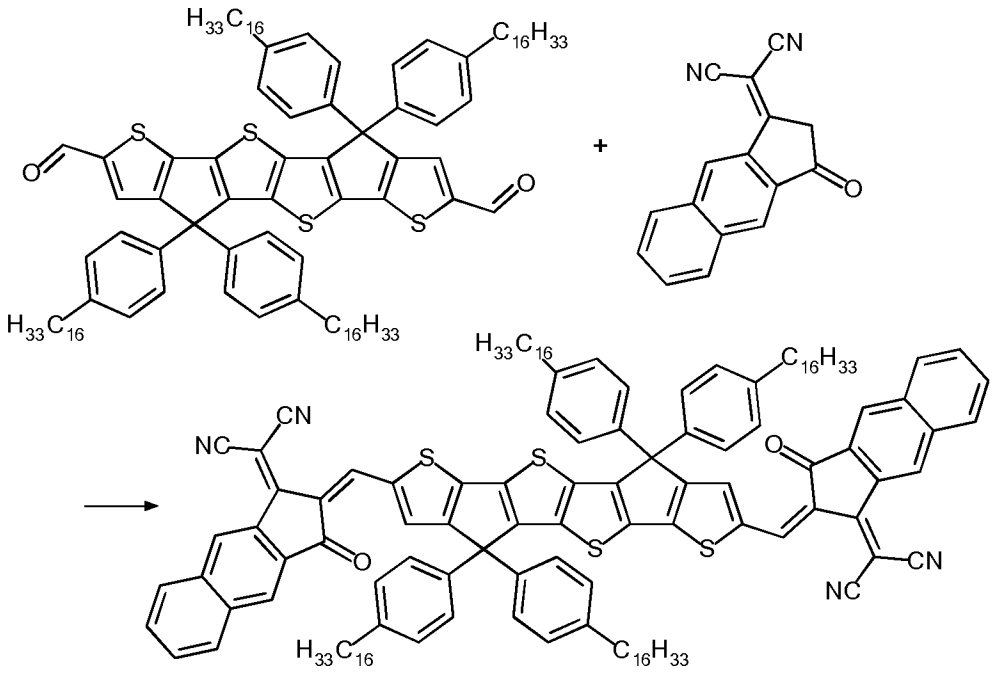
Intermediate 10



To a nitrogen flushed solution of intermediate 9 (5.0 g, 2.9 mmol) in toluene (200 cm^3) at 55 °C is added *p*-toluene sulphonic acid (1.67 g, 8.8 mmol), the reaction is further flushed with nitrogen for 10 minutes. The reaction is stirred at 55 °C for 16 hours. Upon cooling to 23 °C the reaction is filtered, concentrated *in vacuo* and purified by column chromatography (40-60 petrol:dichloromethane; 9:1). The purified material is taken up in chloroform (100 cm^3), cooled to 0 °C and *N,N*-dimethylformamide (12 g) and phosphorus oxychloride (6.72 g, 43.8 mmol) added. The reaction is heated at 65 °C for 16 hours. Water (25 cm^3) is slowly added to the mixture followed by an aqueous sodium acetate solution (250 cm^3, 5 M). The biphasic solution is stirred for 1 hour and the aqueous phase is extracted with dichloromethane (2 x 30 cm^3). The combined organic phase is washed with water (2 x 50 cm^3), dried over magnesium sulphate, filtered and concentrated *in vacuo*. The product is triturated in acetone and filtered off. The solid is purified by column chromatography (40-60 petrol:dichloromethane; 4:1). The resulting solid is triturated in boiling 40-60 petrol, and the solid collected by filtration to give intermediate 10 (1.59 g, 34%) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.82 (2H, s), 7.70

(2H, s), 7.08 - 7.18 (16H, m), 2.53 - 2.60 (8H, m), 1.53 - 1.65 (8H, m), 1.26 (104H, d, J 3.4), 0.89 (12H, t, J 6.8).

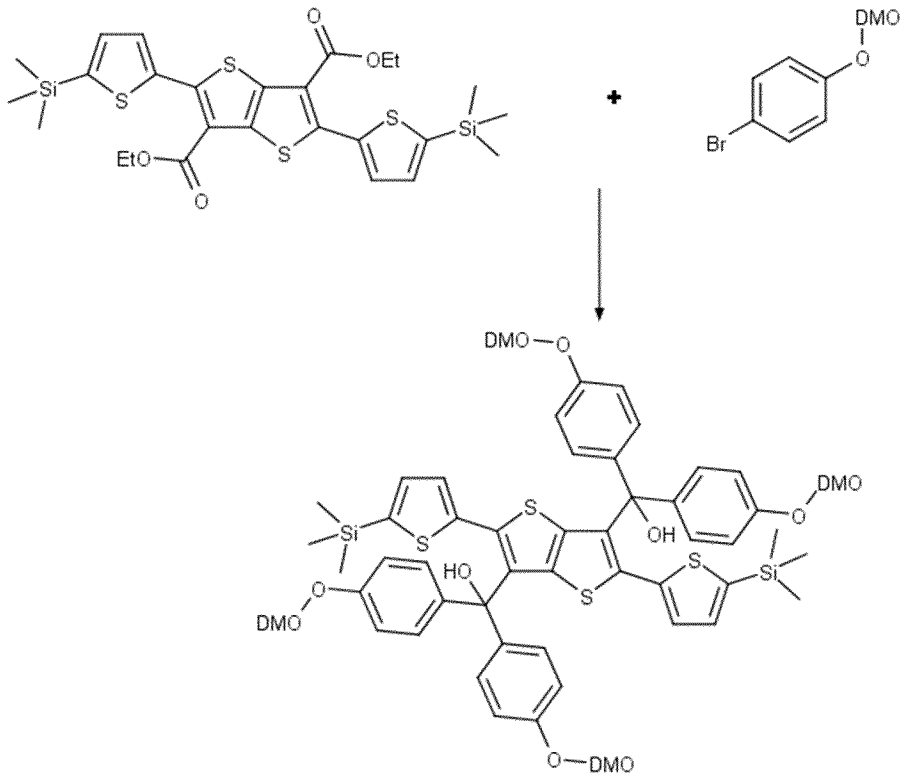
Compound 4



To a nitrogen purged suspension of intermediate 10 (100 mg, 0.06 mmol) and 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (77 mg, 0.32 mmol) in chloroform (2.5 cm^3) is added pyridine (0.36 cm^3) and the solution flushed with nitrogen for a further 10 minutes. The reaction is stirred at 23 °C for 18 hours, diluted with methanol (20 cm^3) and filtered. The solid is washed with methanol (2 x 5 cm^3). The crude material is dissolved in chloroform (20 cm^3) at 40 °C. Acetone (40 cm^3) is added slowly to the mixture followed by methanol (5 cm^3). The suspension is cooled to 23 °C and filtered to give compound 4 (22 mg, 18%) as a green solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.18 (2H, s), 8.94 (2H, s), 8.37 (2H, s), 8.00 - 8.14 (4H, m), 7.75 (2H, s), 7.64 - 7.72 (4H, m), 7.17 (16H, s), 2.61 (8H, t, J 7.9), 1.51 - 1.71 (8H, m), 1.25 (84H, s), 0.87 (12H, t, J 6.6).

Example 5

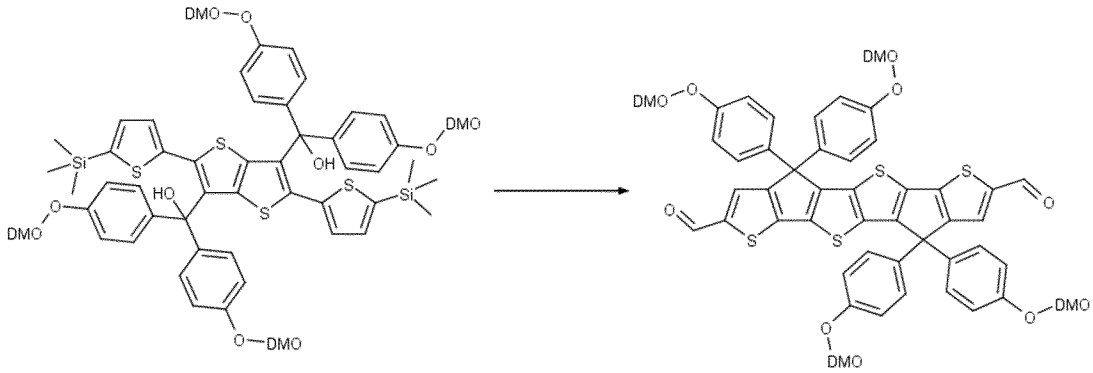
Intermediate 11



Anhydrous tetrahydrofuran (2 cm^3) is added to a flask containing oven dried magnesium turnings (246 mg, 10.1 mmol) and an iodine crystal. The mixture is maintained at reflux while a solution of 1-bromo-4-(3,7-dimethyl-octyloxy)-benzene (3.07 g, 10.1 mmol) in anhydrous tetrahydrofuran (5 cm^3) is added portionwise over 10 minutes. The reaction is then heated to reflux for 2 hours. The resulting Grignard reagent is transferred over 5 minutes to a flask containing intermediate 6 (1.00 g, 1.69 mmol) dissolved in anhydrous tetrahydrofuran (10 cm^3) and maintained at 65 °C. The mixture is heated at 65 °C for 6 hours. Upon cooling to 23 °C, the solution is partioned between water (30 cm^3) and ether (30 cm^3). Hydrochloric acid (2 N) is added slowly until the phases become clear. The organic phase is washed with water (2 x 30 cm^3), dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo*. The crude product is purified by column chromatography (40-60 petrol:dichloromethane; 1:1) to give intermediate 11 (1.26 g, 53%) as a yellow/green oil. ^1H NMR (400 MHz, $CDCl_3$) 7.16 - 7.23 (8H, m), 6.88 (2H, d, J 3.4), 6.79 - 6.86 (8H, m), 6.52 (2H, d, J 3.4), 3.95 - 4.06 (8H, m), 3.38 (2H, s), 1.07 - 1.91 (40H, m), 0.95

(12H, d, J 6.5), 0.87 - 0.92 (24H, m), 0.25 (18H, s).

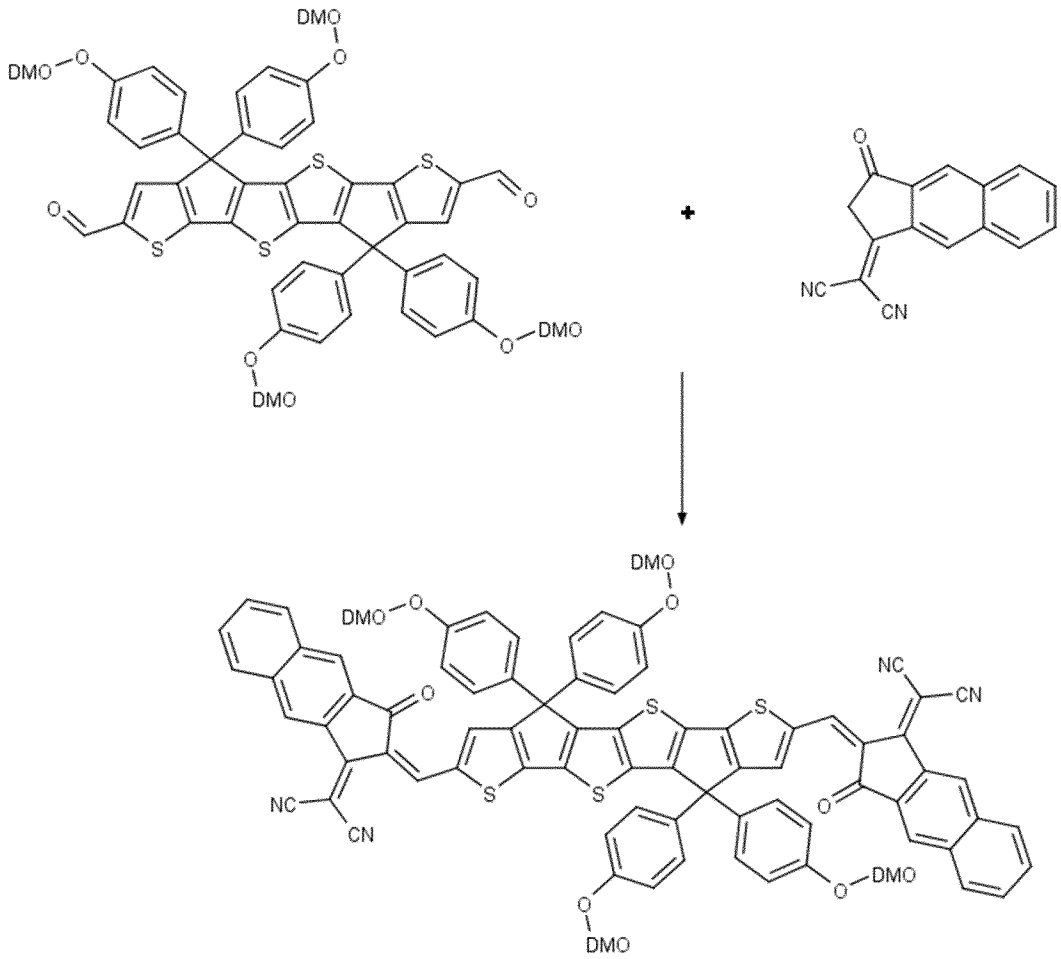
Intermediate 12



DMO = 3,7- dimethyloctyl

Intermediate 11 (1.26 g, 0.89 mmol) is dissolved in toluene (50 cm^3) and heated at 75 °C. The resulting solution is flushed with nitrogen for 20 minutes. Amberlyst 15 strong acid (5.0 g) is added. The nitrogen flush is maintained for a further 10 minutes and the reaction mixture is stirred for 17 hours. The reaction mixture is filtered and the solid washed with hot toluene (3 x 10 cm^3). The filtrate is concentrated *in vacuo* and passed through a silica plug (40-60 petrol:dichloromethane; 5:1). The resulting solid is dissolved in *N,N*-dimethylformamide (1.04 g, 14.3 mmol) and chloroform (25 cm^3) and cooled in an ice-bath. Phosphorus oxychloride (2.05 g, 13.4 mmol) is added portionwise over 5 minutes. The reaction is stirred for 30 minutes at 0 °C and then heated at 65 °C for 16 hours. Upon cooling to 23 °C, water (5 cm^3) is slowly added followed by slow addition of aqueous sodium acetate (50 cm^3, 10 M). The biphasic suspension is stirred for 1 hour and then cooled to 23 °C. The aqueous phase is extracted with dichloromethane (20 cm^3). The combined organic phase is washed with water (2 x 20 cm^3), dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo*. The resulting solid is triturated in acetone (10 cm^3), filtered and washed with acetone (2 x 2 cm^3) to give intermediate 12 (200 mg, 17%) as an orange solid. ^1H NMR (400 MHz, $CDCl_3$) 9.73 (2H, s), 7.59 (2H, s), 7.02 - 7.09 (8H, m), 6.71 - 6.78 (8H, m), 3.86 (8H, ddt, J 9.4, 7.1, 3.3), 0.98 - 1.78 (40H, m), 0.83 (12H, d, J 6.5), 0.78 (24H, d, J 6.6).

Compound 5



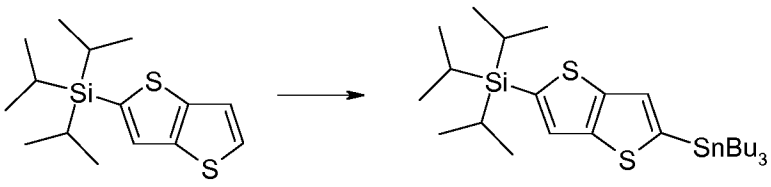
DMO = 3,7- dimethyloctyl

A solution of intermediate 12 (100 mg, 0.08 mmol) and 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (92.9 mg, 0.38 mmol) in chloroform (2.5 cm^3) is purged with nitrogen for 10 minutes before addition of pyridine (0.43 cm^3). The solution is purged with nitrogen for a further 10 minutes and then stirred for 16 hours at 23 °C. The mixture is diluted with methanol (20 cm^3) and filtered. The solid is washed with methanol (2 x 5 cm^3) and purified by column chromatography (40-60 petrol:dichloromethane; 3:2). The solid is dissolved in chloroform (6 cm^3) and acetone (12 cm^3) added at 40 °C followed by methanol (2 cm^3). The solid is collected by filtration to give compound 5 (26 mg, 19%) as a green solid. ^1H NMR (400 MHz, $CDCl_3$) 9.19 (2H, s), 8.96 (2H, s), 8.38 (2H, s), 8.08 (4H, dt, J 9.6, 5.8), 7.66 - 7.77 (6H, m), 7.14 - 7.23 (8H, m), 6.84 -

6.93 (8H, m), 3.99 (8H, q, J 6.0), 1.07 - 1.94 (40H, m), 1.20 (40H, s), 0.94 (12H, d, J 6.5), 0.87 (24H, d, J 6.6).

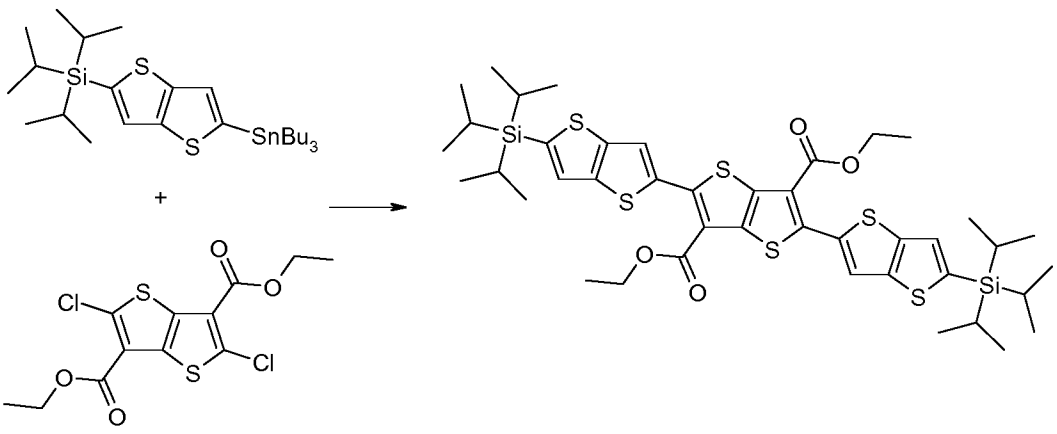
Example 6

Intermediate 13



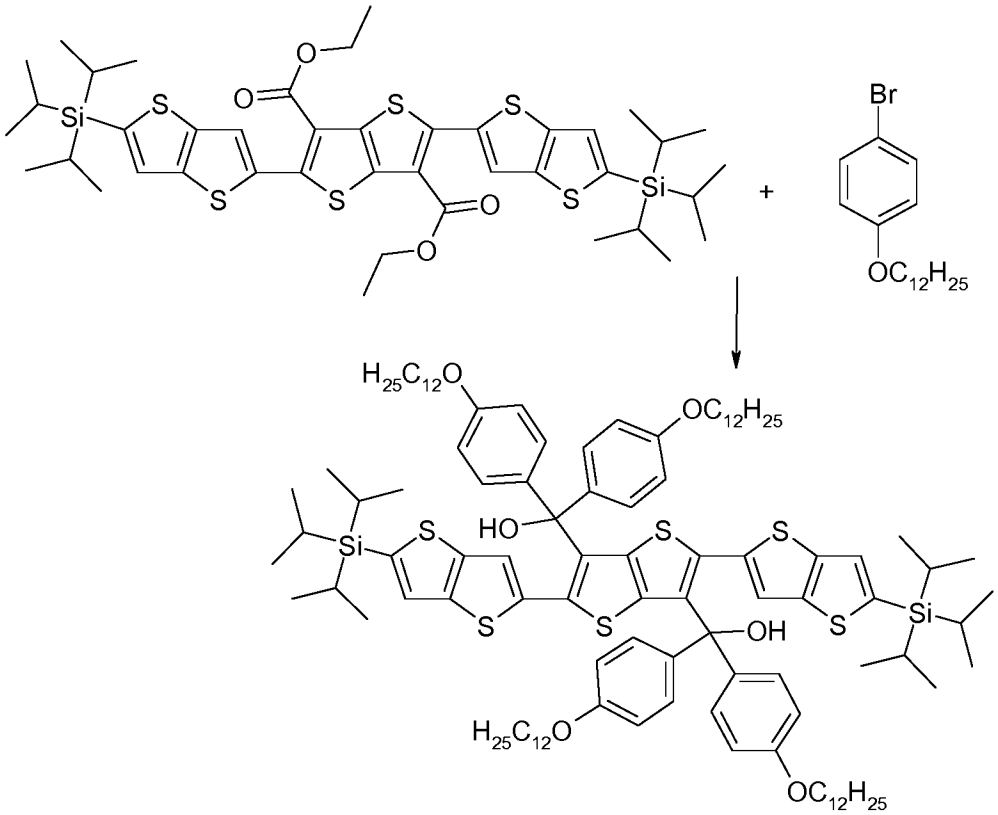
To a solution of triisopropyl-thieno[3,2-*b*]thiophen-2-yl-silane (11.9 g, 40.0 mmol) in anhydrous tetrahydrofuran (100 cm^3) at -78 °C is added drop-wise *n*-butyllithium (20.8 cm^3, 52.0 mmol, 2.5 M in hexane) over 20 minutes. After addition, the reaction mixture is stirred at -78 °C for 120 minutes and then tributyltin chloride (15.8 cm^3, 56.0 mmol) is added. The mixture is then allowed to warm to 23 °C over 17 hours and the solvent removed *in vacuo*. The crude is diluted in 40-60 petrol (250 cm^3) and filtered through a zeolite plug (50 g). The plug is washed with additional 40-60 petrol (250 cm^3). The solvent is removed *in vacuo* to give intermediate 13 (23.1 g, 99%) as a clear oil. ^1H NMR (400 MHz, CD_2Cl_2) 7.27 (1H, d, J 0.7), 7.1 (1H, s), 1.35 - 1.63 (9H, m), 1.17 - 1.34 (12H, m), 0.98 - 1.13 (18H, m), 0.65 - 0.91 (9H, m).

Intermediate 14



A mixture of intermediate 5 (7.5 g, 21 mmol), intermediate 13 (17.8 g, 30.4 mmol) and anhydrous toluene (300 cm^3) is degassed by nitrogen for 25 minutes. To the mixture is added tetrakis(triphenylphosphine)palladium(0) (500 mg, 0.43 mmol) and the mixture further degassed for 15 minutes. The mixture is stirred at 85 °C for 17 hours. The reaction mixture is filtered hot through a celite plug (50 g) and washed through with hot toluene (100 cm^3). The solvent reduced *in vacuo* to ~100 cm^3 and cooled in an ice bath to form a suspension. The product is filtered, washed with water (100 cm^3) and methanol (100 cm^3), collected to give intermediate 14 (9.5 g, 71%) as a yellow crystalline solid. ^1H NMR (400 MHz, $CDCl_3$) 7.75 (2H, d, J 0.7), 7.30 (2H, d, J 0.7), 4.36 (4H, q, J 7.2), 1.23-1.43 (12H, m), 1.07 (36H, d, J 7.3).

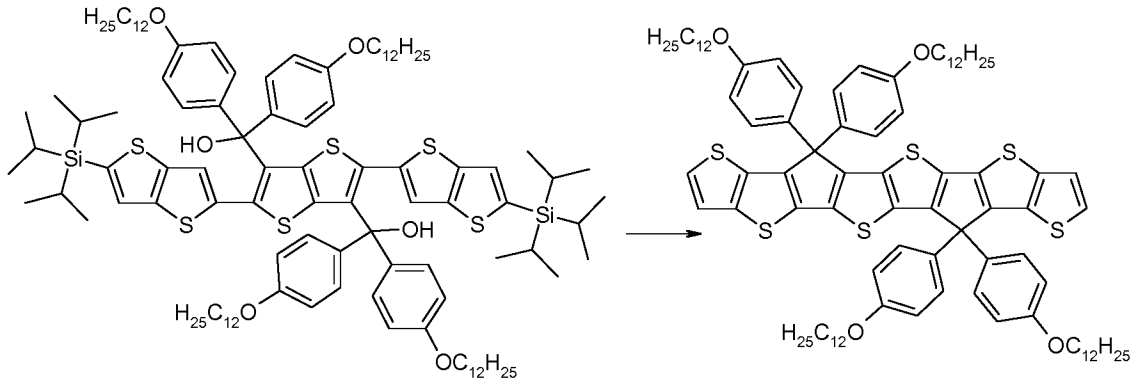
Intermediate 15



To a suspension of 1-bromo-4-dodecyloxy-benzene (10.6 g, 30.9 mmol) in anhydrous tetrahydrofuran (167 cm^3) at -78 °C is added dropwise *t*-butyllithium (36.4 cm^3, 61.8 mmol, 1.7 M in pentane) over 60 minutes.

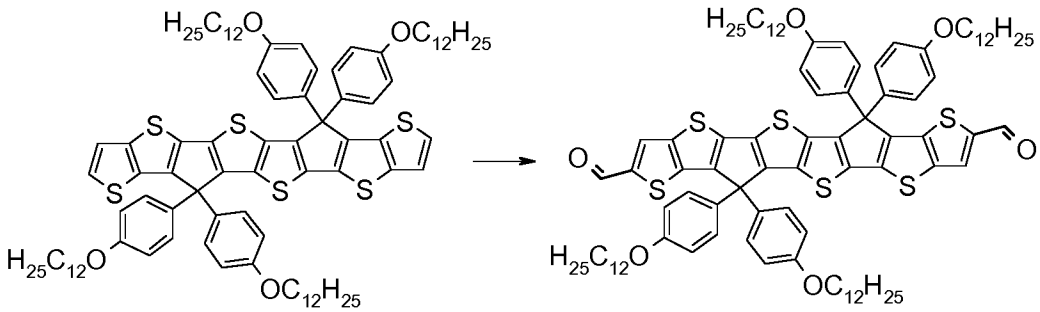
After addition, the reaction mixture is stirred at -78 °C for 120 minutes and then intermediate 14 (6.0 g, 6.9 mmol) added. The mixture is then allowed to warm to 23 °C over 17 hours. Diethyl ether (200 cm^3) and water (200 cm^3) are added and the mixture stirred at 23 °C for 30 minutes. The product is extracted with diethyl ether (3 x 200 cm^3). The combined organics is dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography (40-60 petrol:diethyl ether; 7:3). The solid triturated with methanol (200 cm^3) and collected by filtration to give intermediate 15 (10.3 g, 82%) as a cream solid. ^{1}H NMR (400 MHz, $CDCl_3$) 7.15 - 7.23 (10H, m), 6.77 - 6.85 (8H, m), 6.65 (2H, d, J 0.7), 3.45 (2H, s), 3.95 (8H, s), 1.71 - 1.85 (8H, m), 1.20 - 1.52 (72H, m), 1.11 (36H, d, J 7.3), 0.82 - 0.95 (12H, m).

Intermediate 16



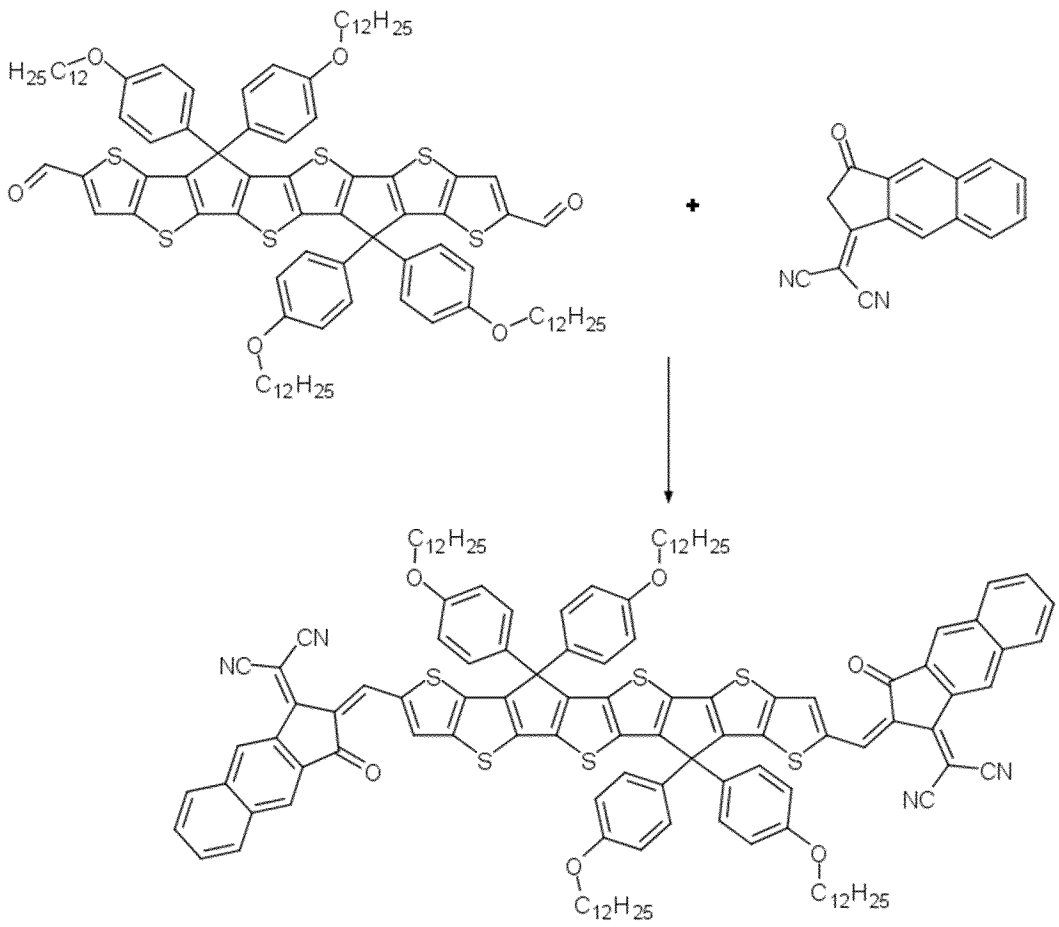
Nitrogen gas is bubbled through a solution of intermediate 15 in anhydrous toluene (250 cm^3) at 0 °C for 60 minutes. Amberlyst 15 strong acid (50 g) is added and the mixture degassed for a further 30 minutes. The resulting suspension is stirred at 70 °C for 2 hours. The reaction mixture allowed to cool to 23 °C, filtered and the solvent removed *in vacuo*. The crude is triturated with acetone (200 cm^3). The solid is collected by filtration to give intermediate 16 (4.2 g, 89%) as a dark orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) 7.26 - 7.32 (4H, m), 7.16 - 7.24 (8H, m), 6.75 - 6.93 (8H, m), 3.91 (8H, t, J 6.5), 1.67 - 1.82 (8H, m), 1.37 - 1.48 (8H, m), 1.19 - 1.37 (64H, m), 0.80 - 1.00 (12H, m).

Intermediate 17



To a solution of intermediate 16 (600 mg, 0.41 mmol) in anhydrous tetrahydrofuran (24 cm^3) at -78 °C is added dropwise *n*-butyllithium (0.7 cm^3, 1.6 mmol, 2.5 M in hexane) over 10 minutes. After addition, the reaction mixture is stirred at -78 °C for 60 minutes. *N,N*-dimethylformamide (0.16 cm^3, 2.4 mmol) is added and the mixture allowed to warm to 23 °C over 2 hours. Diethyl ether (50 cm^3) and water (50 cm^3) are added and the mixture stirred at 23 °C for 30 minutes. The product is extracted with diethyl ether (3 x 100 cm^3). The combined organics are dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography (40-60 petrol:dichloromethane; 8:2) to give intermediate 17 (380 mg, 61%) as a dark red oil. ^{1}H NMR (400 MHz, $CDCl_3$) 9.90 (2H, s), 7.94 (2H, s), 7.08 - 7.23 (8H, m), 6.78 - 6.93 (8H, m), 3.91 (8H, t, J 6.5), 1.65 - 1.85 (8H, m), 1.17 - 1.51 (72H, m), 0.82 - 0.96 (12H, m).

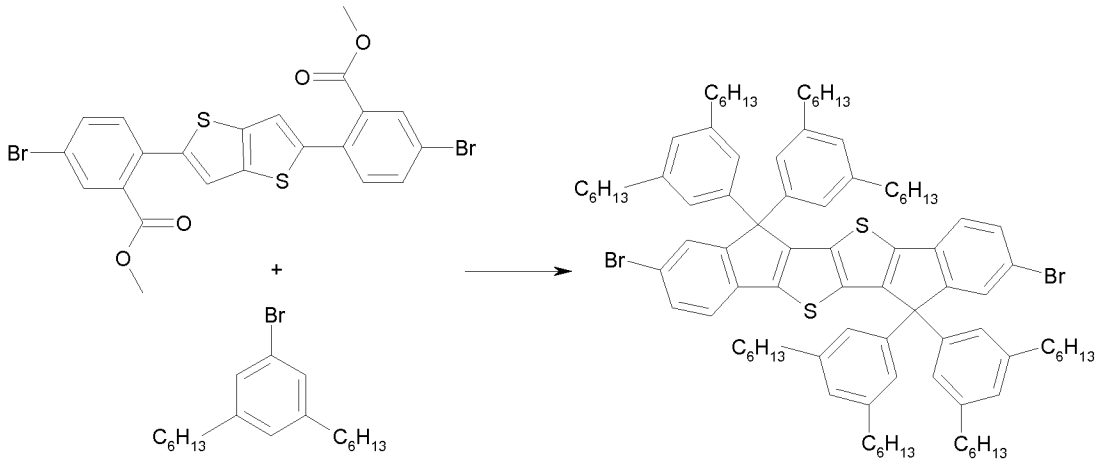
Compound 6



2-(3-Oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (114 mg, 0.47 mmol) is added to a degassed solution of intermediate 16 (240 mg, 0.16 mmol) in a mixture of pyridine (1 cm^3) and anhydrous chloroform (9 cm^3). The mixture is stirred for 4 hours followed by addition of methanol (30 cm^3). The precipitate is collected by filtration and rinsed with methanol (5 cm^3). The solid is purified by column chromatography (chloroform) followed by trituration (dichloromethane) to give compound 6 (235 mg, 76%) as a green solid. ^1H NMR (400 MHz, $CDCl_3$) 9.11 (2H, s), 8.91 (2H, s), 8.37 (2H, s), 8.10 (2H, s), 7.99 - 8.07 (4H, m), 7.64 - 7.74 (4H, m), 7.22 - 7.27 (8H, m), 6.88 - 6.95 (8H, m), 3.93 (8H, t, J 6.5), 1.74 (8H, q, J 6.9), 1.38 - 1.47 (8H, m), 1.16 - 1.36 (64H, m), 0.86 (12H, t, J 6.6).

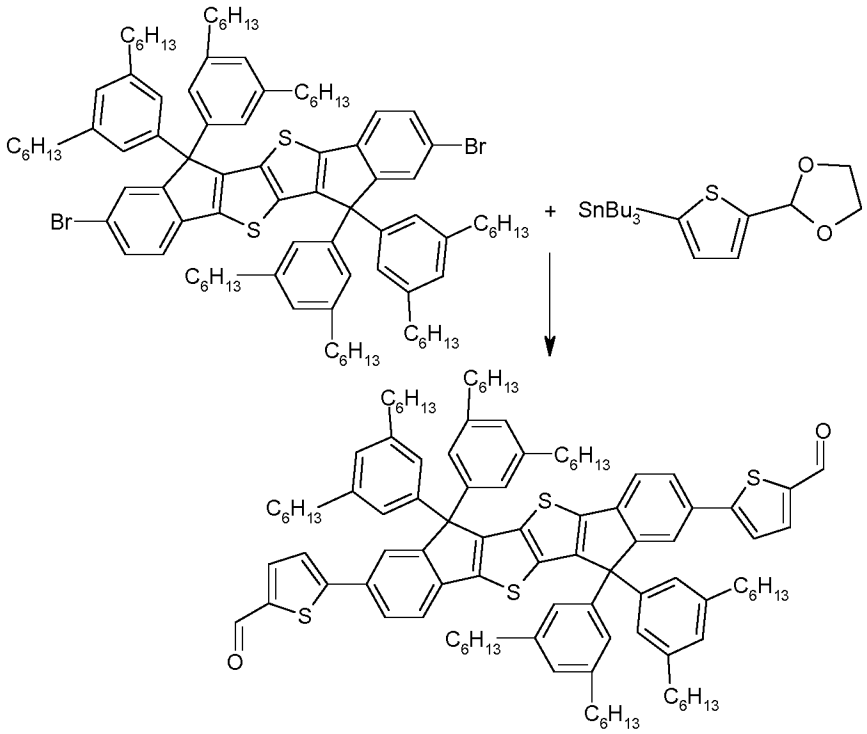
Example 7

Intermediate 17



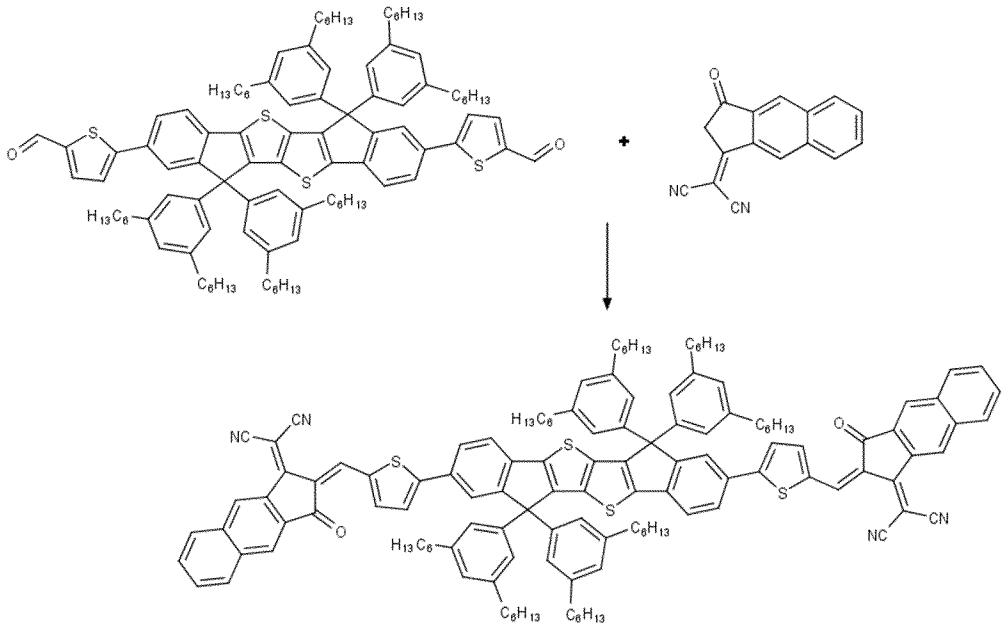
To a solution of 1-bromo-3,5-dihexyl-benzene (9.00 g, 27.7 mmol) in anhydrous tetrahydrofuran (135 cm^3) at -78 °C is added dropwise *n*-butyllithium (11.1 cm^3, 27.7 mmol, 2.5 M in hexanes) over 10 minutes. The reaction is stirred for one hour and methyl 5-bromo-2-[5-(4-bromo-2-methoxycarbonyl-phenyl)thieno[3,2-b]thiophen-2-yl]benzoate (3.13 g, 5.53 mmol) added. The reaction is warmed to 23 °C and stirred for 18 hours. The reaction is partitioned between diethyl ether (50 cm^3) and water (100 cm^3). The organic phase is washed with water (30 cm^3), brine (30 cm^3), dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The crude is triturated with 40-60 petrol, and the solid suspended in toluene (50 cm^3). *p*-Toluene sulphonic acid (2.5 g) is added and the reaction mixture stirred for 17 hours. The suspension is filtered, concentrated *in vacuo* and purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:0 to 1:1). The resulting material is triturated in acetone and the solid collected by filtration to give intermediate 17 (2.71 g, 34%) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) 7.42 (2H, d, J 1.7), 7.32 (2H, dd, J 8.1, 1.8), 7.11 (2H, d, J 8.1), 6.80 (4H, t, J 1.5), 6.71 (8H, d, J 1.5), 2.40 (16H, t, J 7.7), 1.38 - 1.48 (16H, m), 1.11 - 1.24 (48H, m), 0.70 - 0.79 (24H, m).

Intermediate 18



To a degassed solution of intermediate 17 (250 mg, 0.17 mmol), tributyl-(5-[1,3]dioxolan-2-yl-thiophen-2-yl)-stannane (0.18 cm^3, 0.40 mmol) and tris(o-tolyl)phospine (16 mg, 0.05 mmol) in toluene (12.5 cm^3) is added bis(dibenzylideneacetone)palladium(0) (16 mg, 0.02 mmol) and the mixture further degassed. The reaction is then heated to an external temperature of 140 °C for 6 hours. The reaction mixture is allowed to cool to 23 °C and concentrated *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 3:10 to 1:9). The resulting oil is dissolved in chloroform (30 cm^3) and stirred with hydrochloric acid (10 cm^3, 2.5 N) for 18 hours. The organic phase is concentrated *in vacuo* and the residue purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 4:1 to 1:4). The resulting solid is triturated in acetone and the solid collected by filtration to give intermediate 18 (170 mg, 65%) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) 9.78 (2H, s), 7.59 - 7.65 (4H, m), 7.55 (2H, dd, J 8.0, 1.6), 7.31 (2H, d, J 8.0), 7.24 (2H, d, J 3.9), 6.82 (4H, s), 6.78 (8H, s), 2.41 (16H, t, J 7.6), 1.39 - 1.49 (16H, m), 1.17 (48H, m), 0.69 - 0.85 (24H, m).

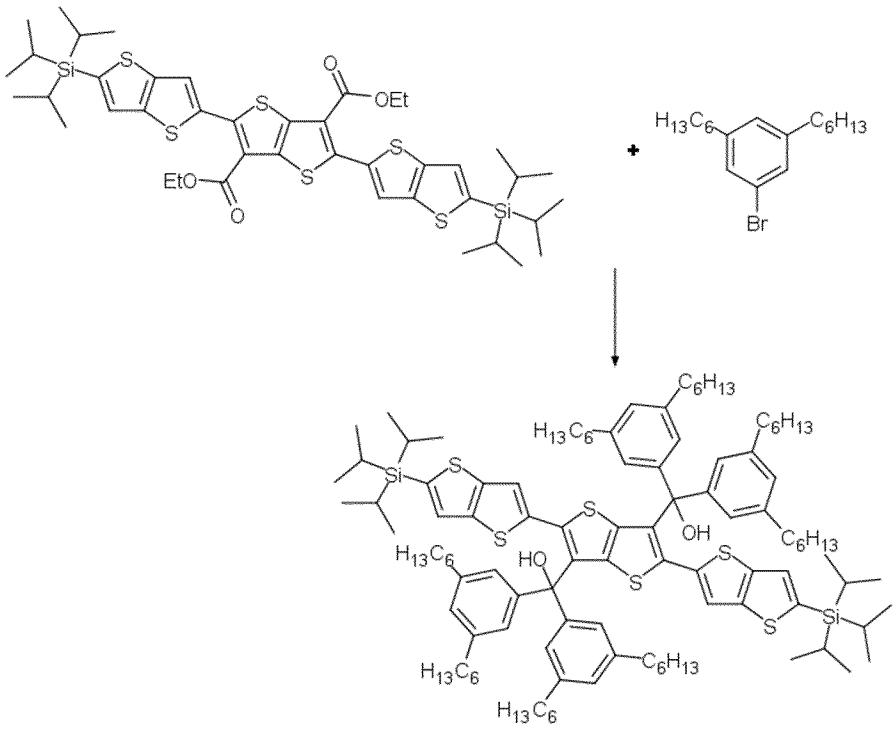
Compound 7



2-(3-Oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (105 mg, 0.43 mmol) is added to a nitrogen purged solution of intermediate 18 (130 mg, 0.09 mmol) in anhydrous chloroform (9 cm^3) and anhydrous pyridine (1 cm^3). The resulting mixture is stirred for 3 hours before methanol (30 cm^3) is added. The resulting precipitate is collected by filtration and rinsed with methanol (50 cm^3). The solid is purified by column chromatography using a graded solvent system (cyclohexane:chloroform; 1:1 to 2:8), followed by trituration (acetone:chloroform) to give compound 7 (105 mg, 62%) as a black solid. ^1H NMR (400 MHz, $CDCl_3$) 9.22 (2H, s), 8.95 (2H, s), 8.41 (2H, s), 8.03 - 8.14 (4H, m), 7.82 - 7.91 (6H, m), 7.67 - 7.77 (4H, m), 7.43 - 7.50 (4H, m), 6.95 (4H, t, J 1.5), 6.92 (8H, d, J 1.5), 2.54 (16H, t, J 7.6), 1.51 - 1.64 (16H, m), 1.20 - 1.37 (48H, m), 0.78 - 0.86 (24H, m).

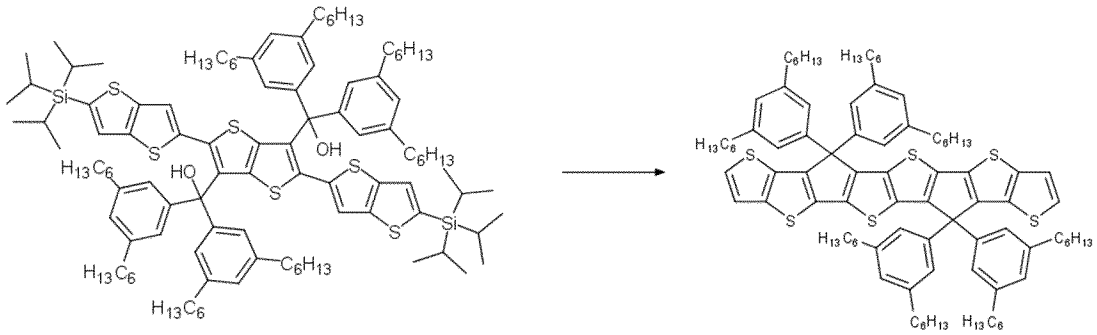
Example 8

Intermediate 19



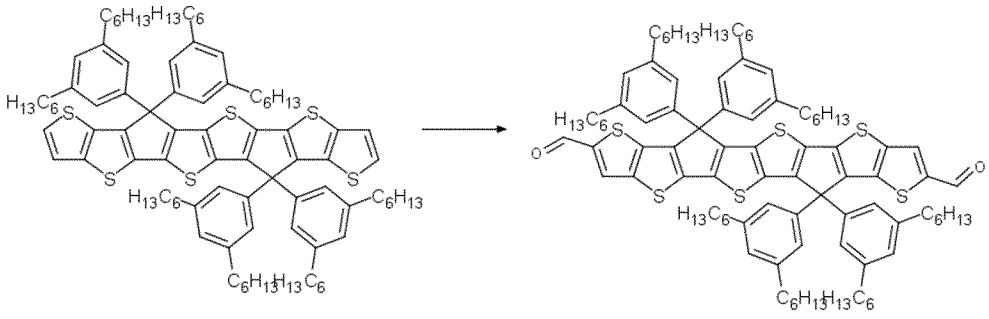
To a solution of 1-bromo-3.5-dihexyl-benzene (5.24 g, 16.0 mmol) in anhydrous tetrahydrofuran (100 cm^3) at -78 °C is added dropwise *n*-butyllithium (6.41 cm^3, 16.0 mmol, 2.5 M in tetrahydrofuran) over 30 minutes. After addition, the reaction mixture is stirred at -78 °C for 120 minutes and then intermediate 14 (2.8 g, 3.2 mmol) added. The mixture is then allowed to warm to 23 °C over 17 hours. Water (100 cm^3) is added and mixture stirred for 1 hour. The product is extracted with diethyl ether (3 x 200 cm^3). The combined organic phase is washed with water (2 x 50 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:diethyl ether; 20:1 to 4:1) to give intermediate 19 (3.54 g, 63%) as a pale cream oil. ^1H NMR (400 MHz, CD_2Cl_2) 7.23 (2H, s), 6.86 - 7.01 (12H, m), 6.51 (2H, s), 3.41 (2H, s), 2.42 - 2.61 (16H, m), 1.49 - 1.61 (16H, m), 1.22 - 1.45 (54H, m), 1.15 (36H, d, J 7.3), 0.78 - 0.95 (24H, m).

Intermediate 20



Intermediate 19 (2.95 g, 1.67 mmol) is added to a degassed suspension of Amberlyst 15 strong acid (12 g) in anhydrous diethyl ether (100 cm^3) at 0 °C. The mixture is further degassed with nitrogen for 30 minutes. The resulting suspension is stirred at 23 °C for 2 hours before it is filtered through a thin celite plug and washed with diethyl ether (200 cm^3). After removing solvent *in vacuo*, the crude material is purified by column chromatography (40-60 petrol). This material is dissolved in anhydrous tetrahydrofuran (50 cm^3) and cooled to 0 °C. Tetrabutylammonium fluoride (3.34 cm^3, 3.34 mmol, 1 M in tetrahydrofuran) is added and the resulting solution is stirred for 30 minutes at 23 °C. The solvent is then removed *in vacuo* and the resulting residue is suspended in methanol (200 cm^3) which is stirred for 30 minutes. The solid is collected by filtration to give intermediate 20 (2.02 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) 7.13 - 7.21 (4H, m), 6.71 - 6.84 (12H, m), 2.33 - 2.49 (16H, m), 1.38 - 1.48 (16H, m), 1.08 - 1.22 (48H, m), 0.70 - 0.80 (24H, m).

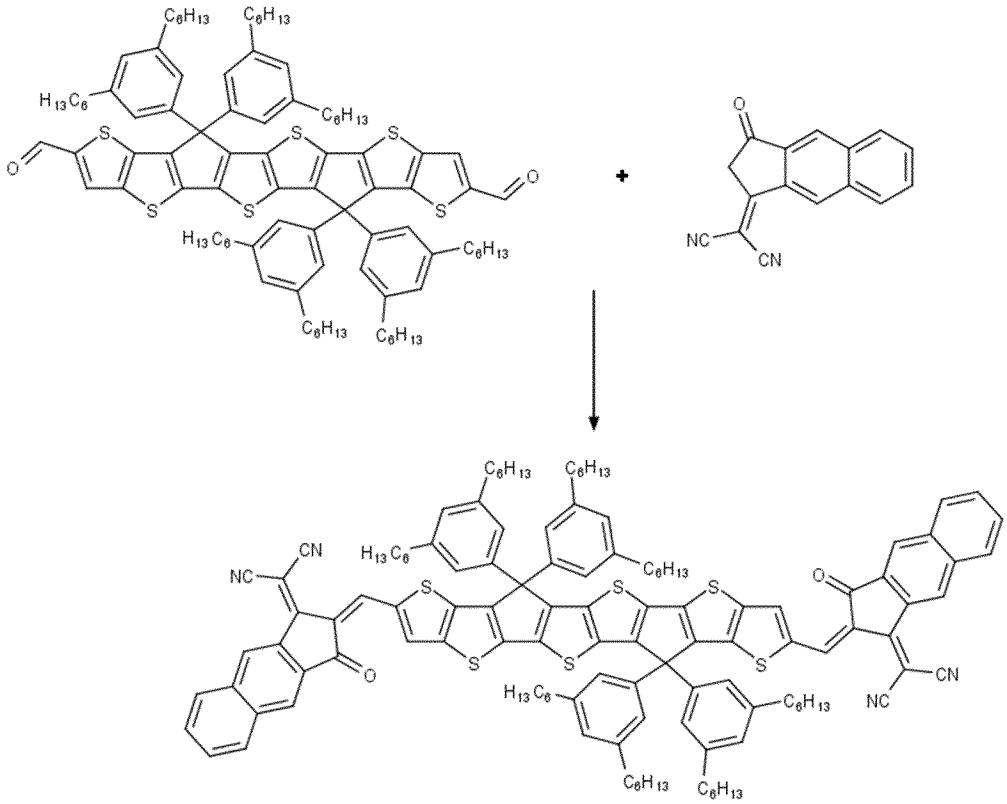
Intermediate 21



To a solution of intermediate 21 (600 mg, 0.42 mmol) in anhydrous tetrahydrofuran (25 cm^3) at -78 °C is added dropwise *n*-butyllithium (0.68

cm^3, 1.7 mmol, 2.5 M in hexane) over 10 minutes. After addition, the reaction mixture is stirred at -78 °C for 60 minutes. *N,N*-Dimethylformamide (0.17 cm^3, 2.5 mmol) is added and the mixture allowed to warm to 23 °C over 2 hours. The reaction is quenched with water (50 cm^3) and the mixture stirred for 30 minutes. The product is extracted with diethyl ether (3 x 50 cm^3) and the combined organics dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography (40-60 petrol:dichloromethane; 8:2) to give intermediate 21 (450 mg, 72%) as a dark red solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.79 (2H, s), 7.85 (2H, s), 6.83 (4H, s), 6.71 (8H, d, J 1.0), 2.41 (16H, t, J 7.6), 1.39 - 1.50 (16H, m), 1.15 (48H, br. s.), 0.70 - 0.80 (24H, m).

Compound 8

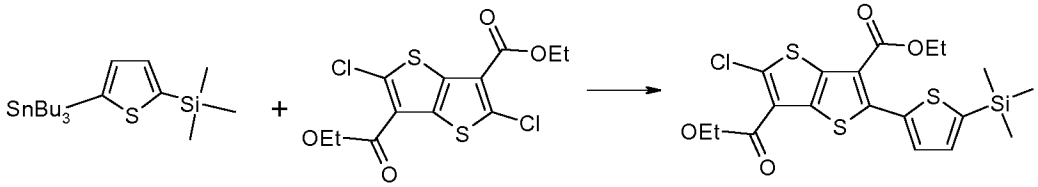


2-(3-Oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (46 mg, 0.19 mmol) is added to a nitrogen saturated solution of intermediate 21 (92 mg, 0.06 mmol) in a mixture of chloroform (1 cm^3) and pyridine (9

cm^3). The solution is stirred for 3 hours. Methanol (30 cm^3) is added, the solid collected by filtration and washed with methanol (50 cm^3). The crude is purified by silica pad (cyclohexane:chloroform; 1:1) followed by trituration (dichloromethane:acetone; 1:1) to give compound 8 (75 mg, 67%) as a black solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.19 (2H, s), 8.98 (2H, s), 8.33 (2H, s), 8.16 (2H, s), 8.10 (2H, dd, J 6.3, 3.4), 8.04 (2H, dd, J 6.2, 3.4), 7.72 (4H, dt, J 6.3, 3.4), 6.97 (4H, t, J 1.5), 6.90 (8H, d, J 1.5), 2.56 (16H, t, J 7.7), 1.50 - 1.64 (16H, m), 1.14 - 1.32 (48H, m), 0.73 - 0.84 (24H, m).

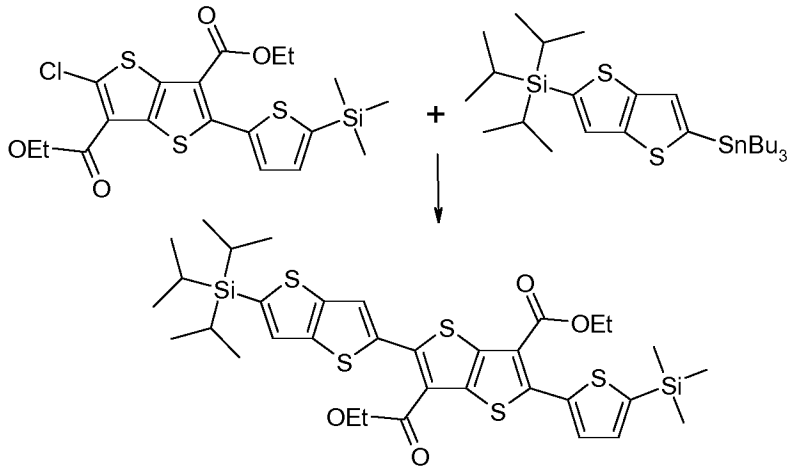
Example 9

Intermediate 22



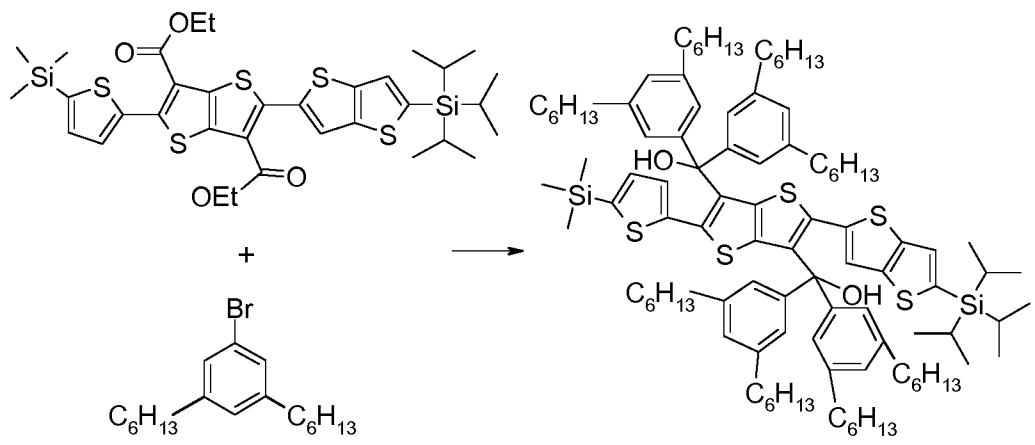
To a degassed mixture of intermediate 5 (7.1 g, 20 mmol), trimethyl-(5-tributylstannanyl-thiophen-2-yl)-silane (10 g, 23 mmol) and anhydrous toluene (300 cm^3) is added tetrakis(triphenylphosphine)palladium(0) (500 mg, 0.4 mmol) and the mixture further degassed for 15 minutes. The mixture is stirred at 85 °C for 17 hours. The reaction mixture is filtered hot through a celite plug and washed through with hot toluene. The crude product is purified by column chromatography (40-60 petrol:dichloromethane: 4:1) to give intermediate 22 (2.3 g, 21%) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) 7.40 (1H, d, J 3.7), 6.99 - 7.03 (1H, m), 4.13 - 4.29 (4H, m), 1.15 - 1.28 (6H, m), 0.10 - 0.37 (9H, s).

Intermediate 23



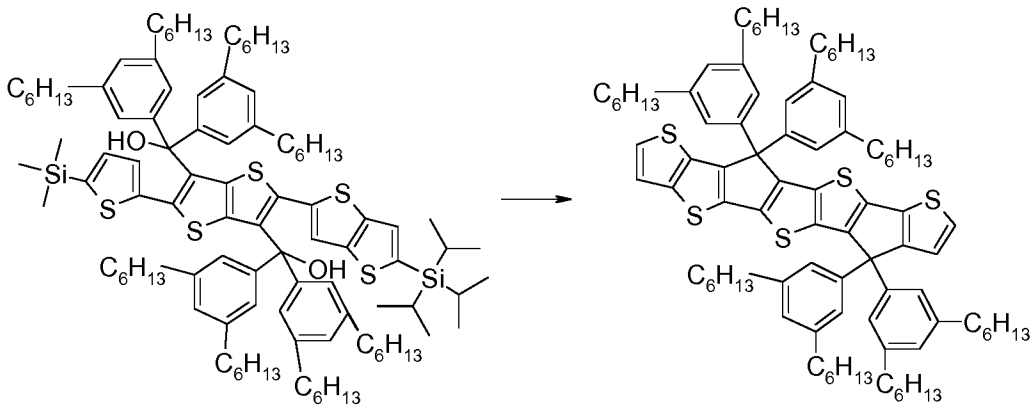
To a degassed mixture of intermediate 22 (2.2 g, 4.6 mmol), intermediate 13 (3.4 g, 5.8 mmol) and anhydrous toluene (300 cm^3) is added tetrakis(triphenylphosphine)palladium(0) (0.5 g, 0.4 mmol) and the mixture further degassed for 15 minutes. The mixture is stirred at 85 °C for 17 hours. The reaction mixture is filtered hot through a celite plug and washed through with hot toluene. The crude product is stirred in acetone (100 cm^3) for 1 hour to form a heavy suspension. The solid is collected by filtration to give intermediate 23 (3.2 g, 75%) as a pale brown solid. ^1H NMR (400 MHz, $CDCl_3$) 7.80 - 7.86 (1H, s), 7.65 (1H, d, J 3.4), 7.38 (1H, s), 7.24 (1H, d, J 3.4), 4.43 (4H, m), 1.31 - 1.51 (10H, m), 1.15 (18H, d, J 7.3), 0.38 (9H, s).

Intermediate 24



To a solution of 1-bromo-3,5-dihexyl-benzene (4.9 g, 15 mmol) in anhydrous tetrahydrofuran (100 cm^3) at -78 °C is added dropwise *n*-butyllithium (6.0 cm^3, 15 mmol, 2.5 M in hexane) over 30 minutes. After addition, the reaction mixture is stirred at -78 °C for 120 minutes. Intermediate 23 (2.2 g, 3.0 mmol) is added and the mixture allowed to warm to 23 °C over 17 hours. Diethyl ether (100 cm^3) and water (100 cm^3) are added and the mixture stirred for 30 minutes. The product is extracted with diethyl ether (3 x 100 cm^3). The organics are combined and dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo* to give intermediate 24 (2.30 g, 47%) as a brown oil. ^{1}H NMR (400 MHz, CD_2Cl_2) 7.21 (1H, s), 7.06 (1H, s), 6.80 - 7.03 (12H, m), 6.42 - 6.55 (2H, m), 3.36 (2H, d, J 4.4), 2.44 - 2.62 (16H, m), 1.48 - 1.65 (16H, m), 1.24 - 1.35 (49H, m), 1.11 - 1.17 (18H, m), 0.83 - 0.94 (24H, m), 0.26 (9H, s).

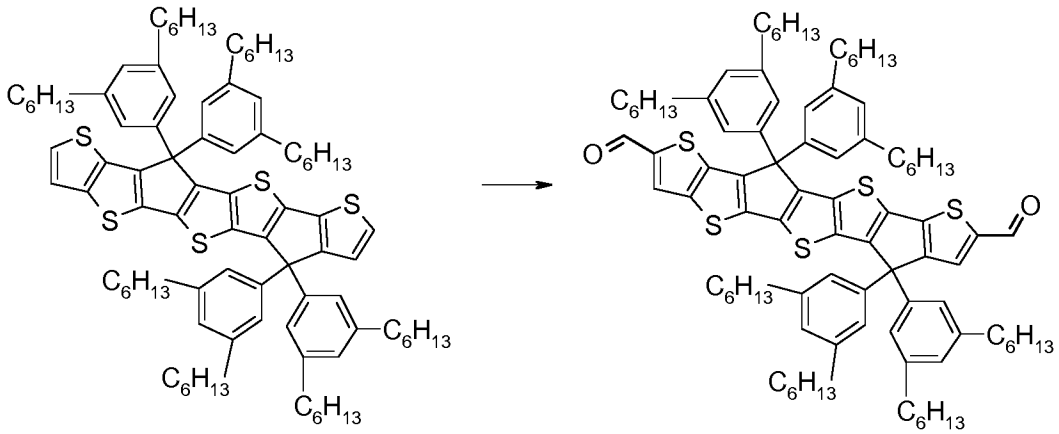
Intermediate 25



Nitrogen gas is bubbled through a suspension of Amberlyst 15 strong acid (8.8 g) in anhydrous diethyl ether (100 cm^3) at 0 °C for 60 minutes. Intermediate 24 (2.2 g, 1.4 mmol) is added whilst the mixture is degassed for a further 30 minutes. The resulting suspension is stirred at 23 °C for 2 hours. The reaction mixture is filtered and the solvent removed *in vacuo*. The crude is taken up in anhydrous tetrahydrofuran (50 cm^3) and tetrabutylammonium fluoride (2.7 cm^3, 2.7 mmol, 1 M in tetrahydrofuran) added. The mixture is stirred for 1 hour, diethyl ether (100 cm^3) and water (200 cm^3) added and the mixture stirred for 30 minutes. The product is extracted with diethyl ether (3 x 100 cm^3). The organics are combined and

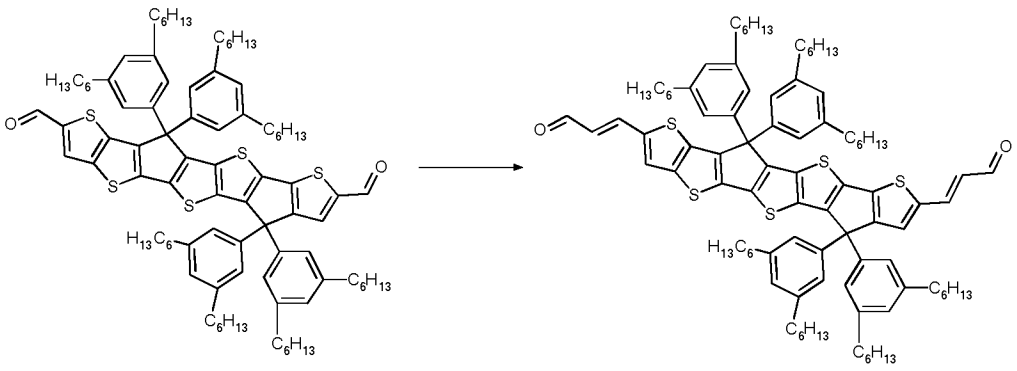
dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography (40-60 petrol:dichloromethane; 9:1) to give intermediate 25 (1.0 g, 54%) as a dark orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) 7.25 - 7.31 (1H, m), 7.21 - 7.25 (1H, m), 7.17 (1H, d, J 4.9), 7.05 (1H, d, J 4.9), 6.81 - 6.91 (12H, m), 2.40 - 2.57 (16H, m), 1.54 (16H, d, J 6.8), 1.25 (48H, d, J 7.3), 0.85 (24H, q, J 6.2).

Intermediate 26



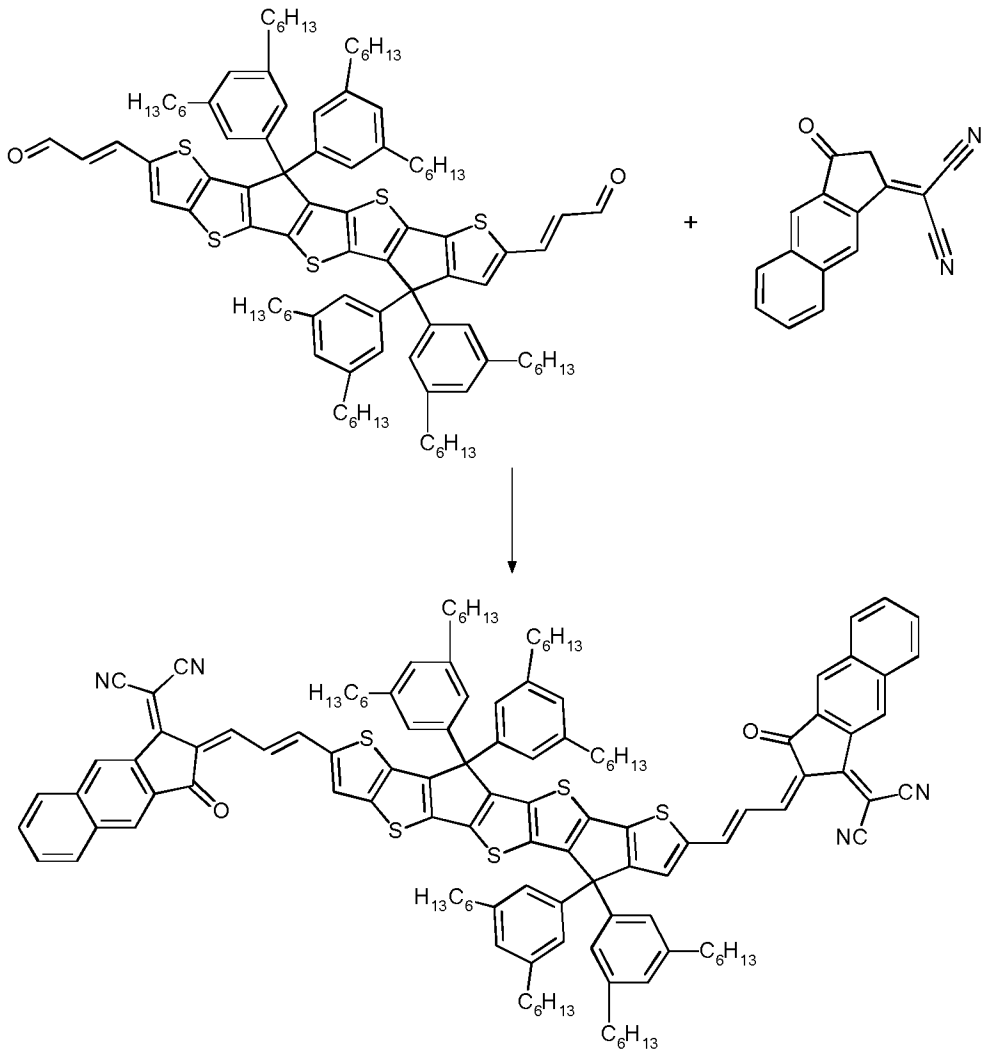
To a solution of intermediate 25 (500 mg, 0.37 mmol) in anhydrous tetrahydrofuran (22 cm^3) at -78 °C is added dropwise *n*-butyllithium (0.6 cm^3, 1.5 mmol, 2.5 M in hexane) over 10 minutes. After addition, the reaction mixture is stirred at -78 °C for 60 minutes. *N,N*-Dimethylformamide (0.15 cm^3, 2.2 mmol) is added and the mixture allowed to warm to 23 °C over 17 hours. Diethyl ether (50 cm^3) and water (50 cm^3) are added and the mixture stirred for 30 minutes. The product is extracted with diethyl ether (3 x 100 cm^3) and the combined organics dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography (40-60 petrol:dichloromethane; 8:2) to give intermediate 26 (95 mg, 18%) as a dark red oil. ^{1}H NMR (400 MHz, $CDCl_3$) 9.70 - 9.85 (1H, s), 9.69 - 9.75 (1H, s), 7.83 - 7.87 (1H, s), 7.56 (1H, s), 6.83 (4H, s), 6.71 (8H, dd, J 12.8, 1.3), 2.29 - 2.53 (16H, m), 1.36 - 1.55 (16H, m), 1.05 - 1.27 (48H, m), 0.76 (24H, q, J 6.8).

Intermediate 27



To a solution of intermediate 26 (1.00 g, 0.71 mmol) and tributyl(1,3-dioxolan-2-ylmethyl)-phosphonium bromide (573 mg, 1.55 mmol) in tetrahydrofuran (50 cm^3) is added sodium hydride (169 mg, 4.23 mmol, 60 % dispersion in mineral oil). The reaction is then stirred for 18 hours. The reaction is cooled to 0 °C and hydrochloric acid (5 cm^3, 10% in water) is added and the mixture stirred at 0 °C for 40 minutes and at 23 °C for 2 hours. Water (25 cm^3) is added and the mixture extracted with ether (3 x 50 cm^3). The combined organic layer is washed with brine (50 cm^3) before drying over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is triturated in acetonitrile (100 cm^3) at 50 °C for 1 hour. The solvent is decanted and the material dried to give intermediate 27 (920 mg, 89%) as a dark purple oil. ^1H NMR (400 MHz, $CDCl_3$) 9.48 - 9.55 (2H, m), 7.41 - 7.52 (3H, m), 7.18 (1H, s), 6.64 - 6.89 (12H, m), 6.27 - 6.42 (2H, m), 2.34 - 2.50 (16H, m), 1.39 - 1.54 (16H, m), 1.10 - 1.29 (48H, m), 0.70 - 0.80 (24H, m).

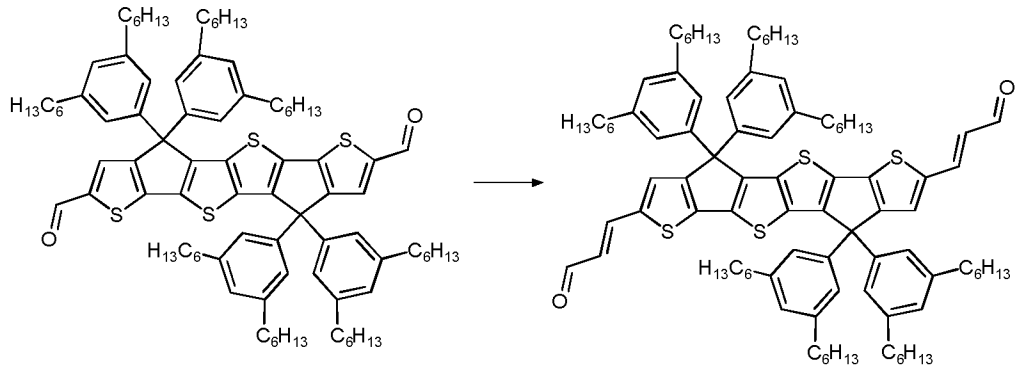
Compound 9



To a solution of intermediate 27 (120 mg, 0.082 mmol) in anhydrous chloroform (6.5 cm^3) at 0 °C is added 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (79.7 mg, 0.326 mmol) followed by pyridine (0.46 cm^3). The resulting solution is then degassed for 15 minutes. The ice bath is removed and the mixture allowed to warm to 23 °C and stirred for 15 minutes. Acetonitrile (50 cm^3) is added to form a heavy suspension and the solid collected by filtration to give compound 9 (145 mg, 92%) as a dark brown solid. ^{1}H NMR (400 MHz, CD_2Cl_2) 9.07 (2H, d, J 5.4), 8.53 - 8.67 (2H, m), 8.36 - 8.44 (2H, m), 8.23 - 8.29 (2H, m), 7.94 - 8.05 (4H, m), 7.46 - 7.66 (7H, m), 7.34 (1H, s), 6.73 - 6.92 (12H, m), 2.35 - 2.48 (16H, m), 1.40 - 1.56 (16H, m), 1.17 (48H, d, J 2.4), 0.66 - 0.81 (24H, m).

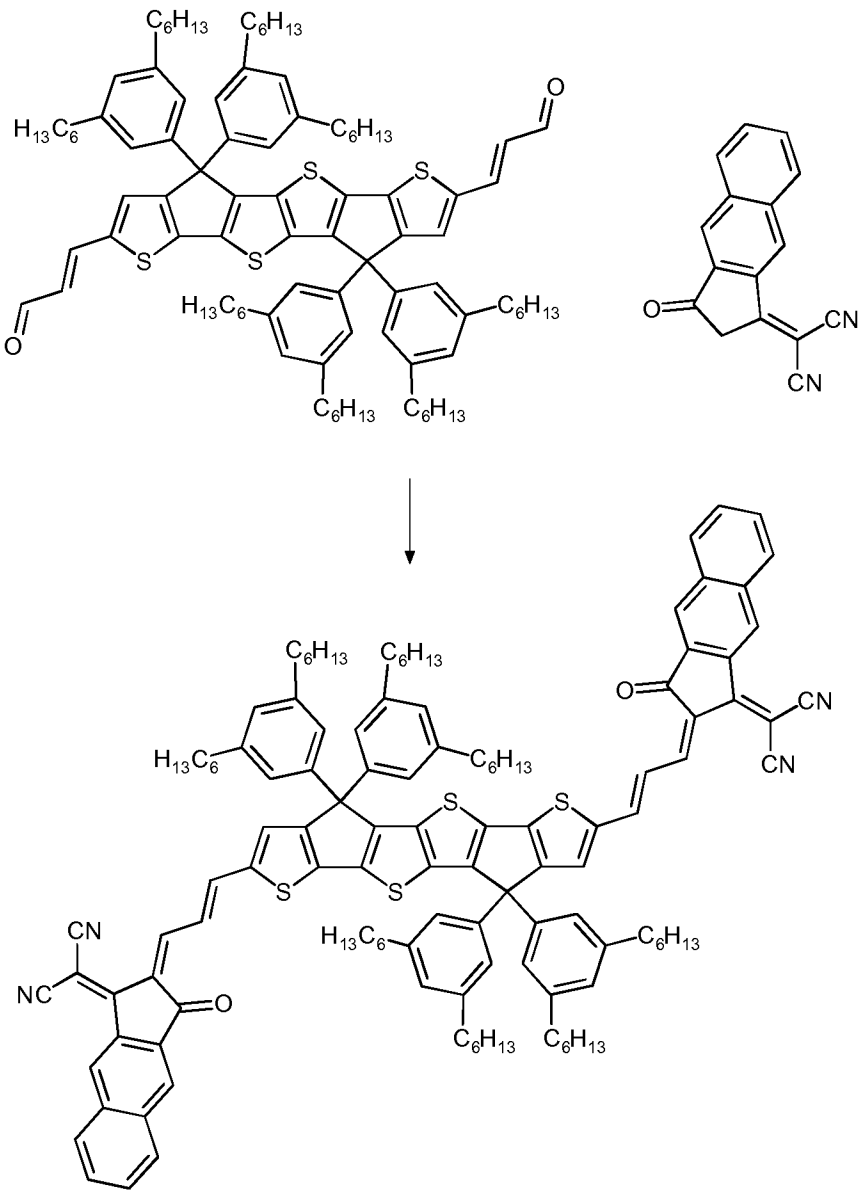
Example 10

Intermediate 28



To a solution of tributyl(1,3-dioxolan-2-ylmethyl)-phosphonium bromide (1.03 g, 2.77 mmol) and intermediate 2 (1.72 g, 1.26 mmol) in anhydrous tetrahydrofuran (70 cm^3) is added sodium hydride (303 mg, 7.57 mmol, 60% dispersion in mineral oil) and the reaction stirred for 17 hours. The reaction is cooled to 0 °C before addition of hydrochloric acid (11 cm^3, 10% in water). The mixture is then stirred at 0 °C for 40 minutes and at 23 °C for 47 hours. Ethyl acetate (100 cm^3) and water (100 cm^3) are then added. The organic layer is then washed with water (100 cm^3) and brine (25 cm^3) before drying over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is then purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:0 to 3:7) to give intermediate 10 (1.53 g, 86%) as a dark oily solid. ^1H NMR (400 MHz, $CDCl_3$) 9.57 (2H, d), 7.48 - 7.56 (2H, m), 7.24 - 7.26 (2H, m), 6.90 (4H, s), 6.78 (8H, s), 6.37 - 6.49 (2H, m), 2.42 - 2.55 (16H, m), 1.43 - 1.60 (16H, m), 1.17 - 1.30 (48H, m), 0.74 - 0.84 (24H, m).

Compound 10

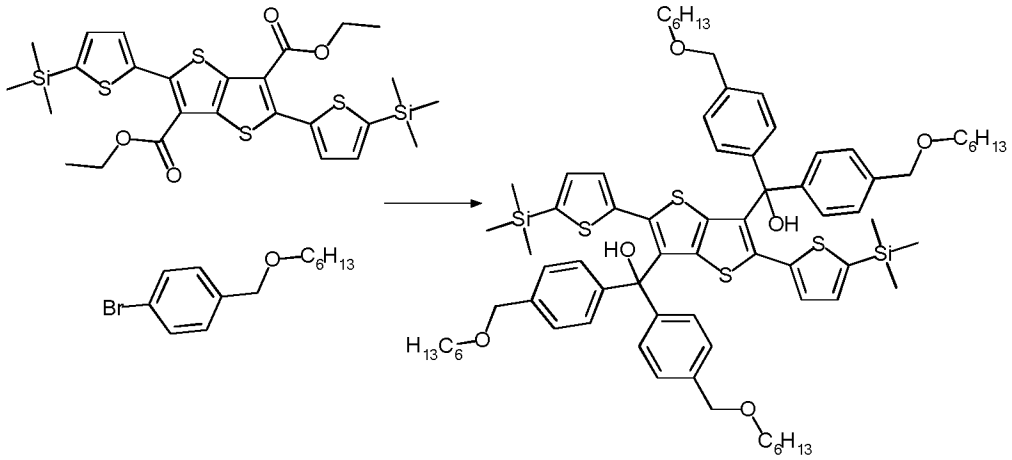


To a degassed solution of intermediate 28 (189 mg, 0.13 mmol) in anhydrous chloroform (10 cm^3) and pyridine (0.76 cm^3) at 0 °C is added 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (131 mg, 0.535 mmol). The reaction mixture is stirred for 2.5 hours at 0 °C and then poured into stirred methanol (150 cm^3). The mixture stirred for 25 minutes, the solid collected by filtration and washed with methanol (3 x 10 cm^3), acetonitrile (3 x 10 cm^3) and 40-60 petrol (3 x 10 cm^3). The crude is then recrystallised (80-100 petrol:acetone) to give compound 10 (26 mg, 10%) as a black solid. ^1H NMR (400 MHz, $CDCl_3$) 9.16 (2H, s), 8.69 (2H, dd, J 14.6, 11.9), 8.50 (2H, d, J 11.7), 8.35 (2H, s), 8.01 - 8.11 (4H, m),

7.66 - 7.73 (4H, m), 7.55 (2H, d, J 14.4), 7.38 (2H, s), 6.95 (4H, s), 6.81 (8H, d, J 1.2), 2.53 (16H, t, J 7.7), 1.49 - 1.66 (16H, m), 1.21 - 1.35 (48H, m), 0.81 - 0.89 (24H, m).

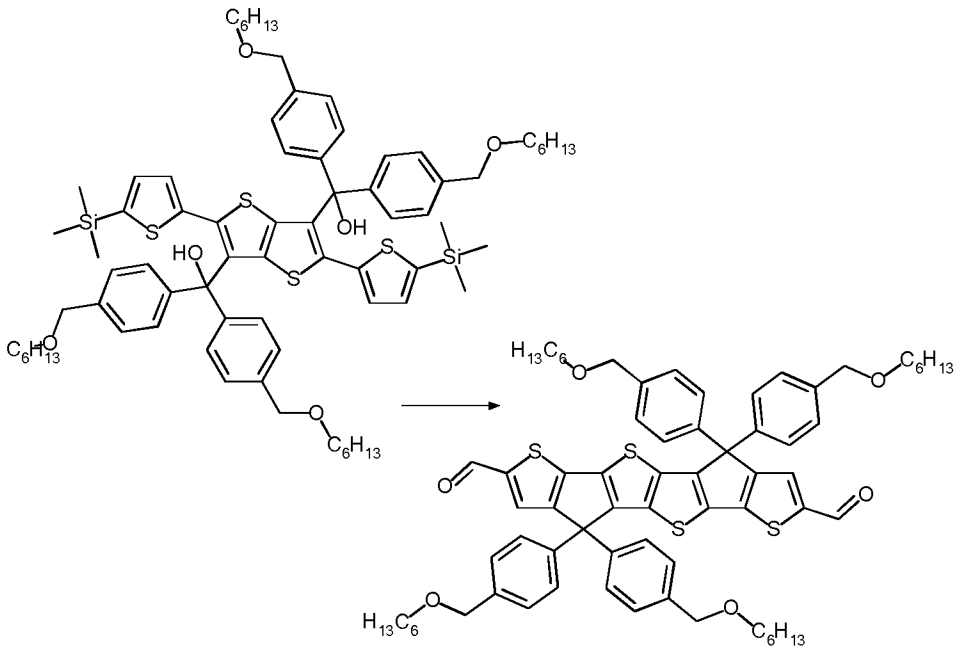
Example 11

Intermediate 29



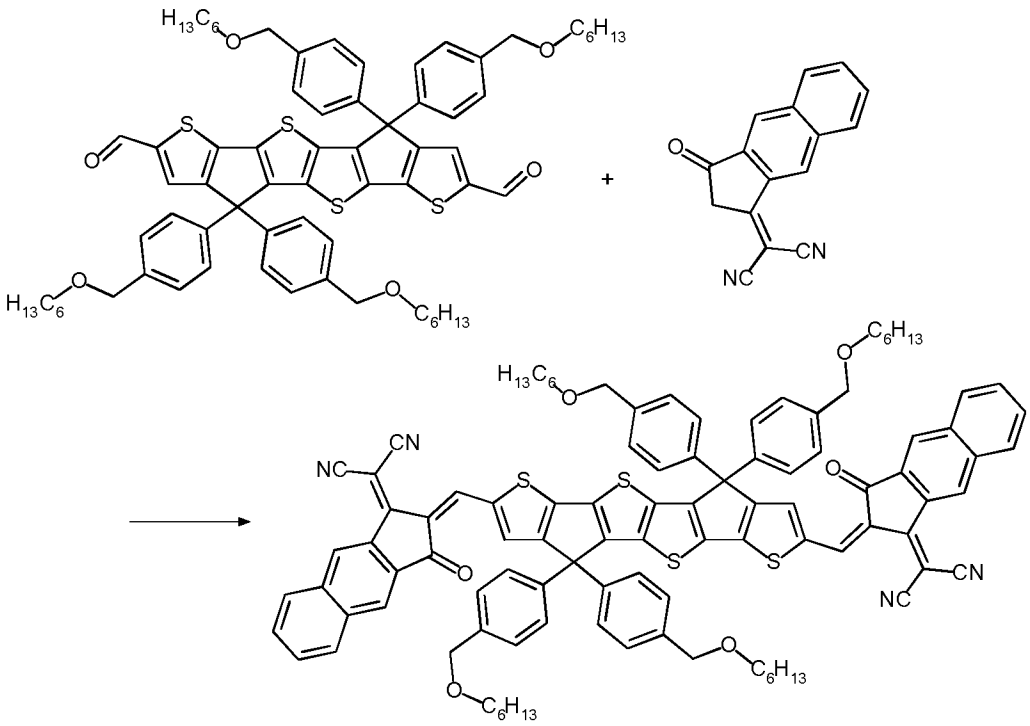
To a solution of 1-bromo-4-hexyloxymethyl-benzene (2.27 g, 8.37 mmol) in anhydrous tetrahydrofuran (68 cm^3) at -78 °C is slowly added *t*-butyllithium (9.9 cm^3, 17 mmol, 1.7 M in pentanes). The solution is stirred for 2 hours, warmed to -30 °C and then cooled again to -70 °C. Intermediate 6 (993 mg, 1.67 mmol) is added, the reaction slowly warmed to 23 °C and stirred for 16 hours. Water (50 cm^3) and ether (100 cm^3) are added. The organic phase is washed with water (3 x 30 cm^3), dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo*. The resulting yellow oil (2.50 g) is taken through to the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) 7.26 - 7.31 (16H, m), 6.83 (2H, d, J 3.4), 6.46 (2H, d, J 3.4), 4.53 (8H, s), 3.43 - 3.48 (10H, m), 1.54 - 1.70 (8H, m), 1.20 - 1.43 (24H, m), 0.83 - 0.97 (12H, m), 0.23 (18H, s).

Intermediate 30



To a nitrogen saturated solution of intermediate 29 (2.5 g) in toluene (100 cm^3) at 50 °C is added Amberlyst 15 strong acid (8.0 g). The suspension is purged with nitrogen for a further 5 minutes and stirred for 16 hours. The reaction mixture is filtered and washed with toluene (3 x 20 cm^3) and the combined filtrate concentrated *in vacuo*. The crude is purified by column chromatography (dichloromethane). The oil is dissolved in chloroform (50 cm^3) and cooled in an ice bath. *N,N*-Dimethylformamide (2.30 g, 31.5 mmol) and phosphorus oxychloride (4.52 g, 29.5 mmol) are slowly added. The reaction is stirred for 1 hour at 23 °C, 60 °C for 8 hours and for 48 hours at 23 °C. Water (20 cm^3) is slowly added and the biphasic solution is heated to 60 °C. Saturated aqueous sodium acetate (20 cm^3) is added and the mixture stirred for a further 3 hours, then cooled to 23 °C. The aqueous phase is extracted with dichloromethane (20 cm^3). The combined organics are washed with water (50 cm^3), dried over magnesium sulphate, filtered and concentrated *in vacuo*. The residue is purified by column chromatography using a graded solvent system (dichloromethane:acetone; 1:0 to 9:1) followed by trituration (80-100 petrol) to give intermediate 30 (380 mg, 17%) as an orange solid. ^1H NMR (400 MHz, $CDCl_3$) 9.82 (2H, s), 7.66 (2H, s), 7.29 - 7.34 (8H, m), 7.19 - 7.24 (8H, m), 4.47 (8H, s), 3.49 (8H, t, J 6.6), 1.55 - 1.67 (8H, m), 1.24 - 1.41 (24H, m), 0.89 (12H, t, J 6.7).

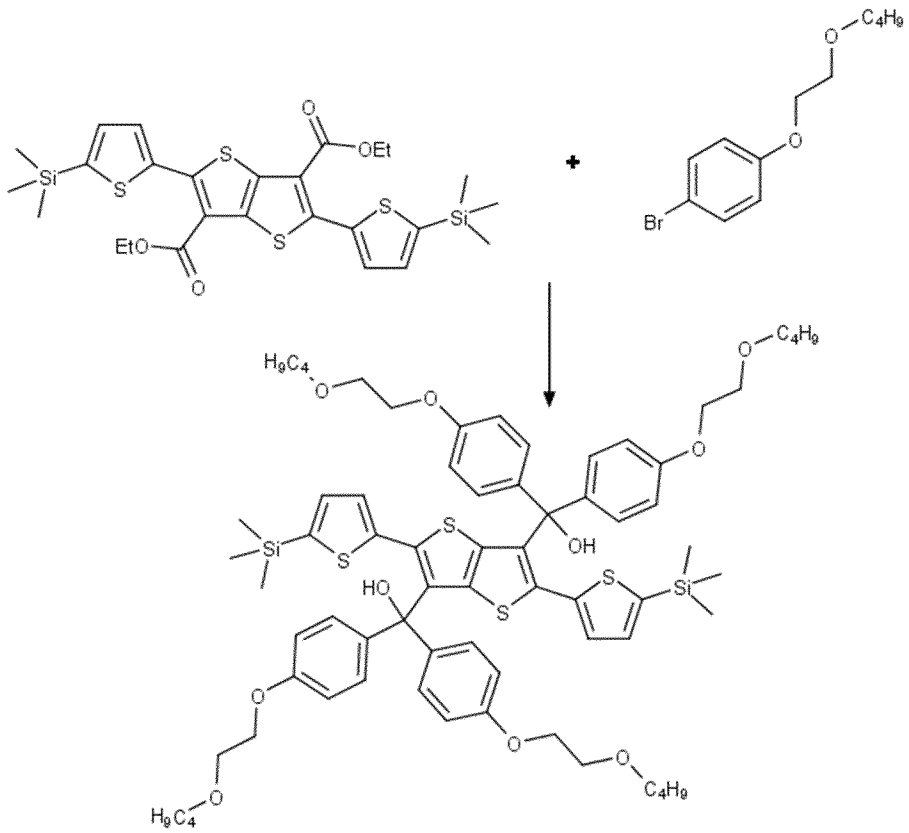
Compound 11



Intermediate 30 (100 mg, 0.09 mmol) and 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (107 mg, 0.44 mmol) are suspended in chloroform (10 cm^3) and saturated with nitrogen. Pyridine (0.49 cm^3) is added and the solution stirred for 16 hours at 23 °C and at 60 °C for 1 hour. Methanol (25 cm^3) is added slowly over 15 minutes, the mixture stirred for 30 minutes and then cooled to 23 °C, filtered and washed with methanol (2 x 25 cm^3). The crude is purified by column chromatography using a graded solvent system (dichloromethane:diethyl ether; 1:0 to 33:1) to give compound 11 (46 mg, 33%) as a green solid. ^1H NMR (400 MHz, $CDCl_3$) 9.18 (2H, s), 8.93 (2H, s), 8.37 (2H, s), 8.02 - 8.11 (4H, m), 7.73 (2H, s), 7.63 - 7.71 (4H, m), 7.36 (8H, d, J 8.3), 7.26 (8H, d, J 8.4), 4.51 (8H, s), 3.51 (8H, t, J 6.6), 1.56 - 1.69 (8H, m), 1.19 - 1.44 (24H, m), 0.84 - 0.95 (12H, m).

Example 12

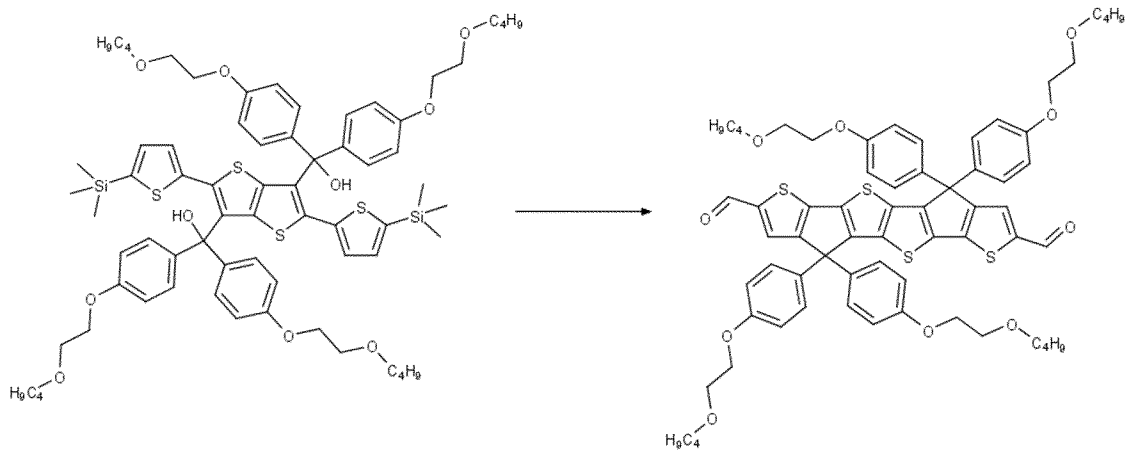
Intermediate 31



Anhydrous tetrahydrofuran (2 cm^3) is added to a flask containing oven dried magnesium turnings (246 mg, 10.1 mmol) and an iodine crystal. The mixture is maintained at reflux while a solution of 1-bromo-4-(2-butoxy-ethoxy)-benzene (2.77 g, 10.1 mmol) in anhydrous tetrahydrofuran (5 cm^3) is added portion wise over 10 minutes. The reaction is then heated at reflux for 2 hours. The resulting Grignard reagent is transferred over 5 minutes to a flask containing intermediate 6 (1.00 g, 1.69 mmol) dissolved in anhydrous tetrahydrofuran (10 cm^3) and maintained at 65 °C. The mixture is heated at 65 °C for 6 hours, followed by 16 hours at 23 °C. The solution is partioned between water (30 cm^3) and diethyl ether (30 cm^3). Hydrochloric acid (2 N) is added slowly until the phases become clear. The organic phase is washed with water (2 x 20 cm^3), dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo.* The residue is recrystallised (40-60 petrol) to give intermediate 31 (1.59 g, 74%) as a beige solid. ^1H NMR (400 MHz, $CDCl_3$) 7.14 - 7.23 (8H, m), 6.88 (2H, d, J

3.4), 6.81 - 6.87 (8H, m), 6.48 (2H, d, J 3.4), 4.13 (8H, t, J 4.1), 3.79 (8H, t, J 4.1), 3.54 (8H, t, J 6.7), 3.39 (2H, s), 1.55 - 1.67 (8H, m), 1.32 - 1.47 (8H, m), 0.94 (12H, t, J 7.4), 0.25 (18H, s).

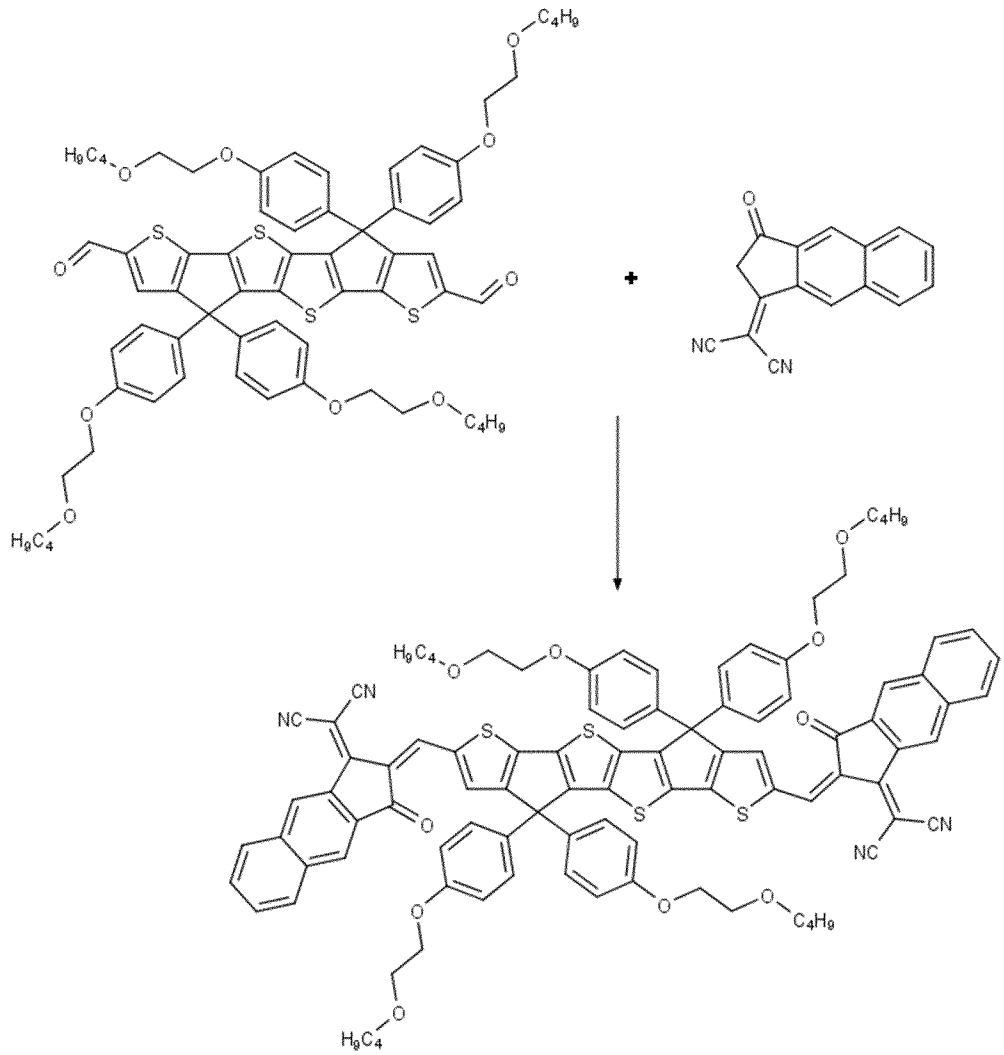
Intermediate 32



Intermediate 31 is dissolved in toluene (64 cm^3). The solution is saturated with nitrogen and Amberlyst 15 strong acid (6.0 g) is added. Nitrogen is bubbled through the suspension for a further 10 minutes and the mixture is stirred for 16 hours. The reaction is filtered and the solid washed with hot toluene (3 x 10 cm^3). The combined filtrates are concentrated *in vacuo* and purified by silica plug (dichloromethane). The intermediate is dissolved in chloroform (32 cm^3), *N,N*-dimethylformamide (1.46 g) added and the solution cooled in an ice-bath. Phosphorus oxychloride (2.86 g, 18.7 mmol) is added over 5 minutes. The solution is warmed to 23 °C and then heated at 65 °C for 16 hours. Water (5 cm^3) is slowly added followed by aqueous sodium acetate (50 cm^3, 10 M) and the biphase is stirred for 1 hour at 65 °C. The aqueous phase is extracted with dichloromethane (20 cm^3) and the combined organics washed with water (2 x 20 cm^3), dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo*. The residue is then triturated in boiling 40-60 petrol (15 cm^3), filtered and washed with 40-60 petrol (2 x 5 cm^3) to give intermediate 32 (670 mg, 47%) as an orange solid. ^1H NMR (400 MHz, $CDCl_3$) 9.73 (2H, s), 7.58 (2H, s), 7.05 (8H, d, J 8.6), 6.78 (8H, d, J 8.7), 4.00 (8H, t, J 4.9), 3.68 (8H, t, J 4.7), 3.43 (8H, t, J 6.7), 1.43 - 1.56 (8H, m), 1.29 (8H, q, J 7.5), 0.83

(12H, t, J 7.3).

Compound 12

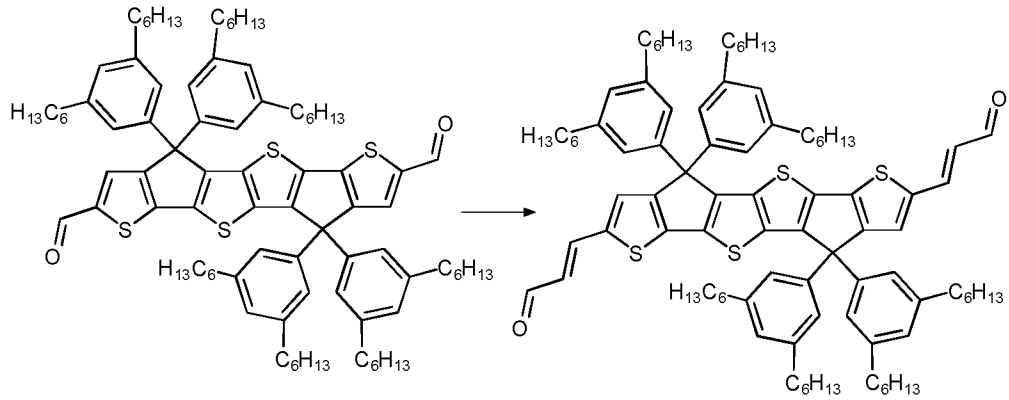


Intermediate 32 (100 mg, 0.09 mmol) and 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (106 mg, 0.43 mmol) are dissolved in chloroform (2.5 cm^3). Nitrogen is bubbled through the suspension for 10 minutes. Pyridine (0.49 cm^3) is added and the nitrogen inlet removed after a further 10 minutes. The reaction is stirred for 18 hours, diluted with methanol (20 cm^3) and stirred for 10 minutes. The resulting suspension is filtered and washed with methanol (2 x 5 cm^3). The material is purified by column chromatography using a graded solvent system (dichloromethane:methanol; 10:0 to 49:1) followed by

recrystallisation (chloroform:acetone) to give compound 12 (97 mg, 70%) as a green solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.10 (2H, s), 8.87 (2H, s), 8.29 (2H, s), 7.94 - 8.05 (4H, m), 7.58 - 7.67 (6H, m), 7.05 - 7.14 (8H, m), 6.78 - 6.87 (8H, m), 4.03 (8H, t, J 4.6), 3.69 (8H, t, J 4.7), 3.44 (8H, t, J 6.7), 1.45 - 1.56 (8H, m), 1.23 - 1.35 (8H, m), 0.83 (12H, t, J 7.4).

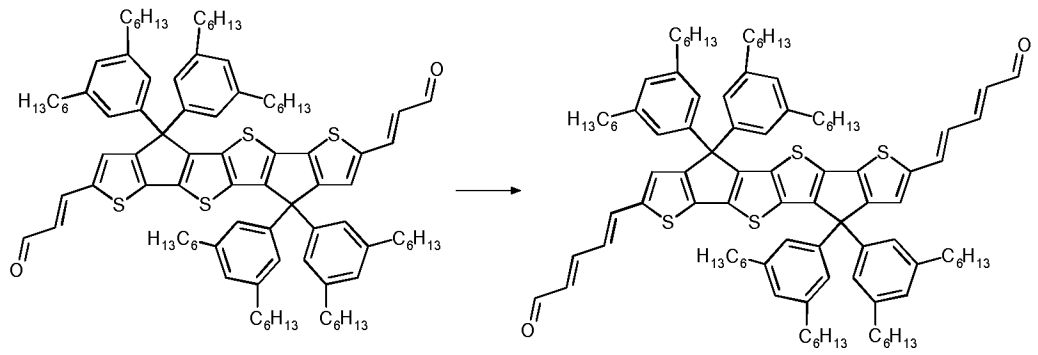
Example 13

Intermediate 33



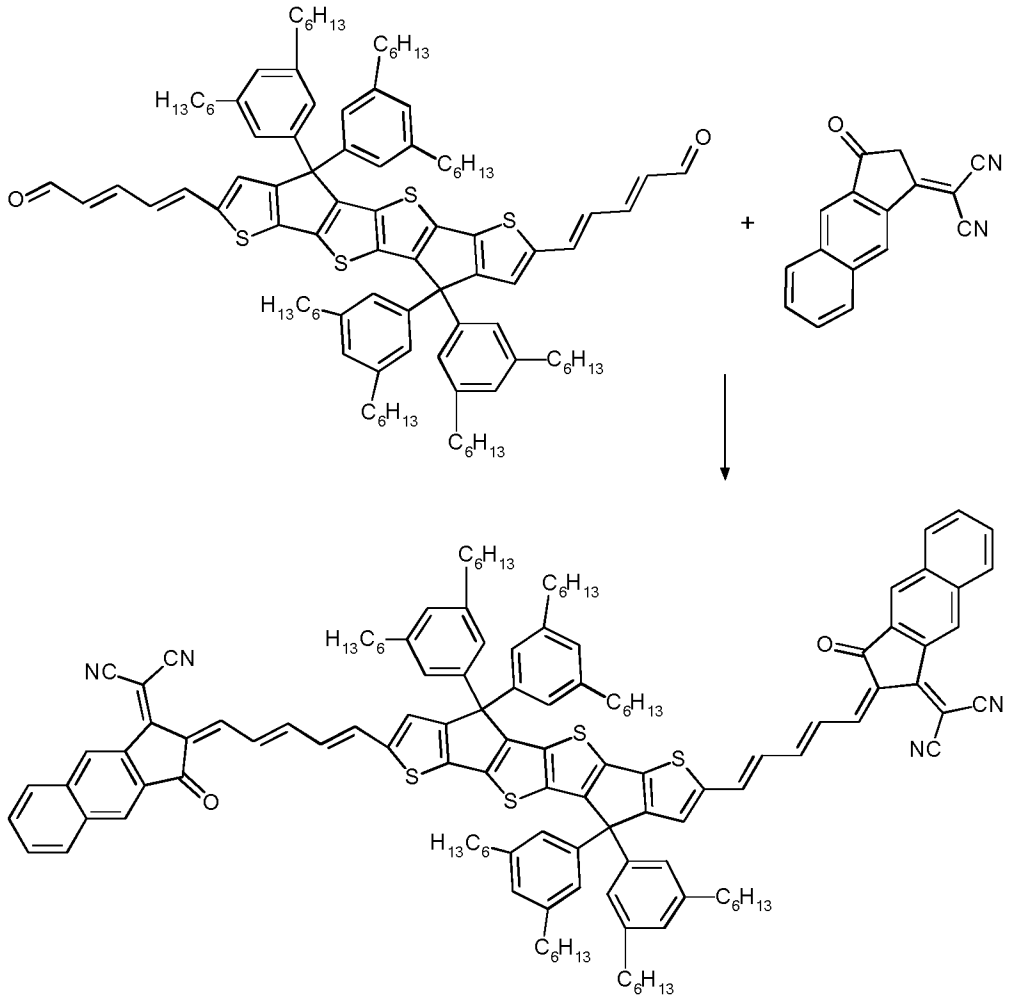
To a solution of tributyl(1,3-dioxolan-2-ylmethyl)-phosphonium bromide (1.03 g, 2.77 mmol) and intermediate 2 (1.72 g, 1.26 mmol) in anhydrous tetrahydrofuran (70 cm^3) is added sodium hydride (303 mg, 7.57 mmol, 60% dispersion in mineral oil) and the reaction stirred for 17 hours. The reaction is cooled to 0 °C before addition of hydrochloric acid (11 cm^3, 10% in water). The mixture is then stirred at 0 °C for 40 minutes and at 23 °C for 47 hours. Ethyl acetate (100 cm^3) and water (100 cm^3) are then added. The organic layer is washed with water (100 cm^3), brine (25 cm^3) before drying over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is then purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:0 to 3:7) to give intermediate 33 (1.53 g, 86%) as a dark oily solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.54 - 9.60 (2H, m), 7.48 - 7.56 (2H, m), 7.24 - 7.26 (2H, m), 6.90 (4H, s), 6.78 (8H, s), 6.37 - 6.49 (2H, m), 2.42 - 2.55 (16H, m), 1.43 - 1.60 (16H, m), 1.17 - 1.30 (48H, m), 0.74 - 0.84 (24H, m).

Intermediate 34



To a solution of tributyl(1,3-dioxolan-2-ylmethyl)-phosphonium bromide (591 mg, 1.60 mmol), intermediate 33 (1.03 g, 0.73 mmol) and anhydrous tetrahydrofuran (40 cm^3) at 0 °C is added sodium hydride (174 mg, 4.36 mmol, 60% dispersion in mineral oil). The reaction is then stirred at 23 °C for 16 hours and then cooled to 0 °C before hydrochloric acid (10 cm^3, 10% in water) is added. The mixture is then stirred at 0 °C for 20 minutes and at 23 °C for 6 hours. Ethyl acetate (100 cm^3) and water (100 cm^3) are added and the organic layer washed with water (100 cm^3) and brine (100 cm^3) before drying over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:ethyl acetate; 1:0 to 9:1) to give intermediate 34 (781 mg, 73%) as a purple/black oily solid. ^1H NMR (400 MHz, CD_2Cl_2) 9.55 (2H, d, J 7.9), 7.20 (2H, dd, J 15.0, 11.1), 7.08 - 7.15 (4H, m), 6.91 (4H, s), 6.70 - 6.84 (10H, m), 6.16 (2H, dd, J 15.0, 7.9), 2.48 (16H, t, J 7.6), 1.45 - 1.57 (16H, m), 1.19 - 1.33 (48H, m), 0.80 - 0.87 (24H, m).

Compound 13

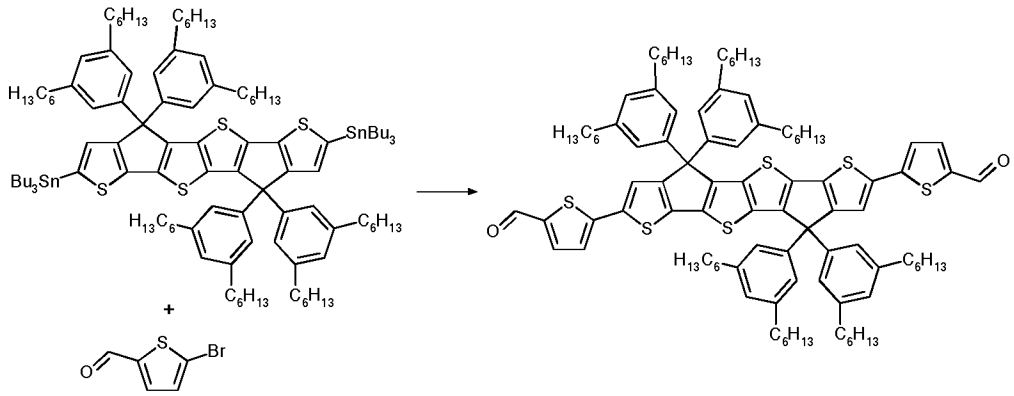


To a degassed solution of intermediate 34 (200 mg, 0.14 mmol), anhydrous chloroform (15 cm^3) and pyridine (0.77 cm^3, 9.6 mmol) at 0 °C is added 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (133 mg, 0.55 mmol). The reaction mixture is then stirred at 0 °C for 110 minutes before adding to stirred methanol (150 cm^3) and the mixture stirred for 15 minutes at 23 °C. The solid collected by filtration, washed with methanol (5 x 10 cm^3), acetonitrile (3 x 10 cm^3), 40-60 petrol (3 x 10 cm^3), cyclohexane (3 x 10 cm^3), ethyl acetate (3 x 10 cm^3), diethyl ether (3 x 10 cm^3), acetone (3 x 10 cm^3) and 2-butanone (3 x 10 cm^3). The solid is triturated with boiling ether (2 x 50 cm^3) and the collected solid washed with ether (2 x 50 cm^3) to give compound 13 (143 mg, 55%) as a black solid. ^1H NMR (400 MHz, CD_2Cl_2) 9.15 (2H, s), 8.30 - 8.49 (6H, m), 8.03 - 8.13 (4H, m), 7.66 - 7.74 (4H, m), 7.18 - 7.34 (6H, m), 7.01 (2H, dd,

J 14.6, 11.6), 6.93 (4H, s), 6.83 (8H, s), 2.50 (16H, t, J 7.5), 1.46 - 1.61 (16H, m), 1.18 - 1.36 (48H, m), 0.78 - 0.90 (24H, m).

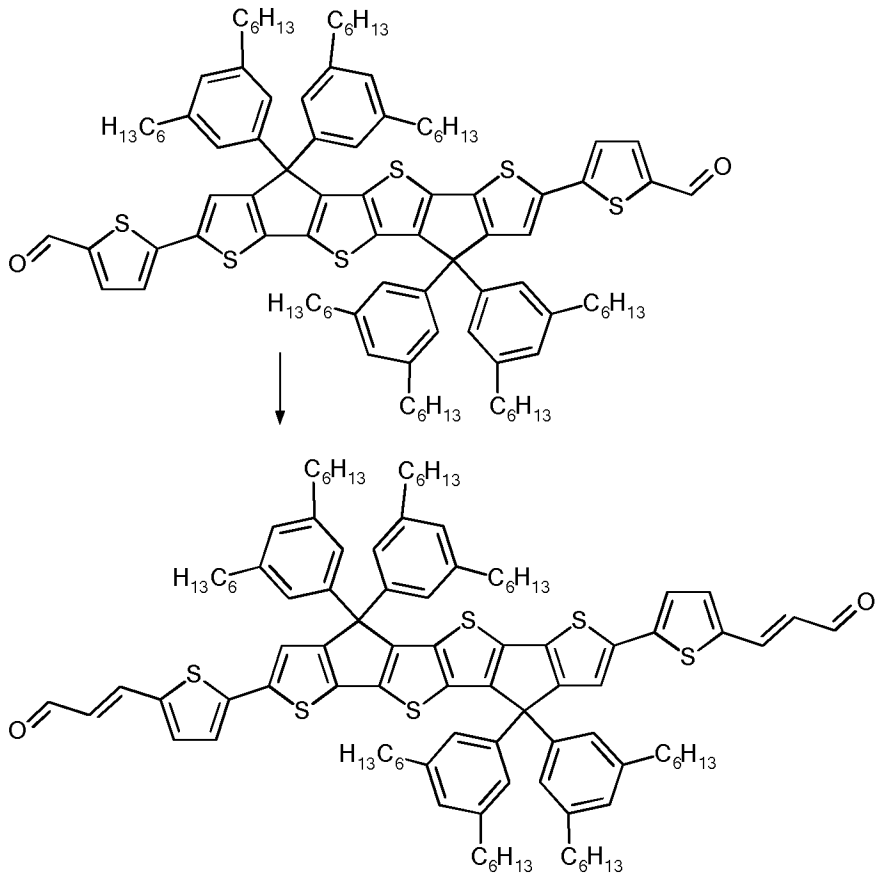
Example 14

Intermediate 35



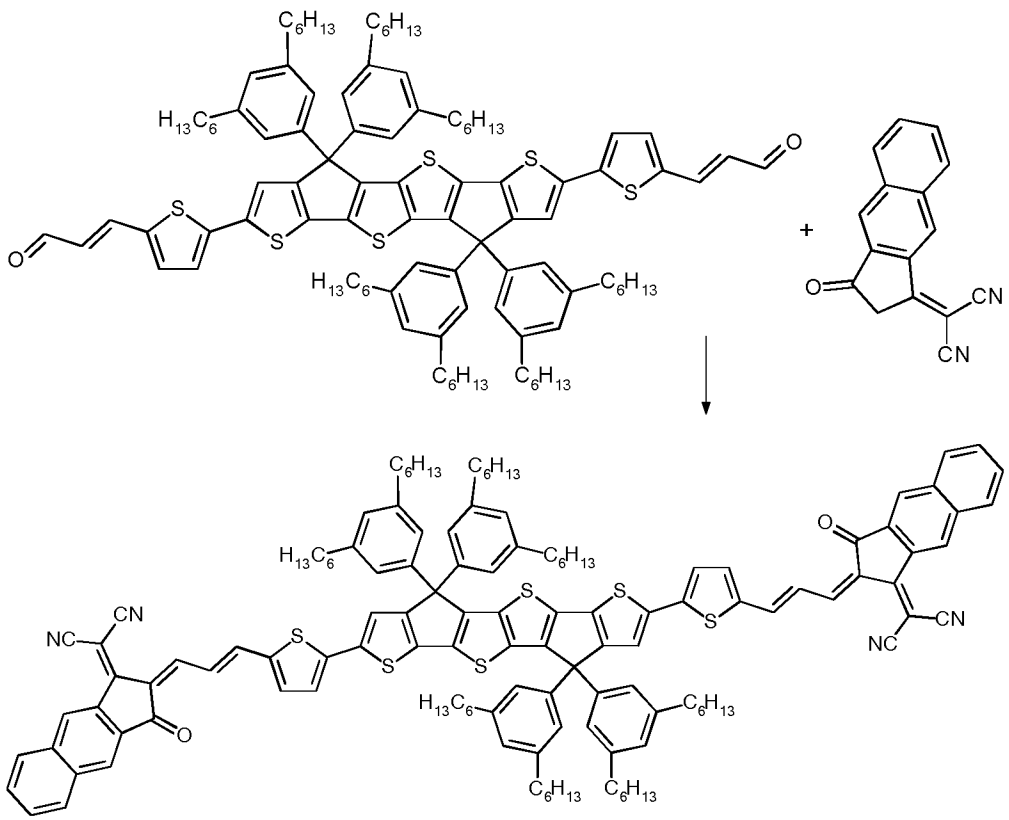
To a degassed solution of 5-bromo-thiophene-2-carbaldehyde (1.05 cm^3, 8.83 mmol), anhydrous toluene (240 cm^3) and intermediate 3 (7.56 g, 4.01 mmol) is added tris(dibenzylideneacetone)dipalladium(0) (294 mg, 0.32 mmol) and tris(*o*-tolyl)phosphine (366 mg, 1.20 mmol). The reaction mixture is then further degassed before heating at 80 °C for 45 hours. The reaction mixture is allowed to cool to 23 °C and the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:0 to 0:1) followed by trituration in acetonitrile (20 cm^3) to give intermediate 35 (1.30 g, 21%) as a dark red solid. ^1H NMR (400 MHz, $CDCl_3$) 9.82 (2H, s), 7.63 (2H, d, J 4.0), 7.29 (2H, s), 7.18 (2H, d, J 4.0), 6.90 (4H, s), 6.82 (8H, d, J 1.1), 2.49 (16H, t, J 7.6), 1.47 - 1.57 (16H, m), 1.19 - 1.32 (48H, m), 0.80 - 0.87 (24H, m).

Intermediate 36



To a mixture of tributyl(1,3-dioxolan-2-ylmethyl)-phosphonium bromide (692 mg, 1.87 mmol), intermediate 35 (1.30 g, 0.85 mmol) and anhydrous tetrahydrofuran (46 cm^3) is added sodium hydride (204 mg, 5.11 mmol, 60% dispersion in mineral oil) and the reaction stirred at 23 °C for 70 hours. Hydrochloric acid (12 cm^3, 10% in water) is added and the mixture stirred for 3 hours. Ethyl acetate (75 cm^3) and water (75 cm^3) are then added and the organic layer extracted with ethyl acetate (10 cm^3). The combined organic layer is washed with water (75 cm^3) and brine (75 cm^3) before drying over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is triturated in warm acetonitrile (2 x 20 cm^3) to give intermediate 36 (1.29 g, 96%) as a purple solid. ^1H NMR (400 MHz, $CDCl_3$) 9.60 (2H, d, J 7.7), 7.50 (2H, d, J 15.5), 7.23 (2H, d, J 3.9), 7.20 (2H, s), 7.10 (2H, d, J 4.0), 6.89 (4H, s), 6.82 (8H, d, J 1.5), 6.40 (2H, dd, J 15.4, 7.7), 2.49 (16H, t, J 7.7), 1.47 - 1.56 (16H, m), 1.18 - 1.32 (48H, m), 0.78 - 0.87 (24H, m).

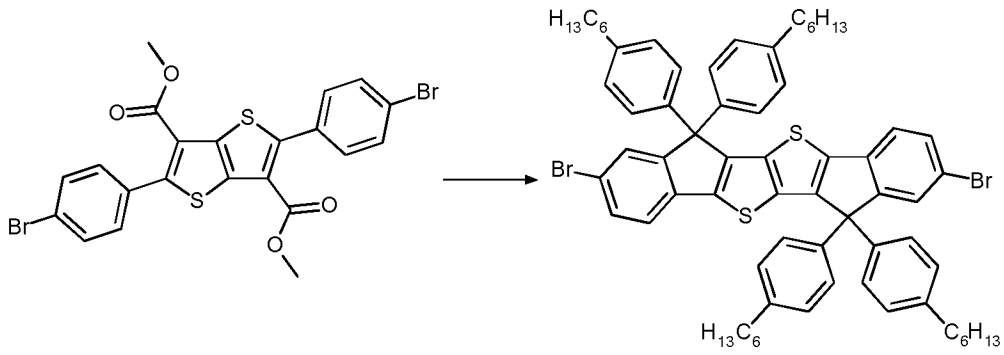
Compound 14



To a degassed solution of intermediate 36 (200 mg, 0.13 mmol), anhydrous chloroform (13 cm^3) and pyridine (0.72 cm^3) at 0 °C is added 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (124 mg, 0.51 mmol). The reaction mixture is stirred for 165 minutes and then added to stirred acetonitrile (75 cm^3) and the mixture stirred for 45 minutes. The solid is collected by filtration and washed with acetonitrile until the filtrate runs colourless. The solid is further washed with 40-60 petrol (2 x 10 cm^3), cyclohexane (2 x 10 cm^3), acetone (2 x 10 cm^3) and ether (2 x 10 cm^3) to give compound 14 (186 mg, 72%) as a black solid. ^1H NMR (400 MHz, 1,2-dichlorobenzene-d4, 100 °C) 9.02 (2H, s), 8.65 (2H, dd, J 14.7, 11.6), 8.39 (2H, d, J 11.5), 8.16 (2H, s), 7.68 - 7.79 (4H, m), 7.38 - 7.46 (6H, m), 7.10 - 7.15 (10H, m), 7.00 (2H, d, J 4.1), 6.96 (2H, d, J 4.0), 6.94 (4H, s), 2.51 (16H, t, J 7.5), 1.51 - 1.61 (16H, m), 1.18 - 1.30 (48H, m), 0.78 - 0.84 (24H, m).

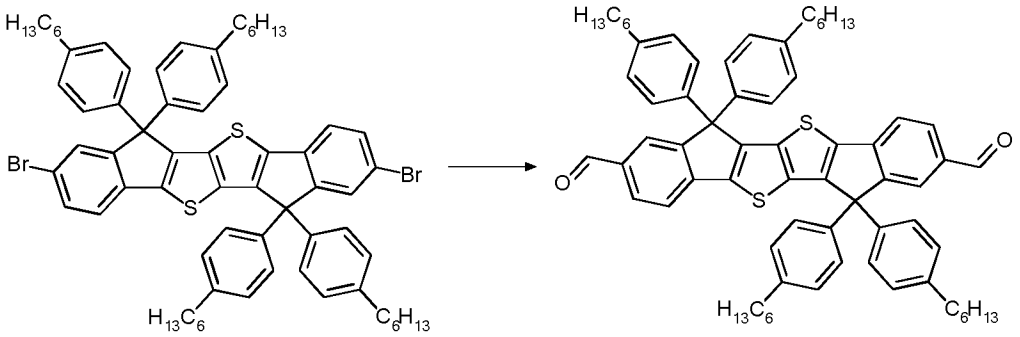
Example 15

Intermediate 37



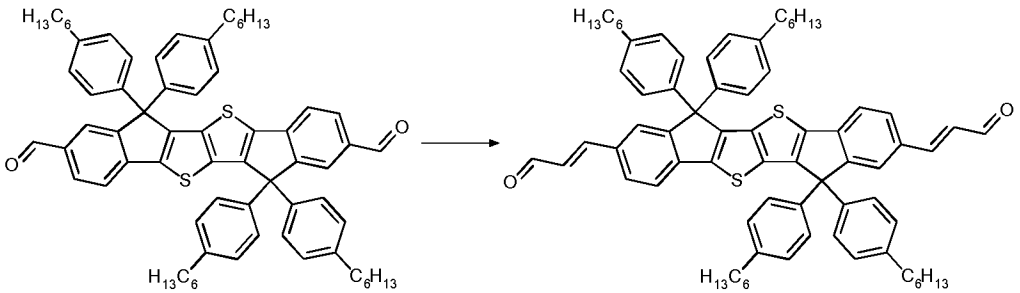
To a solution of 1-bromo-4-hexyl-benzene (10.0 g, 41.5 mmol) in anhydrous tetrahydrofuran (70 cm^3) at -78 °C is added *n*-butyllithium (16.6 cm^3, 41.5 mmol, 2.5 M in tetrahydrofuran) over 10 minutes. The reaction mixture is then stirred for 1 hour before methyl 5-bromo-2-[5-(4-bromo-2-methoxycarbonyl-phenyl)thieno[3,2-b]thiophen-2-yl]benzoate (4.70 g, 8.29 mmol) is added. The reaction mixture is then allowed to warm to 23 °C and stirred for 17 hours. Water (100 cm^3) is added and the mixture stirred for 1 hour. Ether (100 cm^3) is added and the organic washed with water (2 x 50 cm^3), brine (20 cm^3) and dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The solid triturated in ice-cold 40-60 petrol (30 cm^3) to give a yellow solid. The solid is taken up in toluene (40 cm^3) and *p*-toluene sulfonic acid (2 g) is added. The reaction is stirred at 23 °C for 2 hours and at 50 °C for 1 hour. The mixture is filtered and the solvent removed *in vacuo*. The solid is triturated in acetone to give intermediate 37 (3.40 g, 37%) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) 7.44 (2H, s), 7.19 (2H, s), 7.12 - 7.14 (2H, m), 6.98 - 7.15 (16H, m), 2.42 - 2.53 (8H, m), 1.44 -1.57 (8H, m), 1.12 - 1.28 (24H, m), 0.75 - 0.80 (12H, m).

Intermediate 38



To a solution of intermediate 37 (8.75 g, 7.85 mmol) in anhydrous tetrahydrofuran (95 cm^3) at -78 °C is added dropwise *n*-butyllithium (7.2 cm^3, 18 mmol, 2.5 M in hexanes). The reaction mixture is stirred for 1 hour before *N,N*-dimethylformamide (1.5 cm^3, 20 mmol) is added dropwise. The reaction mixture is allowed to warm to 23 °C and stirred for 17 hours. Water (100 cm^3) is added and the aqueous extracted with dichloromethane (2 x 100 cm^3). The combined organic layer is washed with brine (50 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (heptane:ethyl acetate; 9:1 to 4:1) to give intermediate 38 (3.30 g, 42%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.95 (2H, s), 7.94 (2H, s), 7.81 - 7.83 (2H, m), 7.49 - 7.54 (2H, m), 7.05 - 7.21 (16H, m), 2.51 - 2.62 (8H, m), 1.52 - 1.67 (8H, m), 1.25 - 1.41 (24H, m), 0.84 - 0.91 (12H, m).

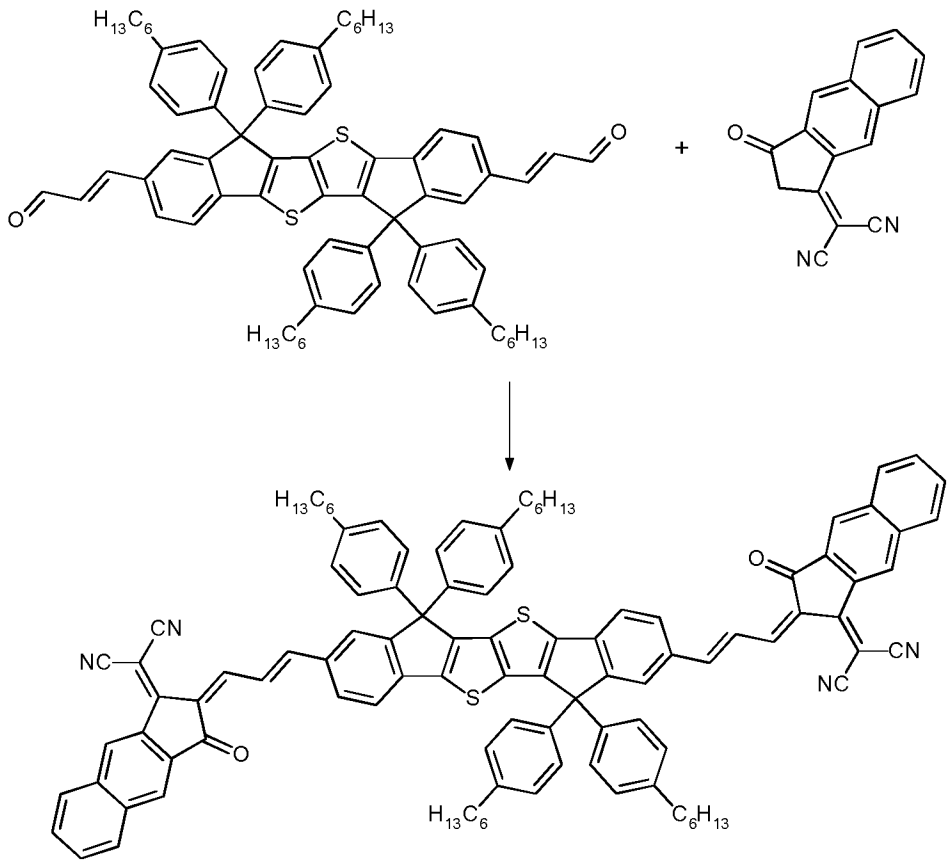
Intermediate 39



To a mixture of tributyl(1,3-dioxolan-2-ylmethyl)-phosphonium bromide (200 mg, 0.54 mmol), intermediate 38 (250 mg, 0.25 mmol) and anhydrous tetrahydrofuran (13 cm^3) at 0 °C is added sodium hydride (59

mg, 1.5 mmol, 60% dispersion in mineral oil). The reaction mixture is allowed to warm to 23 °C and stirred for 17 hours. Dichloromethane (20 cm^3) and hydrochloric acid (40 cm^3, 2N) are added and the mixture stirred for 30 minutes. The organic layer separated, washed with water (20 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 9:11 to 7:13) to give intermediate 39 (228 mg, 87%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.68 (2H, d, J 7.7), 7.61 (2H, s), 7.39 - 7.56 (6H, m), 7.08 - 7.20 (16H, m), 6.68 (2H, dd, J 15.9, 7.6), 2.53 - 2.62 (8H, m), 1.56 - 1.66 (8H, m), 1.26 - 1.39 (24H, m), 0.84 - 0.92 (12H, m).

Compound 15

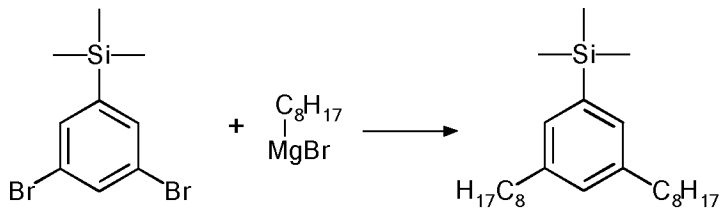


To a degassed mixture of 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (115 mg, 0.469 mmol), intermediate 39 (100 mg, 0.094 mmol) and chloroform (10 cm^3) is added pyridine (520 mg) and the

mixture further degassed. The reaction mixture is stirred for 17 hours and methanol (30 cm^3) added. The solid is collected by filtration and the filtrate concentrated *in vacuo*. To the filtrate is added methanol (30 cm^3) and the solid collected by filtration. The combined solids are then purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 2:3 to 1:4) to give compound 15 (66 mg, 46%) as a green solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.13 (2H, s), 8.74 - 8.86 (2H, m), 8.48 (2H, d, J 11.6), 8.32 (2H, s), 7.96 - 8.05 (4H, m), 7.58 - 7.71 (8H, m), 7.33 - 7.42 (4H, m), 7.12 (8H, d, J 8.4), 7.06 (8H, d, J 8.4), 2.29 - 2.68 (8H, m), 1.53 (8H, t, J 7.5), 1.15 - 1.32 (24H, m), 0.72 - 0.84 (12H, m).

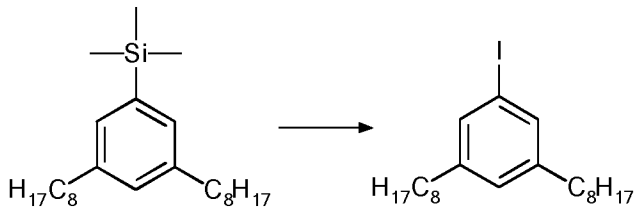
Example 16

Intermediate 40



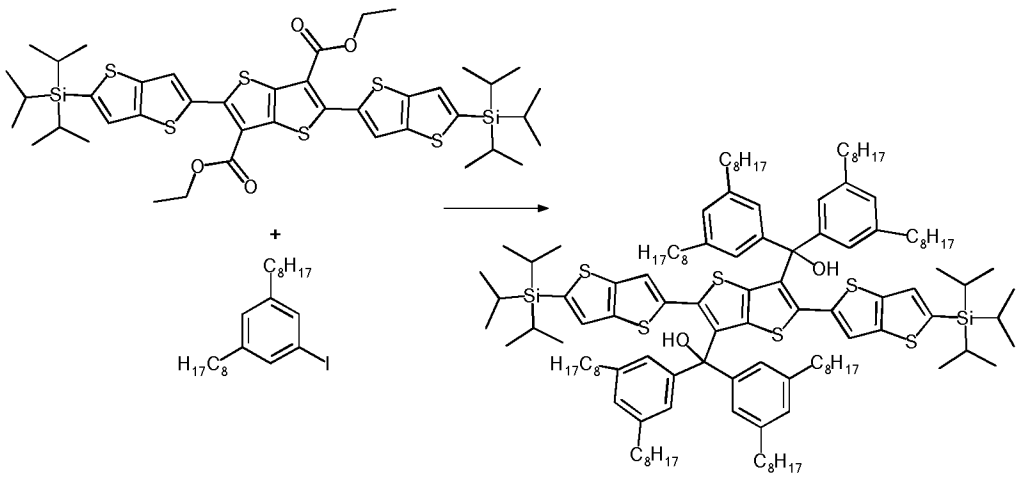
To octylmagnesium bromide solution (183 cm^3, 365 mmol, 2.0 M in ether) and anhydrous tetrahydrofuran (450 cm^3) is added (3,5-dibromophenyl)trimethylsilane (45.0 g, 146 mmol) and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (II) (1.60 g, 2.19 mmol). The reaction mixture is heated at 55 °C for 16 hours before it is cooled to 0 °C and water (250 cm^3) added. The organics extracted with dichloromethane (2 x 250 cm^3). The combined organics are washed with brine (100 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography (heptane) to give intermediate 40 (22.2 g, 41%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) 7.15 (2H, d, J 1.6), 7.00 (1H, s), 2.52 - 2.64 (4H, m), 1.55 - 1.68 (24H, m), 0.84 - 0.89 (6H, m), 0.22 - 0.31 (9H, m).

Intermediate 41



To a solution of intermediate 40 (10.0 g, 26.7 mmol), chloroform (100 cm^3) and methanol (100 cm^3), in the dark, is added silver(I) trifluoroacetate (12.4 g, 56.0 mmol). The mixture is cooled to 0 °C, iodine (13.5 g, 53.4 mmol) added and the mixture stirred for 90 minutes. The reaction mixture is filtered through a plug of silica (dichloromethane) and the orgaic phase washed with saturated aqueous sodium bisulfate (100 cm^3), water (100 cm^3) and brine (100 cm^3) before drying over anhydrous magnesium sulfate. The mixture is filtered, and the solvent removed *in vacuo* to give intermediate 41 (11.4 g, 99%) as a colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) 7.27 (2H, d, J 1.4), 6.85 (1H, d, J 1.5), 2.43 (4H, t, J 7.7), 1.07 - 1.34 (24H, m), 0.70 - 0.85 (6H, m).

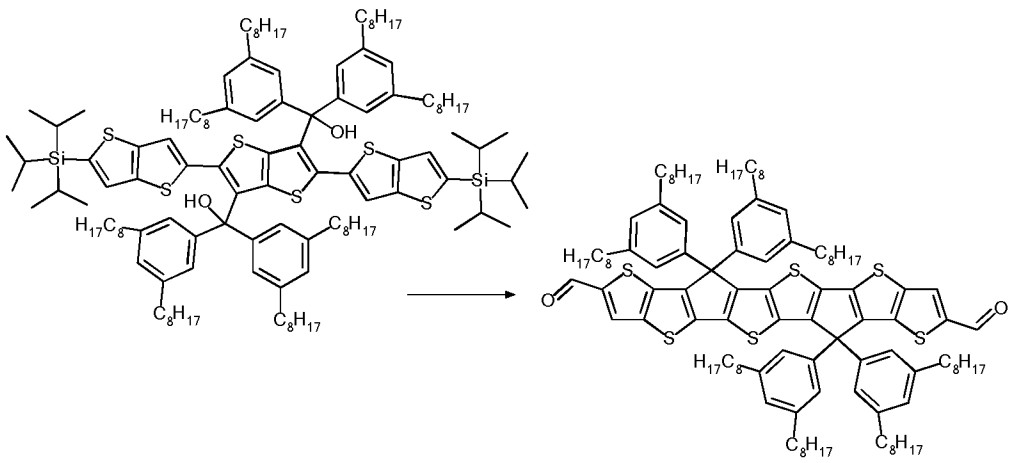
Intermediate 42



To a solution of intermediate 41 (4.99 g, 10.3 mmol) in anhydrous tetrahydrofuran (37 cm^3) at -78 °C is added *t*-butyllithium (12.1 cm^3, 20.6 mmol, 1.7 M in pentane) dropwise over 10 minutes. The solution is stirred for 1 hour; gently warmed to -25 °C for 6 minutes and re-cooled.

Intermediate 14 (1.50 g, 1.72 mmol) is added. The reaction is slowly warmed to 23 °C and stirred for 16 hours. Water (5 cm^3) is slowly added and, after 10 minutes of stirring, the solution portioned between diethyl ether (100 cm^3) and water (50 cm^3). The organic phase is washed with water (3 x 20 cm^3), dried over anhydrous magnesium sulphate and concentrated *in vacuo*. The crude is purified by column chromatography (40-60 petrol:dichloromethane; 9:1) to give intermediate 42 (2.76 g, 73%) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) 7.17 (2H, s), 6.85 - 6.99 (12H, m), 6.46 (2H, s), 3.40 (2H, s), 2.48 (16H, dd, J 8.9, 6.3), 1.43 - 1.67 (16H, m), 1.21 - 1.41 (80H, m), 1.12 (36H, d, J 7.4), 0.81 - 0.92 (30H, m).

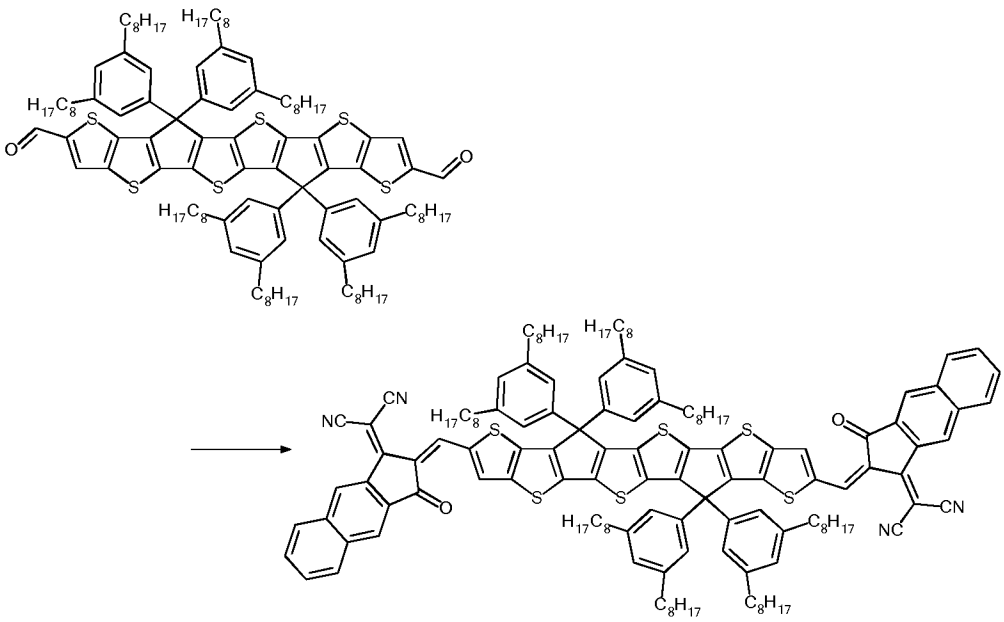
Intermediate 43



To a degassed solution of intermediate 42 (500 mg, 0.251 mmol) in toluene (30 cm^3) at 50 °C is added Amberllyst 15 strong acid (2.0 g) and the reaction mixture heated at 50 °C for 17 hours. The mixture filtered and the solid washed with warm toluene (20 cm^3) and the solvent removed *in vacuo*. To the crude is added *N,N*-dimethylformamide (310 mg, 4.3 mmol) and chloroform (8.8 cm^3) and the mixture cooled to 0 °C. Phosphorus oxychloride (620 mg, 4.02 mmol) is then added dropwise and, after addition, the reaction mixture is stirred for 30 minutes, and then heated at 60 °C for 26 hours. A saturated aqueous solution of potassium acetate (25 cm^3) is added and the mixture stirred for 3 hours before cooling to 23 °C. The aqueous phase is extracted with dichloromethane (20 cm^3) and the combined organics washed with water (20 cm^3), dried over anhydrous

magnesium sulphate, filtered and concentrated *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 4:1 to 3:2) to give intermediate 43 (130 mg, 29%) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.88 (2H, s), 7.94 (2H, s), 6.92 (4H, s), 6.80 (8H, s), 2.50 (16H, t, J 7.7), 1.41 - 1.71 (16H, m), 1.17 - 1.31 (90H, m), 0.67 - 1.04 (24H, m).

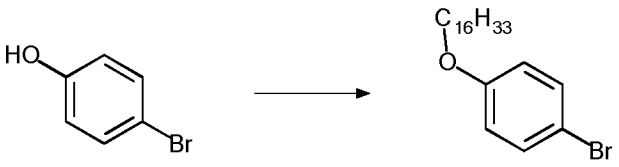
Compound 16



To a degassed solution of intermediate 43 (130 mg, 0.08 mmol) and 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (93.5 mg, 0.38 mmol) in chloroform (3.3 cm^3) is added pyridine (0.43 cm^3, 5.4 mmol) and mixture further degassed. The reaction is stirred at 40 °C for 6 hours, then methanol (30 cm^3) added. After cooling to 23 °C the precipitate is collected by filtration and washed with methanol (20 cm^3). The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 7:3 to 1:1) to give compound 16 (43 mg, 26%) as a green solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.20 (2H, s), 9.00 (2H, s), 8.34 (2H, s), 8.16 (2H, s), 8.10 (2H, dd, J 6.2, 3.4), 8.05 (2H, dd, J 6.2, 3.4), 7.71 (4H, dd, J 6.3, 3.2), 6.97 (4H, d, J 1.6), 6.91 (8H, d, J 1.7), 2.56 (16H, t, J 7.7), 1.58 (16H, s), 1.07 - 1.34 (80H, m), 0.78 (24H, t, J 6.9).

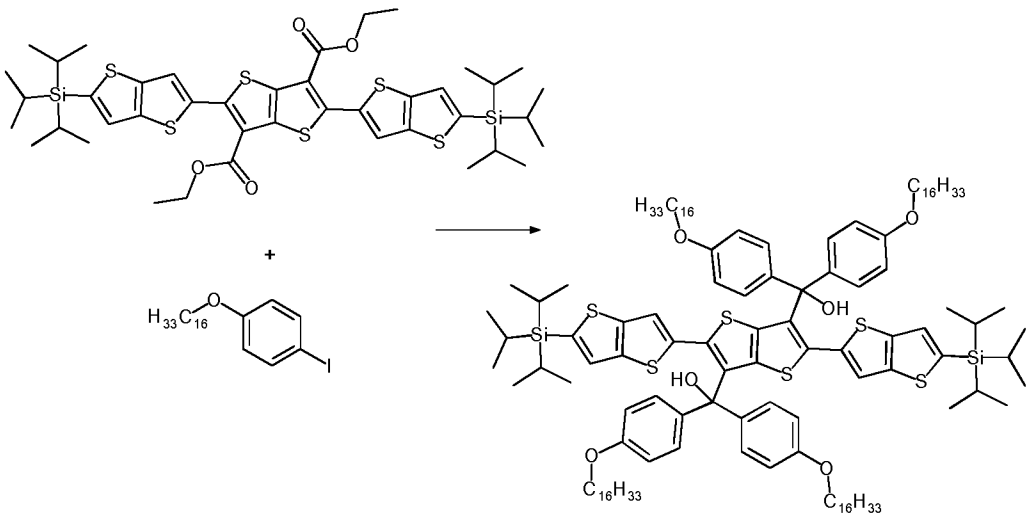
Example 17

Intermediate 44



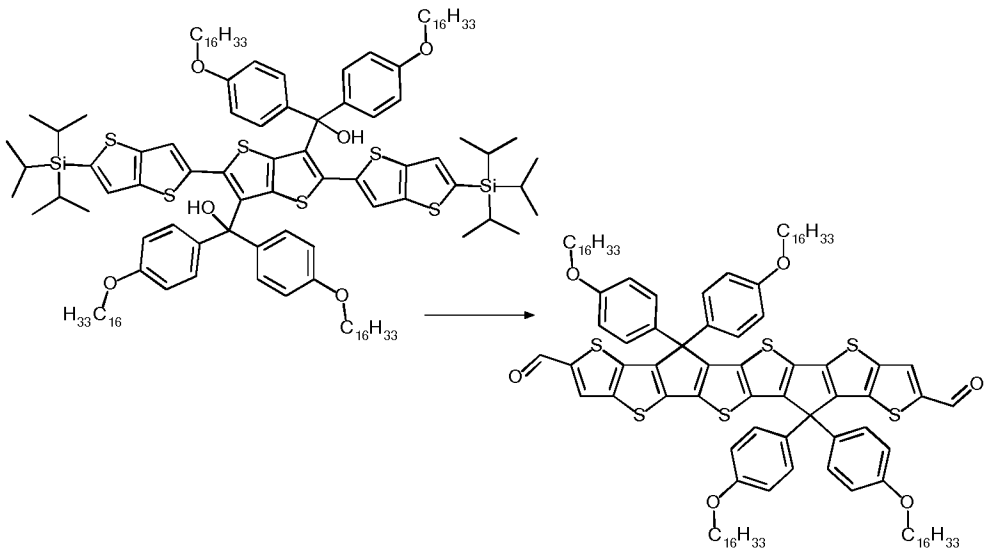
To a suspension of potassium carbonate (39.9 g, 289 mmol) in acetonitrile (160 cm^3) is added 4-bromo-phenol (10.0 g, 57.8 mmol) and 1-bromohexadecane (16.8 g, 54.9 mmol) and the reaction mixture heated at 80 °C for 16 hours. The reaction is hot filtered and the solid washed with dichloromethane (150 cm^3). The combined filtrate is concentrated to 200 cm^3, cooled to 23 °C and then stirred in an ice bath for 10 minutes. The suspension is filtered and washed with ice-cool acetonitrile (50 cm^3) to give intermediate 44 (12.6 g, 55%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) 7.37 (2H, d, J 9.0), 6.78 (2H, d, J 9.0), 3.92 (2H, t, J 6.6), 1.73 - 1.82 (2H, m), 1.39 - 1.50 (2H, m), 1.39 - 1.20 (24H, m), 0.82 - 0.95 (3H, m).

Intermediate 45



To a solution of intermediate 44 (2.73 g, 6.87 mmol) in anhydrous tetrahydrofuran (150 cm^3) at -78 °C is added *t*-butyllithium (8.1 cm^3, 14 mmol, 1.7 M in pentane) over 10 minutes. The resulting suspension is stirred for 90 minutes, warmed to -25 °C over 20 minutes and re-cooled to -70 °C. Then a sonicated suspension of intermediate 14 (1.00 g, 1.14 mmol) in anhydrous tetrahydrofuran (150 cm^3) is added over 5 minutes, the coolant is left to evaporate and the reaction is stirred at 23 °C overnight. Water (5 cm^3) is slowly added and the solution stirred for 10 minutes before partitioning between diethyl ether (100 cm^3) and water (50 cm^3). The organic phase is washed with water (3 x 20 cm^3), dried over anhydrous magnesium sulphate and concentrated *in vacuo*. The residue is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:0 to 0:1) to give intermediate 45 (1.8 g, 76%). ^1H NMR (400 MHz, $CDCl_3$) 7.22 (2H, s), 7.18 - 7.22 (8H, m), 6.80 - 6.84 (8H, m), 6.66 (2H, s), 3.96 (8H, t, J 6.6), 3.45 (2H, s), 1.79 (8H, p, J 6.8), 1.41 - 1.52 (8H, m), 1.31 (96H, s), 1.13 (36H, d, J 7.4), 0.84 - 0.94 (18H, m).

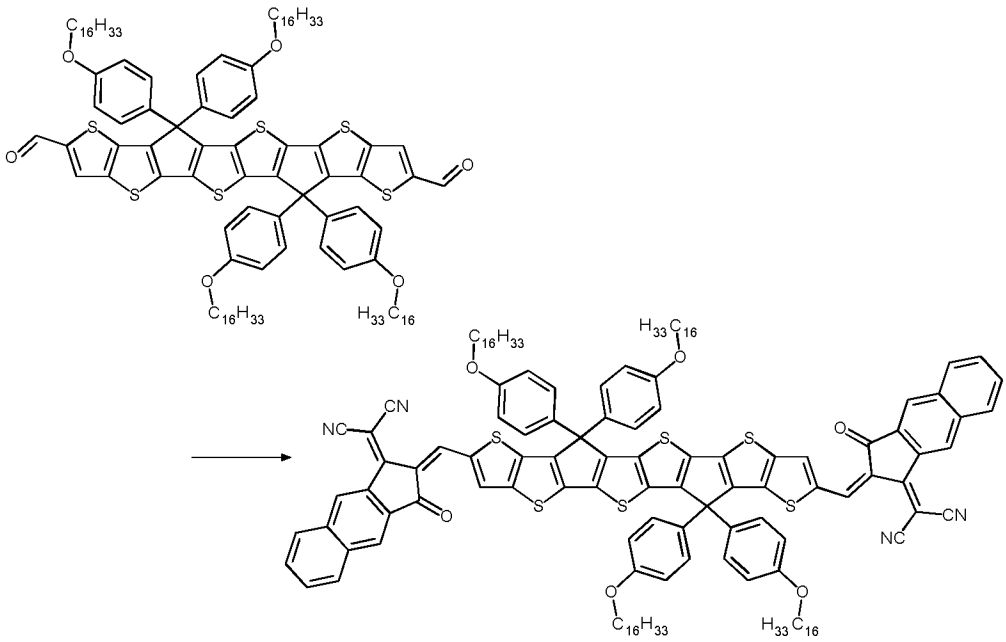
Intermediate 46



To a degassed mixture of intermediate 45 (1.79 g, 0.871 mmol) and toluene (72 cm^3), at 65 °C, is added Amberlyst 15 strong acid (16 g) and the mixture stirred for 16 hours. The reaction mixture is filtered and the solid washed with hot toluene (2 x 30 cm^3). The combined organic phase

is concentrated *in vacuo* and purified by column chromatography (40:60 petrol:dichloromethane; 4:1). The product is dissolved in chloroform (36 cm^3), *N,N*-dimethylformamide (1.02 g, 13.9 mmol) is added, followed by slow addition of phosphorus oxychloride (2.00 g, 13.1 mmol), over 5 minutes. The resulting solution is heated at 55 °C for 16 hours. To the solution is added a saturated aqueous solution of potassium acetate (50 cm^3) and mixture stirred for 2 hours before to cooling to 23 °C. The aqueous phase is extracted with dichloromethane (50 cm^3). The combined organic phase is washed with water (50 cm^3), dried over anhydrous magnesium sulphate and concentrated *in vacuo* before purification by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:0 to 3:4) to give intermediate 46 (763 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) 9.90 (2H, s), 7.94 (2H, s), 7.15 (8H, d, J 8.8), 6.84 (8H, d, J 8.8), 3.91 (8H, t, J 6.5), 1.66 - 1.85 (8H, m), 1.37 - 1.48 (8H, m), 1.20 - 1.37 (96H, m), 0.87 - 0.89 (12H, m).

Compound 17

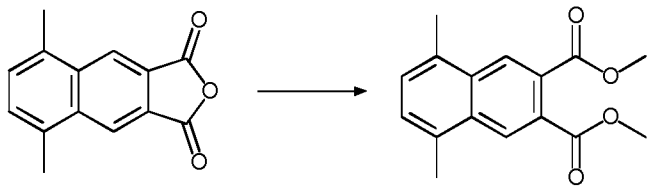


To a degassed solution of intermediate 46 (100 mg, 0.0567 mmol) and 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (97 mg, 0.40 mmol) in chloroform (2.5 cm^3) is added pyridine (0.32 cm^3, 4.0

mmol). The reaction is further degassed and then stirred at 40 °C for 6 hours. Methanol (30 cm^3) is added and the resulting suspension cooled to 23 °C, filtered and washed with methanol (20 cm^3). The resulting solid is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 3:2 to 3:7). The material is precipitated from a hot mixture of chloroform (4 cm^3) and acetone (15 cm^3) to give, upon filtration, compound 17 (51 mg, 41%) as a green solid. ^1H NMR (400 MHz, $CDCl_3$) 9.18 (2H, s), 8.95 (2H, s), 8.39 (2H, s), 8.19 (2H, s), 8.00 - 8.14 (4H, m), 7.78 - 7.66 (4H, m), 7.24 (8H, d, J 8.5), 6.91 (8H, d, J 8.2), 3.93 (8H, t, J 6.4), 1.67 - 1.85 (8H, m), 1.38 - 1.51 (8H, m), 1.17 - 1.38 (32H, m), 0.88 (12H, t, J 6.6).

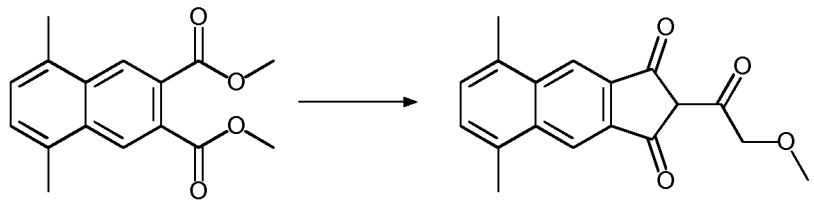
Example 18

Intermediate 47



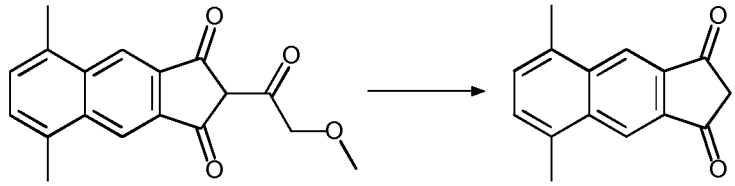
To a solution of 5,8-dimethyl-naphtho[2,3-*c*]furan-1,3-dione (10.0 g, 44.2 mmol) in methanol (50 cm^3) is added concentrated sulfuric acid (920 mg, 9.38 mmol) and the mixture heated at reflux for 12 hours. The reaction mixture is cooled to 23 °C and concentrated *in vacuo*. The residue is diluted with water (250 cm^3) and extracted with ethyl acetate (3 x 100 cm^3). The combined organic layer is washed with saturated aqueous sodium bicarbonate (3 x 100 cm^3), brine (200 cm^3), dried over anhydrous sodium sulphate, filtered and the solvent removed *in vacuo* to give intermediate 47 (10.0 g, 83%) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) 8.44 (2H, s), 7.34 (2H, s), 3.97(6H, s), 2.70 (6H, s).

Intermediate 48



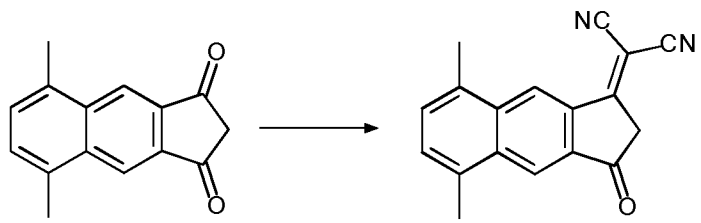
To a solution of intermediate 47 (12.0 g, 44.1 mmol) in anhydrous tetrahydrofuran (100 cm^3) is added sodium hydride (14.1 g, 353 mmol, 60% dispersion in mineral oil) and anhydrous ethyl acetate (35 cm^3). The reaction mixture is then heated at reflux for 12 hours. After cooling to 23 °C the mixture is concentrated *in vacuo*. The residue is triturated in ethyl acetate (100 cm^3) and the solid collected by filtration to give intermediate 48 (30.0 g) as a yellow solid, which is used without further purification.

Intermediate 49



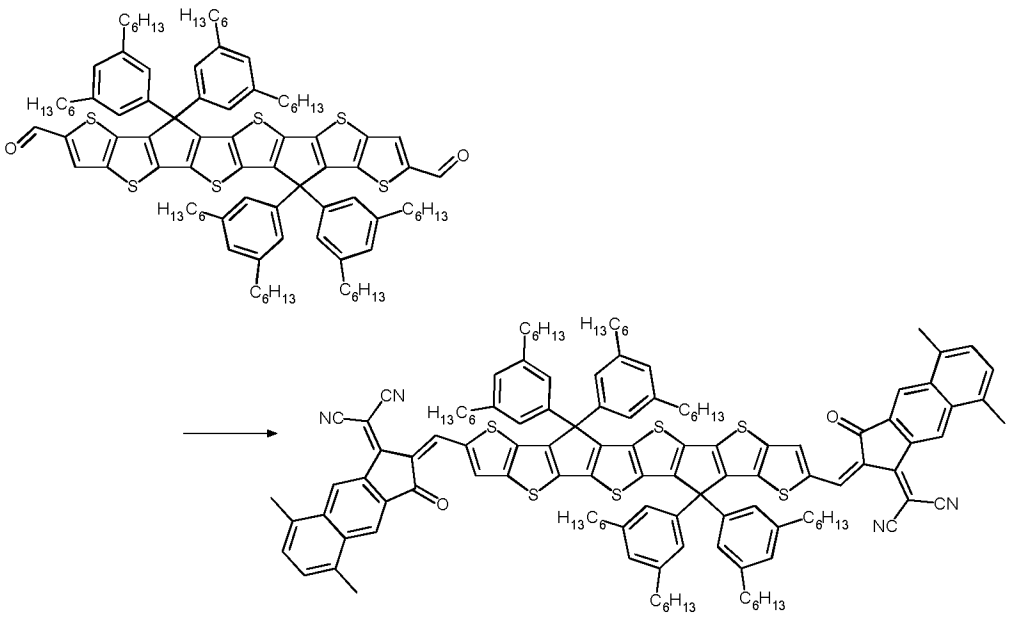
To a mixture of intermediate 48 (30.0 g) and water (200 cm^3) is added hydrochloric acid (7.35 cm^3, 12 M) and the reaction mixture heated at 80 °C for 12 hours. The mixture allowed to cool to 23 °C and the solid collected by filtration to give intermediate 49 (6.0 g) as a brown solid, which is used without any further purification.

Intermediate 50



To a solution of intermediate 49 (4.5 g) and malononitrile (2.52 g, 38.1 mmol) in ethanol (20 cm^3) is added sodium acetate (2.47 g, 30.1 mmol) and the mixture stirred for 12 hours. The reaction mixture is adjusted to pH = 2 with aqueous hydrochloric acid (1 M) and extracted with dichloromethane (3 x 50 cm^3). The combined organic layer is washed with water (2 x 50 cm^3), brine (50 cm^3), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The residue is purified by column chromatography using a graded solvent system (dichloromethane:methanol; 1:0 to 9:1) to give intermediate 50 (1.7 g) as a red solid. ^1H NMR (400 MHz, $CDCl_3$) 9.38 (1H, s), 8.67 (1H, s), 7.51 (2H, s), 3.87 (2H, s), 2.81 (3H, s), 2.77 (3H, s).

Compound 18

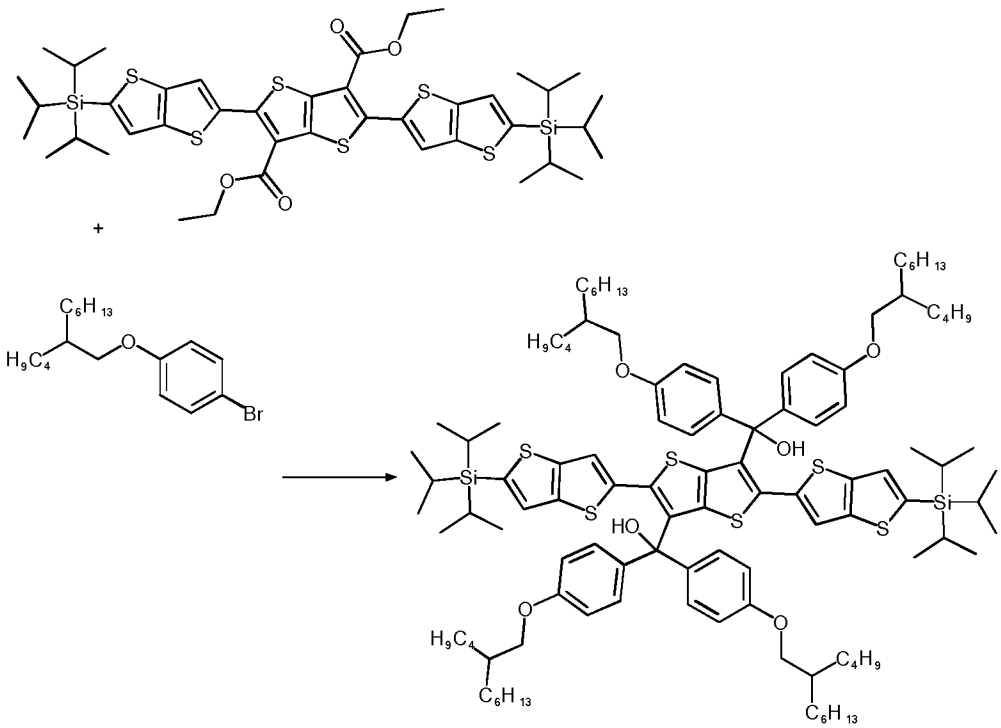


Intermediate 21 (75 mg, 0.05 mmol) and intermediate 50 (69 mg, 0.25 mmol) are dissolved in chloroform (30 cm^3). Pyridine (0.3 cm^3, 4 mmol) is added and the reaction stirred at 55 °C for 17 hours. The reaction mixture is cooled to 23 °C and the solvent removed *in vacuo* before addition of methanol (100 cm^3). The solid is collected by filtration and purified by column chromatography (40-60 petrol:dichloromethane 3:2). The product is dissolved in chloroform (50 cm^3), treated with acetonitrile (50 cm^3) and collected by filtration to give compound 18 (67 mg, 66%). ^1H NMR (400

MHz, CD_2Cl_2) 9.28 (2H, s), 8.86 (2H, s), 8.44 (2H, s), 8.09 (2H,s), 7.36 (4H, s), 6.89 (4H, s), 6.83 (8H, d, J 1.5), 2.67 (12H, d, J 4.9), 2.45 (16H, t, J 7.7), 1.54 - 1.45 (8H, m), 1.26 - 1.05 (56H, m), 0.71 - 0.58 (24H, m).

Example 19

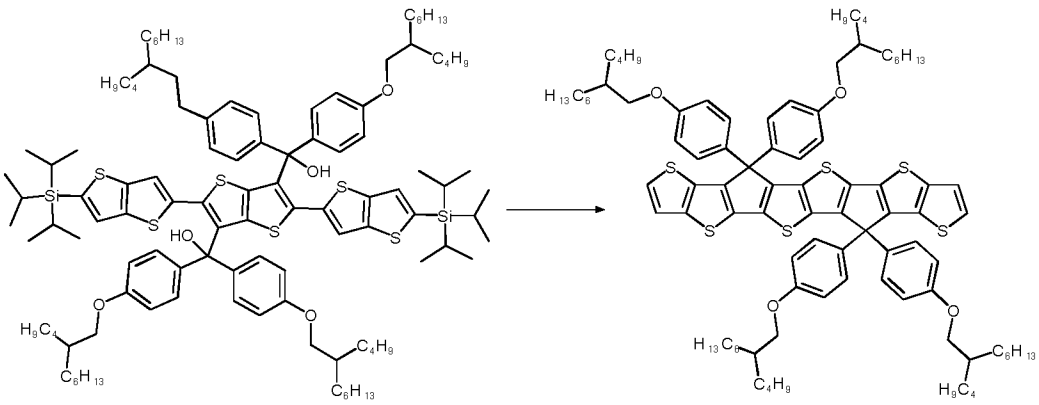
Intermediate 51



To a solution of 1-bromo-4-[(2-butyloctyl)oxy]benzene (3.52 g, 10.3 mmol) in anhydrous tetrahydrofuran (150 cm^3) at -78 °C is added *t*-butyllithium (12.1 cm^3, 20.6 mmol, 1.7 M in pentane) dropwise over 10 minutes. The reaction mixture is stirred for 1.5 hours and warmed to -25 °C. A suspension of intermediate 14 (1.50 g, 1.72 mmol) in anhydrous tetrahydrofuran (50 cm^3) is added and the reaction mixture stirred for 16 hours at 23 °C. Water (100 cm^3) is slowly added and the mixture stirred for 10 minutes before addition of ether (100 cm^3). After phase separation the organic phase is washed with water (3 x 20 cm^3), dried over anhydrous magnesium sulphate, filtered and the solvent removed *in vacuo*. The crude product is purified by column chromatography (40-60

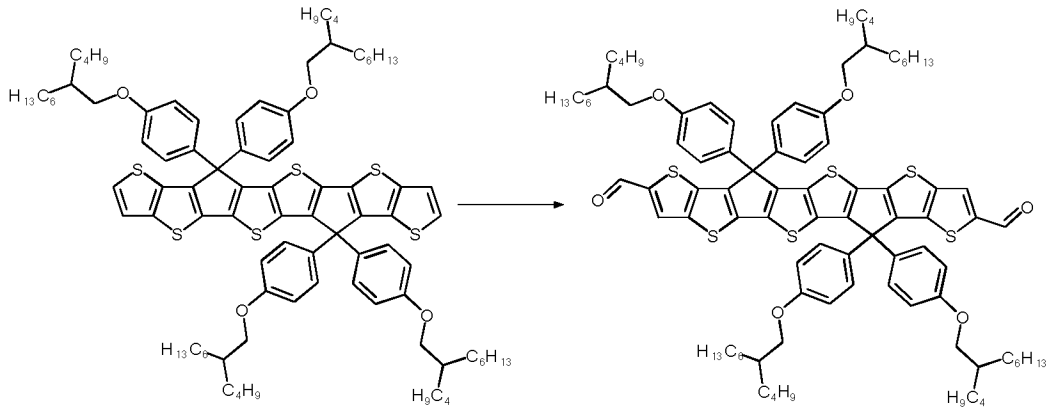
petrol:dichloromethane; 4:1) to give intermediate 51 (1.77 g, 56%). ^{1}H NMR (400 MHz, CD_2Cl_2) 7.15 (2H, s), 7.08 (8H, d, J 8.7), 6.73 (8H, d, J 8.8), 6.56 (2H, s), 3.75 (8H, d, J 6.2), 3.33 (2H, s), 1.64 - 1.72 (4H, m), 0.97 - 1.39 (106H, m), 0.80 (24H, q, J 6.9, 5.8).

Intermediate 52



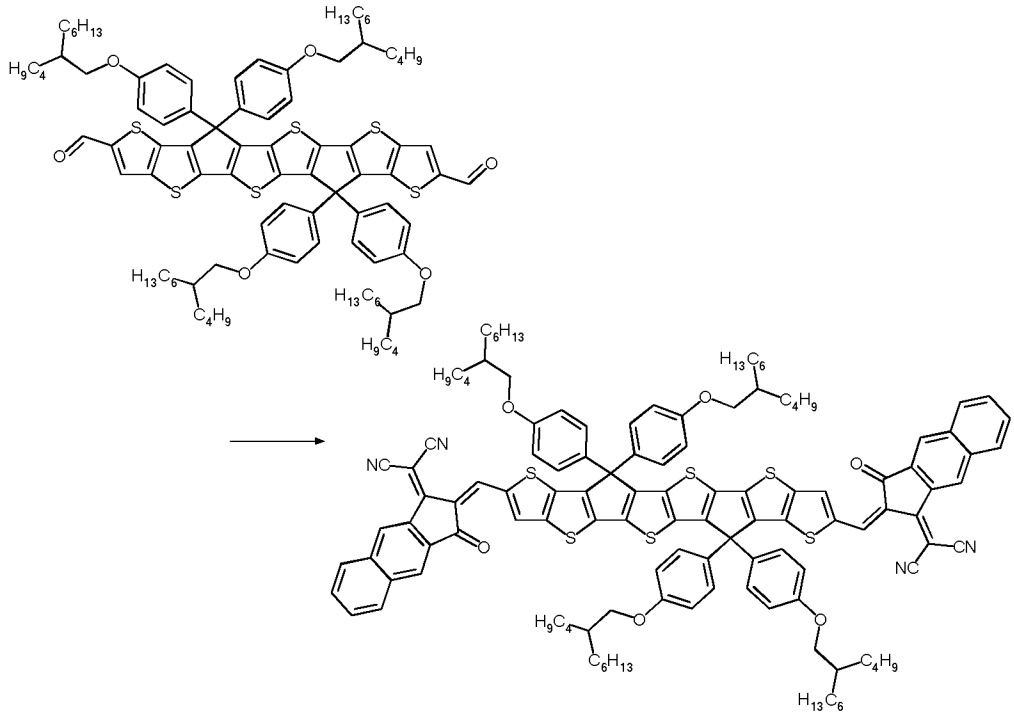
To a solution of intermediate 51 (1.68 g, 0.916 mmol) in toluene (150 cm^3) is added Amberlyst 15 strong acid (8.0 g) and the reaction mixture stirred at 50 °C for 17 hours. The hot reaction mixture is filtered and the filtrate washed with water (50 cm^3). The organic layer is dried over anhydrous magnesium sulphate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography (40-60 petrol:dichloromethane; 19:1) to give intermediate 52 (1.13 g, 83%). ^{1}H NMR (400 MHz, CD_2Cl_2) 7.22 (4H, dd, J 6.7), 7.07 (8H, d, J 8.8), 6.72 (8H, d, J 8.8), 3.69 (8H, d, J 5.6), 1.63 (4H, h, J 5.9), 1.10 - 1.38 (64H, m), 0.70 - 0.84 (24H, m).

Intermediate 53



To a degassed solution of intermediate 52 (1.13 g, 0.762 mmol) in chloroform (30 cm^3) and *N,N*-dimethylformamide (0.70 cm^3, 9.1 mmol) is added phosphorus(V)oxychloride (0.7 cm^3, 8 mmol) and the reaction mixture heated at 60 °C for 17 hours. Saturated aqueous sodium acetate (10 cm^3) is added and the resulting mixture stirred at 50 °C for 1 hour. The resulting mixture is then cooled to 23 °C and the organic solvent removed *in vacuo*. The remaining aqueous phase and material are extracted with ether (3 x 100 cm^3). The combined organic layer is washed with water (2 x 25 cm^3), brine (30 cm^3) and dried over anhydrous magnesium sulphate. The solvent is removed *in vacuo* and the crude product purified by column chromatography (40-60 petrol:dichloromethane: 4:1) to give intermediate 53 (910 mg, 78%) as a red solid. ^1H NMR (400 MHz, CD_2Cl_2) 9.78 (2H, s), 7.88 (2H, s), 7.06 (8H, d, J 8.8), 6.74 (8H, d, J 8.8), 3.69 (8H, d, J 5.6), 1.64 (4H, p, J 5.9), 1.09 - 1.39 (64H, m), 0.70 - 0.84 (24H, m).

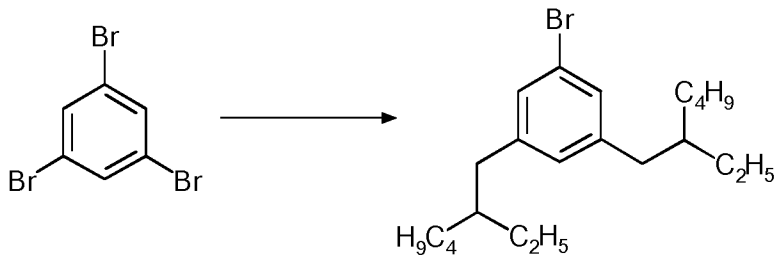
Compound 19



To a solution of intermediate 53 (100 mg, 0.065 mmol) and 2-{3-oxo-1H,2H,3H-cyclopenta[*b*]naphthalen-1-ylidene}propanedinitrile (79.4 mg, 0.325 mmol) in chloroform (30 cm^3) is added pyridine (0.4 cm^3, 5 mmol) and the reaction mixture stirred at 55 °C for 17 hours. The reaction mixture is cooled down to 23 °C and the solvent removed *in vacuo*. The crude product is purified by column chromatography (40-60 petrol:dichloromethane; 3:2). The product is dissolved in chloroform (50 cm^3), treated with acetonitrile (50 cm^3) and collected by filtration to give compound 19 (80 mg, 62%). ^1H NMR (400 MHz, CD_2Cl_2) 9.08 (2H, s), 8.84 (2H, s), 8.28 (2H, s), 8.12 (2H, s), 8.01 (4H, d, J 7.4), 7.63 (4H, dd, J 6.6, 2.9), 7.15 (8H, d, J 8.8), 6.81 (8H, d, J 8.8), 3.73 (8H, d, J 5.6), 1.64 (4H, d, J 7.0), 1.08 - 1.39 (64H, m), 0.69 - 0.85 (24H, m).

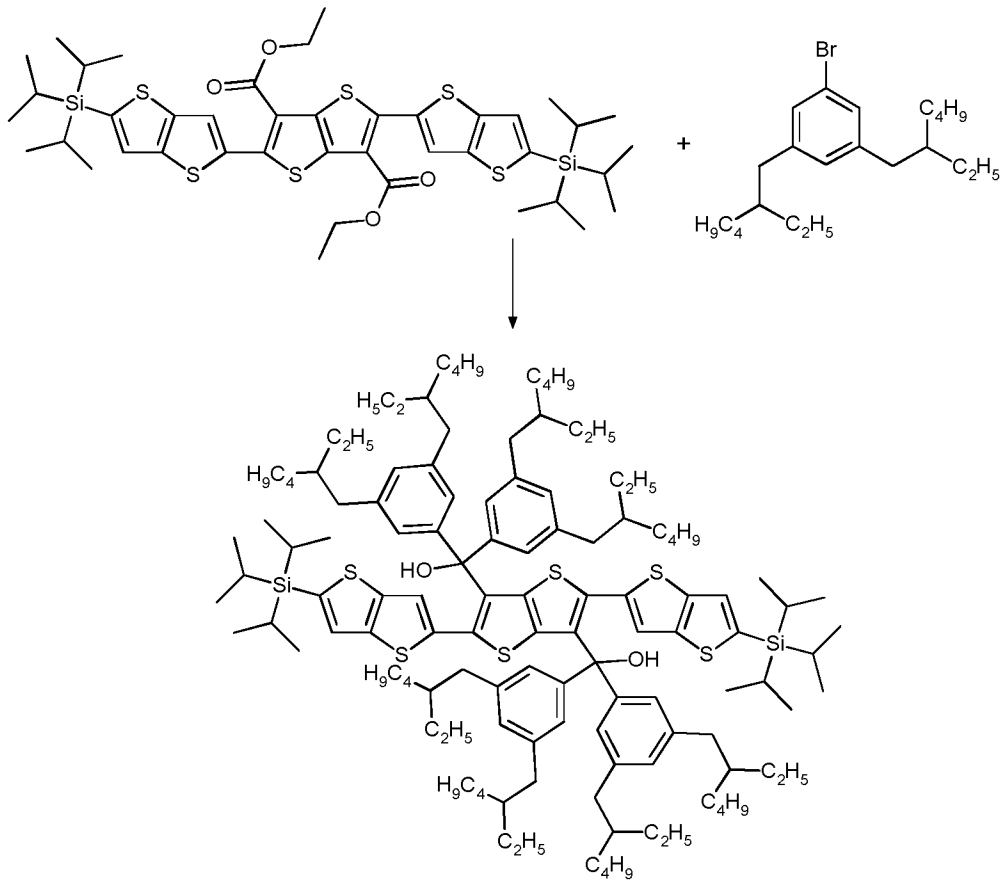
Example 20

Intermediate 54



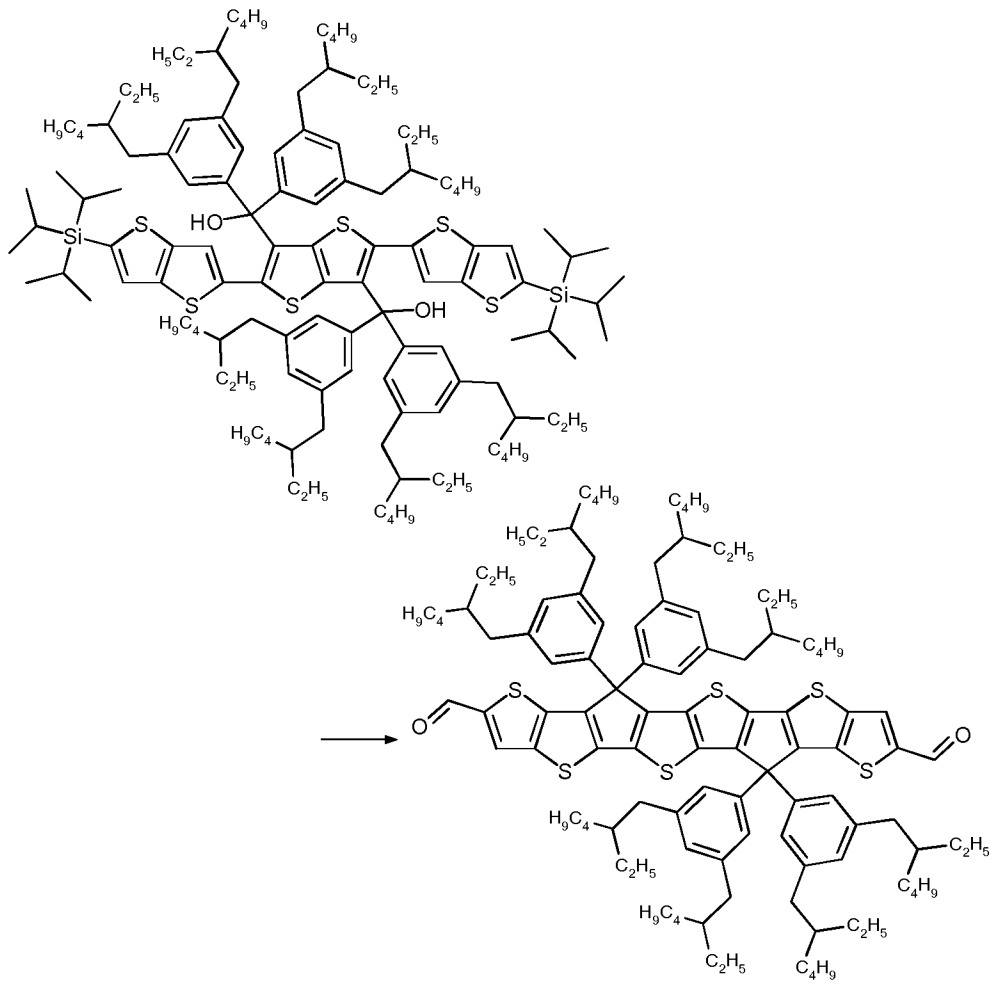
To a suspension of 1,3,5-tribromobenzene (10.0 g, 31.8 mmol) in anhydrous ether (400 cm^3) at -78 °C is added *t*-butyllithium (74.7 cm^3, 127 mmol, 1.7 M in pentane) dropwise over 25 minutes. The reaction mixture is then stirred for 2 hours and 2-ethylhexanal (15.0 g, 117 mmol) is added over 20 minutes. The reaction mixture is allowed to warm to 23 °C and stirred for 16 hours. Water (20 cm^3) is slowly added followed by a saturated aqueous ammonium chloride solution (100 cm^3). The organic is washed with water (2 x 50 cm^3), dried over anhydrous magnesium sulphate, filtered and the solvent removed *in vacuo*. The crude material is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:1 to 0:1). The purified material is then taken up in dichloromethane (42 cm^3), triethylsilane (14.2 g, 122 mmol) added and the mixture cooled to 0 °C. Boron trifluoride diethyl etherate (8.65 g, 61.0 mmol) is then added portion wise over 1 hour, the mixture allowed to warm to 23 °C and stirred for 16 hours. The reaction mixture is then heated at 40 °C for 10 minutes, cooled to 23 °C and a saturated aqueous solution of sodium bicarbonate is added to reach ph ~8. The aqueous solution is extracted with dichloromethane (10 cm^3) and the combined organics dried over anhydrous magnesium sulphate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography (40-60 petrol) to give intermediate 54 (2.39 g, 62%) as a colourless oil. ^1H NMR (400 MHz, $CDCl_3$) 7.12 (2H, s), 6.85 (1H, s), 2.48 (4H, d, J 7.1), 1.49 - 1.57 (2H, m), 1.18 - 1.36 (16H, m), 0.82 - 0.96 (12H, m).

Intermediate 55



To a solution of intermediate 54 (2.25 g, 5.91 mmol) in anhydrous tetrahydrofuran (13 cm^3) at -78 °C is added dropwise *t*-butyllithium (6.95 cm^3, 11.8 mmol, 1.7 M in pentane). The reaction mixture is then stirred for 1 hour, warmed to -18 °C and then re-cooled to -78 °C. A sonicated suspension of intermediate 14 (860 mg, 0.98 mmol) in anhydrous tetrahydrofuran (13 cm^3) is then added, the reaction mixture allowed to warm to 23 °C and stirred for 16 hours. Water (10 cm^3) is added and the biphasic mixture stirred for 5 minutes. Diethyl ether (100 cm^3) is added and the organic phase washed with water (3 x 30 cm^3), dried over anhydrous magnesium sulphate, filtered and the solvent removed *in vacuo*. The residue is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 9:1 to 4:1) to give intermediate 55 (1.21 g, 62%) as an oil. ^1H NMR (400 MHz, $CDCl_3$) 7.17 (2H, s), 6.89 (8H, s), 6.87 (4H, s), 6.58 (2H, s), 3.47 - 3.56 (2H, m), 2.34 - 2.53 (16H, m), 1.51 (4H, s), 1.05 - 1.41 (116H, m), 0.72 - 0.95 (48H, m).

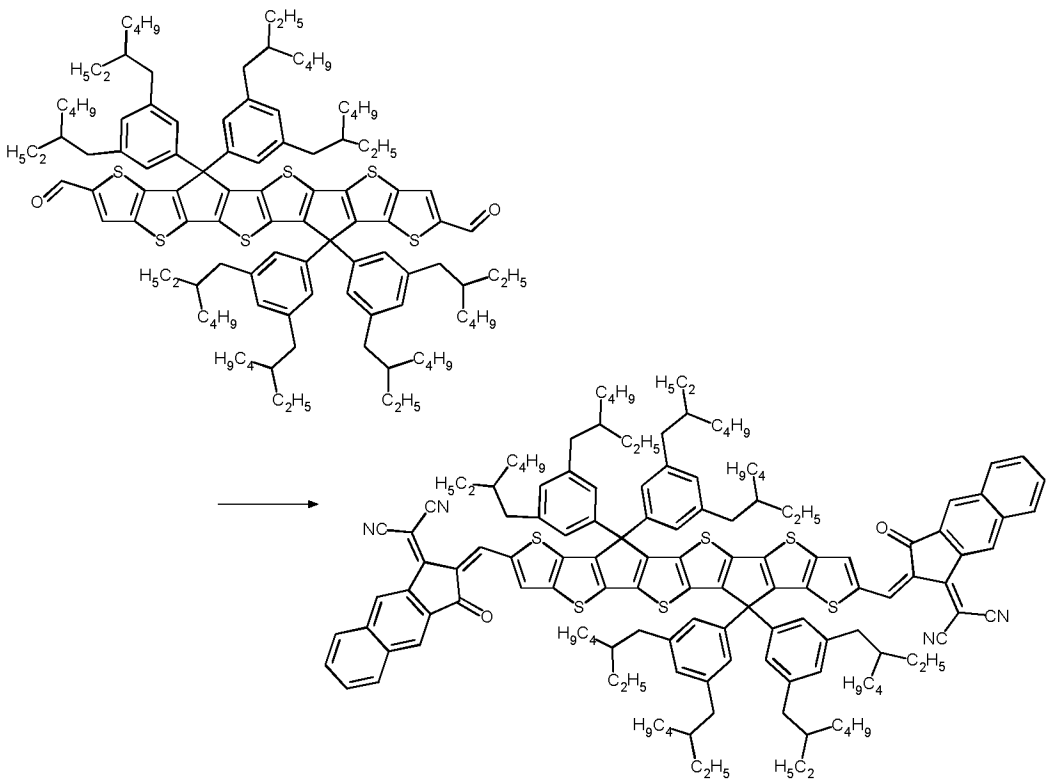
Intermediate 56



To a degassed mixture of intermediate 55 (1.20 g, 0.603 mmol) dissolved in toluene (48 cm^3) at 50 °C is added Amberlyst 15 strong acid (4.0 g) and the reaction mixture stirred for 17 hours. The reaction mixture is filtered, the residue washed with hot toluene (2 x 20 cm^3) and the combined organic phase concentrated *in vacuo*. The residue is dissolved in chloroform (24 cm^3), *N,N*-dimethylformamide (0.70 g, 9.64 mmol) added and the reaction mixture cooled to 0 °C. Phosphorus oxychloride (1.39 g, 9.04 mmol) is added over 5 minutes. The reaction mixture is warmed to 23 °C over 30 minutes and then heated at 55 °C for 16 hours before cooling to 23 °C. Saturated aqueous potassium acetate (50 cm^3) is added and the biphasic solution stirred for 2 hours. The aqueous phase is extracted with chloroform (20 cm^3) and the combined organic phase washed with water

(50 cm^3), dried over anhydrous magnesium sulphate, filtered and the solvent removed *in vacuo*. The residue is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 9:1 to 3:1) to give intermediate 56 (730 mg, 71%) as a dark solid. ^1H NMR (400 MHz, $CDCl_3$) 9.88 (2H, s), 7.93 (2H, s), 6.86 (4H, s), 6.77 (8H, s), 2.37 - 2.45 (16H, m), 1.44 - 1.61 (8H, m), 1.11 - 1.39 (64H, m), 0.72 - 0.95 (48H, m).

Compound 20

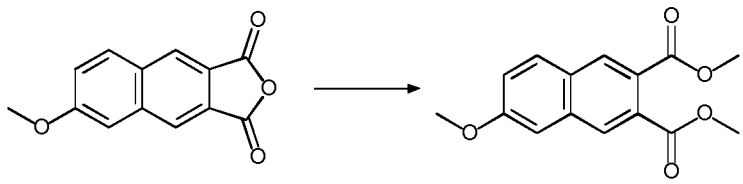


To a solution of intermediate 56 (100 mg, 0.06 mmol) and 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (72 mg, 0.29 mmol) in chloroform (5.0 cm^3) is added pyridine (0.33 cm^3, 4.1 mmol) and the reaction mixture heated at 50 °C for 3 hours. Methanol (50 cm^3) is added, the solid collected by filtration and washed with methanol (2 x 10 cm^3). The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 3:2 to 1:1) to give compound 20 (94 mg, 74%) as a green solid. ^1H NMR (400 MHz, $CDCl_3$)

9.20 (2H, s), 8.96 (2H, s), 8.31 (2H, s), 8.20 (2H, s), 8.10 (2H, dd, J 6.2, 3.4), 8.04 (2H, dd, J 6.2, 3.3), 7.71 (4H, dd, J 6.3, 3.3), 6.89 (4H, s), 6.83 - 6.89 (8H, m), 2.36 - 2.58 (16H, m), 1.10 - 1.36 (72H, m), 0.71 - 0.88 (48H, m).

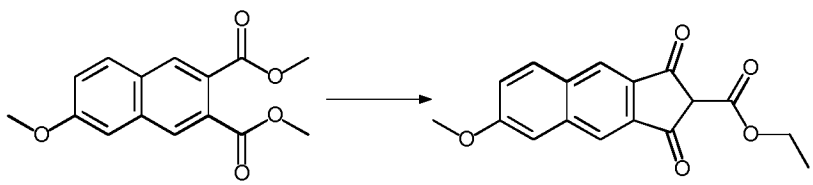
Example 21

Intermediate 57



To a solution of 6-methoxy-naphtho[2,3-*c*]furan-1,3-dione (30.0 g, 131 mmol) in methanol (150 cm^3) is added concentrated sulfuric acid (4.18 g, 42.6 mmol) and the mixture heated at reflux for 12 hours. The mixture is cooled to 23 °C and the solvent removed *in vacuo*. The residue is diluted with water (250 cm^3) and extracted with ethyl acetate (3 x 100 cm^3). The combined organic layer is washed with saturated aqueous sodium bicarbonate (3 x 100 cm^3), brine (200 cm^3), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The residue is purified by column chromatography using a graded solvent system (40-60 petrol: ethyl acetate; 1:0 to 0:1) to give intermediate 57 (15.0 g, 42%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) 8.24 (1H, s), 8.08 (1H, s), 7.82 (1H, d, J 9.2), 7.26 - 7.29 (1H, m), 7.19 (1H, d, J 2.4), 3.96 (3H, s), 3.95 (6H, s).

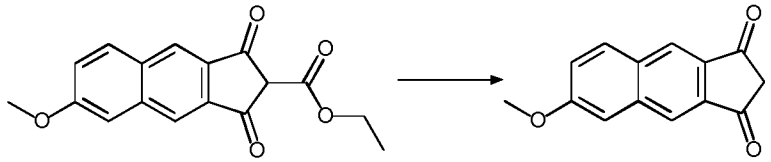
Intermediate 58



To a solution of sodium hydride (5.83 g, 146 mmol, 60% dispersion in mineral oil) in anhydrous tetrahydrofuran (300 cm^3) is added anhydrous

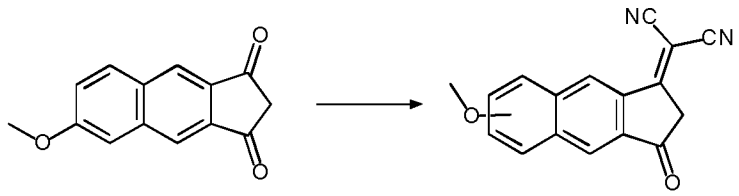
ethyl acetate (14 cm^3) and the mixture stirred for 30 minutes. Intermediate 57 (5.00 g, 18.3 mmol) is then added and the mixture heated at reflux for 12 hours. After cooling to 23 °C, the volatiles are removed *in vacuo* to give intermediate 58 (20.0 g) as a yellow solid, which is used without any further purification.

Intermediate 59



A mixture of intermediate 58 (10.0 g) in aqueous hydrochloric acid (100 cm^3, 2 M) is stirred at 80 °C for 12 hours. The reaction mixture is cooled to 23 °C and the solid collected by filtration. The crude is triturated in ethyl acetate (30 cm^3) and the solid collected by filtration to give intermediate 59 (8.0 g) as a yellow solid, which is used without any further purification.

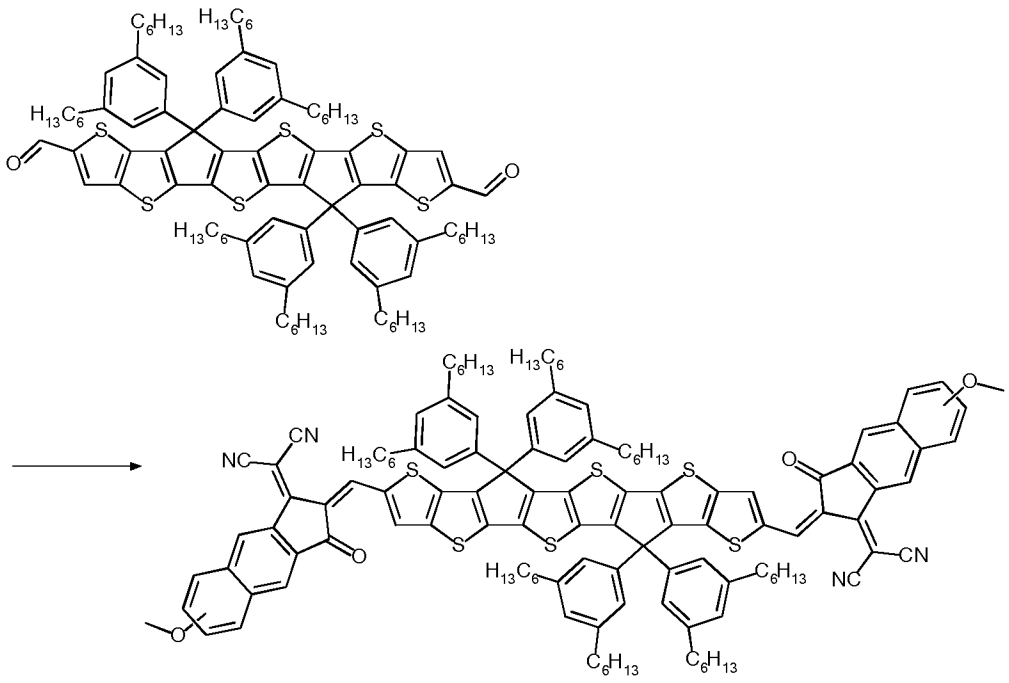
Intermediate 60



To a solution of intermediate 59 (8.00 g) in ethanol (100 cm^3) is added sodium acetate (4.35 g, 53.0 mmol) and malononitrile (4.44 g, 67.2 mmol) and the mixture stirred for 12 hours. The reaction mixture is adjusted to pH ~1-2 with aqueous hydrochloric acid (1 M). The residue is diluted with water (100 cm^3) and extracted with dichloromethane (3 x 100 cm^3). The combined organic layer is washed with water (2 x 100 cm^3), brine (100 cm^3), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The residue is purified by column chromatography using a graded solvent system (dichloromethane:methanol; 0:1 to 1:0) followed by trituration in acetonitrile. The solid is collected by filtration to give

intermediate 60 (3.00 g) as a yellow solid. ^{1}H NMR (400 MHz $CDCl_3$) 9.04 - 9.10 (1H, m), 8.38 - 8.41 (1H, m), 7.98 - 8.06 (1H, m), 7.34 - 7.44 (2H, m), 4.02 (3H, s), 3.83 (2H, s).

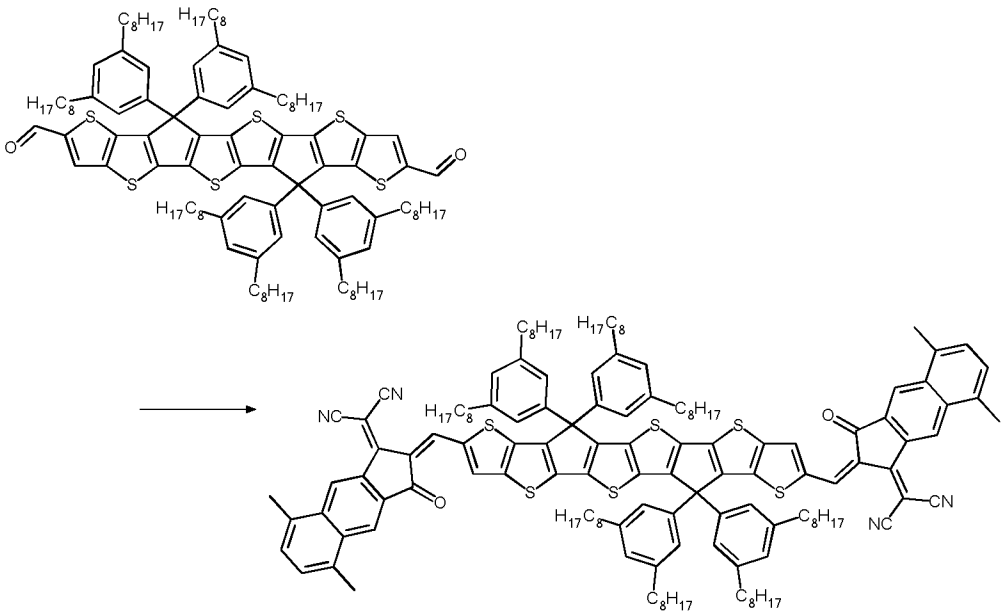
Compound 21



To a degassed solution of intermediate 21 (120 mg, 0.0814 mmol) and intermediate 60 (111 mg, 0.407 mmol) in chloroform (30 cm^3) is added pyridine (0.5 cm^3, 6 mmol) and the reaction mixture stirred at 55 °C for 16 hours. The solvent is removed *in vacuo* and the crude material purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 3:2 to 0:1). The product dissolved in a minimum dichloromethane, treated with acetonitrile and the solid collected by filtration to give compound 21 (132 mg, 82%) as a green solid. ^{1}H NMR (400 MHz, CD_2Cl_2) 8.77 - 9.07 (4H, m), 8.05 - 8.17 (4H, m), 7.84 - 7.92 (2H, m), 7.21 - 7.34 (4H, m), 6.89 (4H, s), 6.83 (8H, s), 3.89 (6H, s), 2.45 (16H, t, J 7.7), 1.47 (16H, s), 1.06 - 1.28 (48H, m), 0.60 - 0.75 (24H, m).

Example 22

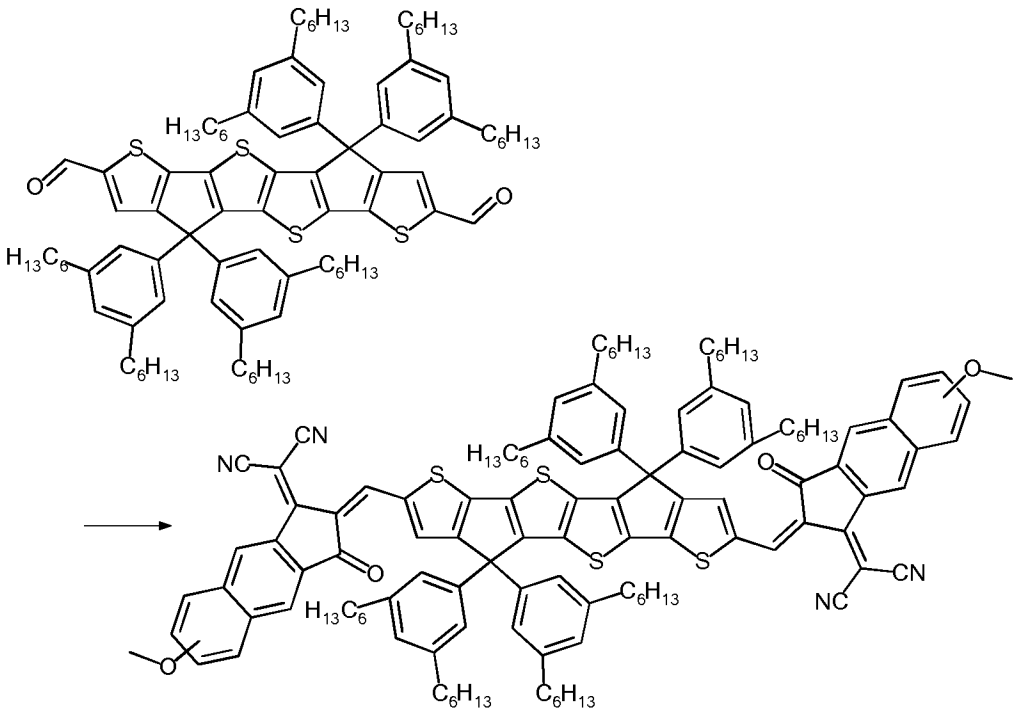
Compound 22



To a degassed solution of intermediate 43 (100 mg, 0.059 mmol) and intermediate 50 (80 mg, 0.29 mmol) in chloroform (30 cm^3) is added pyridine (0.3 cm^3, 4 mmol) and the reaction mixture stirred at 55 °C for 16 hours. The reaction mixture is cooled down to 23 °C and the solvent removed *in vacuo*. The crude product is purified by column chromatography (40-60 petrol:dichloromethane; 3:2) and the solid washed with ether (50 cm^3) to give compound 22 (39 mg, 30%) as a dark solid. ^1H NMR (400 MHz, CD_2Cl_2) 9.28 (2H, s), 8.87 (2H, s), 8.44 (2H, s), 8.08 (2H, s), 7.35 (4H, s), 6.88 (4H, s), 6.83 (8H, s), 2.67 (12H, s), 2.45 (16H, t, J 7.7), 1.47 - 1.57 (16H, m), 0.91 - 1.28 (80H, m), 0.66 (24H, t, J 6.6).

Example 23

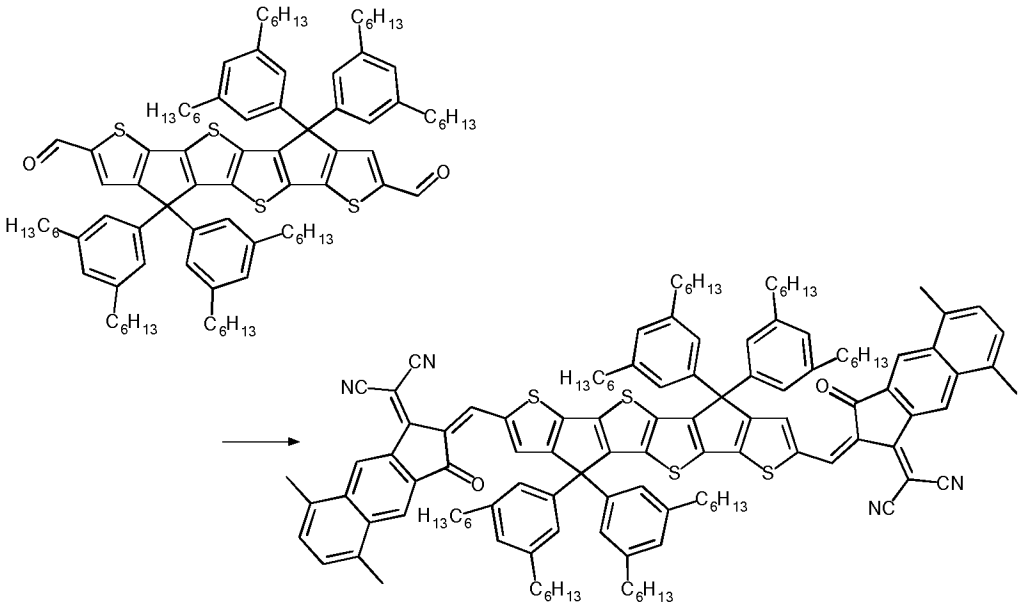
Compound 23



To a solution of intermediate 60 (101 mg, 0.367 mmol) and intermediate 2 (100 mg, 0.073 mmol) in chloroform (10 cm^3) is added pyridine (0.41 cm^3, 5.1 mmol) and the reaction mixture stirred for 16 hours. Methanol (50 cm^3) is slowly added over 15 minutes, the solid collected by filtration and washed with methanol (2 x 5 cm^3). The residue is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane 7:3 to 1:1). The solid is triturated in methanol and collected by filtration to give compound 23 (98 mg, 71%). ^1H NMR (400 MHz, $CDCl_3$) 9.01 - 9.16 (2H, m), 8.86 - 8.99 (2H, m), 8.19 - 8.33 (2H, m), 7.96 (2H, dd, J 15.2, 9.1), 7.73 (2H, d, J 3.2), 7.35 (4H, d, J 8.2), 6.97 (4H, d, J 1.9), 6.84 (8H, d, J 1.5), 3.98 - 4.04 (6H, m), 2.54 (16H, t, J 7.7), 1.57 (16H, d, J 13.9), 1.22 - 1.38 (48H, m), 0.77 - 0.96 (24H, m).

Example 24

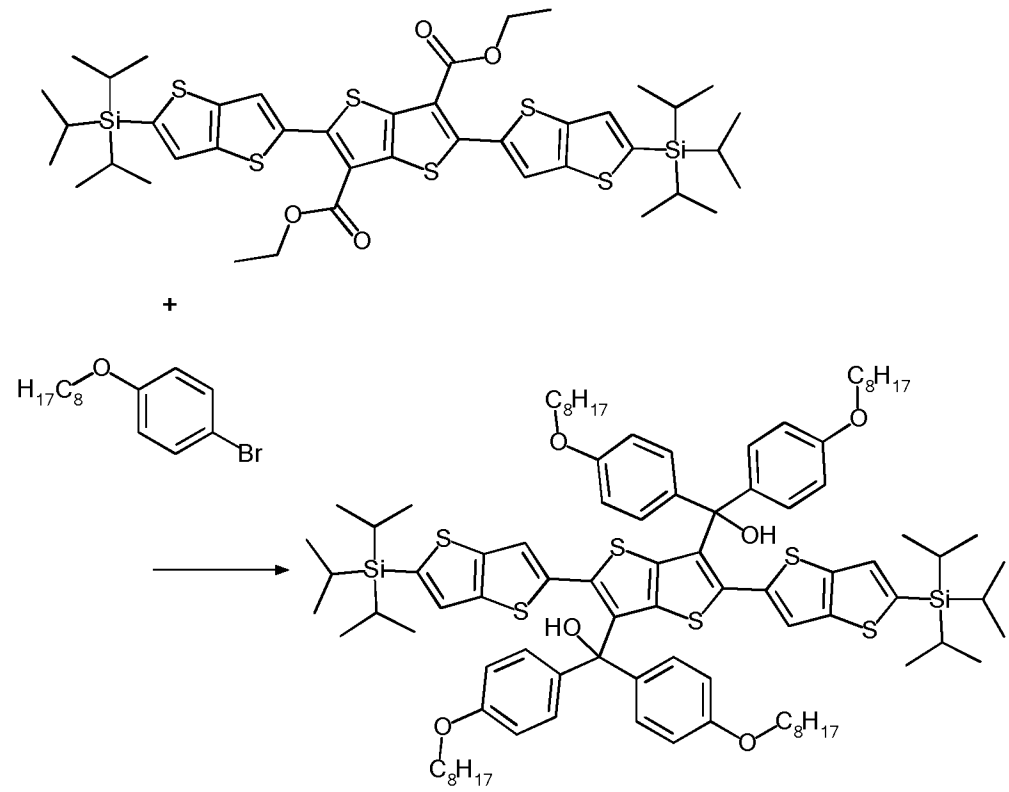
Compound 24



To a solution of intermediate 50 (100 mg, 0.37 mmol) and intermediate 2 (100 mg, 0.073 mmol) in chloroform (10 cm^3) is added pyridine (0.41 cm^3, 5.1 mmol) and the reaction mixture stirred at 23 °C for 16 hours. Methanol (120 cm^3) is added slowly over 15 minutes, the solid collected by filtration and washed with methanol (2 x 5 cm^3). The residue is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane 7:3 to 1:1) to give compound 24 (102 mg, 74%) as a dark solid. ^1H NMR (400 MHz, $CDCl_3$) 9.38 (2H, s), 8.96 (2H, s), 8.56 (2H, s), 7.74 (2H, s), 7.41 (4H, s), 6.98 (4H, s), 6.85 (8H, d, J 1.4), 2.78 (6H, s), 2.77 (6H, s), 2.55 (16H, t, J 7.7), 1.53 - 1.64 (16H, m), 1.24 - 1.38 (48H, m), 0.79 - 0.92 (24H, m).

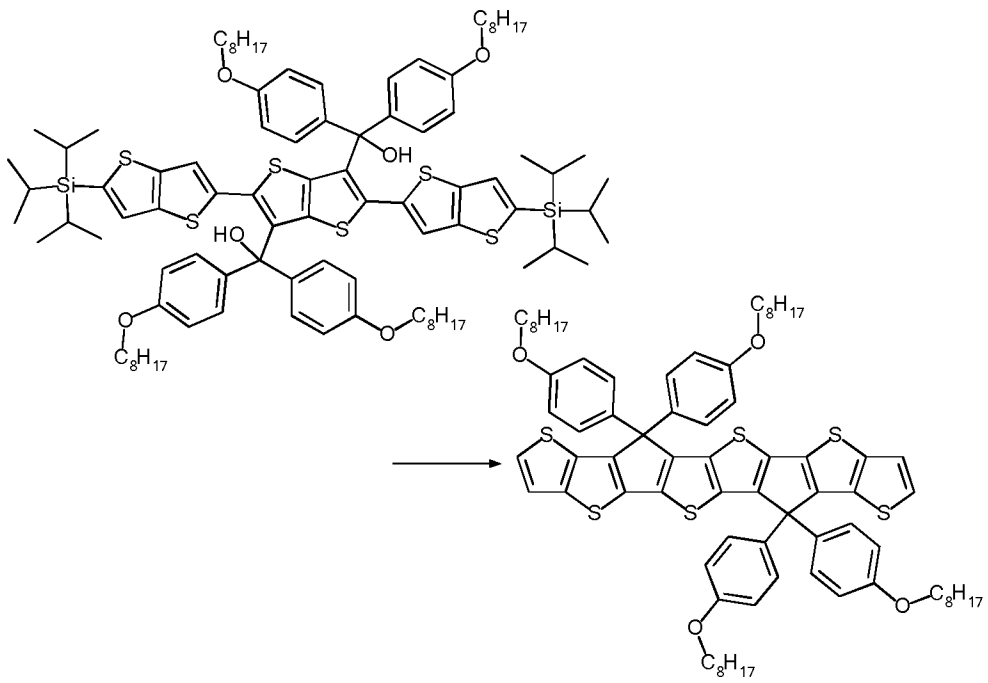
Example 25

Intermediate 61



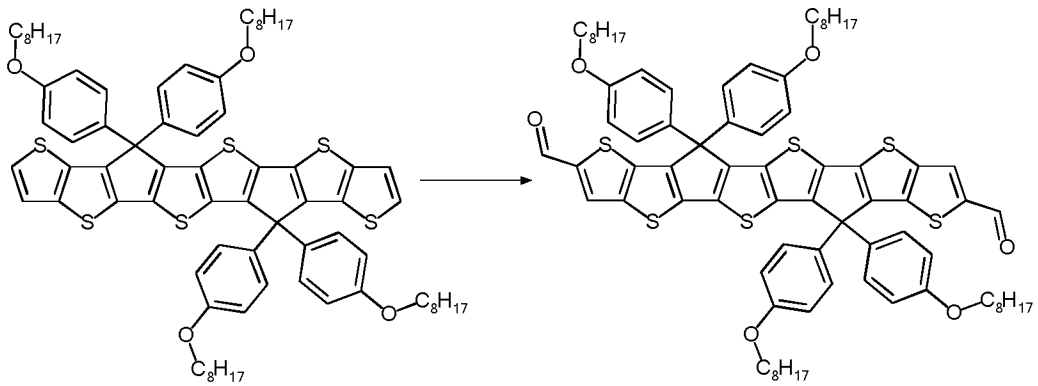
To a solution of 1-bromo-4-(octyloxy)benzene (1.57 g, 5.50 mmol) in anhydrous tetrahydrofuran (24 cm^3) at -78 °C is added dropwise *t*-butyllithium (6.47 cm^3, 11.0 mmol, 1.7 M in pentane). The solution is stirred for 2 hours, warmed to -30 °C and re-cooled to -78 °C. A suspension of intermediate 14 (800 mg, 0.92 mmol) in anhydrous tetrahydrofuran (10 cm^3) is then added. The reaction is slowly warmed to 23 °C and stirred for 16 hours. Water (10 cm^3) is added and the mixture partitioned between ether (50 cm^3) and water (50 cm^3). The aqueous phase is extracted with ether (20 cm^3), the combined organic phase is washed with water (3 x 20 cm^3), dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo*. The residue is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane 7:3 to 1:1) to give intermediate 61 (600 mg, 41%) as a pale brown solid. ^1H NMR (400 MHz, $CDCl_3$) 7.22 (2H, s), 7.17 - 7.22 (8H, m), 6.79 - 6.87 (8H, m), 6.66 (2H, s), 3.96 (8H, t, J 6.6), 3.45 (2H, s), 1.79 (8H, p, J 6.7), 1.41 - 1.51 (8H, m), 1.26 - 1.41 (38 H, m), 1.13 (36H, d, J 7.4), 0.83 - 0.95 (12H, m).

Intermediate 62



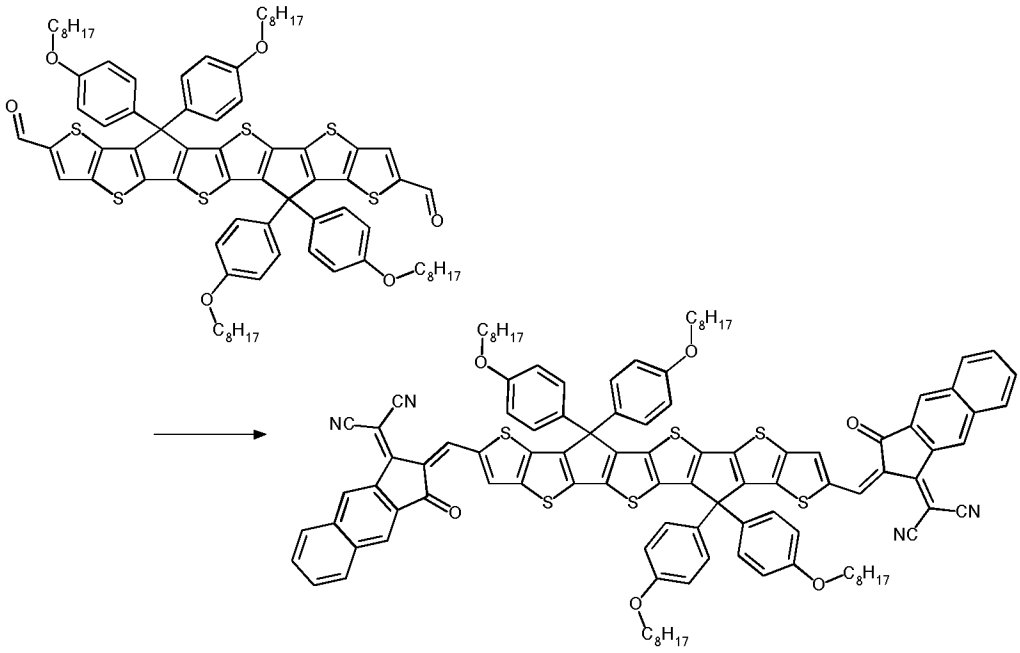
To a solution of intermediate 61 (561 mg, 0.349 mmol) in toluene (80 cm^3) is added Amberlyst 15 strong acid (2.2 g) and the reaction mixture stirred at 50 °C for 16 hours. The hot reaction mixture is filtered and the filtrate washed with water (50 cm^3). The organics dried over anhydrous magnesium sulphate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography (40-60 petrol:dichloromethane; 4:1) to give intermediate 62 (335 mg, 76%). ^1H NMR (400 MHz, CD_2Cl_2) 7.20 (4H, d, J 6.7), 7.07 (8H, d, J 8.8), 6.71 (8H, d, J 8.8), 3.79 (8H, t, J 6.6), 1.56 - 1.68 (8H, m), 1.31 (8H, t, J 7.4), 1.10 - 1.26 (32H, m), 0.68 - 0.84 (12H, m).

Intermediate 63



To a degassed solution of intermediate 62 (335 mg, 0.266 mmol) in chloroform (30 cm^3) and *N,N*-dimethylformamide (0.25 cm^3, 3.2 mmol) is added phosphorus(V) oxychloride (0.25 cm^3, 2.7 mmol) and the reaction mixture heated at 60 °C for 16 hours. Saturated aqueous sodium acetate solution (10 cm^3) is added and the resulting mixture stirred at 50 °C for 1 hour. The mixture is then cooled down to 23 °C and the organic solvent removed *in vacuo*. The remaining aqueous phase and material are extracted with ether (3 x 100 cm^3), the combined organic layer is washed with water (2 x 25 cm^3), and brine (30 cm^3), before drying over anhydrous magnesium sulphate. The mixture is filtered, the solvent removed *in vacuo* and the crude product purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 4:1 to 1:1) to give intermediate 63 (206 mg, 59%). ^{1}H NMR (400 MHz, CD_2Cl_2) 9.76 (2H, s), 7.85 (2H, s), 7.05 (8H, d, J 8.4), 6.71 (8H, d, J 8.5), 3.78 (8H, t, J 6.6), 1.61 (8H, q, J 6.9), 1.25 - 1.36 (8H, m), 1.10 - 1.25 (32H, m), 0.77 (12H, t, J 6.7).

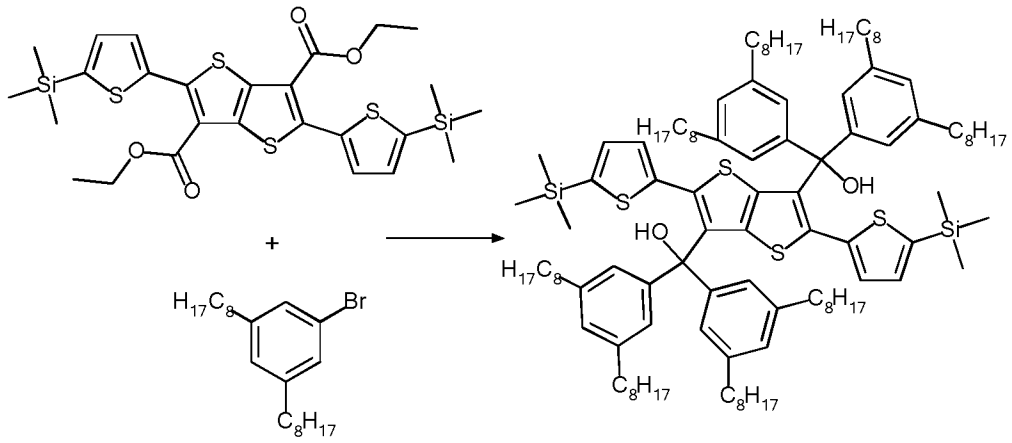
Compound 25



To a degassed solution of intermediate 63 (60 mg, 0.046 mmol) and 2-{3-oxo-1H,2H,3H-cyclopenta[*b*]naphthalen-1-ylidene}propanedinitrile (56 mg, 0.23 mmol) in chloroform (30 cm^3) is added pyridine (0.3 cm^3) and the reaction mixture stirred at 55 °C for 16 hours. The solvent is removed *in vacuo*, and the crude purified by column chromatography (chloroform). The product is dissolved in the minimum chloroform, treated with acetonitrile (50 cm^3) and the solid collected by filtration to give compound 25 (40 mg, 50%) as a dark solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.09 (2H, s), 8.86 (2H, s), 8.30 (2H, s), 8.10 (2H, s), 7.98 (4H, ddd, J 10.5, 6.1, 3.3), 7.62 (4H, dd, J 6.3, 3.2), 7.15 (8H, d, J 8.9), 6.77 - 6.85 (8H, d, J 8.9), 3.84 (8H, t, J 6.5), 1.67 (8H, p, J 6.7), 1.30 - 1.39 (8H, m), 1.10 - 1.28 (32H, m), 0.70 - 0.83 (12H).

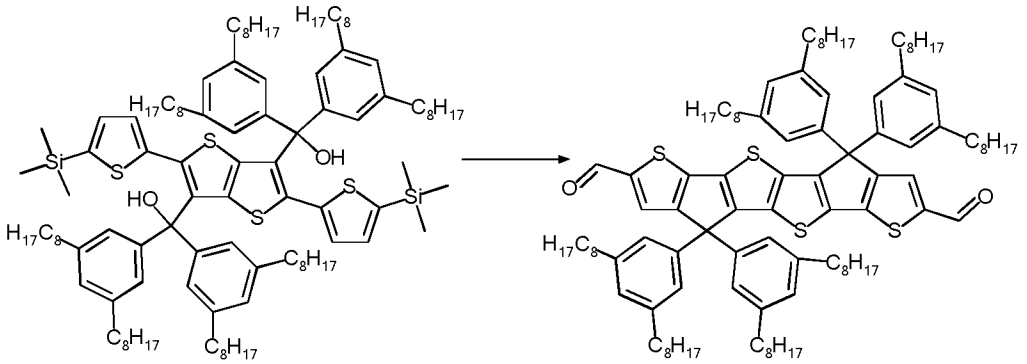
Example 26

Intermediate 64



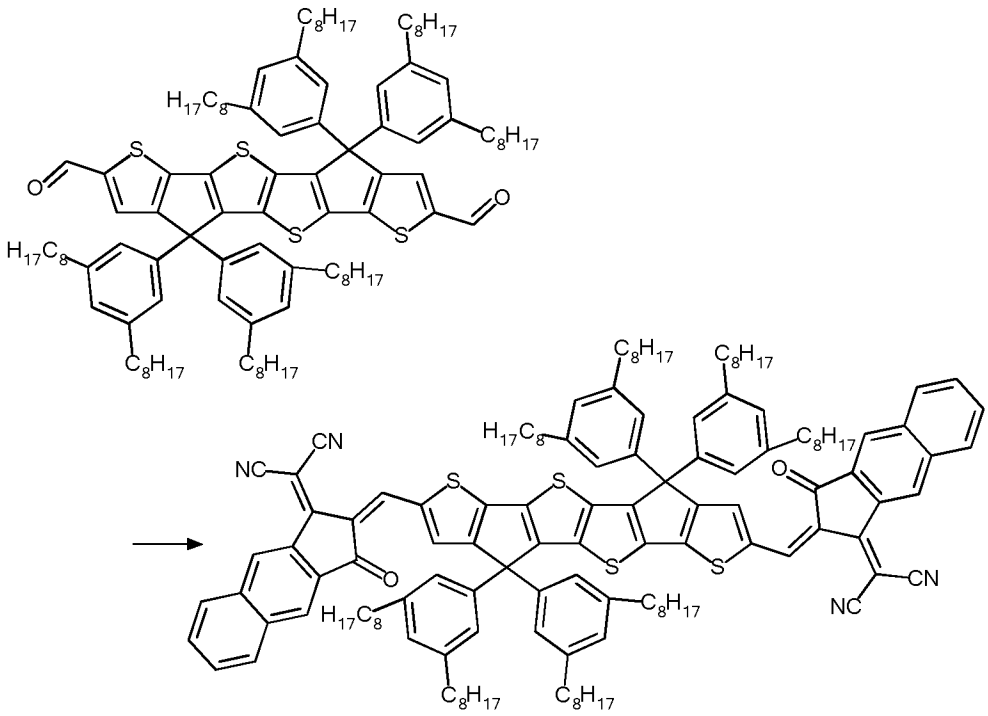
To a solution of 1-bromo-3,5-dioctyl-benzene (3.1 g, 8.1 mmol) in anhydrous tetrahydrofuran (12 cm^3) at -78 °C is added *t*-butyllithium (9.5 cm^3, 16 mmol, 1.7 M in pentane) over 10 minutes and the solution stirred for 2 hours. The cooling is removed for 5 minutes and the reaction mixture is re-cooled to -78 °C. A solution of 2,5-bis-(5-trimethylsilanyl-thiophen-2-yl)-thieno[3,2-b]thiophene-3,6-dicarboxylic acid diethyl ester (0.80 g, 1.35 mmol) in anhydrous tetrahydrofuran (10 cm^3) is added over 5 minutes, the coolant is left to evaporate and the reaction stirred for 16 hours. Water (5 cm^3) is added and the mixture stirred for 5 minutes. The reaction is partitioned between ether (100 cm^3) and water (50 cm^3), the organic phase is washed with water (3 x 20 cm^3), dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo*. The residue is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 9:1 to 4:1) to give intermediate 64 (2.1 g, 89%). ^1H NMR (400 MHz, $CDCl_3$) 6.93 (8H, d, J 1.5), 6.90 (4H, d, J 1.7), 6.79 (2H, d, J 3.4), 6.43 (2H, d, J 3.4), 3.35 (2H, s), 2.50 (16H, t, J 7.7), 1.48 - 1.56 (16H, m), 1.20 - 1.36 (80H, m), 0.80 - 0.94 (24H, m), 0.22 (18H, s).

Intermediate 65



To a degassed solution of intermediate 64 (2.00 g, 1.17 mmol) in toluene (30 cm^3) at 50 °C is added Amberlyst 15 strong acid (8 g). The reaction is stirred for 16 hours, filtered and the solid extracted with toluene (3 x 50 cm^3). The combined organic phase is concentrated *in vacuo* and passed through a silica plug using a graded solvent system (40-60 petrol:dichloromethane; 1:0 to 19:1). Crude material (1.20 g) is dissolved in chloroform (24 cm^3) and *N,N*-dimethylformamide (0.92 g, 13 mmol), and the solution cooled to 0 °C. Phosphorus(V) oxychloride (1.80 g, 11.8 mmol) is added over 5 minutes, stirred at 23 °C for 30 minutes and heated at 55 °C for 16 hours. Saturated aqueous potassium acetate (50 cm^3) is added and the biphasic solution stirred at 55 °C for 1 hour. The aqueous phase is extracted with dichloromethane (20 cm^3) and the combined organics washed with water (20 cm^3), dried over anhydrous magnesium sulphate, filtered and concentrated *in vacuo*. The residue is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 4:1 to 3:1) to give intermediate 65 (545 mg, 44%). ^1H NMR (400 MHz, $CDCl_3$) 9.82 (2H, s), 7.66 (2H, s), 6.93 (4H, t, J 1.5), 6.80 (8H, d, J 1.5), 2.50 (16H, t, J 7.7), 1.53 (16H, t, J 7.7), 1.26 (80H, t, J 7.5), 0.83 - 0.91 (24H, m).

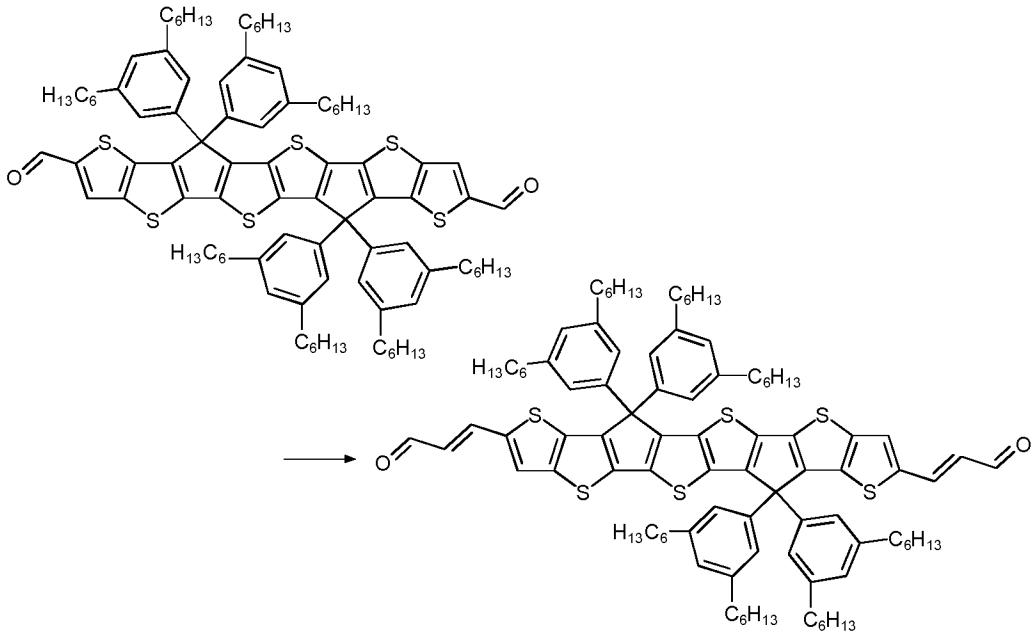
Compound 26



To a solution of intermediate 65 (100 mg, 0.063 mmol) and 2-{3-oxo-1H,2H,3H-cyclopenta[*b*]naphthalen-1-ylidene}propanedinitrile (100 mg, 0.410 mmol) in chloroform (10 cm^3) is added pyridine (0.36 cm^3, 4.4 mmol) and the reaction stirred at 55 °C for 6 hours. Methanol (30 cm^3) is added, the suspension cooled to 23 °C, filtered and the solid washed with methanol (5 cm^3). The solid is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 7:3 to 11:9) to give compound 26 (56 mg, 44%) as a green solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.19 (2H, s), 8.98 (2H, s), 8.36 (2H, s), 8.05 - 8.11 (4H, m), 7.68 - 7.78 (6H, m), 6.98 (4H, s), 6.83 (8H, d, J 1.5), 2.54 (16H, t, J 7.8), 1.45 - 1.70 (8H, m), 1.21 - 1.32 (88H, m), 0.81 - 0.90 (24H, m).

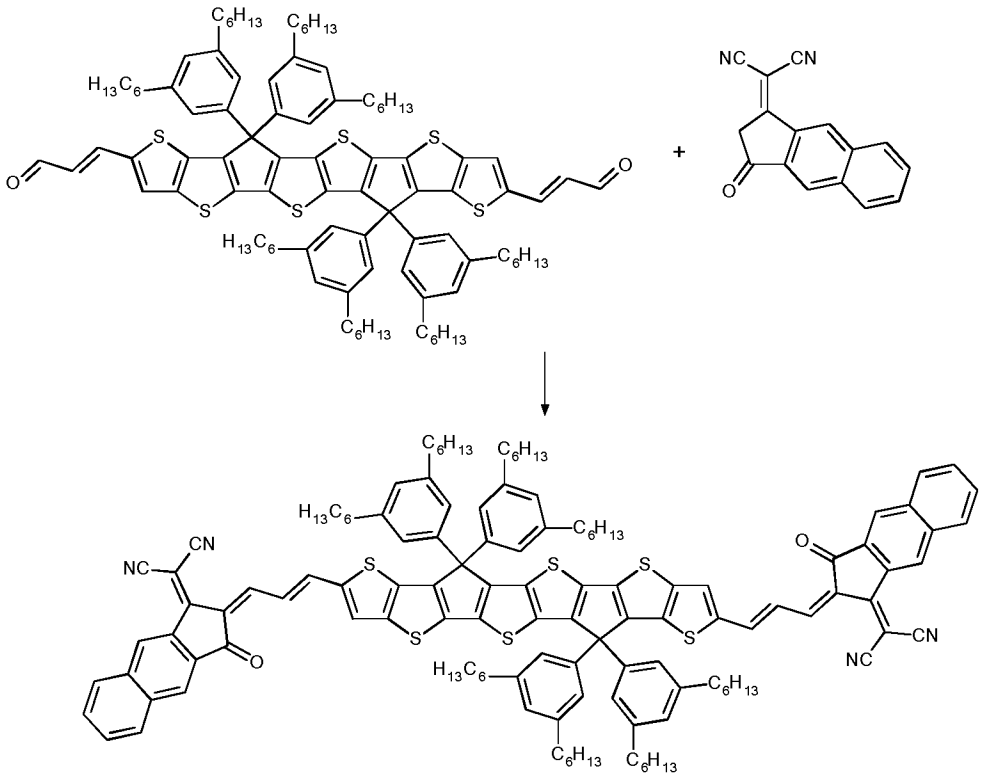
Example 27

Intermediate 66



To a solution of intermediate 21 (500 mg, 0.34 mmol) and tributyl(1,3-dioxolan-2-ylmethyl)-phosphonium bromide (276 mg, 0.75 mmol) in tetrahydrofuran (19 cm^3) at 0 °C is added sodium hydride (81.4 mg, 2.03 mmol, 60% dispersion in mineral oil). The reaction is slowly warmed to 23 °C and stirred for 16 hours. Aqueous hydrochloric acid (60 cm^3, 10%) is added and the reaction mixture heated at 45 °C for 24 hours. The mixture allowed to cool, and the organics extracted with ether (40 cm^3). The organic layer is then washed with water (2 x 20 cm^3), dried over anhydrous magnesium sulphate, filtered and the solvent removed *in vacuo*. Purification by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 5:1 to 3:2) gives intermediate 66 (480 mg, 93%) as a purple solid. ^1H NMR (400 MHz, $CDCl_3$) 9.62 (2H, d, J 7.6), 7.58 (2H, d, J 15.4), 7.54 (2H, s), 6.93 (4H, d, J 1.5), 6.82 (8H, d, J 1.5), 6.41 (2H, dd, J 15.4, 7.6), 2.51 (16H, t, J 7.6), 1.53 (16H, q, J 7.6, 7.0), 1.19 - 1.34 (48H, m), 0.80 - 0.88 (24H, m).

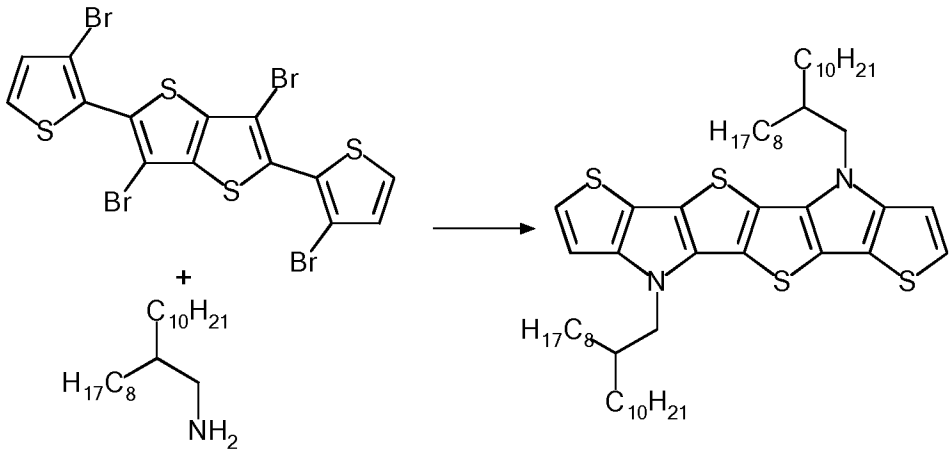
Compound 27



Intermediate 66 (100 mg, 0.066 mmol) and 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (35.2 mg, 0.144 mmol) are suspended in chloroform (5.0 cm^3), pyridine (0.37 cm^3, 4.6 mmol) added and the reaction mixture stirred at 23 °C for 16 hours. Methanol (30 cm^3) is added, the solid collected by filtration and washed with methanol (10 cm^3). The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 5:1 to 3:7) to give compound 27 (68 mg, 53%) as a dark solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.20 (2H, s), 8.72 (2H, s), 8.53 (2H, d, J 11.7), 8.35 (2H, s), 8.00 - 8.18 (4H, m), 7.67 - 7.77 (4H, m), 7.65 (2H, s), 7.57 (2H, d, J 14.3), 6.96 (4H, s), 6.86 (8H, s), 2.56 (16H, t, J 7.6), 1.54 - 1.65 (16H, m), 1.19 - 1.40 (48H, m), 0.79 - 0.86 (24H, m).

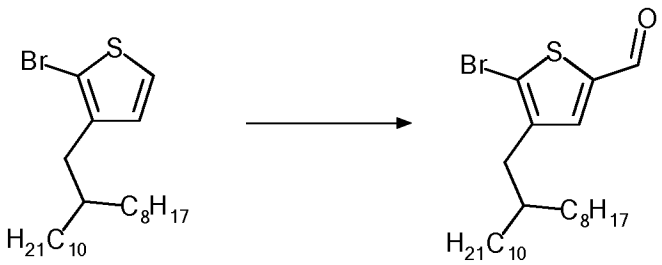
Example 28

Intermediate 67



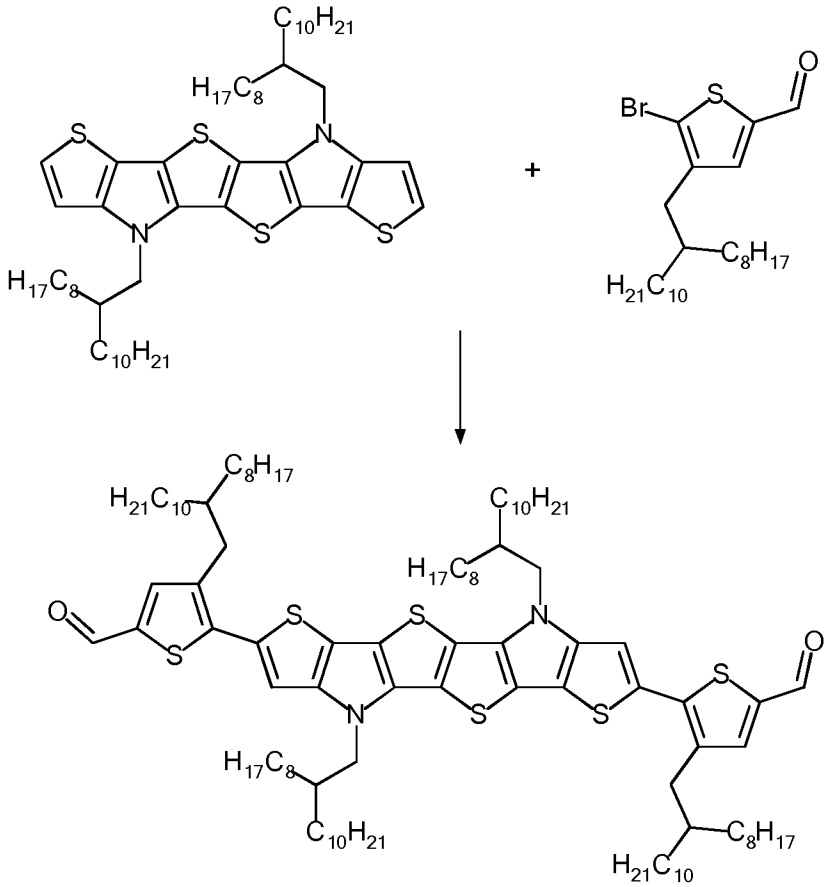
To a degassed solution of 3,6-dibromo-2,5-bis(3-bromo-2-thienyl)-thieno[3,2-b]thiophene (1.00 g, 1.61 mmol), sodium 2-methylpropan-2-olate (3.10 g, 32.3 mmol), 1,1'-bis(diphenylphosphino)ferrocene (358 mg, 0.645 mmol) and tris(dibenzylideneacetone)dipalladium(0) (148 mg, 0.161 mmol) in anhydrous toluene (30 cm^3) is added 2-octyl-1-dodecylamine (1.44 g, 4.838 mmol). The reaction mixture is then heated at 110 °C for 20 hours. The mixture is cooled to 23 °C and water (50 cm^3) added. The aqueous phase is extracted with cyclohexane (2 x 25 cm^3) and the combined organics dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography (40-60 petrol:dichloromethane; 19:1) to give intermediate 67 (606 mg, 42%) as an orange solid. ^1H NMR (400 MHz, CD_2Cl_2) 7.17 (2H, d, J 5.3), 7.07 (2H, d, J 5.3), 4.21 (4H, d, J 7.6), 2.12 - 2.23 (2H, m), 1.19 - 1.48 (64H, m), 0.83 - 0.96 (12H, m).

Intermediate 68



To a solution of 2-bromo-3-(2-octyldodecyl)thiophene (5.90 g, 13.3 mmol) in anhydrous tetrahydrofuran (50 cm^3) at -78 °C is added lithium diisopropylamine (9.98 cm^3, 20.0 mmol, 2.0 M in tetrahydrofuran) and the mixture stirred for 90 minutes. Anhydrous *N,N*-dimethylformamide (1.5 cm^3, 20 mmol) is added and the cooling bath removed. The mixture is stirred at 23 °C for 1 hour and then cooled back to -78 °C. Saturated aqueous ammonium chloride solution (20 cm^3) is added and the mixture allowed to warm to 23 °C where the solvent is removed *in vacuo*. The organic residue is taken into 40-60 petrol (100 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 9:1 to 7:3) to give intermediate 68 (6.01 g, 96%) as a pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.78 (1H, s), 7.44 (1H, s), 2.55 (2H, d, J 7.1), 1.63 - 1.73 (1H, m), 1.20 - 1.38 (32H, m), 0.87 - 0.94 (6H, m).

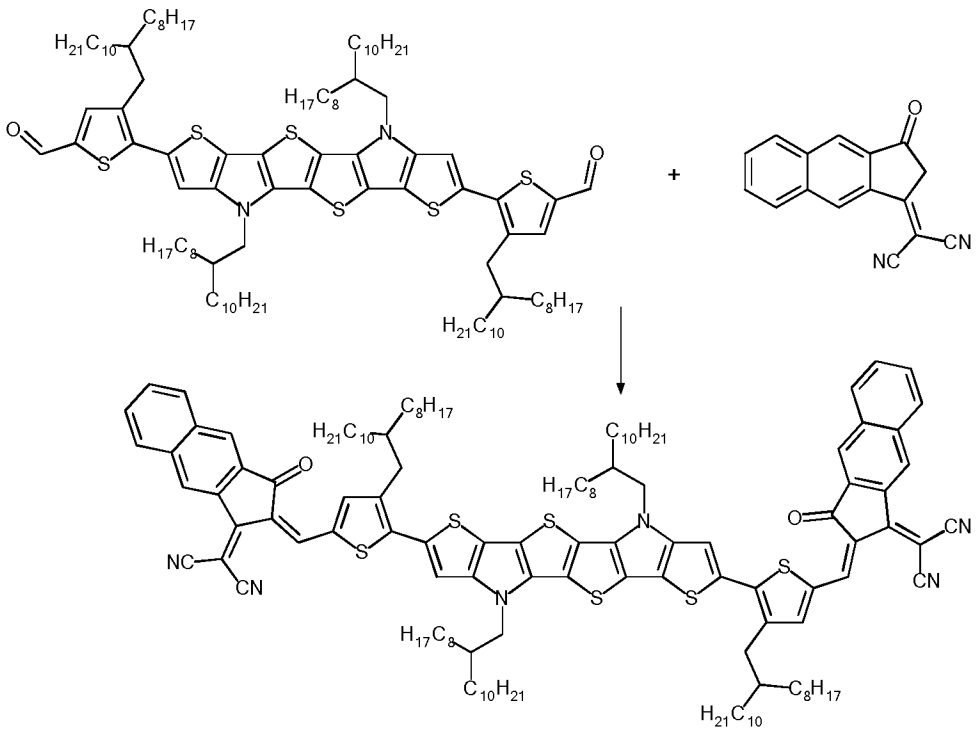
Intermediate 69



To a solution of intermediate 67 (710 mg, 0.796 mmol) in anhydrous tetrahydrofuran (15 cm^3) at -78 °C is added *t*-butyllithium (1.4 cm^3, 2.4 mmol, 1.7 M in pentane) batchwise over 10 minutes. The mixture is stirred for 6 hours. Chlorotrimethylstannane (4.8 cm^3, 4.8 mmol) is added, the reaction mixture allowed to warm to 23 °C and stirred for 17 hours. The solvent removed *in vacuo*, the residue triturated in 40-60 petrol (40 cm^3) and then passed through a plug of celite. The solid is taken up in anhydrous toluene (25 cm^3) and anhydrous *N,N*-dimethylformamide (5.0 cm^3) and intermediate 68 (970 mg, 2.1 mmol) added. The solution is degassed followed by addition of tris(dibenzylideneacetone)dipalladium(0) (75 mg, 0.082 mmol) and tri(*o*-tolyl)phosphine (100 mg, 0.33 mmol). The reaction mixture is then stirred at 120 °C (external) for 2 hours. The mixture is allowed to cool to 23 °C and the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 7:3 to 1:1) followed by trituration in methanol to give intermediate 69 (860 mg, 63%) as a brown-red solid. ^1H

NMR (400 MHz, CD_2Cl_2) 9.73 (2H, s), 7.49 (2H, s), 7.12 (2H, s), 4.08 (4H, d, J 7.6), 2.75 (4H, d, J 7.2), 2.00 - 2.13 (2H, m), 1.63 - 1.76 (2H, m), 1.00 - 1.39 (128H, m), 0.71 - 0.83 (24H, m).

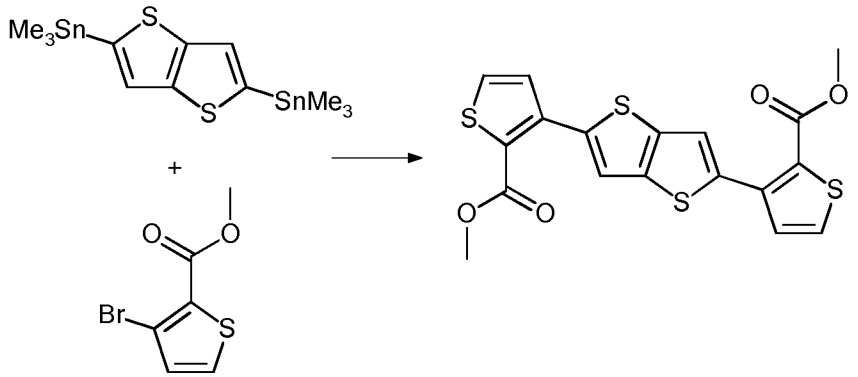
Compound 28



To a solution of intermediate 69 (250 mg, 0.149 mmol) in chloroform (20 cm^3) and ethanol (5 cm^3) is added pyridine (20 mg, 0.25 mmol) and 2-{3-oxo-1H,2H,3H-cyclopenta[*b*]naphthalen-1-ylidene}propanedinitrile (110 mg, 0.448 mmol). The solution is stirred for 48 hours before the volatiles are removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (cyclohexane:chloroform; 2:3 to 0:1) to give compound 28 (281 mg, 89%) as a brown solid. ^{1}H NMR (400 MHz, tetrahydrofuran-d8) 8.90 (2H, s), 8.66 (2H, s), 8.14 (2H, s), 7.86 - 7.96 (4H, m), 7.68 (2H, br. s), 7.51 - 7.60 (4H, m), 7.44 (2H, s), 4.26 (4H, d, J 7.6), 2.91 (4H, d, J 7.2), 2.12 - 2.25 (2H, m), 1.91 - 2.04 (2H, m), 1.08 - 1.59 (128H, m), 0.76 - 0.93 (24H, m).

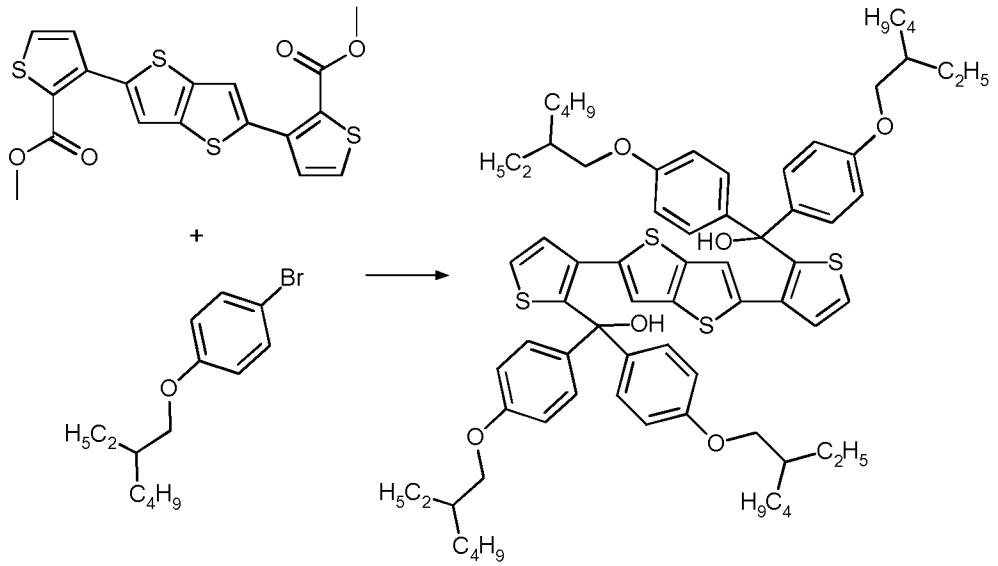
Example 29

Intermediate 70



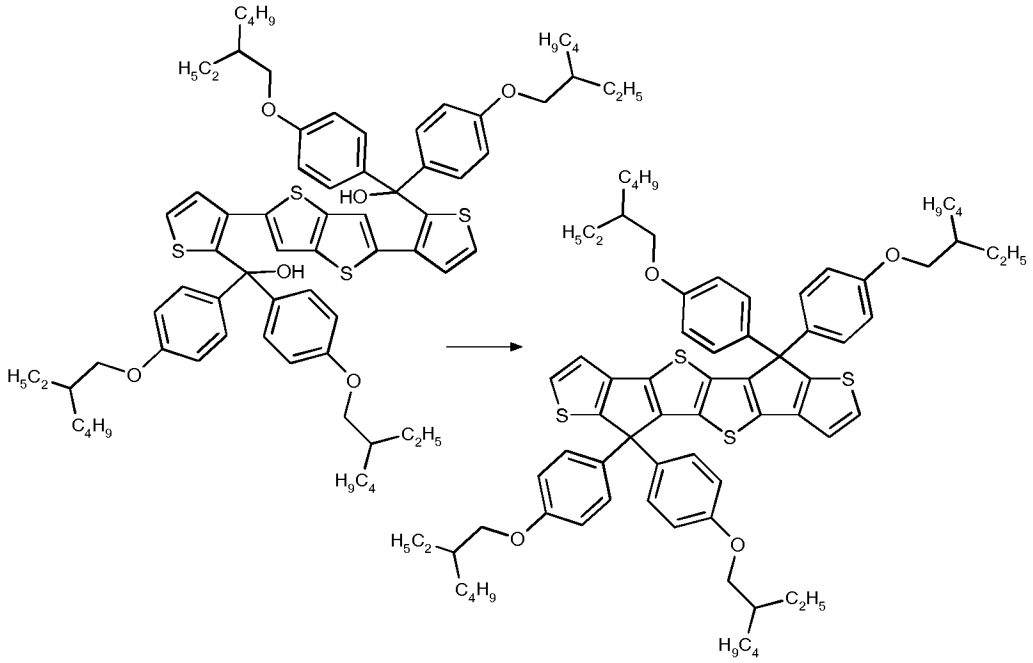
To a degassed solution of 3-bromothiophene-2-carboxylate (10.4 g, 47.2 mmol), toluene (500 cm^3) and trimethyl[5-(trimethylstannyl)thieno[3,2-b]thiophen-2-yl]stannane (10.0 g, 21.5 mmol) is added tris(dibenzylideneacetone)dipalladium(0) (983 mg, 1.07 mmol) and 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (2.05 g, 4.29 mmol). The reaction is then degassed for a further 15 minutes before heating to 80 °C for 45 minutes. The reaction is then heated at 110 °C for a further 15 minutes before cooling to 23 °C and stirring for 17 hours. The solid is collected by filtration, washed with ether (4 x 50 cm^3) and 40-60 petrol (3 x 70 cm^3) to give intermediate 70 (8.76 g, 97%) as a beige solid. ^{1}H NMR (400 MHz, $CDCl_3$) 8.19 (2H, s), 7.56 (2H, d, *J* 5.2), 7.47 (2H, d, *J* 5.2), 4.02 (6H, s).

Intermediate 71



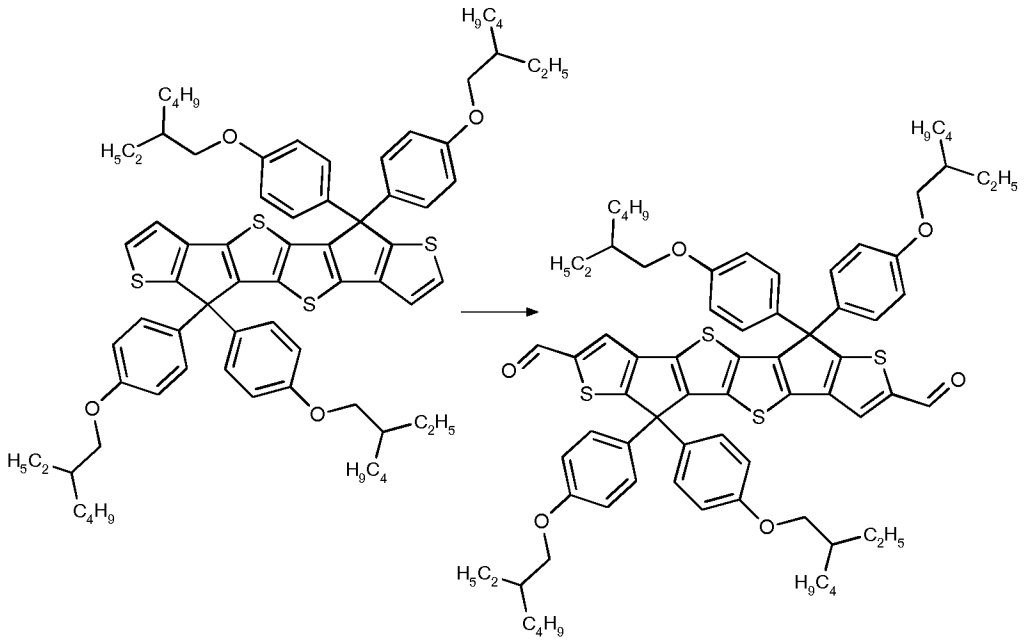
To a solution of 1-bromo-4-[(2-ethylhexyl)oxy]benzene (10.2 g, 35.7 mmol) in anhydrous tetrahydrofuran (127 cm^3) at -78 °C is added dropwise *t*-butyllithium (35.0 cm^3, 59.4 mmol, 1.7 M in pentane) over 35 minutes keeping the reaction temperature below -50 °C. Once the addition is finished the reaction mixture is stirred for 2 hours. The ice-bath is then removed and the reaction is allowed to warm to about -40 °C and stirred for 15 minutes. The reaction mixture is then cooled to -78 °C, intermediate 70 (2.50 g, 5.95 mmol) added and the reaction mixture stirred for 1 hour. The cooling is then removed and the resulting suspension stirred at 23 °C for 17 hours. Water (100 cm^3) is added and the mixture stirred for 1 hour. The organics are extracted with ether (3 x 100 cm^3) and the combined organics washed with water (100 cm^3), brine (100 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude product is suspended in acetonitrile (150 cm^3) and stirred for 1 hour. The mixture is then let stand for 10 minutes and the upper solution decanted. The crude is further purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 9:1 to 1:1) to give intermediate 71 (3.72 g, 53%) as a pale brown oil. ^1H NMR (400 MHz, $CDCl_3$) 7.17 - 7.25 (8H, m), 7.15 (2H, d, J 5.1), 7.09 (2H, d, J 5.1), 6.79 - 6.86 (8H, m), 6.61 (2H, s), 3.85 (8H, d, J 5.9), 3.54 (2H, s), 1.73 (4H, quin, J 6.1), 1.25 - 1.55 (32H, m), 0.87 - 0.99 (24H, m).

Intermediate 72



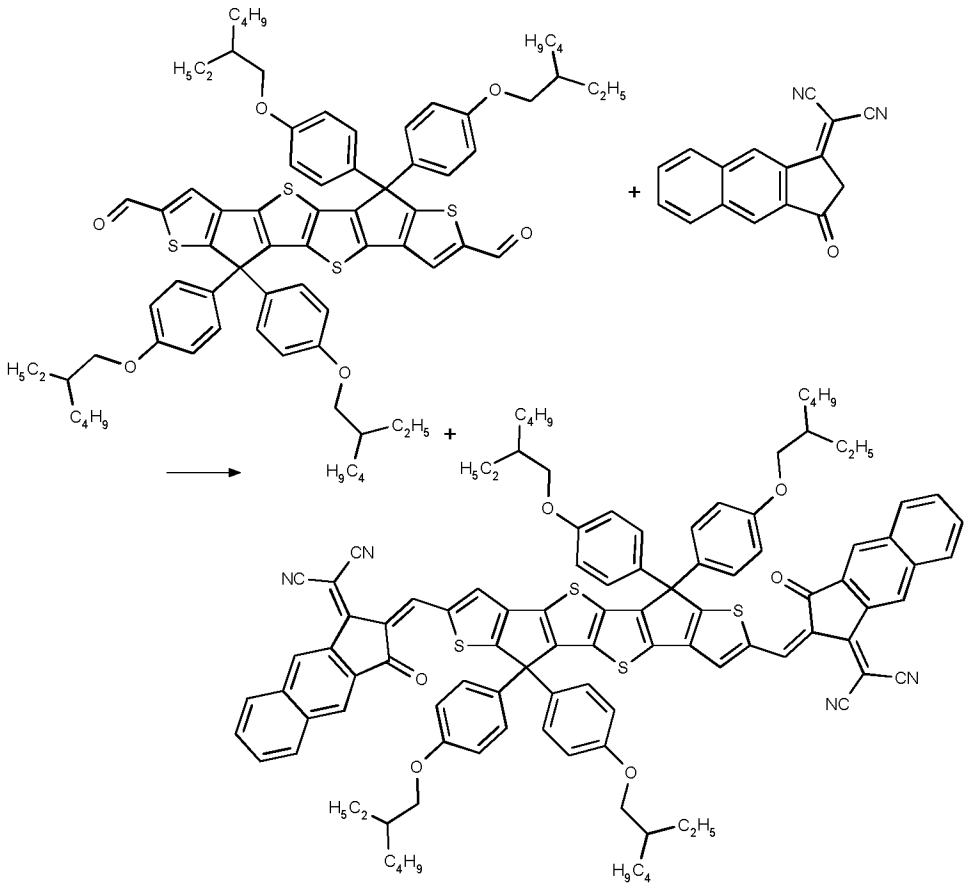
To a solution of *p*-toluene sulfonic acid monohydrate (1.32 g, 6.96 mmol) in chloroform (75 cm^3) at 70 °C is added a solution of compound 71 (1.50 g, 1.16 mmol) in chloroform (75 cm^3). The reaction mixture is heated at 70 °C for 65 hours. The reaction mixture is then cooled to 23 °C and the solvent removed *in vacuo* before water (50 cm^3) is added. The organics are then extracted with ether (3 x 50 cm^3). The combined organic layer is washed with brine (50 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. Purification by column chromatography using a graded solvent system (40-60 petrol:dichloromethane: 9:1 to 7:3) gives intermediate 72 (585 mg, 44%) as a pale cream solid. ^1H NMR (400 MHz, $CDCl_3$) 7.36 (2H, d, J 4.9), 7.14 - 7.24 (8H, m), 7.01 (2H, d, J 4.9), 6.76 - 6.87 (8H, m), 3.74 - 3.87 (8H, m), 1.63 - 1.77 (4H, m), 1.20 - 1.57 (32H, m), 0.81 - 0.96 (24H, m).

Intermediate 73



To a solution of *N,N*-dimethylformamide (0.22 cm^3) in anhydrous chloroform (80 cm^3) at 0 °C is added dropwise phosphorus(V) oxychloride (0.22 cm^3, 2.40 mmol). After 15 minutes at 0 °C, the reaction is stirred at 23 °C for 30 minutes. Intermediate 72 (550 mg, 0.480 mmol) is then added and the reaction heated at reflux for 48 hours. Saturated aqueous sodium acetate solution (50 cm^3) is then added and the resulting mixture heated at 50 °C for 1 hour. The solution is cooled to 23 °C and the solvent removed *in vacuo*. The organics extracted with ether (3 x 80 cm^3) and the combined organics washed with brine (30 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:1 to 1:4) to give intermediate 73 (480 mg, 83%) as pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.72 - 9.88 (2H, m), 7.50 - 7.62 (2H, m), 7.01 - 7.14 (8H, m), 6.66 - 6.82 (8H, m), 3.62 - 3.84 (8H, m), 1.60 (4H, dq, *J* 12.1, 5.8), 1.09 - 1.46 (32H, m), 0.71 - 0.92 (24H, m).

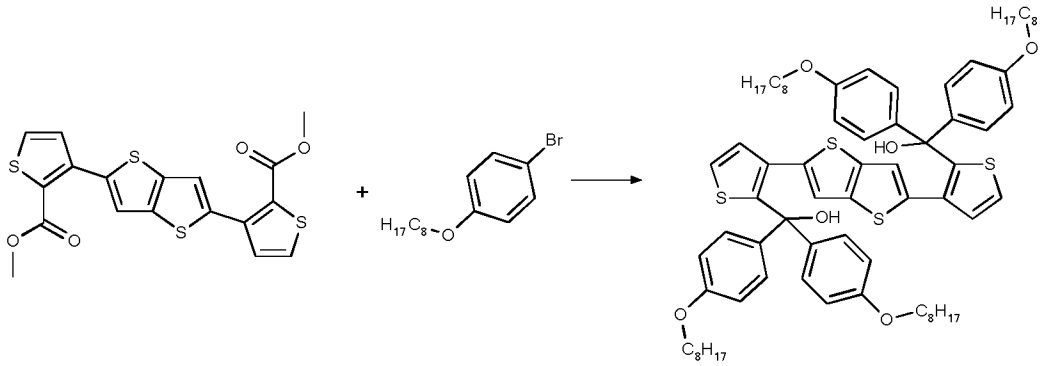
Compound 29



A degassed solution of intermediate 73 (150 mg, 0.13 mmol), pyridine (0.71 cm^3), 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (152 mg, 0.624 mmol) in anhydrous chloroform (10 cm^3) is stirred for 17 hours. The reaction mixture is diluted with methanol (150 cm^3) and stirred for 1 hour. The solid is collected by filtration and washed with acetonitrile (100 cm^3). The crude is triturated in ether (100 cm^3) and the solid collected by filtration to give compound 29 (205 mg, 99%) as a dark solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.11 (2H, s), 8.88 (2H, s), 8.24 - 8.37 (2H, m), 7.97 (4H, ddd, *J* 12.2, 6.0, 3.6), 7.72 - 7.81 (2H, m), 7.56 - 7.68 (4H, m), 7.11 - 7.23 (8H, m), 6.75 - 6.86 (8H, m), 3.67 - 3.81 (8H, m), 1.57 - 1.68 (4H, m), 1.11 - 1.45 (32H, m), 0.76 - 0.87 (24H, m).

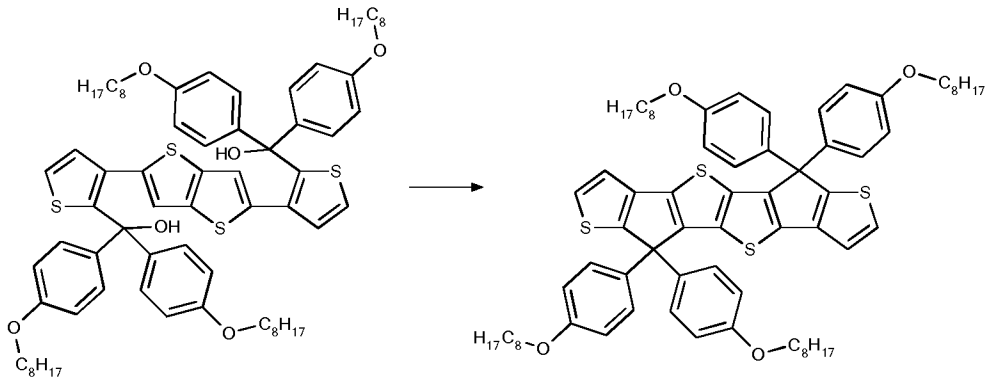
Example 30

Intermediate 74



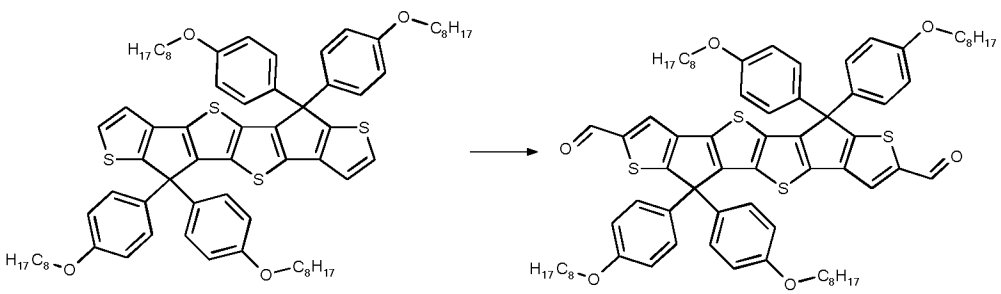
To a solution of 1-bromo-4-(octyloxy)benzene (6.06 g, 21.3 mmol) in anhydrous tetrahydrofuran (90 cm^3) at -78 °C is added dropwise *t*-butyllithium (25.0 cm^3, 42.5 mmol, 1.7 M in pentane) keeping the reaction temperature below -60 °C. After 20 minutes stirring at -78 °C the reaction is allowed to warm to -40 °C over 10 minutes before re-cooling to -78 °C. After stirring at -78 °C for 15 minutes, additional 1-bromo-4-octyloxybenzene (606 mg, 2.13 mmol) is added to the reaction mixture and the reaction stirred for a further 15 minutes before addition of intermediate 71 (1.79 g, 4.25 mmol). The reaction mixture is stirred at -78 °C for 25 minutes before removing the cooling and allowing the reaction to warm to 23 °C over 17 hours. Water (10 cm^3) is then added before the reaction mixture is added to a separating funnel with ether (100 cm^3) and additional water (100 cm^3). The organic layer is then washed with water (100 cm^3), brine (100 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:0 to 1:3) to give intermediate 74 (4.20 g, 84%) as a brown/green glassy oil. ^1H NMR (400 MHz, $CDCl_3$) 7.17 - 7.22 (8H, m), 7.14 (2H, d, *J* 5.2), 7.08 (2H, d, *J* 5.2), 6.77 - 6.83 (8H, m), 6.60 (2H, s), 3.95 (8H, t, *J* 6.6), 3.52 (2H, s), 1.78 (8H, p, *J* 6.7), 1.45 (8H, p, *J* 6.8), 1.23 - 1.39 (32H, m), 0.85 - 0.91 (12H, m).

Intermediate 75



To a degassed solution of intermediate 74 (3.85 g, 3.26 mmol) in toluene (250 cm^3) is added *p*-toluene sulfonic acid monohydrate (1.24 g, 6.51 mmol) and the mixture degassed for a further 10 minutes before stirring for 50 minutes and then heating at 50 °C for 16 hours. The reaction mixture is cooled to 23 °C and concentrated *in vacuo*. Water (100 cm^3) and ether (100 cm^3) are then added. The organic layer is washed with water (100 cm^3), brine (100 cm^3) and dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:0 to 7:3) to give intermediate 75 (1.03 g, 28%) as a yellow/brown oil. ^1H NMR (400 MHz, $CDCl_3$) 7.34 (2H, d, *J* 5.0), 7.14 - 7.19 (8H, m), 6.98 (2H, d, *J* 5.0), 6.76 - 6.82 (8H, m), 3.89 (8H, t, *J* 6.5), 1.68 - 1.77 (8H, m), 1.36 - 1.45 (8H, m), 1.18 - 1.36 (32H, m), 0.84 - 0.92 (12H, m).

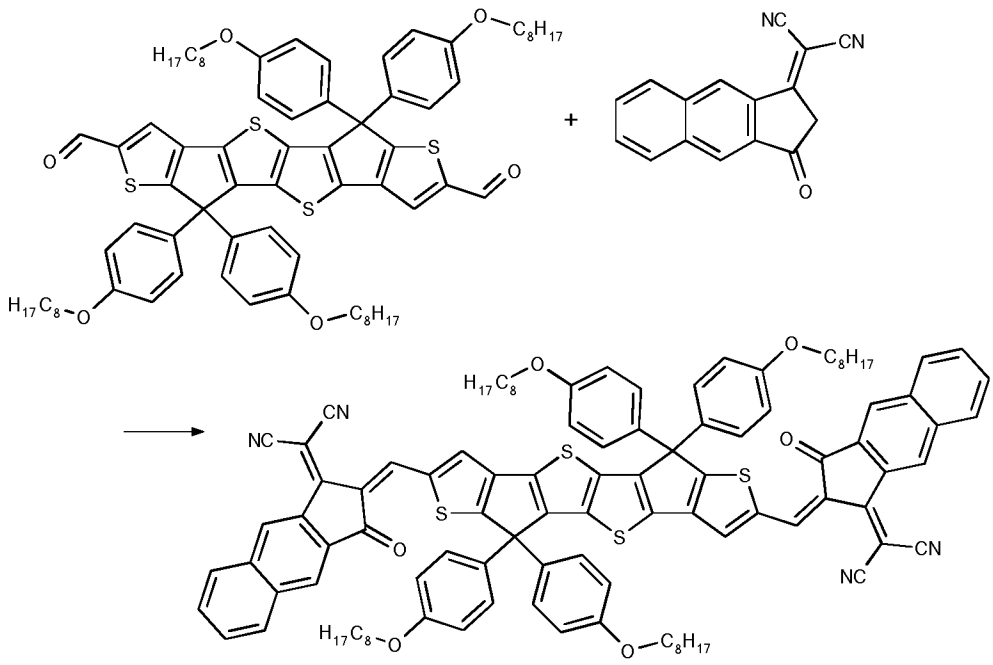
Intermediate 76



To a solution of *N,N*-dimethylformamide (0.41 cm^3, 5.25 mmol) in anhydrous chloroform (30 cm^3) at 0 °C is added dropwise phosphorous(V)

oxychloride (0.41 cm^3, 4.4 mmol). The mixture is then stirred for 10 minutes at 0 °C and at 23 °C for 30 minutes. A solution of intermediate 75 (1.00 g, 0.87 mmol) in chloroform (20 cm^3) is then added to the reaction mixture which is then stirred at 23 °C for 35 minutes before heating at 65 °C for 66 hours. The reaction is then cooled to 23 °C before adding *N,N*-dimethylformamide (0.82 cm^3, 10.5 mmol). After 5 minutes the reaction is cooled to 0 °C before adding phosphorous(V) oxychloride (0.82 cm^3, 8.8 mmol). The reaction is stirred at 0 °C for 15 minutes before heating at reflux for 6 hours. The reaction is then cooled to 23 °C before adding *N,N*-dimethylformamide (0.82 cm^3, 10.5 mmol). After 5 minutes the reaction is cooled to 0 °C before adding phosphorous(V) oxychloride (0.82 cm^3, 8.8 mmol). The reaction is stirred at 0 °C for 10 minutes before heating at reflux for 19 hours. Saturated aqueous sodium acetate solution (20 cm^3) is then added slowly. After a further 40 minutes at 75 °C the reaction is then cooled to 23 °C. Water (100 cm^3) and dichloromethane (50 cm^3) are added. The organic layer is washed with water (100 cm^3) and dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude product is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:0 to 3:7) to give intermediate 76 (763 mg, 73%) as a glassy yellow/brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.87 (2H, s), 7.63 (2H, s), 7.11 - 7.17 (8H, m), 6.78 - 6.84 (8H, m), 3.90 (8H, t, *J* 6.5), 1.74 (8H, p, *J* 6.6), 1.37 - 1.45 (8H, m), 1.22 - 1.36 (32H, m), 0.84 - 0.89 (12H, m).

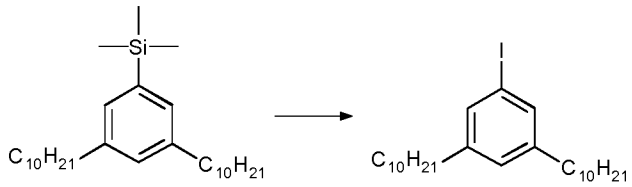
Compound 30



To a degassed solution of intermediate 76 (160 mg, 0.13 mmol), anhydrous chloroform (40 cm^3) and pyridine (0.75 cm^3) at 0 °C is added 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (130 mg, 0.53 mmol). The reaction is stirred at 0 °C for 70 minutes, 23 °C for 85 minutes and at 40 °C for 110 minutes. The reaction mixture is then stirred at 23 °C for 10 minutes before the reaction mixture is poured into stirred methanol (150 cm^3). The solid is collected by filtration and washed with methanol (4 x 10 cm^3). The solid is then triturated in acetone (75 cm^3) and the collected solid washed with acetone (2 x 10 cm^3) and ether (3 x 10 cm^3). The solid is then triturated in boiling acetone (50 cm^3) and the collected solid washed with acetone (2 x 10 cm^3) to give compound 30 (89 mg, 40%) as a black solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.19 (2H, s), 8.97 (2H, s), 8.37 (2H, s), 8.00 - 8.11 (4H, m), 7.84 (2H, m), 7.66 - 7.74 (4H, m), 7.18 - 7.25 (8H, m), 6.82 - 6.90 (8H, m), 3.92 (8H, t, *J* 6.5), 1.75 (8H, p, *J* 6.6), 1.37 - 1.47 (8H, m), 1.19 - 1.37 (32H, m), 0.81 - 0.91 (12H, m).

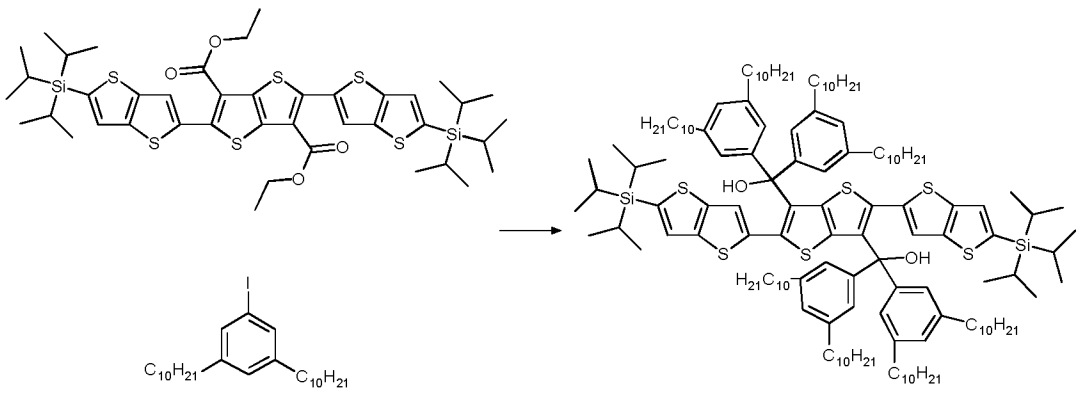
Example 31

Intermediate 77



To a solution of 3,5-bis(decyl)phenyl]trimethylsilane (7.28 g, 16.9 mmol) in chloroform (10 cm^3) and methanol (10 cm^3), in the dark, is added silver trifluoroacetate (7.84 g, 35.5 mmol). The mixture cooled to 0 °C, iodine (8.58 g, 33.8 mmol) added and the mixture stirred for 90 minutes. The mixture is filtered through a plug of silica (40-60 petrol) and the organic phase washed with saturated aqueous sodium thiosulfate (100 cm^3), water (100 cm^3) and brine (100 cm^3). The organics are dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo* to give intermediate 77 (6.98 g, 85%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) 7.27 (2H, s), 6.85 (1H, s), 2.43 (4H, t, J 7.8), 1.44 - 1.55 (4H, m), 1.13 - 1.29 (28H, m), 0.78 - 0.84 (6H, m).

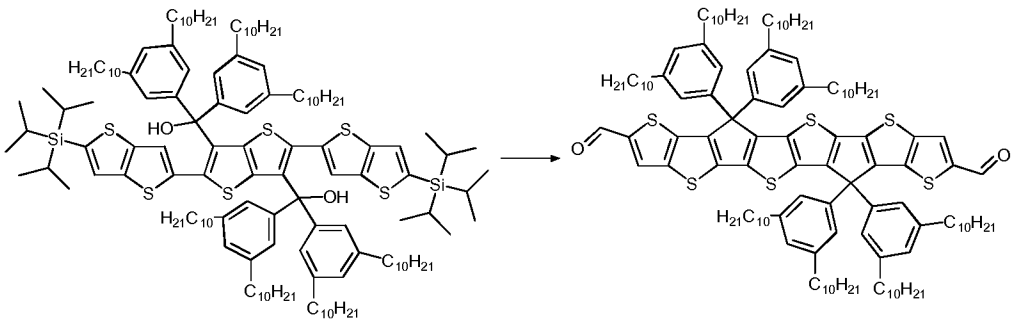
Intermediate 78



To a solution of intermediate 77 (4.99 g, 10.3 mmol) in anhydrous tetrahydrofuran (37.5 cm^3) at -78 °C is added dropwise *t*-butyllithium (12.1 cm^3, 20.6 mmol, 1.7 M in pentane) over 10 minutes. The reaction mixture is then stirred for 1 hour before the cooling is removed for 6 minutes and then the mixture cooled back to -78 °C. Intermediate 14 (1.50 g, 1.71 mmol) is then added and the reaction mixture allowed to warm to 23 °C and stirred for 17 hours. Water (5 cm^3) is added and the mixture stirred for

a further 10 minutes. Ether (100 cm^3) and water (50 cm^3) are added and the organic layer washed with water (3 x 20 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:0 to 3:1) to give intermediate 78 (2.76 g, 73%) as a pale brown oil. ^1H NMR (400 MHz, $CDCl_3$) 7.17 (2H, s), 6.93 (8H, s), 6.88 (4H, s), 6.45 (2H, s), 3.39 (2H, s), 2.42 - 2.53 (16H, m), 1.48 - 1.61 (16H, m), 1.07 - 1.41 (118H, m), 0.83 - 0.94 (60H, m).

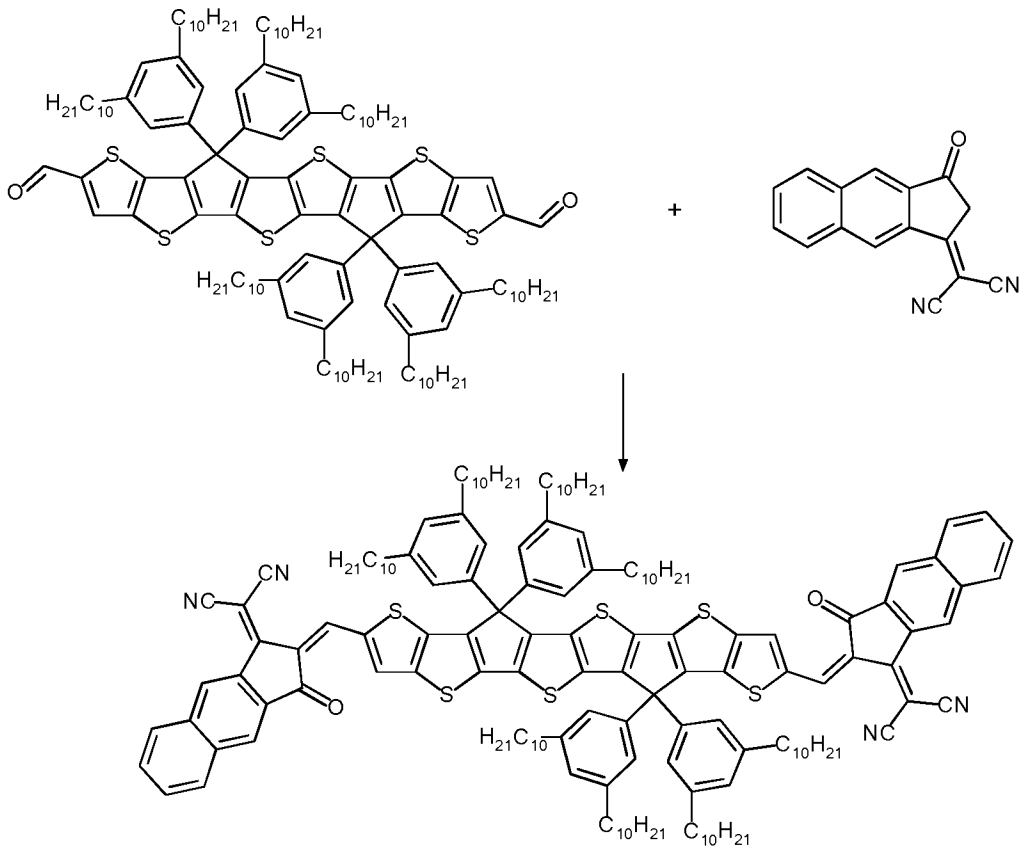
Intermediate 79



To a degassed solution of intermediate 78 (2.76 g, 1.25 mmol) in toluene (110 cm^3) at 60 °C is added Amberlyst 15 strong acid (10.0 g) and the reaction mixture stirred for 17 hours. The hot mixture is filtered and the filtered solid washed with hot toluene (3 x 20 cm^3). The filtrates combined, and the solvent removed *in vacuo*. The intermediate is then purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:0 to 17:3). The solid is then dissolved in chloroform (55.2 cm^3) and *N,N*-dimethylformamide (1.46 g, 19.9 mmol) added. Phosphorus(V) oxychloride (2.86 g, 18.7 mmol) is then added slowly over 5 minutes and then the reaction mixture stirred for 30 minutes and heated at 55 °C for 17 hours. The reaction mixture is allowed to cool to 23 °C and aqueous potassium acetate (150 cm^3, 3 M) is added and the mixture stirred for 1 hour. The organics are extracted with dichloromethane (2 x 200 cm^3) and the combined organics washed with water (50 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 9:1 to 3:1) to give

intermediate 79 (1.37 g, 57%) as a red oil. ^{1}H NMR (400 MHz, $CDCl_3$) 9.89 (2H, s), 7.93 (2H, s), 6.92 (4H, s), 6.80 (8H, s), 2.50 (16H, t, J 7.7), 1.52 (16H, q, J 7.2), 1.09 - 1.40 (112H, m), 0.87 (24H, t, J 6.8).

Compound 31

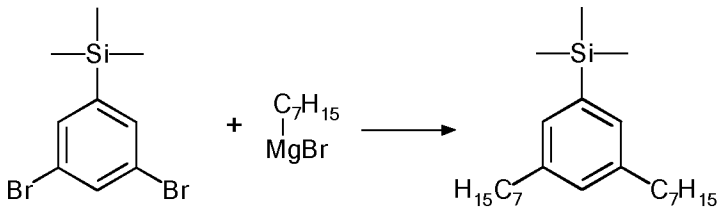


To a degassed mixture of intermediate 79 (100 mg, 0.05 mmol) and 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (51 mg, 0.21 mmol) in chloroform (2.5 cm^3) is added pyridine (0.29 cm^3, 3.6 mmol) and the mixxture degassed for a further 10 minutes. The solution is heated at 40 °C for 6 hours and then cooled to 23 °C before methanol (30 cm^3) is added. The solid is collected by filtration and washed with methanol (20 cm^3). The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 3:2 to 1:1) to give compound 31 (51 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) 9.20 (2H, s), 9.00 (2H, s), 8.33 (2H, s), 7.98 - 8.22 (6H, m), 7.63 - 7.80 (4H, m), 6.96 (4H, s),

6.90 (8H, s), 2.55 (16H, t, J 7.7), 1.51 - 1.63 (16H, m), 0.99 - 1.41 (112H, m), 0.82 (24H, t, J 7.0).

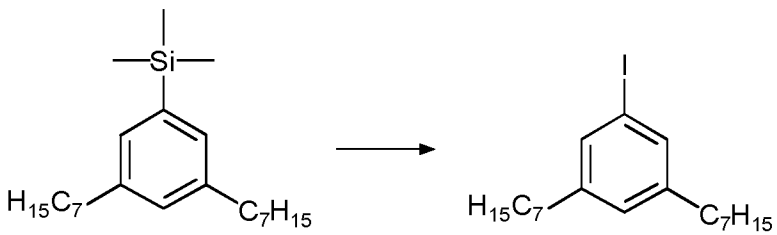
Example 32

Intermediate 80



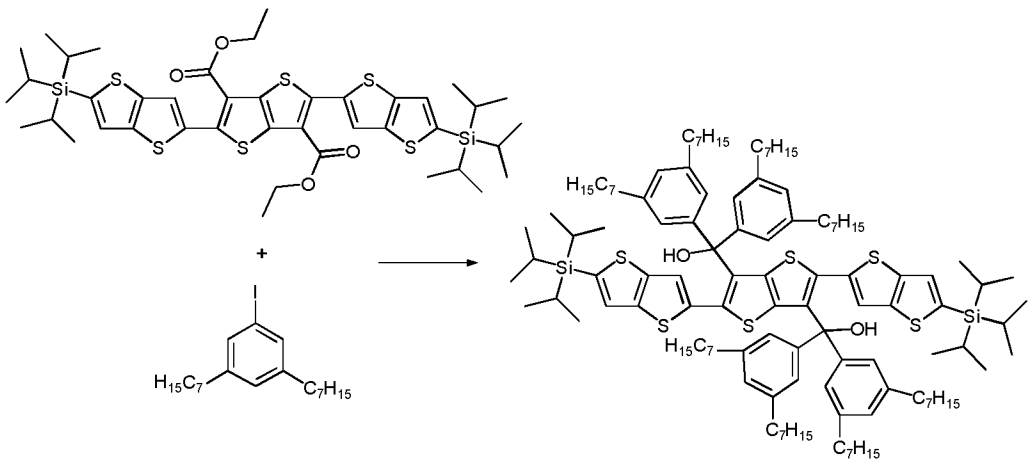
To a solution of bromo(octyl)magnesium (183 cm^3, 365 mmol, 2.0 M in tetrahydrofuran) in anhydrous tetrahydrofuran (450 cm^3) is added (3,5-dibromophenyl)trimethylsilane (45.0 g, 146 mmol) and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (II) (1.60 g, 2.19 mmol) and the reaction mixture heated at reflux for 17 hours. The reaction mixture is then cooled to 0 °C, water (250 cm^3) added and the mixture stirred for 1 hour. The organics are extracted with dichloromethane (2 x 250 cm^3). The combined organics are washed with brine (100 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography (heptane) to give intermediate 80 (22.2 g, 41%) as a colourless oil. ^1H NMR (400 MHz, $CDCl_3$) 7.15 (2H, s), 7.00 (1H, s), 2.53 - 2.65 (4H, m), 1.56 - 1.70 (4H, m), 1.20 - 1.43 (16H, m), 0.82 - 0.96 (6H, m), 0.27 (9H, s).

Intermediate 81



To a solution of intermediate 80 (9.89 g, 28.5 mmol) in chloroform (100 cm^3) and methanol (100 cm^3), in the dark, is added silver(I) trifluoroacetate (13.2 g, 59.9 mmol) and the mixture cooled to 0 °C. Iodine (14.5 g, 57.0 mmol) is added and the mixture stirred for 1.5 hours. The mixture is filtered through a silica plug (dichloromethane) and the filtrate washed with saturated aqueous sodium bisulfite (200 cm^3), water (200 cm^3) and brine (200 cm^3). The solution is then dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo* to give intermediate 81 (9.51 g, 83%). ^{1}H NMR (400 MHz, CD_2Cl_2) 7.27 (2H, s), 6.88 (1H, s), 2.43 (4H, t, J 7.5), 1.43 - 1.53 (4H, m), 1.15 - 1.28 (16H, m), 0.76 - 0.83 (6H, m).

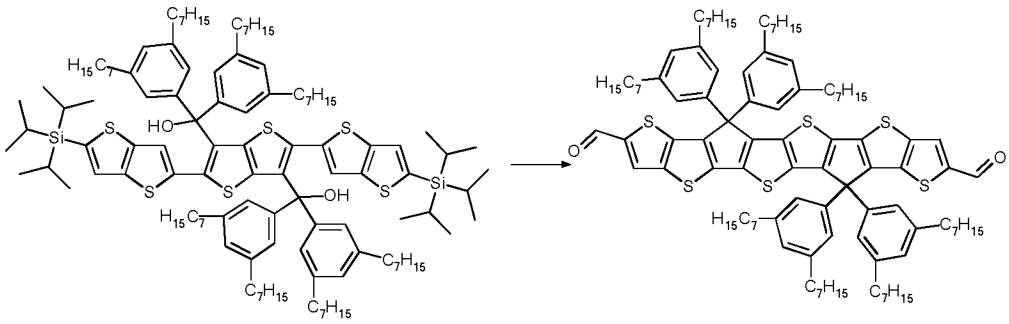
Intermediate 82



To a solution of intermediate 81 (4.13 g, 10.3 mmol) in anhydrous tetrahydrofuran (38 cm^3) at -78 °C is added *t*-butyllithium (12.1 cm^3, 20.6 mmol, 1.7 M in pentane) over 10 minutes. The reaction mixture is then stirred for 1 hour, the cooling bath removed for 6 minutes and then the mixture cooled back to -78 °C. Intermediate 14 (1.50 g, 1.72 mmol) is added, the reaction mixture allowed to warm to 23 °C and stirred for 17 hours. Water (5 cm^3) is slowly added and the mixture stirred for 10 minutes. Ether (100 cm^3) is then added, the mixture washed with water (3 x 50 cm^3) and then dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is then purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:0 to 17:3) to give intermediate 82 (1.83 g, 57%).

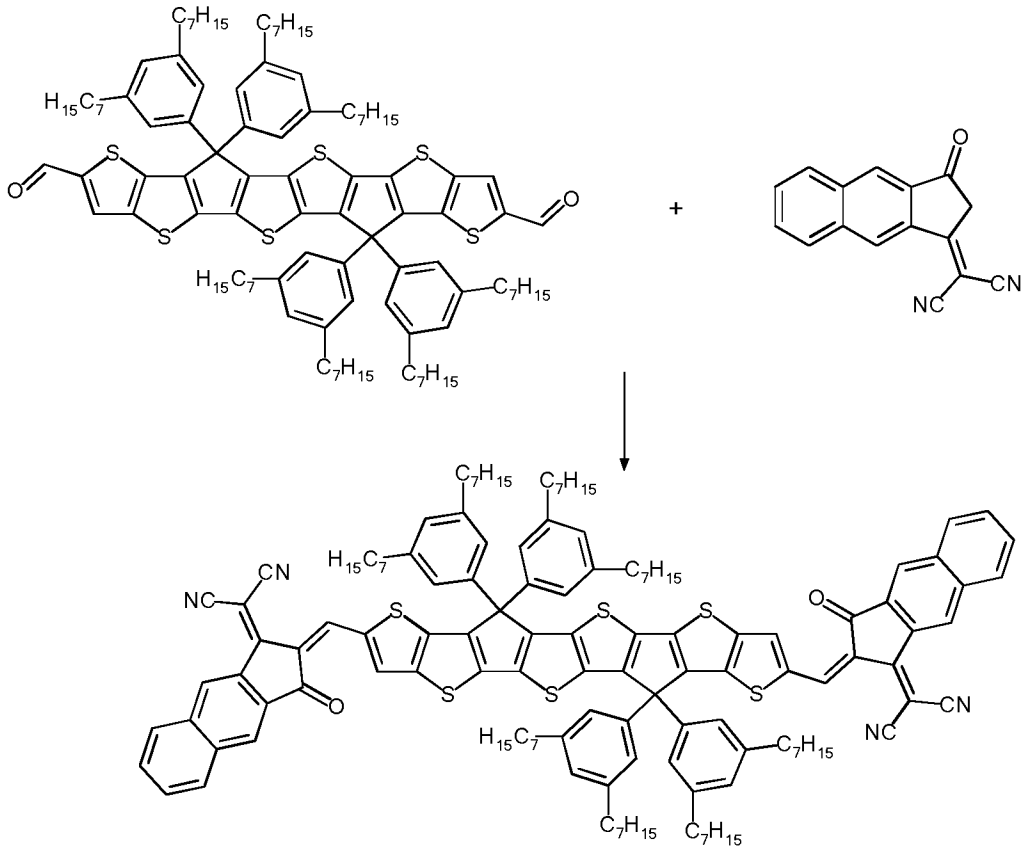
^{1}H NMR (400 MHz, $CDCl_3$) 7.17 (2H, s), 6.92 - 6.96 (8H, m), 6.87 - 6.90 (4H, m), 6.46 (2H, s), 3.42 (2H, s), 2.44 - 2.54 (16H, m), 1.49 - 1.61 (16H, m), 1.20 - 1.36 (70H, m), 1.12 (36H, d, J 7.4), 0.83 - 0.93 (24H, m).

Intermediate 83



To a degassed solution of intermediate 82 (1.83 g, 0.975 mmol) in toluene (73 cm^3) at 60 °C is added Amberlyst 15 strong acid (6.0 g) and the reaction mixture stirred for 17 hours. The hot reaction mixture is filtered and the solid washed with hot toluene (3 x 20 cm^3). The filtrate is then concentrated *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 19:1 to 3:1). The purified material is then taken up in chlorofom (37 cm^3) and *N,N*-dimethylformamide (1.14 g, 15.6 mmol) added followed by phosphorus(V) oxychloride (2.24 g, 14.6 mmol) over 5 minutes. The reaction mixture is then stirred for 30 minutes and then heated at 55 °C for 17 hours. The mixture is allowed to cool to 23 °C, aqueous potassium acetate (150 cm^3, 3 M) added and the mixture stirred for 1 hour. The organics are extracted with dichloromethane (20 cm^3) and the organic layer washed with water (50 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 9:1 to 7:3) to give intermediate 83 (890 mg, 58) as an orange/red solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.89 (2H, s), 7.93 (2H, s), 6.90 - 6.94 (4H, m), 6.79 - 6.82 (8H, m), 2.50 (16H, t, J 7.7), 1.47 - 1.59 (16H, m), 1.16 - 1.33 (64H, m), 0.83 - 0.92 (24H, m).

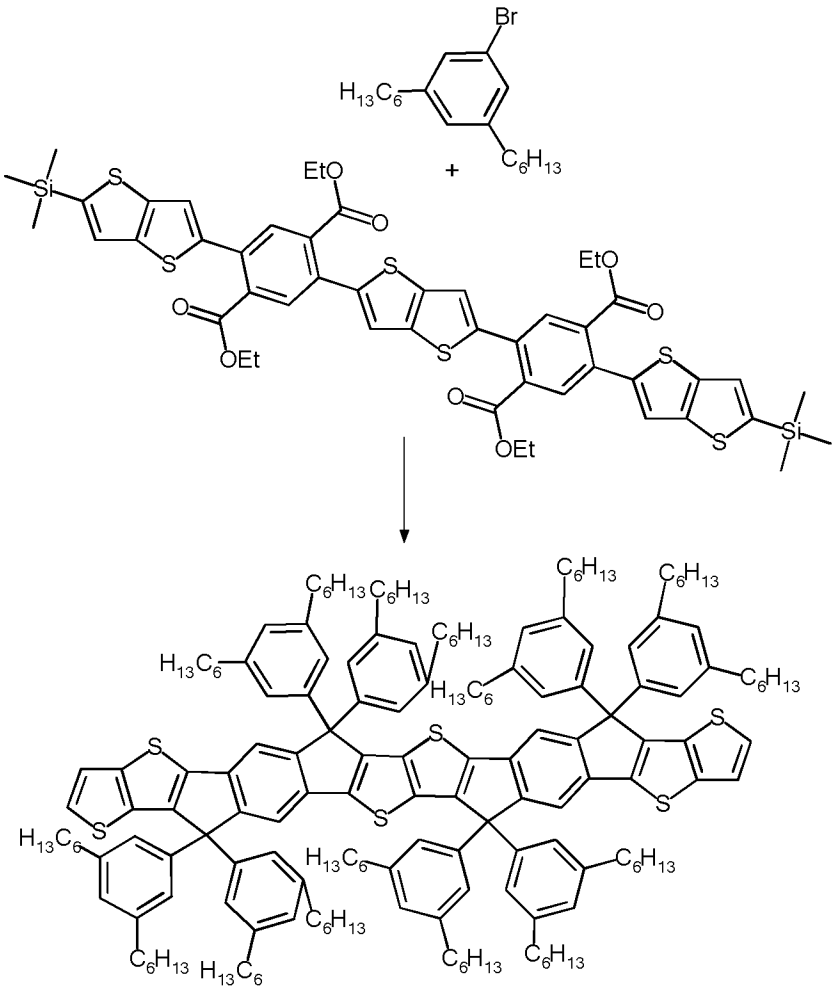
Compound 32



To a degassed mixture of intermediate 83 (100 mg, 0.06 mmol) and 2-(3-oxo-2,3-dihydro-cyclopenta[*b*]naphthalen-1-ylidene)-malononitrile (62 mg, 0.25 mmol) in chloroform (3 cm^3) is added pyridine (0.36 cm^3, 4.4 mmol) and the solution further degassed. The reaction mixture is stirred for 6 hours and then heated at 50 °C for a further 1 hour. The reaction is cooled to 23 °C, methanol (30 cm^3) added and the solid is collected by filtration which is then washed with methanol (20 cm^3). The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:1 to 2:3) to give compound 32 (74 mg, 57%) as a dark solid. ^1H NMR (400 MHz, $CDCl_3$) 9.19 (2H, s), 8.99 (2H, s), 8.33 (2H, s), 8.16 (2H, s), 8.01 - 8.14 (4H, m), 7.67 - 7.76 (4H, m), 6.97 (4H, d, J 1.7), 6.90 (8H, d, J 1.5), 2.56 (16H, t, J 7.7), 1.48 - 1.65 (16H, m), 1.12 - 1.34 (64H, m), 0.74 - 0.82 (24H, m).

Example 33

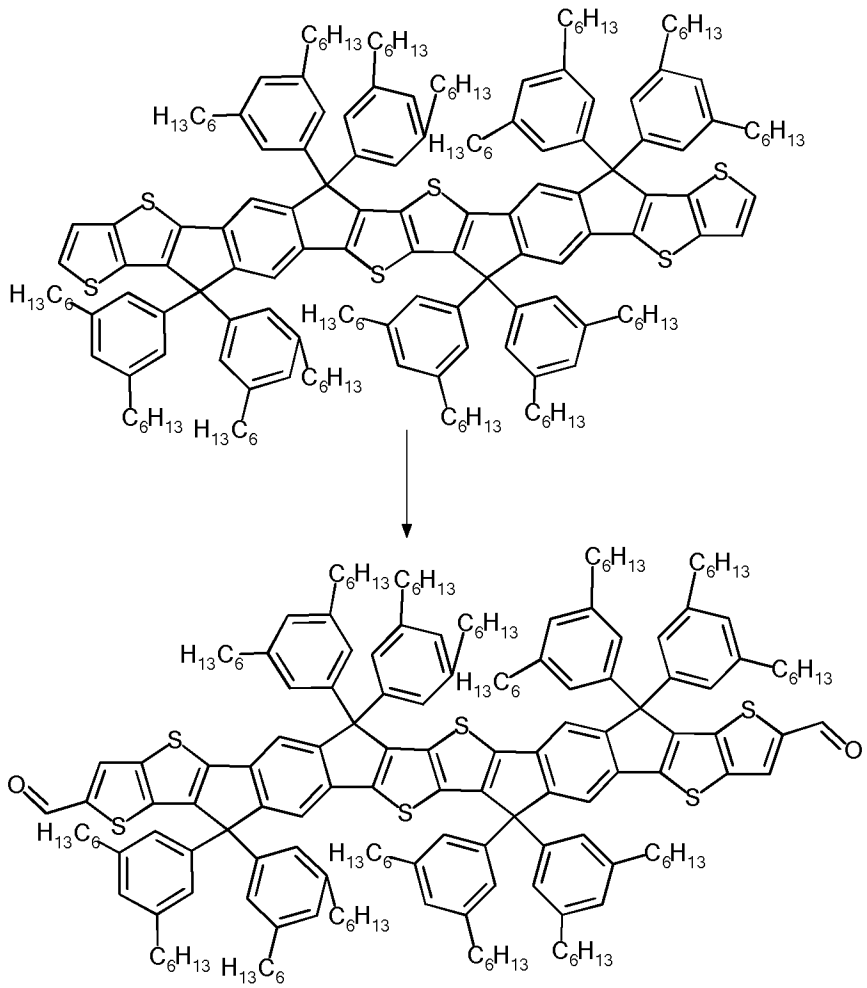
Intermediate 84



To a soluton of 1-bromo-3,5-dihexylbenzene (5.06 g, 14.9 mmol) in anhydrous tetrahydrofuran (50 cm^3) at -78 °C is added *t*-butyllithium (8.8 cm^3, 15 mmol, 1.7 M in pentane) over 20 minutes. The solution is then stirred at -78 °C for 2 hours. 1,1',4,4'-Tetraethyl ester-2,2'-thieno[3,2-b] thiophene-2,5-diylbis[5-[5-(trimethylsilyl)thieno[3,2-b]thien-2-yl]-1,4-benzenedicarboxylic acid (1.50 g, 1.49 mmol) is added and the reaction mixture stirred for 17 hours in the cooling bath allowing the temperature to slowly rise to 23 °C. The soluton is then heated at 50 °C for 1 hour before cooling to 23 °C. Water (10 cm^3) is added and the mixture stirred for 5 minutes. The volatiles are removed *in vacuo* and the residue extracted with ether (2 x 25 cm^3). The combined organics are dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude

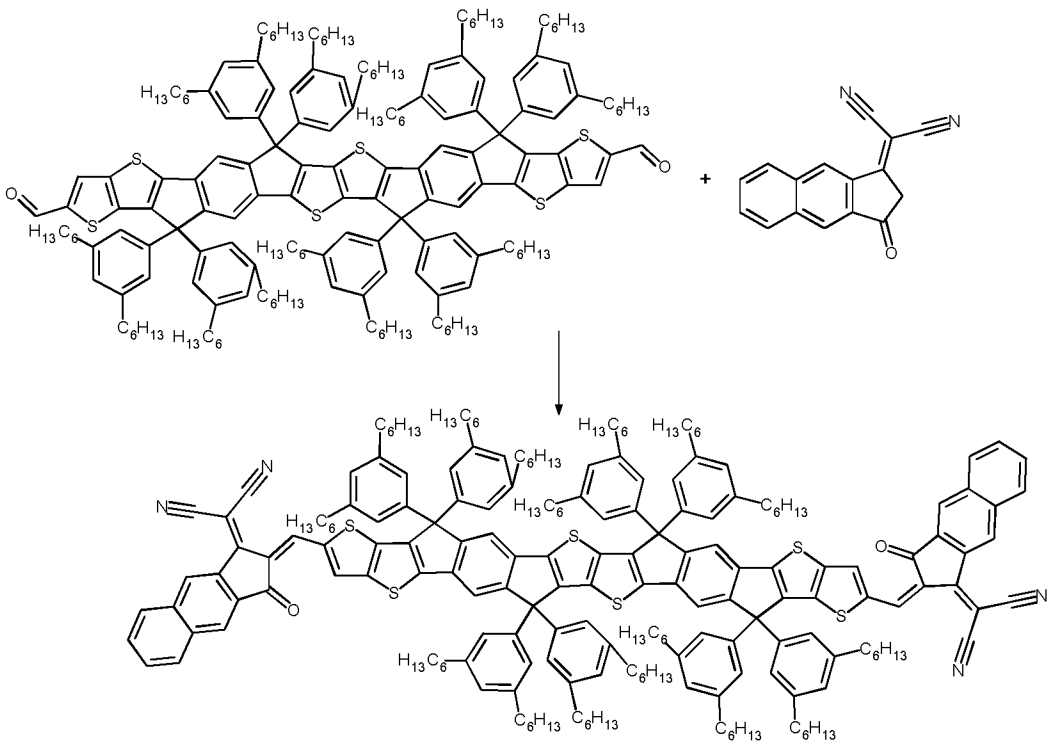
is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:0 to 1:1). The purified material is taken up in anhydrous dichloromethane (50 cm^3) and a solution of *p*-toluenesulfonic acid monohydrate (100 mg, 0.526 mmol) in acetic acid (2 cm^3) is added. The solution is stirred for 1 hour and the volatiles removed *in vacuo*. The residue is triturated in methanol, the solid collected by filtration and washed with methanol (100 cm^3). The solid is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 19:1 to 9:1) to give intermediate 84 (1.86 g, 48%) as a pale orange solid. ^1H NMR (400 MHz, CD_2Cl_2) 7.38 (2H, s), 7.30 (2H, s), 7.17 - 7.22 (4H, m), 6.77 - 6.82 (16H, m), 6.73 - 6.76 (8H, m), 2.29 - 2.43 (32H, m), 1.33 - 1.50 (32H, m), 1.03 - 1.23 (96H, m), 0.67 - 0.77 (24H, m), 0.58 - 0.67 (24H, m).

Intermediate 85



To a solution of intermediate 84 (1.60 g, 0.622 mmol) and anhydrous *N,N*-dimethylformamide (0.5 cm^3) in anhydrous chloroform (50 cm^3) at 0 °C is added phosphorus(V) oxychloride (0.60 cm^3, 6.4 mmol). The mixture is stirred at 0 °C for 30 minutes and then at 23 °C for 1 hour and finally at 60 °C for 24 hours. The reaction mixture allowed to cool to 23 °C and saturated aqueous sodium acetate solution (20 cm^3) added and the mixture sitrred for 30 minutes. The mixture is then concentrated *in vacuo* and the solid collected by filtration. The solid is then washed with water (50 cm^3) and methanol (50 cm^3) to give intermediate 85 (1.60 g, 98%) as a red/orange solid. ^1H NMR (400 MHz, $CDCl_3$) 9.87 (2H, s), 7.92 (2H, s), 7.52 (2H, s), 7.39 (2H, s), 6.86 - 6.92 (16H, m), 6.78 - 6.82 (8H, m), 2.48 (32H, dt, J 10.5, 7.6), 1.45 - 1.63 (32H, m), 1.13 - 1.33 (96H, m), 0.77 - 0.88 (24H, m), 0.69 - 0.77 (24H, m).

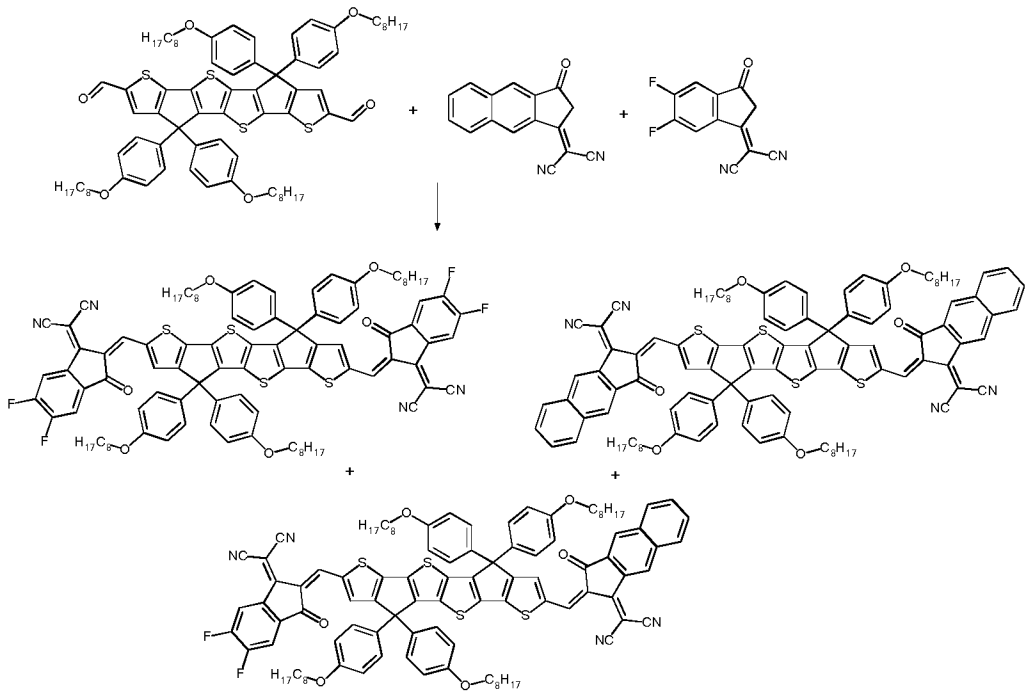
Compound 33



To a solution of intermediate 85 (200 mg, 0.076 mmol) in chloroform (10 cm^3) and ethanol (0.50 cm^3) is added pyridine (0.1 cm^3, 1 mmol) and 2-{3-oxo-1H,2H,3H-cyclopenta[*b*]naphthalen-1-ylidene}propanedinitrile (56 mg, 0.23 mmol). The reaction mixture is then stirred for 12 hours and the volatiles removed *in vacuo*. The residue is triturated in methanol, the solid collected by filtration and washed with methanol until the filtrate runs colourless. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 7:3 to 1:1) to give compound 33 (209 mg, 89%) as a dark green solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.19 (2H, s), 8.97 (2H, s), 8.33 (2H, s), 8.14 - 8.23 (2H, m), 8.07 - 8.13 (2H, m), 7.99 - 8.06 (2H, m), 7.68 - 7.74 (4H, m), 7.54 - 7.60 (2H, m), 7.36 - 7.47 (2H, m), 6.85 - 6.96 (24H, m), 2.45 - 2.56 (32H, m), 1.48 - 1.61 (32H, m), 1.14 - 1.34 (96H, m), 0.69 - 0.80 (48H, m).

Example 34

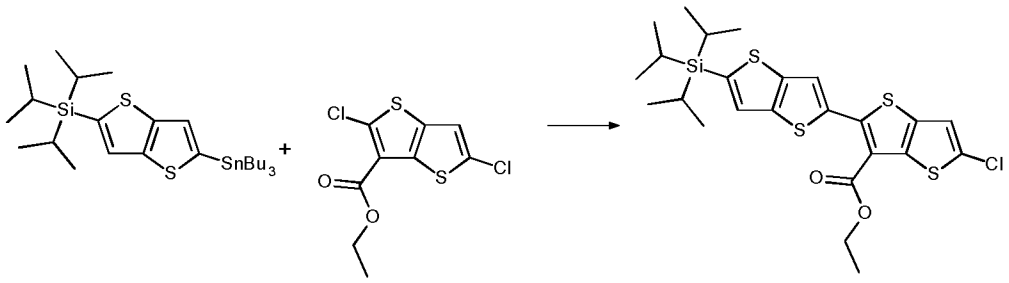
Compound 34



To a degassed solution of intermediate 8 (100 mg, 0.08 mmol), 2-{3-oxo-1H,2H,3H-cyclopenta[*b*]naphthalen-1-ylidene}propanedinitrile (41 mg, 0.17 mmol) and 2-(5,6-difluoro-3-oxo-indan-1-ylidene)-malononitrile (38 mg, 0.17 mmol) in chloroform (2.5 cm^3) is added pyridine (0.47 cm^3, 5.8 mmol) and the mixture degassed for a further 20 minutes. The solution is stirred for 6 hours before addition of methanol (35 cm^3). The solid is collected by filtration and washed with methanol (2 cm^3). The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 3:2 to 1:1) to give compound 34 (56 mg, 41%) as a mixture of 3 compounds. ^{1}H NMR (400 MHz, $CDCl_3$) 9.20 (1H, s), 8.96 (1H, s), 8.86 (1H, s), 8.52 - 8.59 (1H, m), 8.38 (1H, s), 8.04 - 8.12 (2H, m), 6.65 - 7.77 (5H, m), 7.12 - 7.22 (8H, m), 6.82 - 6.92 (8H, m), 3.91 - 3.98 (8H, m), 1.73 - 1.83 (8H, m), 1.40 - 1.50 (8H, m), 1.21 - 1.40 (32H, m), 0.83 - 0.93 (12H, m).

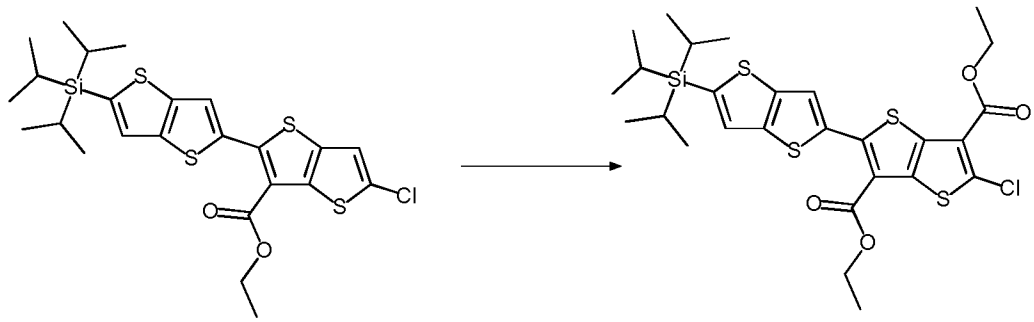
Example 35

Intermediate 86



To a degassed solution of ethyl 2,5-dichlorothieno[3,2-b]thiophene-3-carboxylate (25.0 g, 88.9 mmol) in anhydrous toluene (650 cm^3) at 110 °C is added tris(dibenzylideneacetone)dipalladium (0) (0.81 g, 0.89 mmol), dicyclohexyl-(2,4,6-triisoprpopyl-biphenyl-2-yl-phosphane (0.85 g, 1.8 mmol) and a solution of tris(propan-2-yl)[5-(tributylstannyl)thieno[3,2-b]thiophen-2-yl]silane (41.3 g, 59.2 mmol) in anhydrous toluene (50 cm^3). The reaction mixture is stirred for 2 hours at 120 °C before allowing it to cool to 23 °C. Water (750 cm^3) is added and the organic phase is separated, washed with brine (100 cm^3), dried over anhydrous magnesium sulfate and filtered off. Solvent is then removed *in vacuo* and the residue passed through a silica plug (heptane:dichloromethane; 1:5) to give intermediate 86 (28 g, 87%) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) 7.76 (1H, s), 7.36 (1H, s), 7.12 (1H, s), 4.38 - 4.50 (2H, m), 1.34 - 1.45 (3H, m), 1.10 - 1.22 (21, H).

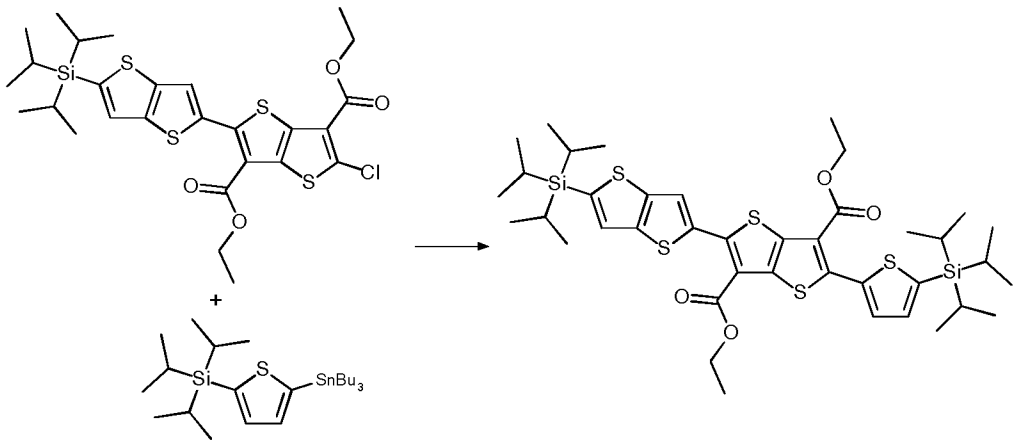
Intermediate 87



To a solution of intermediate 86 (51.2 g, 94.6 mmol) in anhydrous tetrahydrofuran (512 cm^3) at -8 °C is added tetramethylpiperidinylmagnesium chloride lithium chloride complex (142

cm^3, 142 mmol, 1.0 M in tetrahydrofuran/toluene) dropwise over 50 minutes. The reaction mixture is stirred for 1 hour and then ethyl chloroformate (13.6 cm^3, 142 mmol) is added dropwise over 10 minutes. The reaction mixture is left stirring for 16 hours, warming up slowly to 23 °C. Water (250 cm^3) is added followed by dichloromethane (250 cm^3). The aqueous layer is extracted with dichloromethane (2 x 250 cm^3) and then the combined organic layer is washed with brine (100 cm^3), dried over anhydrous magnesium sulfate and filtered off. Removal of the solvent *in vacuo* followed by repeated trituration in heptane gives intermediate 87 (41.8 g, 72%) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) 7.80 (1H, s), 7.36 (1H, s), 4.32 - 4.52 (4H, m), 1.34 - 1.50 (6H, m), 1.10 - 1.22 (21, H).

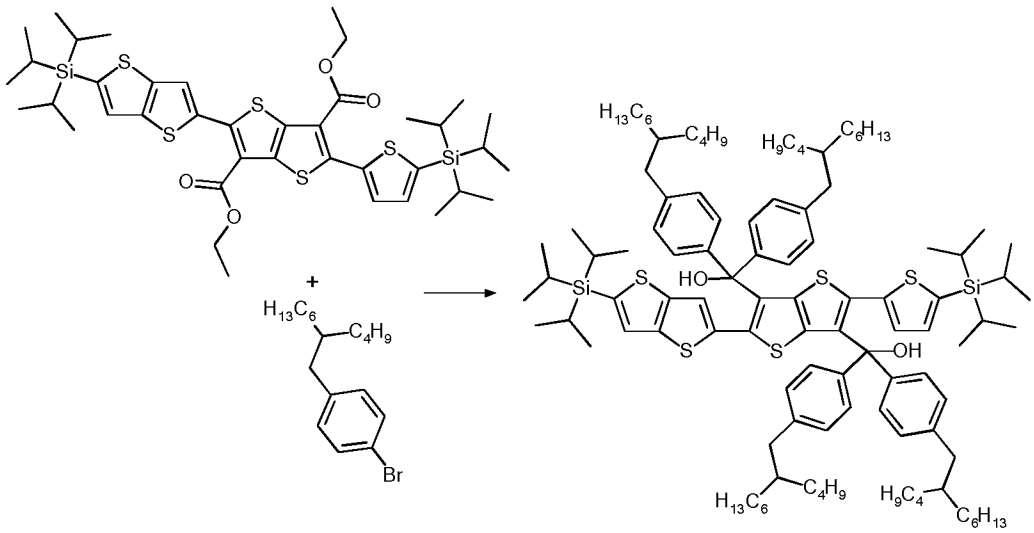
Intermediate 88



To intermediate 87 (48.0 g, 78.3 mmol) and toluene (480 cm^3) is added tris(propan-2-yl)[5-(tributylstannyl)thiophen-2-yl]silane (54.4 g, 82.2 mmol). The mixture is degased for 1 hour before it is heated to 105 °C. Then, tris (dibenzylideneacetone)dipalladium (0) (1.79 g, 1.96 mmol) and dicyclohexyl-(2', 4',6'-triisopropylbiphenyl-2yl)-phosphane (1.87 g, 3.91 mmol) are added and the reaction mixture heated at 120 °C for 2 hours. After cooling down to 23 °C, water (500 cm^3) is added and the aqueous layer is extracted with dichloromethane (3 x 250 cm^3). The combined organic layer is washed with brine (100 cm^3), dried over anhydrous magnesium sulfate and filtered off. The removal of the solvent *in vacuo* followed by column chromatography (heptane:dichloromethane; 7:3) and

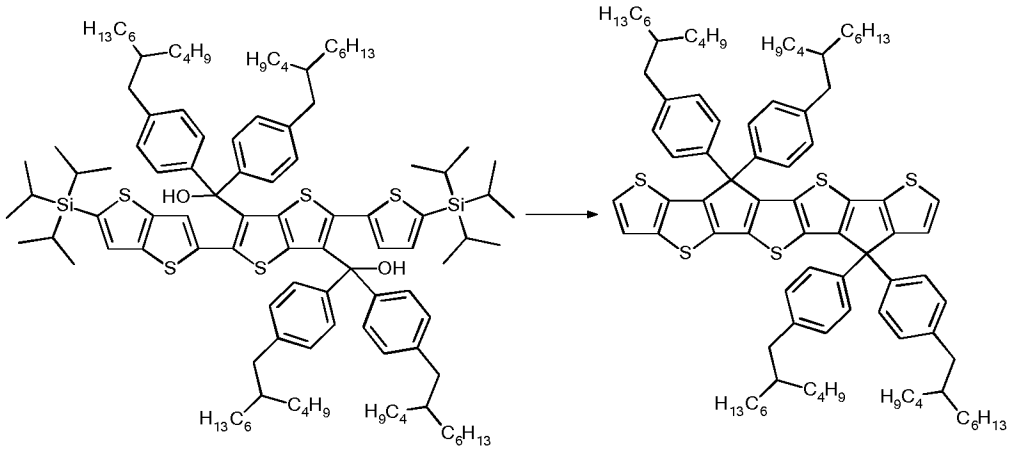
trituation (heptane) gives intermediate 88 (41.5 g, 65%) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) 7.82 (1H, s), 7.68 - 7.72 (1H, d, J 3.5), 7.38 (1H, s), 7.25 - 7.29 (1H, m), 4.35 - 4.48 (4H, m), 1.34 - 1.50 (12H, m), 1.10 - 1.22 (36 H, m).

Intermediate 89



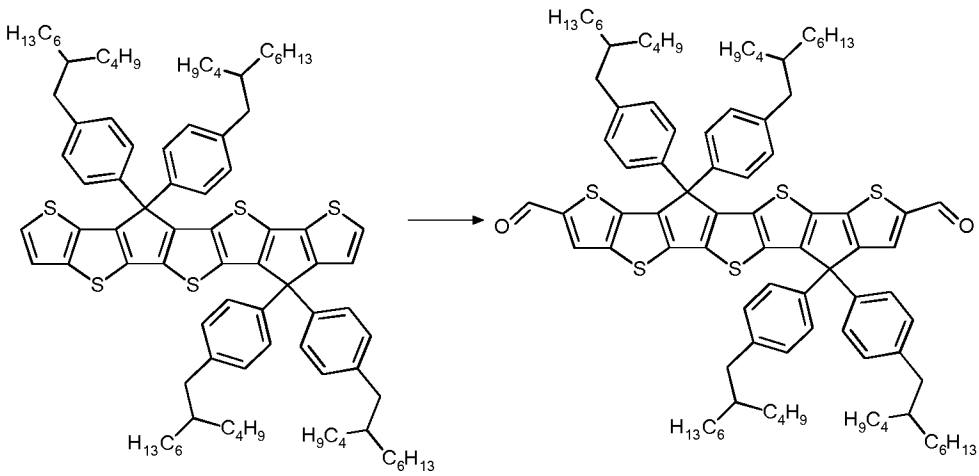
To a solution of 1-bromo-4-(2-butyloctyl)benzene (7.97 g, 0.024 mol) in anhydrous tetrahydrofuran (100 cm^3) at -78 °C is added dropwise *t*-butyllithium (29 cm^3, 0.049 mol, 1.7 M in pentane) over 70 minutes. The reaction mixture is then stirred for 2 hours. Intermediate 88 (4.00 g, 4.90 mmol) is then added and the reaction mixture allowed to warm to 23 °C and stirred for 17 hours. Water (100 cm^3) is added and the mixture stirred for a further 1 hour. Ether (100 cm^3) is added to the mixture, the organic layer separated, and the aqueous layer extracted with ether (2 x 100 cm^3). The combined organics washed with water (2 x 50 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography (40-60 petrol) to give intermediate 89 (7.2 g, 86%) as a pale cream oil. ^{1}H NMR (400 MHz, $CDCl_3$) 7.19 - 7.25 (8H, m), 7.17 (1H, s), 7.06 - 7.12 (8H, m), 6.90 (1H, d, J 3.5), 6.52 - 6.56 (2H, m), 3.54 (1H, s), 3.48 (1H, s), 2.47 - 2.60 (8H, m), 1.53 - 1.69 (4H, m), 0.99 - 1.42 (108H, m), 0.80 - 0.94 (24H, m).

Intermediate 90



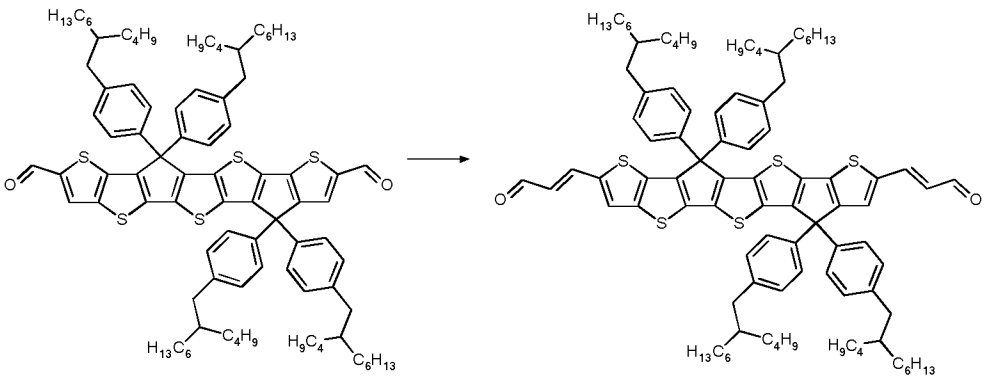
To a solution of 4-methylbenzene-1-sulfonic acid hydrate (4.27 g, 22.4 mmol) in dichloromethane (250 cm^3) at 0 °C is added a solution of intermediate 89 (6.40 g, 3.74 mmol) in dichloromethane (50 cm^3). The reaction mixture is allowed to warm to 23 °C and stirred for 17 hours. The solvent is removed *in vacuo* and the residue passed through a celite plug (pentane). The crude is purified by column chromatography (40-60 petrol) to give intermediate 90 (1.8 g, 35%) as a red oil. ^1H NMR (400 MHz, $CDCl_3$) 7.19 (1H, d, 5.3), 7.15 (1H, d, 5.3), 7.09 (1H, d, 4.9), 7.04 - 7.08 (8H, m), 7.01 (1H, d, 4.9), 6.94 - 7.00 (8H, m), 2.35 - 2.43 (8H, m), 1.42 - 1.55 (4H, m), 1.06 - 1.28 (64H, m), 0.70 - 0.85 (24H, m).

Intermediate 91



To a mixture of *N,N*-dimethylformamide (0.6 cm^3) and chloroform (100 cm^3) at 0 °C is added phosphor(V) oxychloride (1.01 g, 6.61 mmol). The reaction mixture is allowed to warm to 23 °C and stirred for 1 hour before cooling to 0 °C. Intermediate 90 (1.80 g, 1.32 mmol) is added, the reaction mixture allowed to warm to 23 °C and stirred for 72 hours. The reaction mixture is poured onto saturated aqueous sodium acetate (100 cm^3) and stirred for 30 minutes before heating to 50 °C and stirring for an additional 30 minutes. The aqueous layer is extracted with dichloromethane (100 cm^3). The oragnic layer is washed with water (100 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 7:3 to 1:1) to give intermediate 91 (1.8 g, 96%) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.90 (1H, s), 9.82 (1H, s), 7.94 (1H, s), 7.71 (1H, s), 7.04 - 7.18 (16H, m), 2.50 (8H, t, J 6.7), 1.52 - 1.62 (4H, m), 1.16 - 1.33 (64 H, m), 0.79 - 0.91 (24H, m).

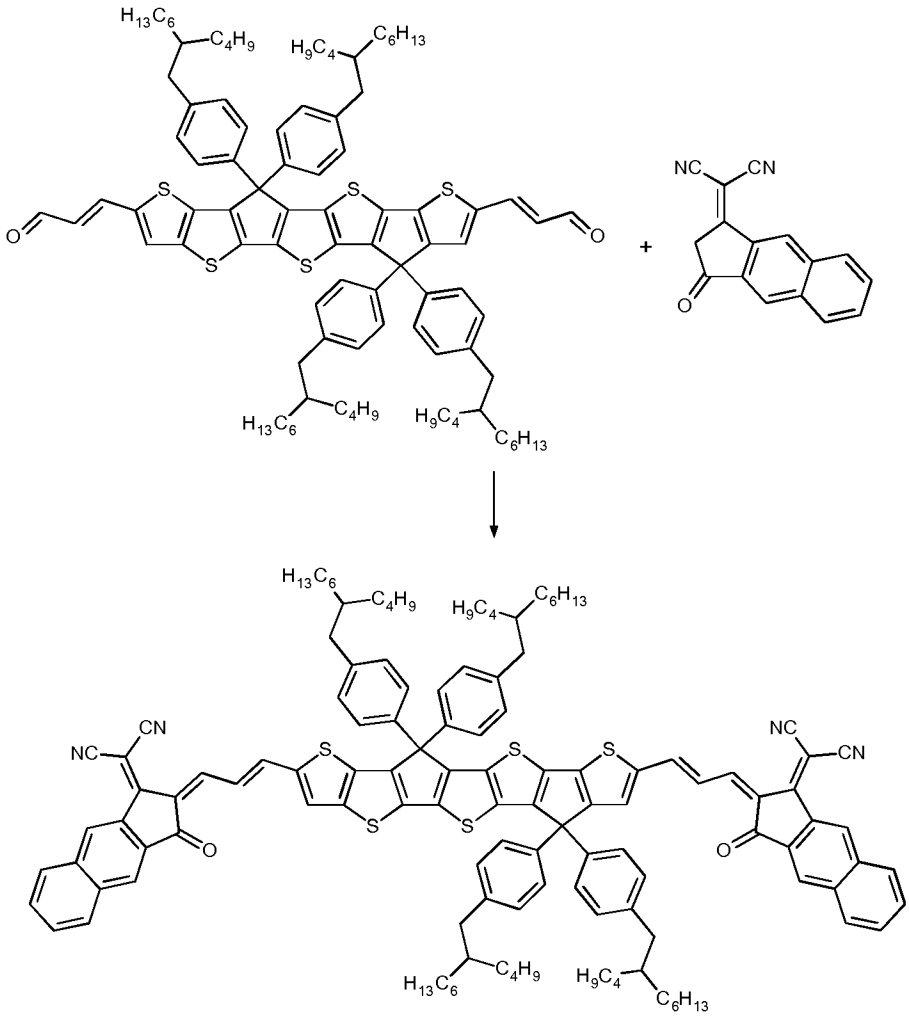
Intermediate 92



To a solution of intermediate 91 (1.40 g, 0.99 mmol) and tributyl(1,3-dioxolan-2-ylmethyl)-phosphonium bromide (802 mg, 2.17 mmol) in tetrahydrofuran (72 cm^3) is added sodium hydride (237 mg, 5.92 mmol, 60% dispersion in mineral oil) and the reaction mixture stirred at 23 °C for 18 hours. The reaction mixture is cooled to 0 °C and aqueous hydrochloric acid (20 cm^3, 10%) added. The reaction mixture is stirred at 0 °C for 40 minutes and then at 23 °C for 2 hours. Water (100 cm^3) is added and the organics extracted with ether (3 x 100 cm^3). The combined organics washed with brine (100 cm^3), dried over anhydrous magnesium sulfate,

filtered and the sovent removed *in vacuo*. The crude is triturated (acetonitrile), the solid collected by filtration and washed with methanol (100 cm^3) to give intermediate 92 (1.2 g, 83%) as a red solid. ^1H NMR (400 MHz, $CDCl_3$) 9.53 (1H, d, J 7.6), 9.50 (1H, d, J 7.6), 7.40 - 7.52 (3H, m), 7.24 (1H, s), 6.96 - 7.10 (8H, m), 6.30 - 6.41 (2H, m), 2.35 - 2.47 (8H, m), 1.43 - 1.55 (4H, m), 1.04 - 1.27 (64H, m), 0.68 - 0.84 (24H, m).

Compound 35

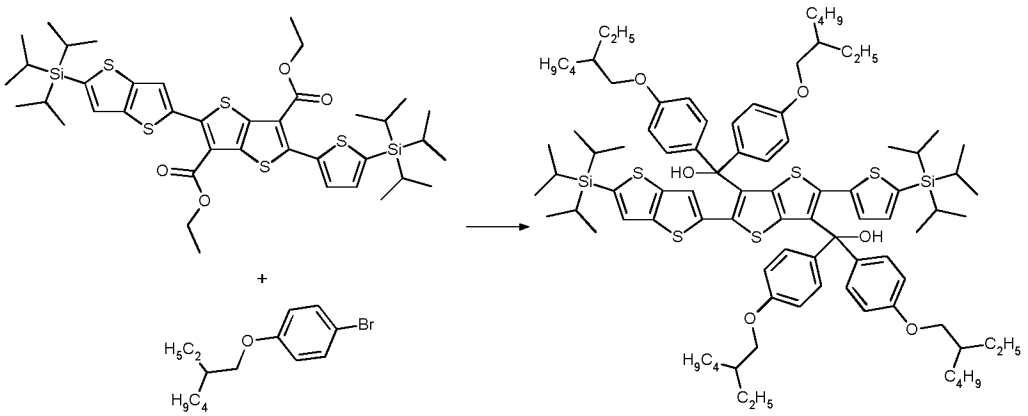


To a solution of intermediate 92 (250 mg, 0.17 mmol) in anhydrous chloroform (10 cm^3) is added 2-{3-oxo-1H,2H,3H-cyclopenta[*b*]naphthalen-1-ylidene}propanedinitrile (125 mg, 0.510 mmol) followed by pyridine (0.1 cm^3, 1 mmol). The resulting solution is stirred for 4 hours at 40 °C. The

mixture is allowed to cool to 23 °C and the volatiles removed *in vacuo*. The residue is triturated in methanol and the solid washed with further methanol until the filtrate runs colourless. The crude is purified by column chromatography (cyclohexane:chloroform; 7:13) to give compound 35 (94 mg, 29%) as a brown/green solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.05 - 9.11 (2H, m), 8.50 - 8.67 (2H, m), 8.38 - 8.47 (2H, m), 8.24 - 8.31 (2H, m), 7.93 - 8.04 (2H, m), 7.57 - 7.68 (4H, m), 7.36 - 7.54 (4H, m), 6.99 - 7.16 (16H, m), 2.37 - 2.51 (8H, m), 1.45 - 1.60 (4H, m), 1.08 - 1.27 (64H, m), 0.69 - 0.82 (24H, m).

Example 36

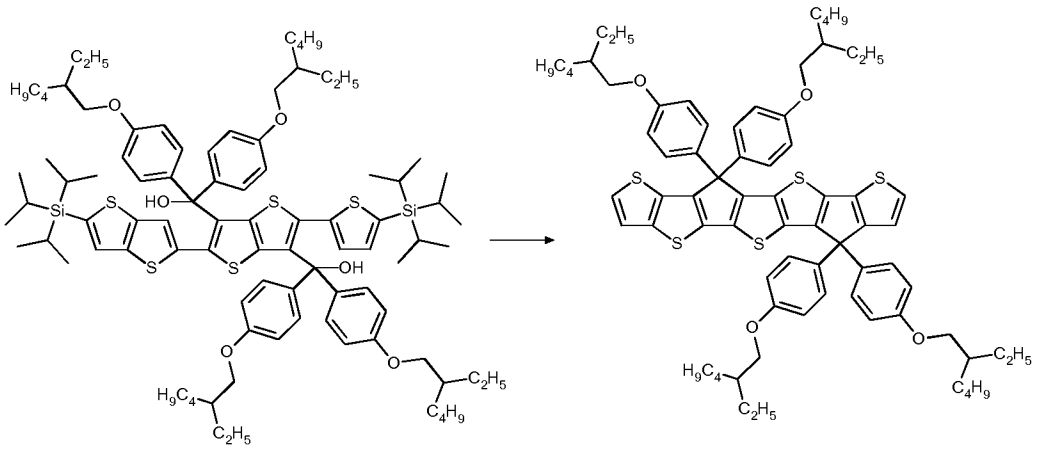
Intermediate 93



To a solution of 1-bromo-4-[(2-ethylhexyl)oxy]benzene (6.98 g, 24.5 mmol) in anhydrous tetrahydrofuran (100 cm^3) at -78 °C is added dropwise *t*-butyllithium (28.8 cm^3, 48.9 mmol, 1.7 M in pentane) over 70 minutes. The reaction mixture is then stirred for 2 hours. Intermediate 88 (4.00 g, 4.89 mmol) is then added as a single portion and the reaction mixture allowed to warm to 23 °C and stirred for 17 hours. Water (100 cm^3) is added and the mixture stirred for a further 1 hour. Ether (100 cm^3) is added and the aqueous layer extracted with ether (2 x 100 cm^3). The combined organic layer is washed with water (2 x 50 cm^3), dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (pentane:dichloromethane; 1:0 to 0:1) to give intermediate 93 (6.70 g,

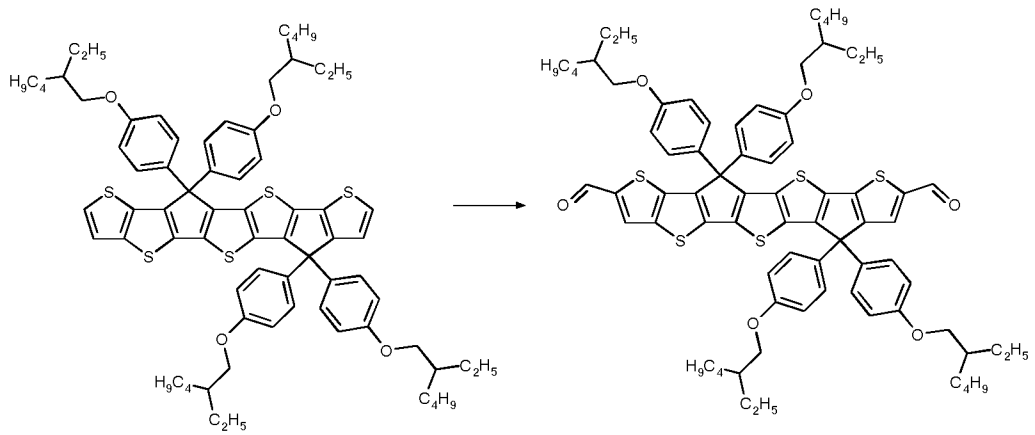
88%) as a yellow oil. ^{1}H NMR (400 MHz, CD_2Cl_2) 7.14 (1H, s), 7.04 - 7.12 (8H, m), 6.86 (1H, d, J 3.5), 6.69 - 6.75 (8H, m), 6.61 (1H, d, J 3.5), 6.54 (1H, m), 3.68 - 3.82 (8H, m), 3.30 (1H, s), 3.25 (1H, s), 1.56 - 1.68 (4H, m), 1.53 - 1.69 (4H, m), 1.11 - 1.42 (38H, m), 0.99 - 1.04 (18H, m), 0.92 - 0.97 (18H, m), 0.77 - 0.86 (24H, m).

Intermediate 94



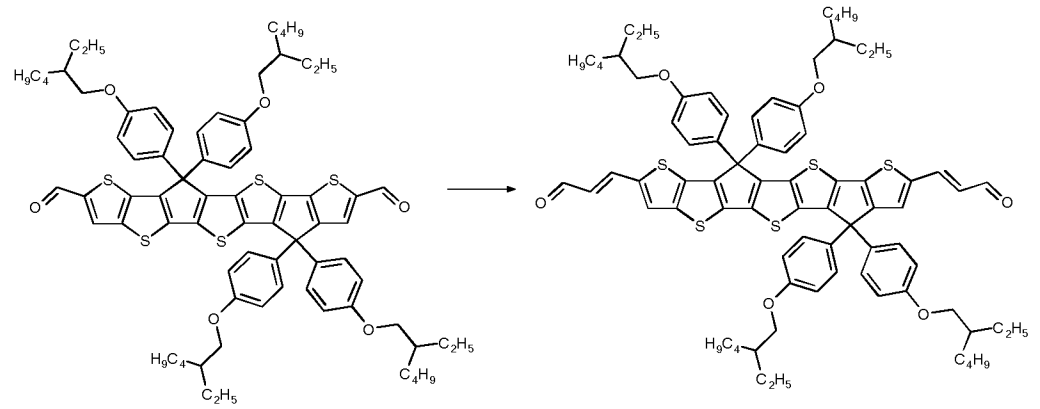
To a stirred solution of intermediate 93 (6.00 g, 3.87) in dichloromethane (50 cm^3) is added a solution of 4-methylbenzene-1-sulfonic acid hydrate (0.10 mg, 0.001 mmol) in acetic acid (1.0 cm^3). The mixture is then stirred at 40 °C for 12 hours. The mixture allowed to cool to 23 °C and the volatiles removed *in vacuo*. The residue taken up in ether (50 cm^3) and the solution washed with saturated aqueous potassium carbonate until the solution is basic. The solution is then dried over potassium carbonate, filtered and the solvent removed *in vacuo*. The residue is taken up in tetrahydrofuran (40 cm^3) and tetrabutylammonium fluoride (10 cm^3, 10 mmol, 1.0 M in tetrahydrofuran) is added. The mixture is stirred for 15 minutes and then the solvent removed *in vacuo*. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 19:1 to 17:3) to give intermediate 94 (2.15 g, 46%) as a pale orage solid. ^{1}H NMR (400 MHz, $CDCl_3$) 7.29 (1H, d, J 5.2), 7.25 (1H, d, J 5.2), 7.16 - 7.21 (9H, m), 7.06 (1H, d, J 4.9), 6.80 - 6.85 (8H, m), 3.76 - 3.83 (8H, m), 1.64 - 1.75 (4H, m), 1.24 - 1.54 (32H, m), 0.84 - 0.96 (24H, m).

Intermediate 95



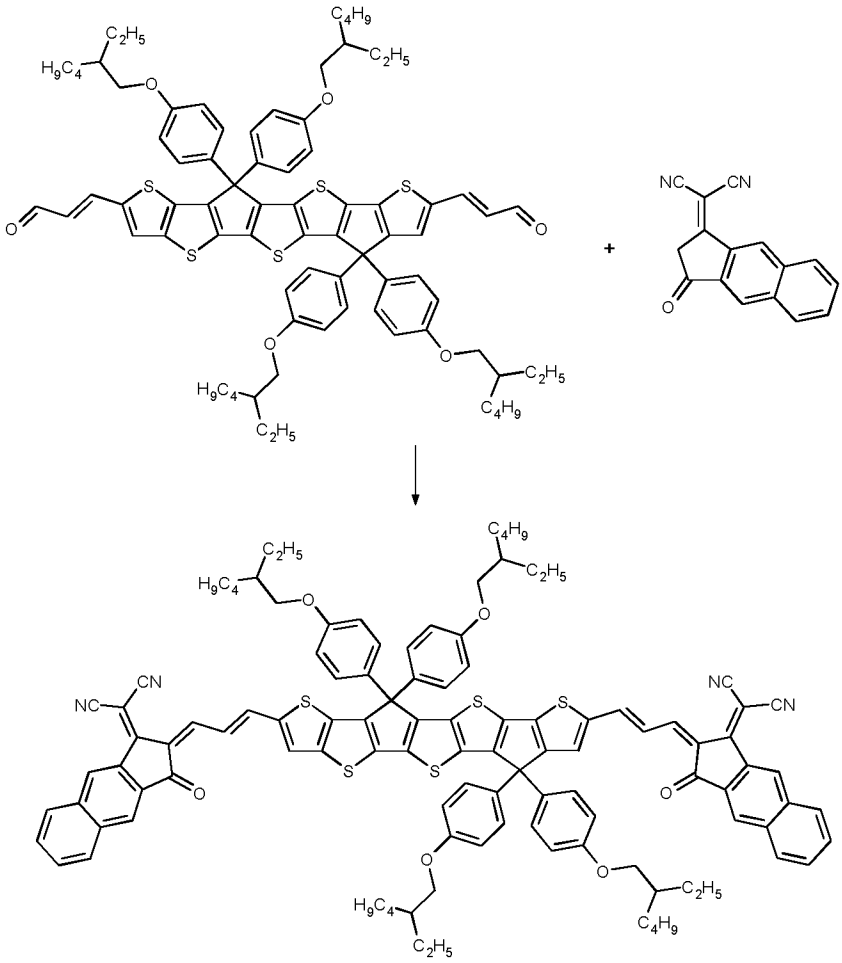
To a solution of intermediate 94 (1.98 g, 1.65 mmol), anhydrous *N,N*-dimethylformamide (0.65 cm^3, 8.4 mmol) and anhydrous chloroform (50 cm^3) at 0 °C is added phosphorus(V) oxychloride (0.80 cm^3, 8.6 mmol). The mixture is then stirred at 0 °C for 30 minutes and at 50 °C for 16 hours before allowing to cool to 23 °C. The volatiles are removed *in vacuo* and tetrahydrofuran (25 cm^3) and water (5 cm^3) are added. The mixture is then stirred for 30 minutes before the volatiles are removed *in vacuo*. The residue is triturated (methanol), the solid collected by filtration and washed with methanol (50 cm^3) to give intermediate 95 (2.0 g, 99%) as an orange solid. ^1H NMR (400 MHz, CD_2Cl_2) 9.91 (1H, s), 9.83 (1H, s), 8.01 (1H, s), 7.72 (1H, s), 7.13 - 7.23 (8H, m), 6.81 - 6.91 (8H, m), 3.78 - 3.88 (8H, m), 1.69 - 1.79 (4H, m), 1.24 - 1.57 (32H, m), 0.85 - 1.00 (24H, m).

Intermediate 96



To a solution of intermediate 95 (1.70 g, 1.35 mmol) and tributyl(1,3-dioxolan-2-ylmethyl)-phosphonium bromide (1.50 g, 4.05 mmol) in anhydrous tetrahydrofuran (25 cm^3) is added sodium hydride (270 mg, 6.76 mmol, 60% dispersion in mineral oil) and the reaction mixture stirred for 4 hours and then heated at 40 °C for 2 hours. The reaction mixture is cooled to 0 °C and aqueous hydrochloric acid (4.6 cm^3, 10%) added. The reaction mixture is stirred at 0 °C for 10 minutes. The volatiles are removed *in vacuo*, the aqueous phase decanted, and the residue washed with water (2 x 10 cm^3). The crude is triturated in methanol, the solid collected by filtration and washed with methanol (50 cm^3). The product is further purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 3:17 to 0:1) followed by recrystallisation (chloroform:acetonitrile) to give intermediate 96 (1.63 g, 92%) as a red solid. ^1H NMR (400 MHz, CD_2Cl_2) 9.50 (1H, d, J 7.6), 9.48 (1H, d, J 7.6), 7.41 - 7.54 (3H, m), 7.22 (1H, s), 7.00 - 7.10 (8H, m), 6.69 - 6.78 (8H, m), 6.26 - 6.39 (2H, m), 3.64 - 3.77 (8H, m), 1.52 - 1.65 (4H, m), 1.11 - 1.45 (32H, m), 0.72 - 0.86 (24H, m).

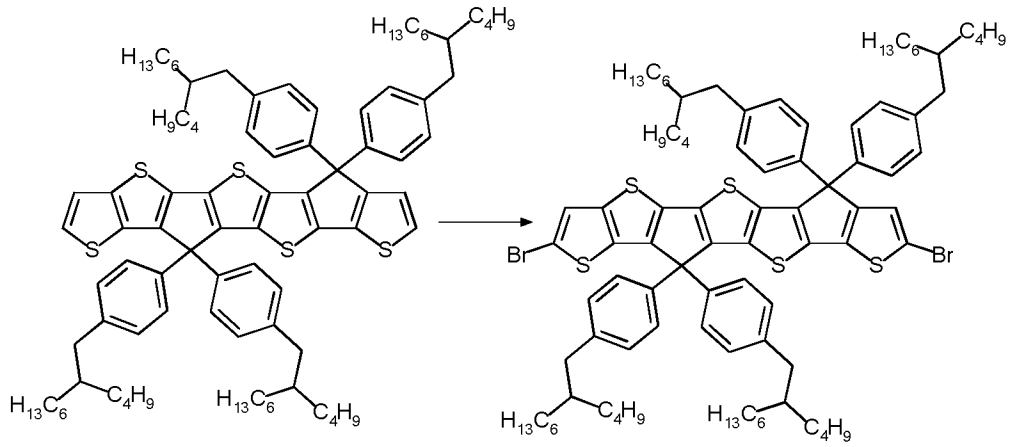
Compound 36



To a solution of intermediate 96 (250 mg, 0.191 mmol) in anhydrous chloroform (10 cm^3) and ethanol (0.5 cm^3) is added 2-{3-oxo-1H,2H,3H-cyclopenta[*b*]naphthalen-1-ylidene}propanedinitrile (140 mg, 0.573 mmol) followed by pyridine (0.1 cm^3, 1.2 mmol). The resulting solution is stirred for 12 hours at 40 °C. The mixture is allowed to cool to 23 °C and the volatiles removed *in vacuo*. The residue is triturated in methanol and the solid washed with further methanol until the filtrate runs colourless. The crude is purified by column chromatography using a graded solvent system (40-60 petrol:chloroform; 3:17 to 1:19) to give compound 36 (138 mg, 41%) as a dark green solid. ^1H NMR (400 MHz, $CDCl_3$) 9.15 - 9.19 (2H, m), 8.61 - 8.74 (2H, m), 8.47 - 8.54 (2H, m), 8.34 - 8.39 (2H, m), 8.03 - 8.11 (4H, m), 7.66 - 7.75 (4H, m), 7.49 - 7.63 (3H, m), 7.42 (1H, s), 7.14 - 7.22 (8H, m), 6.83 - 6.96 (8H, m), 3.77 - 3.90 (8H, m), 1.64 - 1.77 (4H, m), 1.23 - 1.59 (32H, m), 0.83 - 0.97 (24H, m).

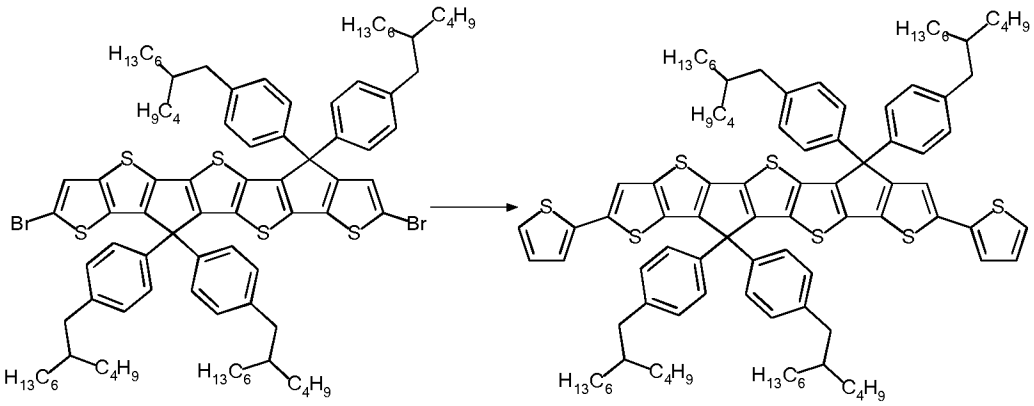
Example 37

Intermediate 97



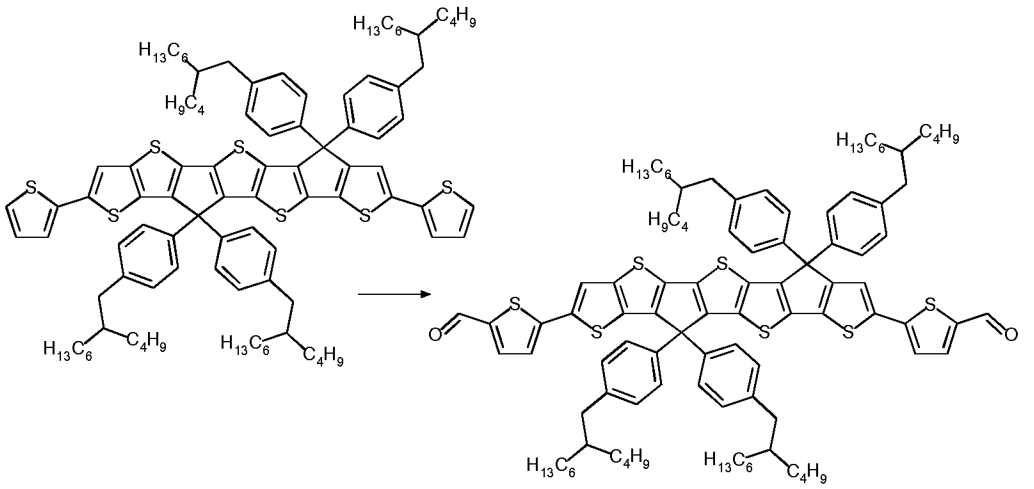
To a solution of intermediate 90 (1.10 g, 0.807 mmol) in tetrahydrofuran (50 cm^3) at 0 °C is added *N*-bromosuccinimide (302 mg, 1.70 mmol) in two portions over 10 minutes. The reaction mixture is then stirred at 23 °C for 17 hours. Dichloromethane (25 cm^3) and water (75 cm^3) are added and the aqueous layer extracted with dichloromethane (25 cm^3). The combined organic extracts are washed with water (50 cm^3) and brine (50 cm^3) before drying over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*, to give intermediate 97 (1.0 g, 82%) as a brown oily solid. ^1H NMR (400 MHz, CD_2Cl_2) 6.89 - 7.31 (18H, m), 2.39 (8H, dd, J 6.9), 1.42 - 1.57 (4H, m), 1.07 - 1.26 (64H, m), 0.67 - 0.83 (24H, m).

Intermediate 98



To a degassed mixture of intermediate 97 (1.00 g, 0.658 mmol), toluene (80 cm^3), tributyl(thiophen-2-yl)stannane (0.46 cm^3, 1.4 mmol) and tris(o-tolyl)phosphine (40 mg, 0.13 mmol) is added tris(dibenzylideneacetone)dipalladium(0) (30 mg, 0.033 mmol). The reaction is then heated at 110 °C for 4 hours before cooling to 23 °C. The volatiles are removed *in vacuo*, ethanol (100 cm^3) added and the mixture stirred for 17 hourrs. The solid is collected by filtration and washed with ethanol (100 cm^3) to give intermediate 98 (905 mg, 90%) as a light yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2) 7.30 (1H, s), 6.88 - 7.21 (23H, m), 2.40 (8H, t, J 7.2), 1.46 (4H, br. s.), 1.01 - 1.26 (64H, m), 0.65 - 0.84 (24H, m).

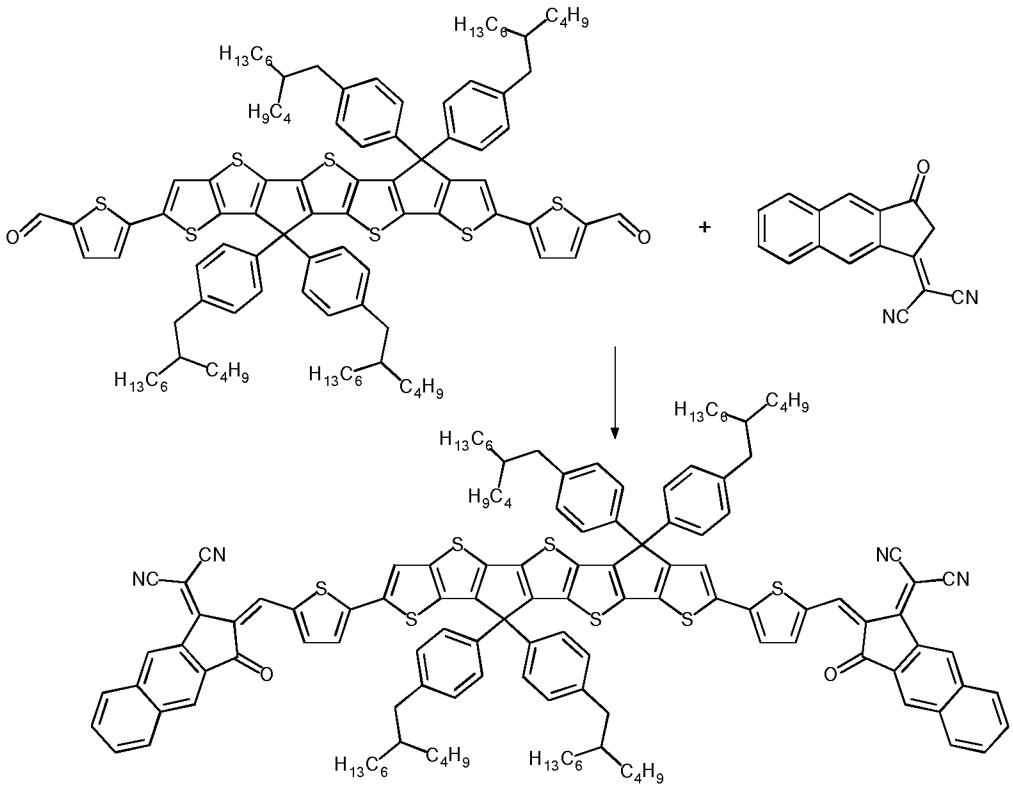
Intermediate 99



To a solution of *N,N*-dimethylformamide (0.4 cm^3) in anhydrous chloroform (80 cm^3) at 0 °C is added dropwise phosphorus(V) oxychloride (0.41 cm^3,

4.4 mmol). After 10 minutes at 0 °C, the reaction mixture is stirred at 23 °C for 30 minutes before intermediate 98 (900 mg, 0.590 mmol) is added. The reaction mixture is stirred for 17 hours at 23 °C and then heated at reflux for 17 hours. After cooling to 23 °C, saturated aqueous sodium sulphate solution (50 cm^3) is then added and the resulting mixture heated at 50 °C for 1 hour. The mixture allowed to cool to 23 °C and the volatiles removed *in vacuo*. The organics are extracted with ether (3 x 100 cm^3) and the combined organics washed with water (2 x 25 cm^3), brine (30 cm^3) and dried over anhydrous magnesium sulfate. Filtration and removal of the solvent *in vacuo* gives the crude product which is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 4:1 to 2:3) to give intermediate 99 (750 mg, 80%) as a dark red solid. ^1H NMR (400 MHz, $CDCl_3$) 9.83 (1H, s), 9.82 (1H, s), 7.65 (1H, d, J 3.7), 7.66 (1H, d J 3.7), 7.58 (1H, s), 7.32 (1H, s), 7.23 (1H, d, J 3.9), 6.95 - 7.17 (17H, m), 2.49 (4H, d, J 6.9), 2.45 (4H, d, J 7.0), 1.47 - 1.63 (4H, m), 1.05 - 1.37 (64H, m), 0.73 - 0.89 (24H, m).

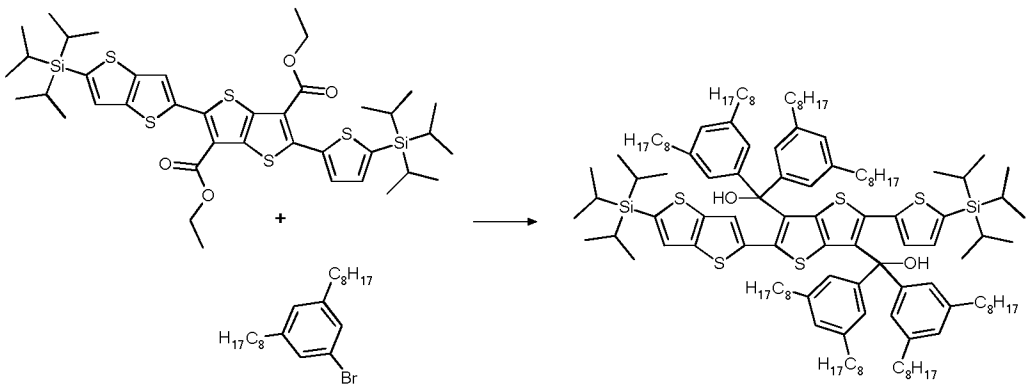
Compound 37



To a degassed solution of intermediate 99 (190 mg, 0.120 mmol) and 2-{3-oxo-1H,2H,3H-cyclopenta[*b*]naphthalen-1-ylidene}propanedinitrile (176 mg, 0.720 mmol) in anhydrous chloroform (40 cm^3) at 10 °C is added pyridine (0.68 cm^3, 8.4 mmol). The resulting solution is then degassed for a further 30 minutes. The reaction mixture is warmed to 23 °C and stirred for 3 hours. Acetonitrile (500 cm^3) is added and the mixture stirred for 1 hour. The solid collected by filtration, washed with acetone (20 cm^3) and ether (20 cm^3) to give compound 37 (224 mg, 92%) as a dark grey solid. ^1H NMR (400 MHz, $CDCl_3$) 9.08 (2H, d, J 18.9), 8.85 (2H, d, J 10.5), 8.33 (2H, s), 7.91 - 8.02 (3H, m), 7.82 (1H, d, J 8.1), 7.67 - 7.73 (2H, m), 7.50 - 7.65 (6H, m), 7.00 - 7.29 (18H, m), 2.48 - 2.61 (8H, m), 1.57 - 1.69 (4H, m), 1.14 - 1.36 (64H, m), 0.78 - 0.92 (24H, m).

Example 38

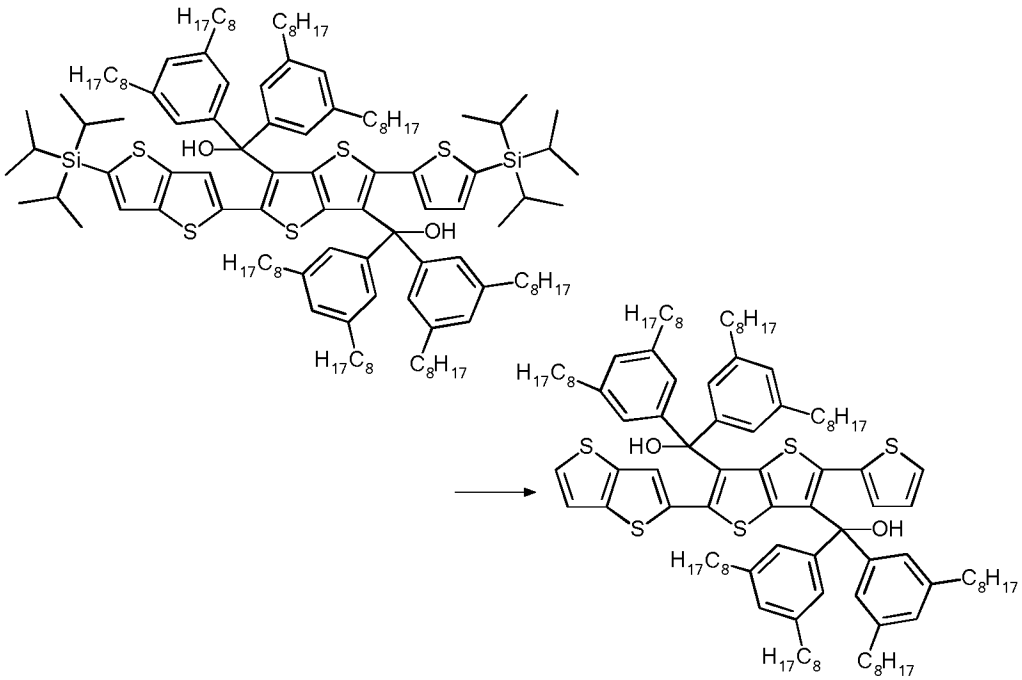
Intermediate 100



To a mixture of intermediate 88 (5.72 g, 15.0 mmol) and anhydrous tetrahydrofuran (40 cm^3) at -78 °C is added *t*-butyllithium (17.6 cm^3, 30.0 mmol, 1.7 M in pentane) over 10 minutes The mixture is then stirred for 2 hours before intermediate 43 (2.45 g, 3.00 mmol) is added, the mixture allowed to warm to 23 °C and stirred for 17 hours. Water (25 cm^3) is added and the mixture stirred for a further 1 hour. The aqueous layer is extracted with ether (2 x 50 cm^3) and the combined organics dried over anhydrous magnesium sulfate. Filtration and removal of the solvent *in vacuo* followed by column chromatography using a graded solvent system (40-60

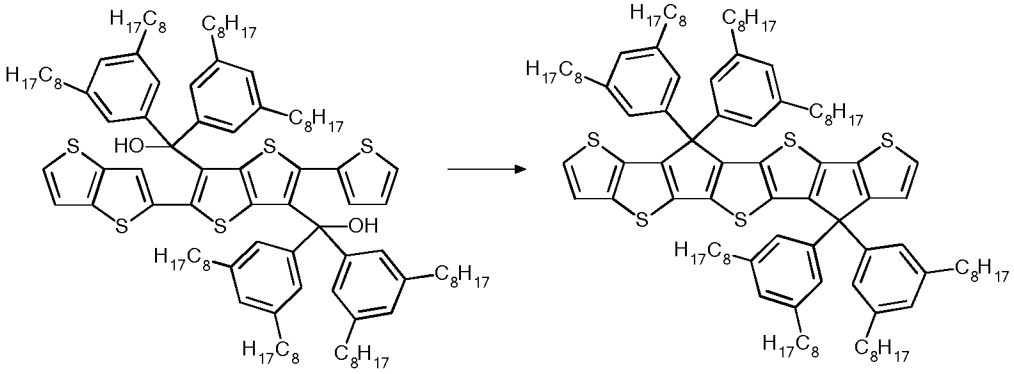
petrol:dichloromethane; 1:0 to 17:3) gives intermediate 100 (3.03 g, 52%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) 7.15 (1H, s), 6.95 - 7.00 (4H, m), 6.89 - 6.94 (6H, m), 6.89 (1H, d, J 3.4), 6.84 - 6.88 (2H, m), 6.62 (1H, d, J 3.4), 6.37 (1H, s), 3.50 (1H, s), 3.34 (1H, s), 2.40 - 2.59 (16H, m), 1.46 - 1.63 (16H, m), 1.19 - 1.42 (86H, m), 1.10 - 1.15 (18H, m), 1.02 - 1.07 (18H, m), 0.81 - 0.95 (24H, m).

Intermediate 101



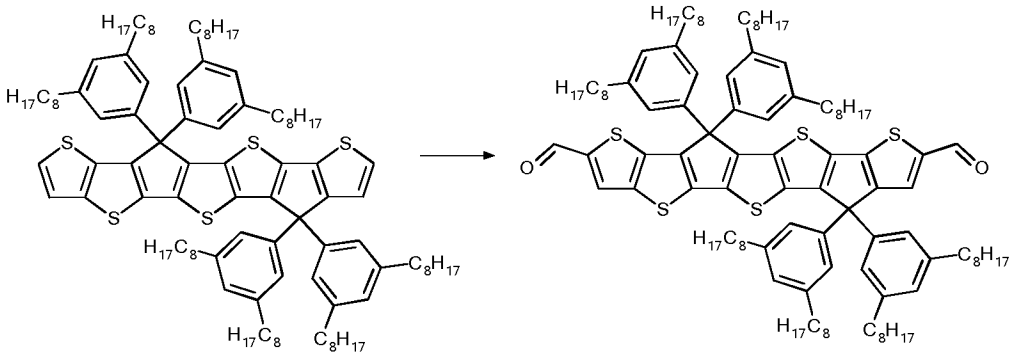
To a solution of intermediate 100 (2.20 g, 1.14 mmol) in tetrahydrofuran (20 cm^3) is added tetrabutylammonium fluoride (2.84 cm^3, 2.84 mmol, 1.0 M in tetrahydrofuran) and the mixture stirred for 2 hours. The volatiles are then removed *in vacuo* and the crude purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 9:1 to 3:1) to give intermediate 101 (1.64 g, 89%) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) 7.25 - 7.27 (1H, m), 7.09 - 7.13 (1H, m), 7.03 - 7.05 (1H, m), 6.86 - 6.94 (12H, m), 6.68 - 6.72 (1H, m), 6.43 - 6.46 (2H, m), 3.34 (1H, s), 3.32 (1H, s), 2.42 - 2.55 (16H, m), 1.46 - 1.58 (16H, m), 1.14 - 1.34 (80H, m), 0.82 - 0.92 (24H, m).

Intermediate 102



To a solution of intermediate 101 (910 mg, 0.560 mmol) in cyclohexane (50 cm^3) is added Amberlyst 15 strong acid (3.5 g). The mixture is then heated at 50 °C for 25 minutes and the solution filtered. The volatiles are removed from the filtrate *in vacuo* and the residue purified by column chromatography (40-60 petrol) to give intermediate 102 (600 mg, 67%) as an orange oil. ^1H NMR (400 MHz, CD_2Cl_2) 7.21 (1H, d, 5.2), 7.17 (1H, d, 5.2), 7.13 (1H, d, 4.9), 6.98 (1H, d, 4.9), 6.78 - 6.82 (4H, m), 6.72 - 6.76 (8H, m), 2.33 - 2.44 (16H, m), 1.35 - 1.50 (16H, m), 1.04 - 1.27 (80H, m), 0.71 - 0.84 (24H, m).

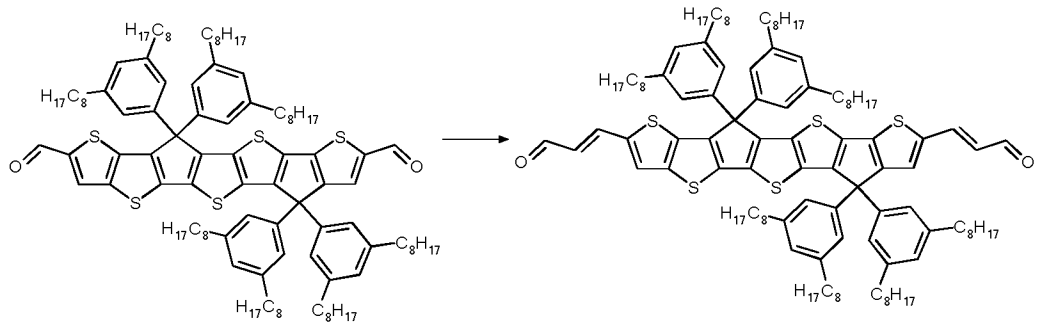
Intermediate 103



To a solution of intermediate 102 (590 mg, 0.372 mmol), anhydrous *N,N*-dimethylformamide (0.25 cm^3, 3.2 mmol) and anhydrous chloroform (20 cm^3) at 0 °C is added phosphorus(V) oxychloride (0.25 cm^3, 2.7 mmol). The mixture is then stirred at 0 °C for 30 minutes and at 60 °C for 16 hours

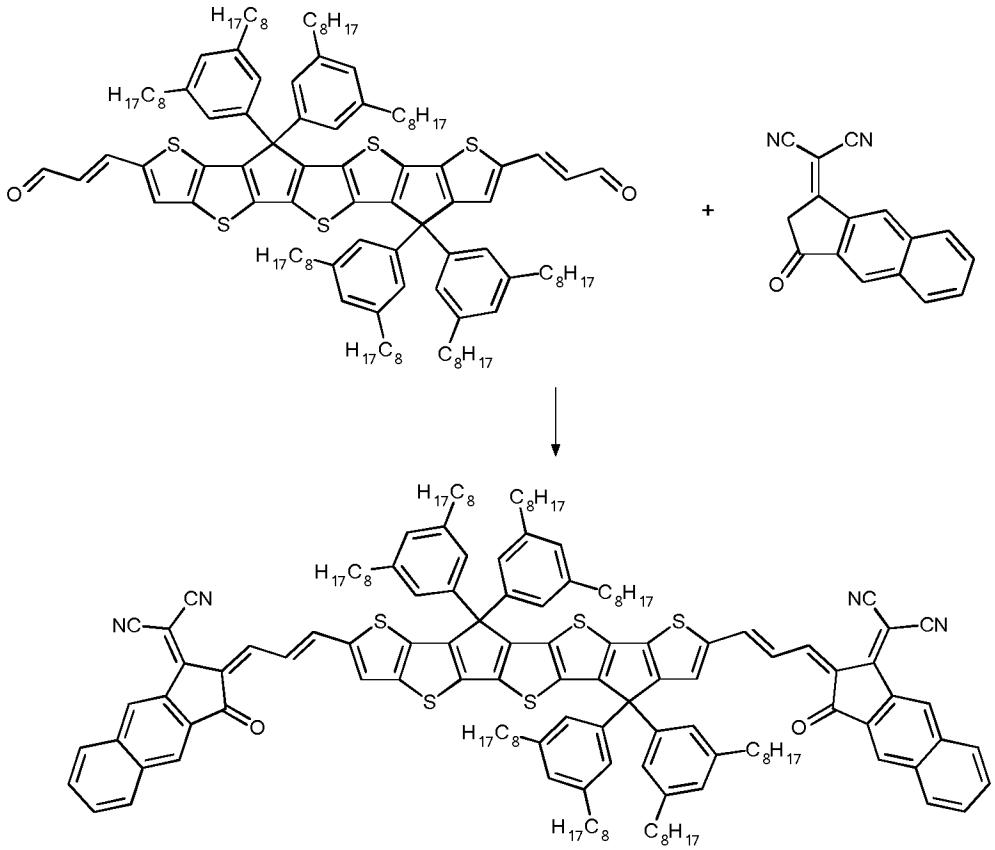
before allowing to cool to 23 °C. The volatiles are removed *in vacuo* and tetrahydrofuran (10 cm^3) and water (2 cm^3) are added. The mixture is then stirred for 15 minutes before the volatiles are removed *in vacuo*. The aqueous is decanted and the residue purified by column chromatography using a graded solvent system (cyclohexane:dichloromethane; 3:1 to 13:7) to give intermediate 103 (590 mg, 97%) as an orange solid. ^{1}H NMR (400 MHz, CD_2Cl_2) 9.78 (1H, s), 9.71 (1H, s), 7.88 (1H, s), 7.58 (1H, s), 6.84 (4H, s), 6.74 (4H, s), 6.70 (4H, s), 2.32 - 2.47 (16H, m), 1.30 - 1.50 (16H, m), 1.04 - 1.25 (80H, m), 0.67 - 0.83 (24H, m).

Intermediate 104



To a solution of intermediate 103 (630 mg, 0.384 mmol) and tributyl(1,3-dioxolan-2-ylmethyl)-phosphonium bromide (425 mg, 1.15 mmol) in anhydrous tetrahydrofuran (10 cm^3) is added sodium hydride (77 mg, 1.9 mmol, 60% dispersion in mineral oil) and the reaction mixture stirred for 4 hours. The reaction mixture is cooled to 0 °C and aqueous hydrochloric acid (1.8 cm^3, 10%) added. The reaction mixture is stirred at 0 °C for 10 minutes. The volatiles are removed *in vacuo*, the aqueous phase decanted, and the residue washed with water (2 x 10 cm^3). The crude is then purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 11:9 to 2:3) to give intermediate 104 (460 mg, 71%) as an orange solid. ^{1}H NMR (400 MHz, CD_2Cl_2) 9.50 (1H, d, J 7.6), 9.47 (1H, d, J 7.6), 7.42 - 7.54 (3H, m), 7.21 (1H, s), 6.81 - 6.85 (4H, m), 6.69 - 6.75 (8H, m), 6.25 - 6.37 (2H, m), 2.34 - 2.45 (16H, m), 1.37 - 1.49 (16H, m), 1.05 - 1.23 (80H, m), 0.69 - 0.81 (24H, m).

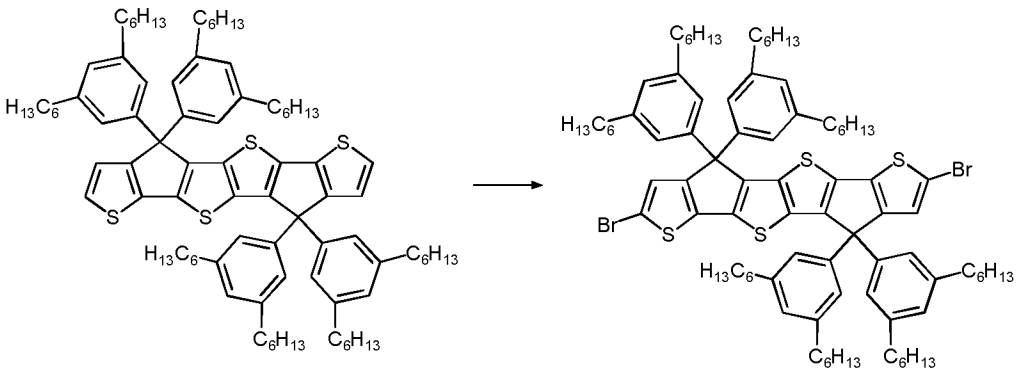
Compound 38



To a solution of intermediate 104 (139 mg, 0.082 mmol) in chloroform (10 cm^3) is added pyridine (0.1 cm^3, 1 mmol) and 2-{3-oxo-1H,2H,3H-cyclopenta[*b*]naphthalen-1-ylidene}propanedinitrile (59.0 mg, 0.241 mmol). The solution is stirred for 12 hours and then heated at 40 °C for 3 hours and then allowed to cool to 23 °C. The volatiles are removed *in vacuo* and the residue triturated with methanol. The solid is collected by filtration and washed with methanol until the filtrate is colourless. The crude is then further purified by column chromatography (chloroform) to give compound 38 (133 mg, 76%) as a green solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.06 - 9.13 (2H, m), 8.56 - 8.70 (2H, m), 8.39 - 8.47 (2H, m), 8.23 - 8.29 (2H, m), 7.92 - 8.07 (4H, m), 7.58 - 7.66 (4H, m), 7.55 (1H, s), 7.43 - 7.53 (2H, m), 7.30 (1H, s), 6.71 - 6.93 (12H, m), 2.39 - 2.51 (16H, m), 1.40 - 1.56 (16H, m), 1.00 - 1.28 (80H, m), 0.65 - 0.80 (24H, m).

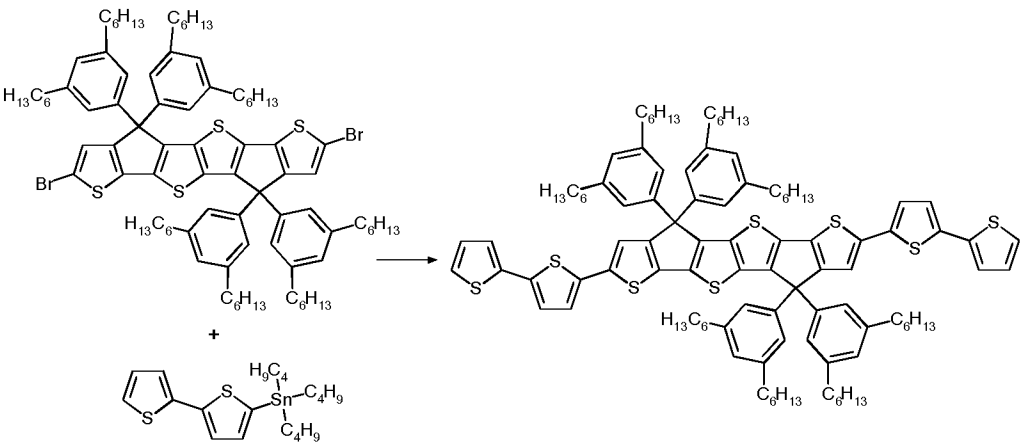
Example 39

Intermediate 105



To a stirred solution of intermediate 1 (620 mg, 0.475 mmol) in tetrahydrofuran (30 cm^3), in the dark, is added *N*-bromosuccinimide (175 mg, 0.973 mmol). The reaction mixture is stirred for 15 hours and the solvent removed *in vacuo*. The crude is purified by column chromatography (cyclohexane) to give intermediate 105 (690 mg, 99%) as an orange-yellow solid. ^1H NMR (400 MHz, CD_2Cl_2) 7.09 (2H, s), 6.92 - 6.94 (4H, m), 6.82 (8H, d, J 1.6), 2.51 (16H, t, J 7.7), 1.50 - 1.61 (16H, m), 1.22 - 1.36 (48H, m), 0.84 - 0.93 (24H, m).

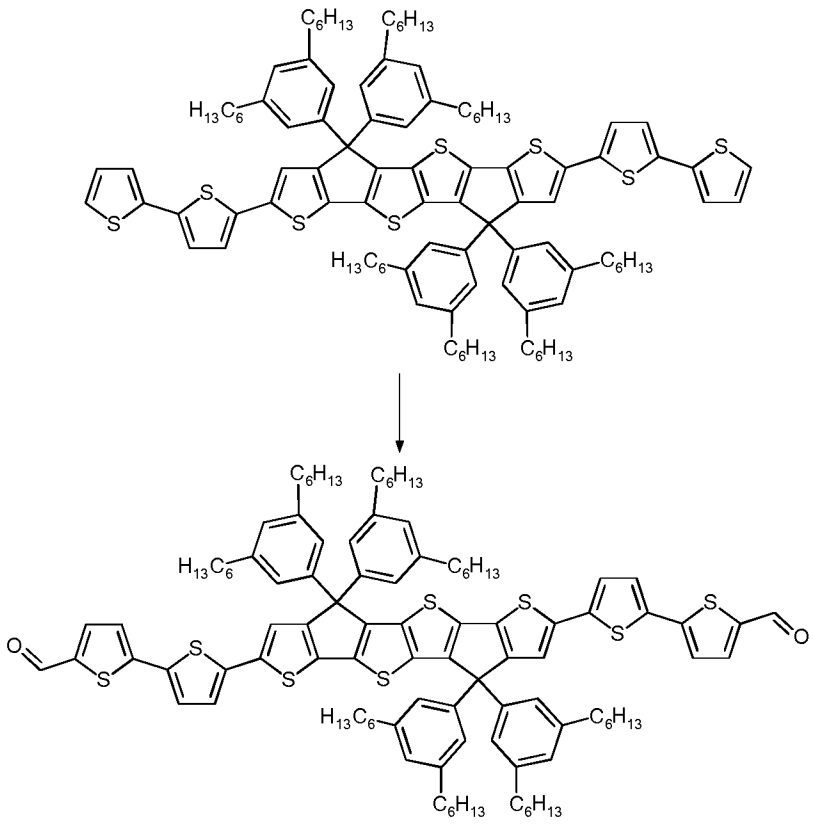
Intermediate 106



A mixture of intermediate 105 (900 mg, 0.615 mmol), {[2,2'-bithiophen]-5-yl}tributylstannane (729 mg, 1.54 mmol), tris(dibenzylideneacetone)dipalladium(0) (11 mg, 0.012 mmol), tris(*o*-

tolyl)phosphine (15 mg, 0.049 mmol), anhydrous toluene (25 cm^3) and anhydrous *N,N*-dimethylformamide (5 cm^3) is stirred at 110 °C for 90 minutes. The mixture allowed to cool to 23 °C and the volatiles removed *in vacuo*. Methanol (20 cm^3) is added, the solid collected by filtration and washed with methanol (20 cm^3). The crude is purified by column chromatography using a graded solvent system (cyclohexane:chloroform; 49:1 to 19:1) to give intermediate 106 (990 mg, 99%) as a dark-red solid. ^{1}H NMR (400 MHz, CD_2Cl_2) 7.16 (2H, dd, J 5.1, 1.2), 7.09 (2H, dd, J 3.6, 1.2), 7.07 (2H, s), 6.97 - 7.02 (4H, m), 6.94 (2H, dd, J 5.1, 3.6), 6.80 - 6.84 (4H, m), 6.76 - 6.79 (8H, m), 2.41 (16H, t, J 7.7), 1.39 - 1.51 (16H, m), 1.10 - 1.25 (48H, m), 0.71 - 0.80 (24H, m).

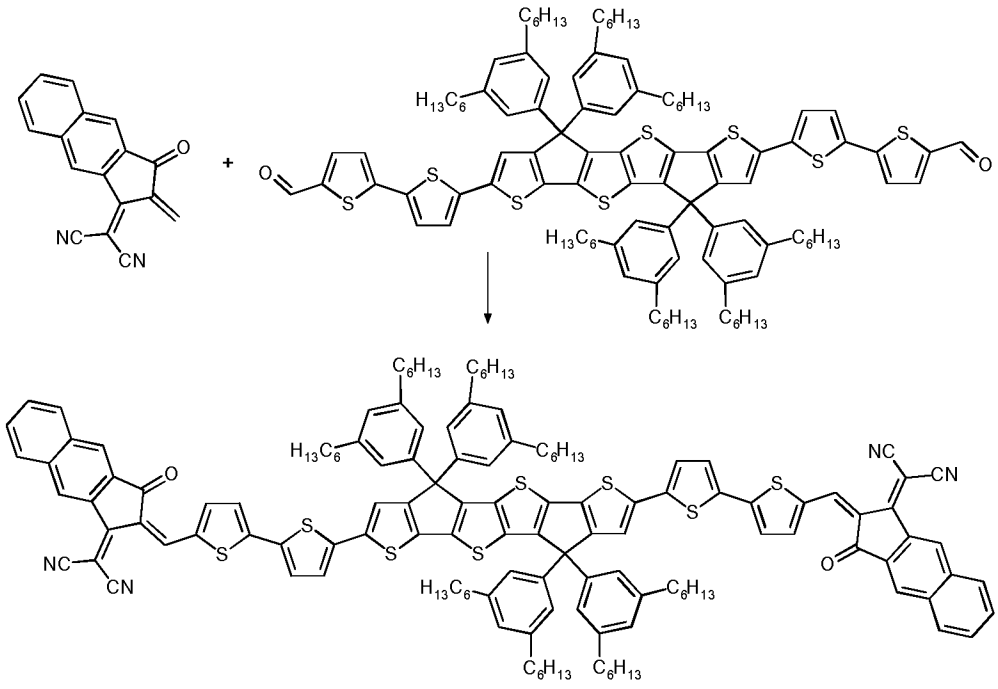
Intermediate 107



To a solution of intermediate 106 (990 mg, 0.606 mmol) and anhydrous *N,N*-dimethylformamide (0.30 cm^3, 3.9 mmol) in anhydrous chloroform (30 cm^3) at 0 °C is added phosphorus(V) oxychloride (0.35 cm^3, 3.8 mmol). The mixture is then stirred at 0 °C for 30 minutes and at 60 °C for 16

hours. The mixture is cooled to 23 °C and the volatiles removed *in vacuo*. Tetrahydrofuran (25 cm^3) and water (5 cm^3) are added and the mixture sitrred for 30 minutes. The volatiles are removed *in vacuo* and the residue triturated with acetonitrile. The solid is collected by filtration and washed with acetonitrile (50 cm^3). The crude is purified by column chromatography using a graded solvent system (40-60 petrol:dichloromethane; 1:1 to 7:13), followed by trituration in acetonitrile. The solid is collected by filtration and washed with acetonitrile (50 cm^3) to give intermediate 107 (610 mg, 60%) as a red/brown solid. ^1H NMR (400 MHz, CD_2Cl_2) 9.75 (2H, s), 7.60 (2H, d, J 4.0), 7.21 (2H, d, J 3.9), 7.16 (2H, d, J 3.9), 7.13 (2H, s), 7.04 (2H, d, J 4.0), 6.82 - 6.84 (4H, m), 6.76 - 6.79 (8H, m), 2.42 (16H, t, J 7.6), 1.40 - 1.52 (16H, m), 1.10 - 1.25 (48H, m), 0.70 - 0.81 (24H, m).

Compound 39

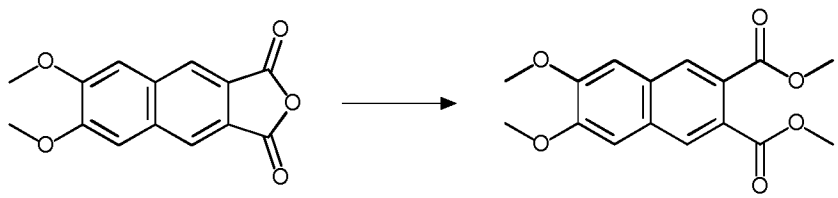


To a solution of intermediate 107 (200 mg, 0.118 mmol) in chloroform (10 cm^3) is added pyridine (0.1 cm^3, 1 mmol) and 2-{3-oxo-1H,2H,3H-cyclopenta[*b*]naphthalen-1-ylidene}propanedinitrile (86.7 mg, 0.355 mmol). The reaction mixture is stirred for 4 hours and then heated at 40 °C for 12 hours. The mixture allowed to cool to 23 °C, the volatiles removed *in*

vacuo and the residue triturated in methanol. The solid is collected by filtration, washed with methanol until the eluent is colourless. The crude is then purified by column chromatography (chloroform) to give compound 39 (230 mg, 91%) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) 9.07 (2H, s), 8.81 (2H, s), 8.29 (2H, s), 7.91 - 7.98 (4H, m), 7.67 - 7.73 (2H, m), 7.53 - 7.60 (4H, m), 7.33 - 7.41 (2H, m), 7.09 - 7.23 (6H, m), 6.83 - 6.88 (4H, m), 6.75 - 6.82 (8H, m), 2.46 (16H, t, J 7.6), 1.42 - 1.55 (16H, m), 1.13 - 1.28 (48H, m), 0.72 - 0.83 (24H, m).

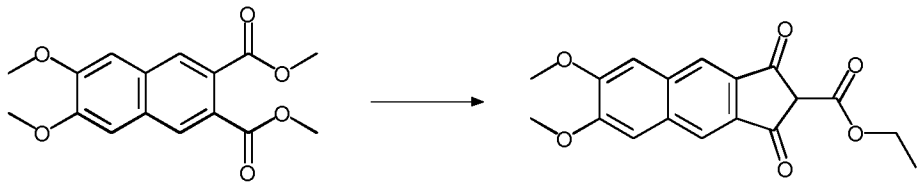
Example 39

Intermediate 108



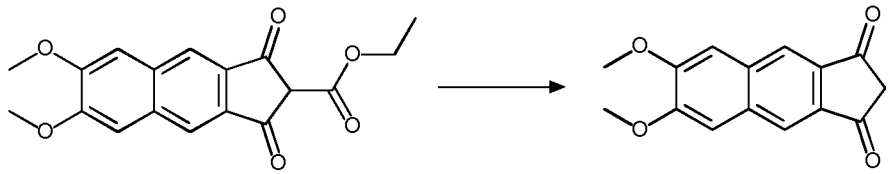
Sulphuric acid (2 cm^3) is added to a solution of 6,7-dimethoxy-naphtho[2, 3-c]furan-1,3-dione (40.0 g, 155 mmol) in methanol (200 cm^3). The mixture is stirred at 70 °C for 12 hours before cooling to 23 °C and the volatiles removed *in vacuo*. Water (200 cm^3) is added and the organics extracted with ethyl acetate (3 x 200 cm^3). The combined organic layer is washed with saturated aqueous sodium carbonate solution (2 x 200 cm^3) and brine (200 cm^3), dried over anhydrous sodium sulphate, filtered and concentrated *in vacuo*. The residue is purified by column chromatography using a graded solvent system (40-60 petrol:ethyl actetate; 1:0 to 0:1) to give intermediate 108 (28.0 g, 59%) as a yellow solid. ^{1}HNMR (400 MHz, $CDCl_3$) 8.08 (2H, s), 7.17 (2H, s), 4.02 (6H, s), 3.95 (6H, s).

Intermediate 109



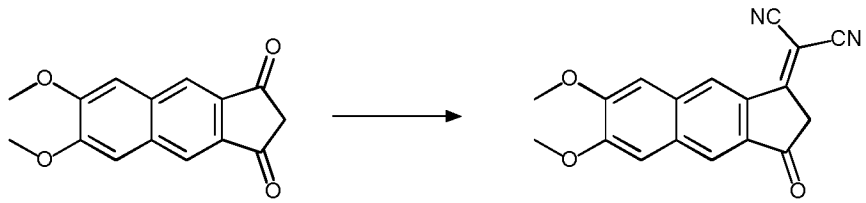
Intermediate 108 (20.0 g, 65.7 mmol) is added to a solution of sodium hydride (21.0 g, 525 mmol, 60% dispersion in mineral oil) in anhydrous ethyl acetate (51 cm^3) and anhydrous tetrahydrofuran (400 cm^3), and the mixture stirred at reflux for 12 hours. Upon cooling to 23 °C the mixture is concentrated *in vacuo* to give intermediate 109 (25 g) as a yellow solid, which is used without further purification.

Intermediate 110



Intermediate 109 (25 g, 76 mmol) is dissolved in hydrochloric acid (333 cm^3, 2.0 M) and he mixture stirred at 80 °C for 1 hour. The reaction mixture is filtered, and resulting solid, is triturated with ethyl acetate (30 cm^3). Filtration gives intermediate 110 (10.0 g) as a yellow solid, which is used without further purification.

Intermediate 111



Sodium acetate (4.80 g, 58.5 mmol) and malononitrile (4.90 g, 74.1 mmol) are added to a solution of intermediate 110 (10.0 g, 39.0 mmol) in ethanol (100 cm^3). The mixture is stirred at 25 °C for 12 hours before the reaction

mixture is acidified (pH = 1-2) by addition of hydrochloric acid (1 M). Water (100 cm^3) is added and the organics extracted with dichloromethane (3 x 100 cm^3). The combined organic layer is washed with water (2 x 100 cm^3) and brine (100 cm^3), dried over anhydrous sodium sulphate, filtered and concentrated *in vacuo*. The crude is purified by column chromatography using a graded solvent system (dichloromethane:methanol; 1:0 to 0:1) to give intermediate 111 (3.80 g) as a brown solid. ^1H NMR (400 MHz, $CDCl_3$) 8.98 (1H, s), 8.30 (1H, s), 7.36 (1H, s), 7.31 (1H, s), 4.09 (6H, s), 3.80 (2H, s).

Use Example 1

Current-voltage characteristics are measured using a Keithley 2400 SMU while the solar cells are illuminated by a Newport Solar Simulator at 100 $mW \cdot cm^{-2}$ white light. The solar simulator is equipped with AM1.5G filters. The illumination intensity is calibrated using a Si photodiode. All the device preparations and characterizations are carried out in a dry-nitrogen atmosphere.

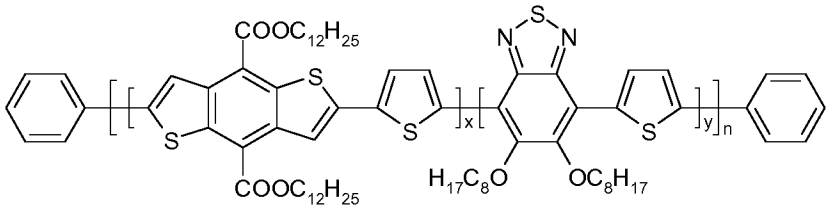
Power conversion efficiency is calculated using the following expression

$$\eta = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}}$$

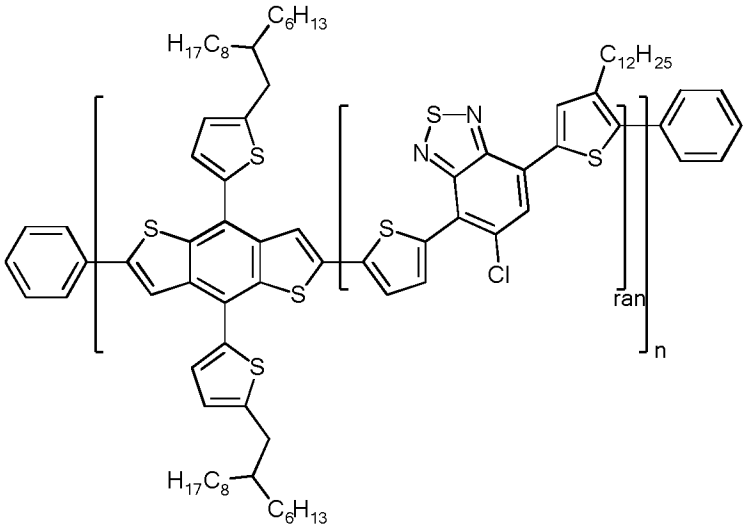
where FF is defined as

$$FF = \frac{V_{\max} \times J_{\max}}{V_{oc} \times J_{sc}}$$

OPV device characteristics are obtained for a composition, which contains Polymer 1 or Polymer 2 as shown below and an acceptor that is a compound of formula I, and is coated from an organic solution. Details of the solution composition are shown in Table 1.



Polymer 1 (x=y=1)



Polymer 2 (x=y=1)

A1: Inverted bulk heterojunction organic photovoltaic devices

Organic photovoltaic (OPV) devices are fabricated on pre-patterned ITO-glass substrates (13Ω/sq.) purchased from LUMTEC Corporation. Substrates are cleaned using common solvents (acetone, iso-propanol, deionized-water) in an ultrasonic bath. A layer of commercially available aluminium zinc oxide (AlZnO, Nanograde) is applied as a uniform coating by doctor blade at 40 °C. The AlZnO Films are then annealed at 100 °C for 10 minutes in air. Active material solutions (i.e. polymer + acceptor) are prepared to fully dissolve the solutes at a 23 $mg.cm^{-3}$ solution concentration. Thin films are blade-coated in air atmosphere to achieve active layer thicknesses between 50 and 800 nm as measured using a profilometer. A short drying period follows to ensure removal of any residual solvent.

Typically, blade-coated films are dried at 60 °C for 2 minutes on a hotplate. Next the devices are transferred into an air atmosphere. On top of the active layer 0.18 mL of a conducting polymer poly(ethylene dioxythiophene) doped with poly(styrene sulfonic acid) [PEDOT:PSS Clevios P VP Al 4083 (Heraeus)] is spread and uniformly coated by doctor blade at 70 °C. Afterwards Ag (100 nm) cathodes are thermally evaporated through a shadow mask to define the cells.

Table 1 shows the characteristics of the individual photoactive formulations.

Table 1: Formulation characteristics

No.	Acceptor	Polymer	Ratio Polymer: Acceptor	Concentration g/L	Solvent
1	1	1	1:1.3	23	o-xylene
2	1	2	1:1.3	23	o-xylene
3	3	1	1:1.3	23	o-xylene
4	3	2	1:1.3	23	o-xylene:3-phenoxytoluene (97:3)
5	4	1	1:1.3	23	o-xylene
6	4	2	1:1.3	23	o-xylene
7	5	1	1:1.3	23	o-xylene
8	5	2	1:1.3	23	o-xylene
9	6	1	1:1.3	23	o-xylene
10	6	2	1:1.3	23	o-xylene
11	7	1	1:1.3	23	o-xylene
12	7	2	1:1.3	23	o-xylene
13	8	1	1:1.3	23	o-xylene
14	8	2	1:1.3	23	o-xylene

15	9	1	1:1.3	23	o-xylene:3-phenoxytoluene (97:3)
16	9	2	1:1.3	23	o-xylene:3-phenoxytoluene (97:3)
17	11	1	1:1.3	23	o-xylene
18	11	2	1:1.3	23	o-xylene
19	12	1	1:1.3	23	o-xylene
20	12	2	1:1.3	23	o-xylene
21	15	1	1:1.3	23	o-xylene
22	16	1	1:1.3	23	o-xylene
23	16	2	1:1.3	23	o-xylene
24	17	1	1:1.3	23	o-xylene
25	17	2	1:1.3	23	o-xylene
26	18	1	1:1.3	23	o-xylene
27	19	1	1:1.3	23	o-xylene
28	19	2	1:1.3	23	o-xylene
29	20	1	1:1.3	23	o-xylene
30	20	2	1:1.3	23	o-xylene
31	21	1	1:1.3	23	o-xylene
32	21	2	1:1.3	23	o-xylene
33	22	1	1:1.3	23	o-xylene
34	22	2	1:1.3	23	o-xylene
35	23	1	1:1.3	23	o-xylene
36	23	2	1:1.3	23	o-xylene
37	24	1	1:1.3	23	o-xylene
38	26	1	1:1.3	23	o-xylene
39	26	2	1:1.3	23	o-xylene
40	27	1	1:1.3	23	o-xylene
41	31	1	1:1.3	23	o-xylene

42	31	2	1:1.3	23	o-xylene
43	32	1	1:1.3	23	o-xylene
44	32	2	1:1.3	23	o-xylene
45	34	1	1:1.3	23	o-xylene
46	35	2	1:1.3	23	o-xylene
47	36	2	1:1.3	23	o-xylene

Table 2: Photovoltaic cell characteristics under simulated solar irradiation at 1 sun (AM 1.5G)

No.	Acceptor	Polymer	Average Performance			
			Voc	Jsc	FF	PCE
			mV	mA cm^{-2}	%	%
1	1	1	705	14.5	54.8	5.6
2	1	2	690	17.7	52.0	6.5
3	3	1	730	10.5	39.2	3.0
4	3	2	688	5.9	33.3	1.4
5	4	1	733	12.6	51.9	4.8
6	4	2	746	11.3	46.8	4.0
7	5	1	721	11.8	50.3	4.3
8	5	2	695	11.9	44.3	3.7
9	6	1	763	14.2	47.2	5.1
10	6	2	748	11.2	42.5	3.6
11	7	1	851	7.6	39.7	2.6
12	7	2	776	13.5	51.3	5.4
13	8	1	750	13.2	56.6	5.6
14	8	2	700	15.2	54.8	5.8
15	9	1	674	7.4	48.0	2.4
16	9	2	669	11.9	52.9	4.2
17	11	1	765	12.4	56.1	5.2
18	11	2	745	11.5	54.7	4.3

19	12	1	775	2.6	43.8	0.8
20	12	2	760	2.3	40.4	0.7
21	15	1	830	4.8	49	1.4
22	16	1	745	19	53	7.08
23	16	2	730	19.5	45.2	6.18
24	17	1	775	13.8	49	4.77
25	17	2	755	15	53.3	4.58
26	18	1	800	12.7	42	4.05
27	19	1	750	13.9	43.2	4.26
28	19	2	735	13.8	47.8	4.71
29	20	1	715	17.3	55.3	6.73
30	20	2	685	18.1	52.9	6.38
31	21	1	790	7.9	52.8	3.06
32	21	2	765	10	50.5	3.53
33	22	1	795	15.6	50.1	5.75
34	22	2	770	16	52.7	6.23
35	23	1	750	13	56.4	5.42
36	23	2	740	17.1	55.7	6.7
37	24	1	780	8.6	58.2	3.53
38	26	1	780	13.4	56	4.7
39	26	2	735	18.5	56	6.6
40	27	2	705	12.3	56	4.5
41	31	1	820	14.7	45	4.8
42	31	2	785	17.7	40	5
43	32	1	745	17	50	6.2
44	32	2	715	17.7	50	6.5
45	34	1	655	15.3	55.7	5.36
46	35	2	655	19.8	47.1	5.09
47	36	2	665	12.7	55	3.35

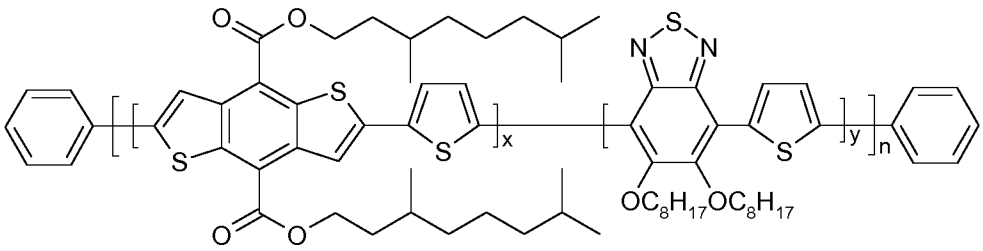
Light stability of synthesised compounds is shown in Table 3.

Table. 3 Light stability of Example devices under constant illumination at 1 Sun

No.	Acceptor	Donor	Initial PCE	PCE after 200h constant illumination
1	16	2	6.6%	4.6%
2	1	2	6.4%	4.8%
3	PC61BM	2	6.9%	4.0%

A1: Bulk heterojunction organic photodetector devices (OPDs)

Devices are fabricated onto glass substrates with six pre-patterned ITO dots of 5 mm diameter to provide the bottom electrode. The ITO substrates are cleaned using a standard process of ultrasonication in Decon90 solution (30 minutes) followed by washing with de-ionized water (x3) and ultrasonication in de-ionized water (30 minutes). The ZnO ETL layer was deposited by spin coating a ZnO nanoparticle dispersion onto the substrate and drying on a hotplate for 10 minutes at a temperature between 100 and 140 °C. A formulation of Polymer 2, Polymer 3 (sourced from Merck KGaA) or Polymer 4 (Lisicon PV-D4650 (sourced from Merck KGaA)) and compound as disclosed herein was prepared at a ratio of 1:1 in o-xylene at a concentration of 20 mg/ml, and stirred for 17 hours at a temperature of between 23 °C and 60 °C. The active layer was deposited using blade coating (K101 Control Coater System from RK). The stage temperature was set to between 20 - 60 °C, the blade gap set between 2-200 µm and the speed set between 2 - 8 m/min targeting a final dry film thickness of 500-1000 nm. Following coating the active layer was annealed at 100 °C for 10 minutes. The MoO_3 HTL layer was deposited by E-beam vacuum deposition from MoO_3 pellets at a rate of 1 Å/s, targeting 15 nm thickness. Finally, the top silver electrode was deposited by thermal evaporation through a shadow mask, to achieve Ag thickness between 30-80 nm.



Polymer 3 (x=y=1)

The J-V curves are measured using a Keithley 4200 system under light and dark conditions at a bias from +5 to -5 V. The light source was a 580 nm LED with power 0.5 mW/cm^2.

The EQE of OPD devices are characterized between 400 and 1100 nm under -2V bias, using an External Quantum Efficiency (EQE) Measurement System from LOT-QuantumDesign Europe.

Table 4 shows the characteristics of the individual formulations.

Table 4: Formulation characteristics

No.	Acceptor	Polymer
1	Compound 1	3
2	Compound 1	4
3	Compound 2	2
4	Compound 2	3
5	Compound 9	2
6	Compound 9	3
7	Compound 10	2
8	Compound 10	3
9	Compound 30	4

Tables 5, 6 and 7 show the EQE values for the individual OPD devices comprising a photoactive layer with a BHJ formed from the photoactive acceptor/polymer formulations of Table 4.

Table 5: EQEs for the devices at 650 nm

No.	EQE %
1	42
2	49
3	15
4	14
5	29
6	14
7	42
8	23
9	18

Table 6: EQEs for the devices at 850 nm

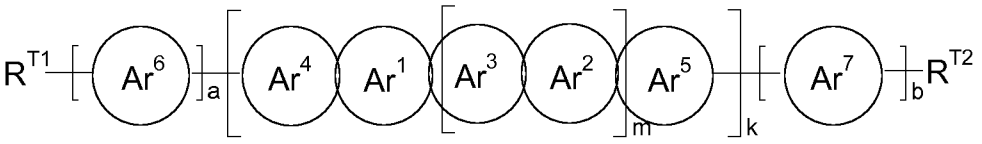
No.	EQE %
1	41
2	46
5	23
6	9
7	36
8	17

Table 7: EQEs for the devices at 940 nm

No.	EQE %
5	15
7	32
8	15

Claims

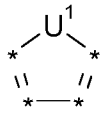
1. A compound of formula I



I

wherein the individual radicals, independently of each other and on each occurrence identically or differently, have the following meanings

Ar^1, Ar^2 a group selected from the following formulae

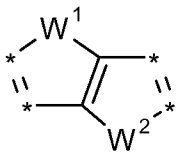


A1

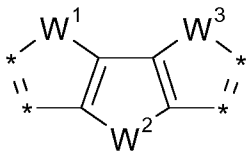


A2

Ar^3 a group selected from the following formulae and their mirror images



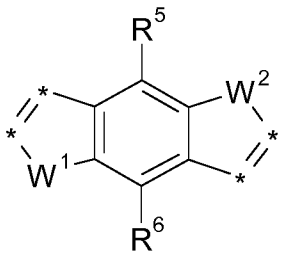
A3a



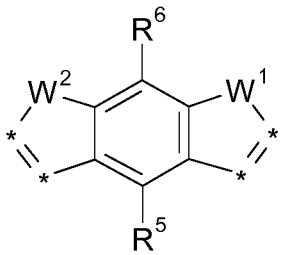
A3b



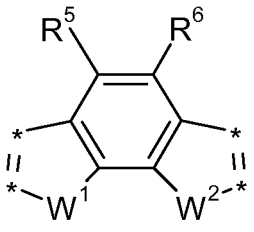
A3c



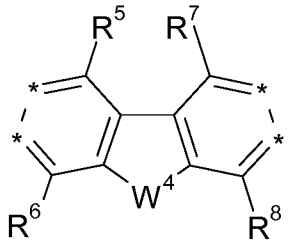
A3d



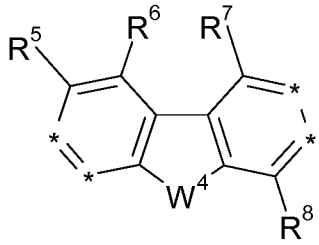
A3e



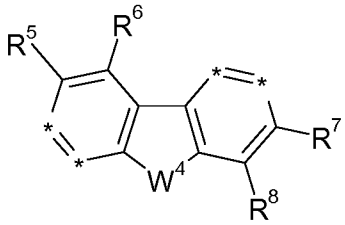
A3f



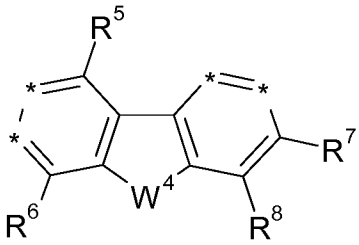
A3g



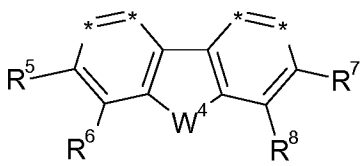
A3h



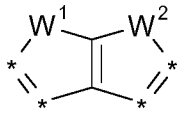
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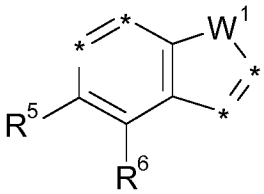
A3j



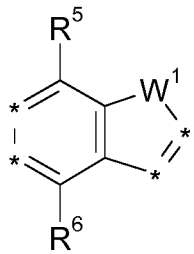
A3k



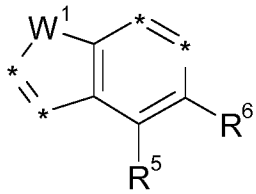
A3l



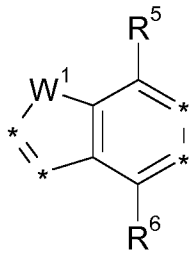
A3m



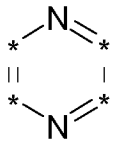
A3n



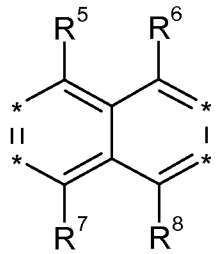
A3o



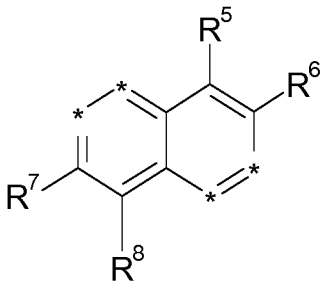
A3p



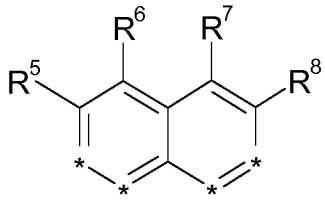
A3q



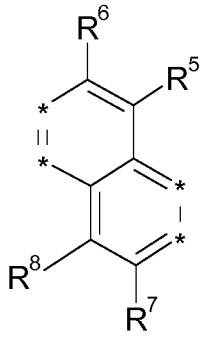
A3r



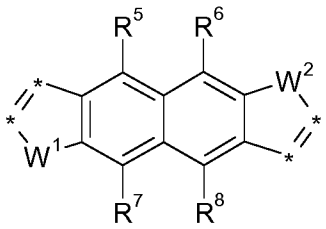
A3s



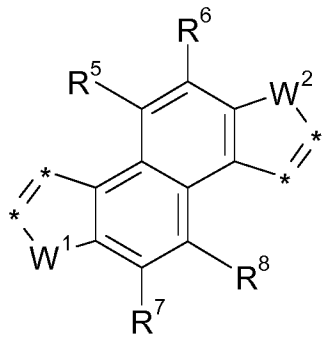
A3t



A3u

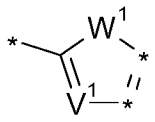


A3v

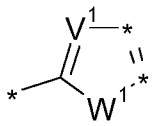


A3w

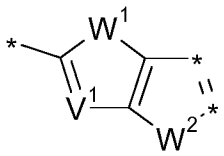
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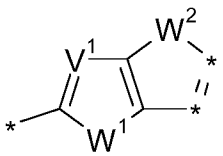
A4a



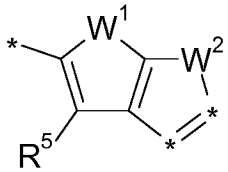
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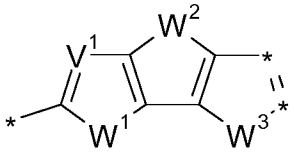
A4c



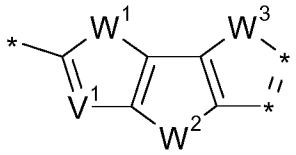
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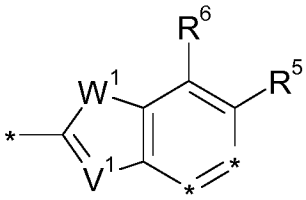
A4e



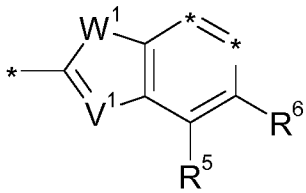
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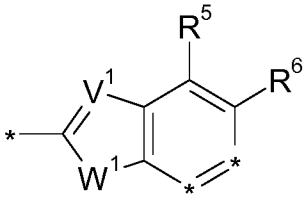
A4g



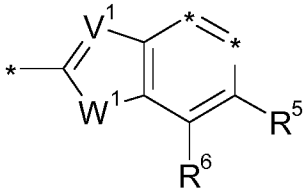
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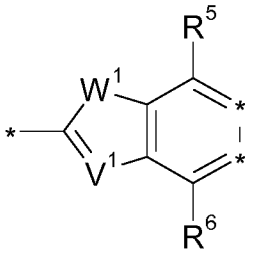
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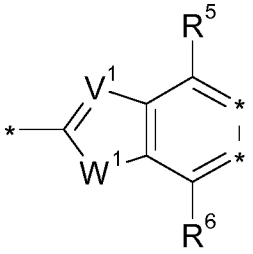
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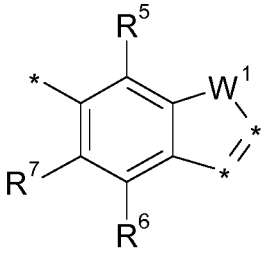
A4k



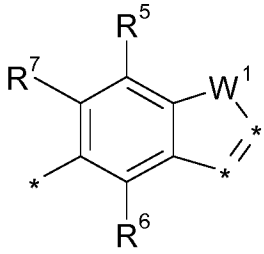
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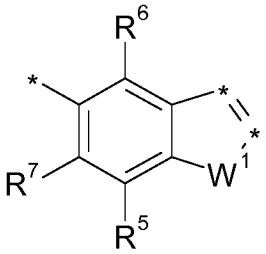
A4m



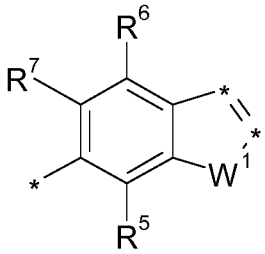
A4n



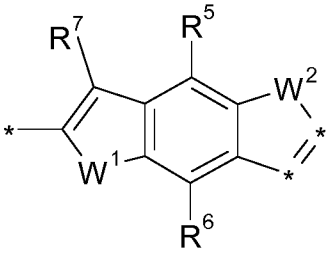
A4o



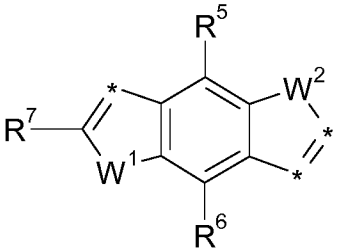
A4p



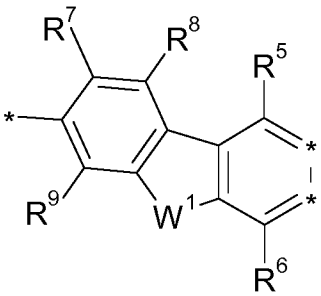
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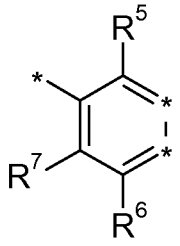
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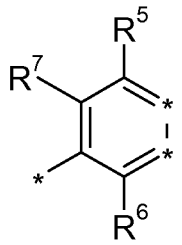
A4s



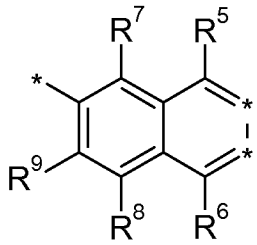
A4t



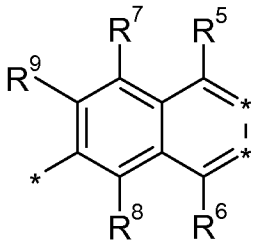
A4u



A4v

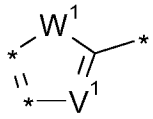


A4w

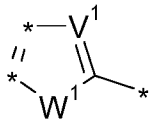


A4x

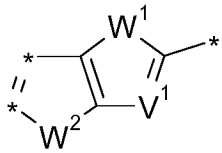
Ar^5 a group selected from the following formulae and their mirror images



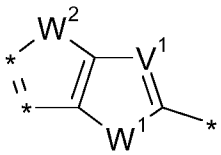
A5a



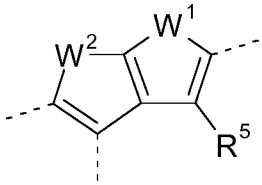
A5b



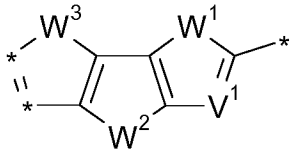
A5c



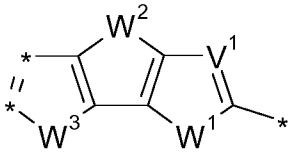
A5d



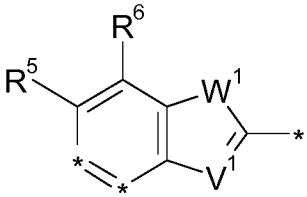
A5e



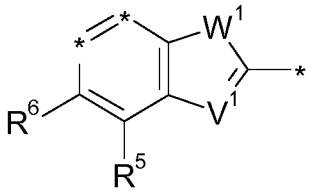
A5f



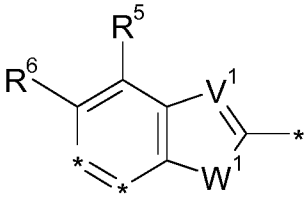
A5g



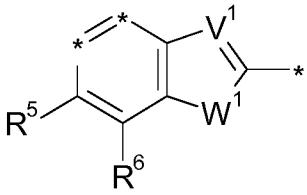
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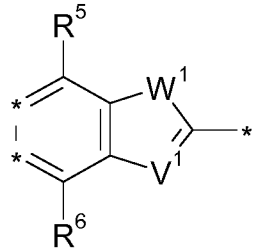
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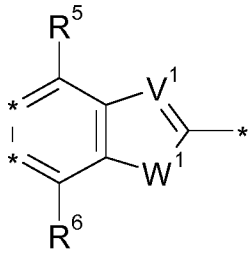
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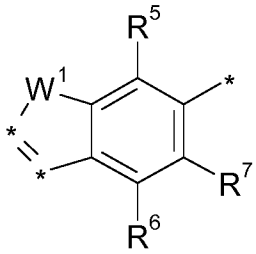
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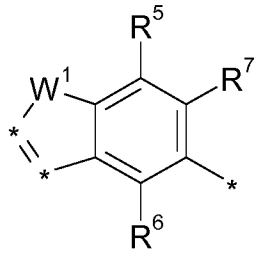
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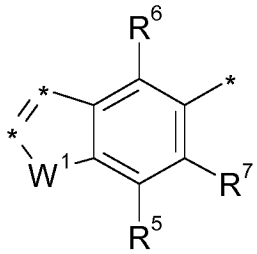
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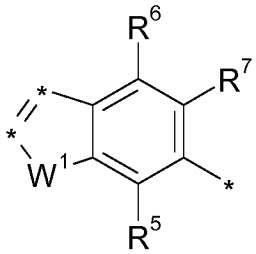
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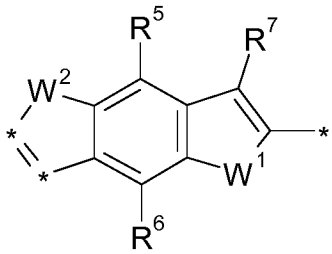
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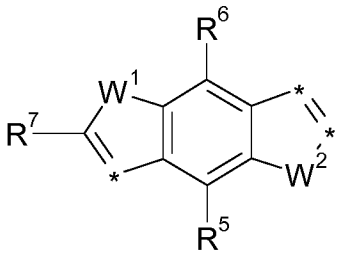
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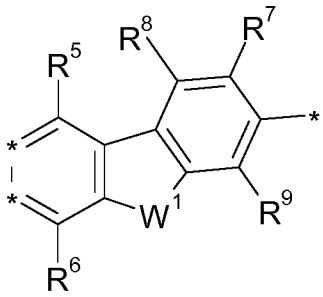
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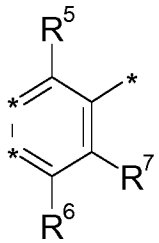
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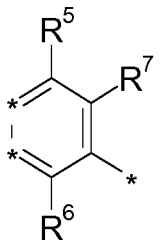
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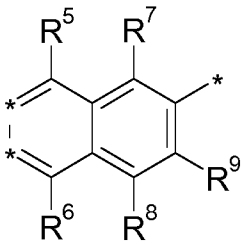
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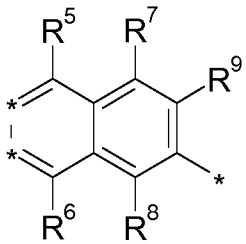
A5u



A5v



A5w



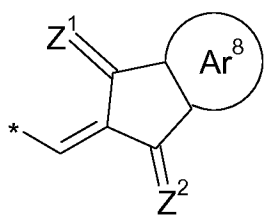
A5x

$Ar^{6,7}$ arylene or heteroarylene that has from 5 to 20 ring atoms, is mono- or polycyclic, optionally contains fused rings, and is unsubstituted or substituted by one or more identical or different groups R^1 or L^S, or $CY^1=CY^2$ or -C≡C-,

U^1, U^2	CR^1R^2, SiR^1R^2, GeR^1R^2, $C=CR^1R^2$, NR^1 or C=O, preferably CR^1R^2,
V^1	CR^3 or N,
W^1, W^2, W^3	S, O, Se or C=O, preferably S,
W^4	S, O, Se, C=O or NR^1,
R^{1-9}	H, F, Cl, CN, or straight-chain, branched or cyclic alkyl with 1 to 30, preferably 1 to 20, C atoms, in which one or more CH_2 groups are optionally replaced by -O-, -S-, -C(=O)-, -C(=S)-, -C(=O)-O-, -O-C(=O)-, $-NR^0$-, $-SiR^0R^{00}$-, $-CF_2$-, $-CR^0=CR^{00}$-, $-CY^1=CY^2$- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, and in which one or more H atoms are optionally replaced by F, Cl, Br, I or CN, and in which one or more CH_2 or CH_3 groups are optionally replaced by a cationic or anionic group, or aryl, heteroaryl, arylalkyl, heteroarylalkyl, aryloxy or heteroaryloxy, wherein each of the aforementioned cyclic groups has 5 to 20 ring atoms, is mono- or polycyclic, does optionally contain fused rings, and is unsubstituted or substituted by one or more identical or different groups L^S, and the pair of R^1 and R^2, together with the C, Si or Ge atom to which they are attached, may also form a spiro group with 5 to 20 ring atoms which is mono- or polycyclic, does optionally contain fused rings, and is unsubstituted or substituted by one or more identical or different groups L^S,
R^{T1}, R^{T2}	an electron withdrawing group,

Y^1, Y^2	H, F, Cl or CN,
L^S	F, Cl, $-NO_2$, -CN, -NC, -NCO, -NCS, -OCN, -SCN, R^0, OR^0, SR^0, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)-OR^0$, $-O-C(=O)-R^0$, $-NH_2$, $-NHR^0$, $-NR^0R^{00}$, $-C(=O)NHR^0$, $-C(=O)NR^0R^{00}$, $-SO_3R^0$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-SF_5$, or optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 30, preferably 1 to 20 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, preferably F, -CN, R^0, $-OR^0$, $-SR^0$, $-C(=O)-R^0$, $-C(=O)-OR^0$, $-O-C(=O)-R^0$, $-O-C(=O)-OR^0$, $-C(=O)-NHR^0$, or $-C(=O)-NR^0R^{00}$,
R^0, R^{00}	H or straight-chain or branched alkyl with 1 to 20, preferably 1 to 12, C atoms that is optionally fluorinated,
X^0	halogen, preferably F or Cl,
a, b	0 or an integer from 1 to 10, preferably 0, 1, 2, 3, 4 or 5, very preferably 0, 1, 2 or 3,
k	an integer from 1 to 10, preferably 1, 2, 3, 4, 5, 6 or 7, very preferably 1, 2 or 3, most preferably 1,
m	0 or an integer from 1 to 10, preferably 0, 1, 2, 3, 4, 5, 6 or 7, very preferably 0, 1, 2 or 3,

wherein at least one of R^{T1} and R^{T2} is an electron withdrawing group of formula TG

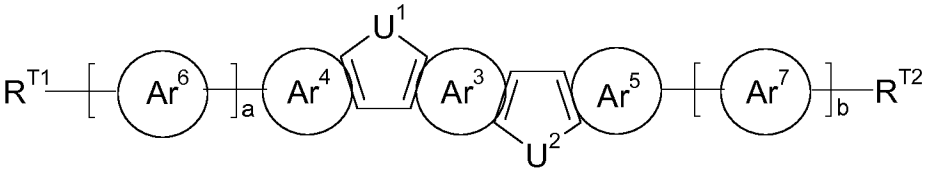


TG

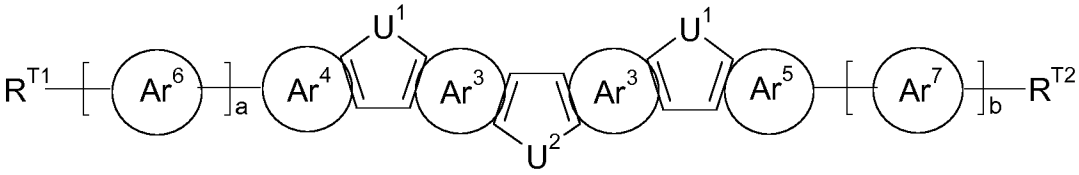
	Ar^8	bi- or polycyclic arylene or heteroarylene having from 5 to 20 ring atoms which is optionally substituted with one or more groups L,
	L	F, Cl, $-NO_2$, -CN, -NC, -NCO, -NCS, -OCN, -SCN, R^0, OR^0, SR^0, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)-OR^0$, $-O-C(=O)-R^0$, $-NH_2$, $-NHR^0$, $-NR^0R^{00}$, $-C(=O)NHR^0$, $-C(=O)NR^0R^{00}$, $-SO_3R^0$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-SF_5$, preferably F, -CN, R^0, $-OR^0$, $-SR^0$, $-C(=O)-R^0$, $-C(=O)-OR^0$, $-O-C(=O)-R^0$, $-O-C(=O)-OR^0$, $-C(=O)-NHR^0$, $-C(=O)-NR^0R^{00}$,
	Z^1, Z^2	O or $C(CN)_2$ or C(CN)(C=O)R, preferably one of Z^1 and Z^2 is O and the other is $C(CN)_2$,

and wherein at least one group Ar^3 denotes thieno[3,2-b]thiophene and/or at least one of the groups Ar^4 and Ar^5 denotes thieno[3,2-b]thiophene that is optionally substituted with R^3.

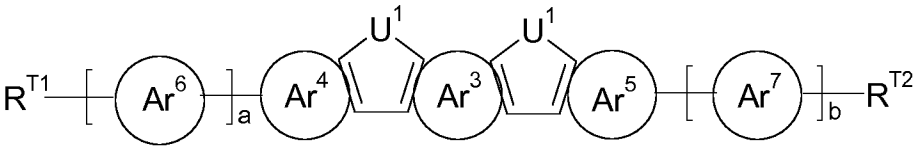
2. The compound according to claim 1, characterized in that it is selected from the following subformulae



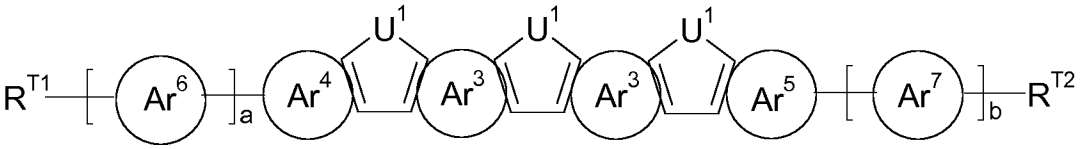
I'

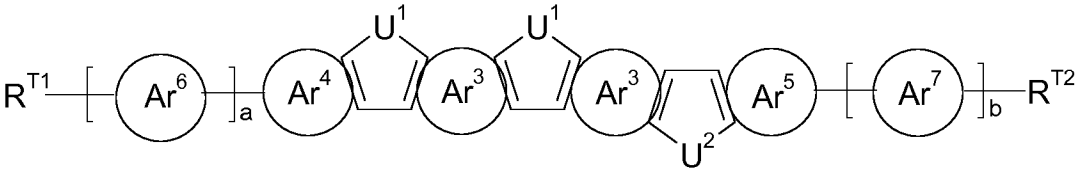


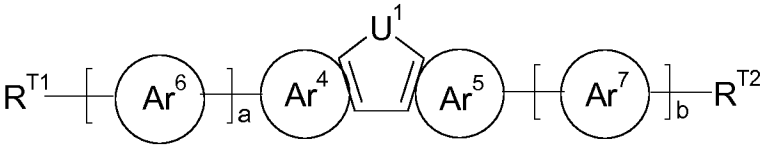
I2



I3

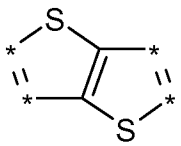




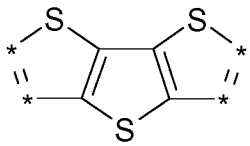


wherein U^1, U^2, Ar^3, Ar^4, Ar^5, Ar^6, Ar^7, R^{T1}, R^{T2}, a and b, independently of each other and on each occurrence identically or differently, have the meanings given in claim 1.

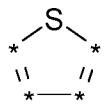
3. The compound according to claim 1 or 2, characterized in that the groups Ar^3 are on each occurrence identically or differently selected from the following formulae and their mirror images



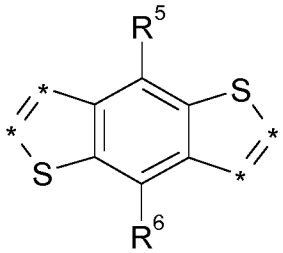
A3a1



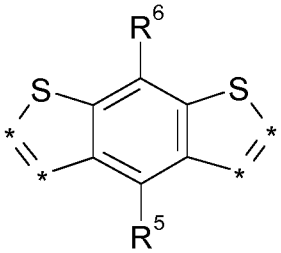
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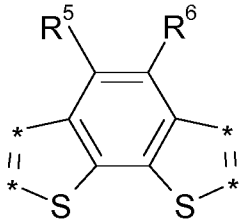
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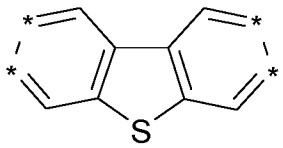
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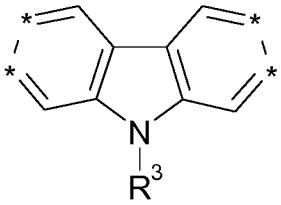
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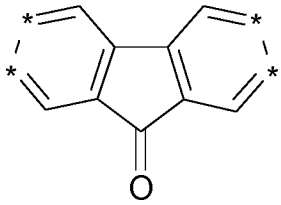
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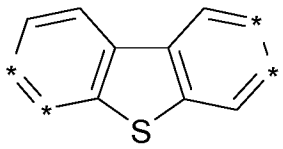
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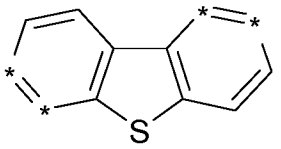
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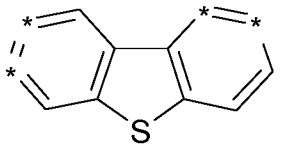
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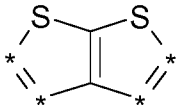
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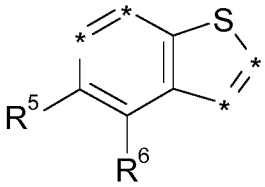
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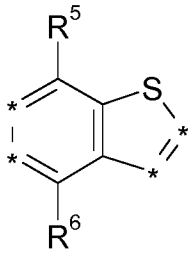
Arj1



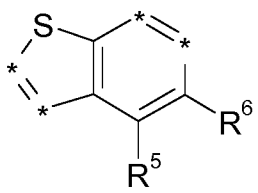
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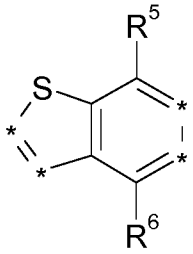
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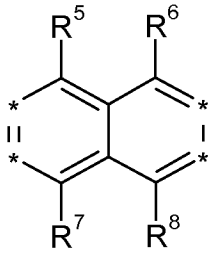
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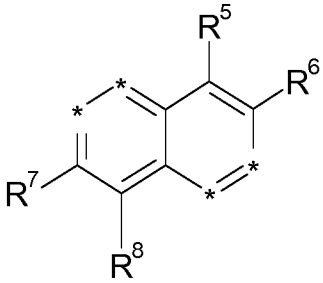
A3n1



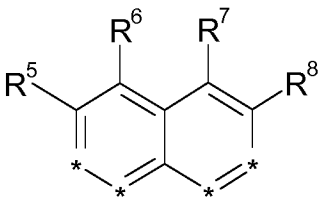
A3o1



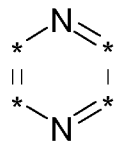
A3p



A3q



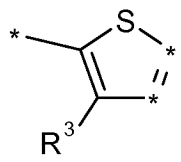
A3r



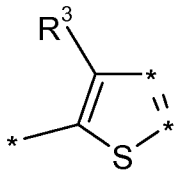
A3s

wherein R^{5-8} have the meanings given in claim 1.

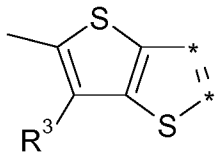
4. The compound according to any of claims 1 to 3, characterized in that the groups Ar^4 are on each occurrence identically or differently selected from the following formulae and their mirror images



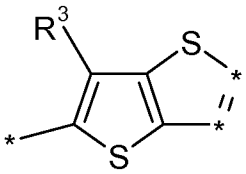
A4a1



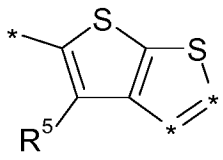
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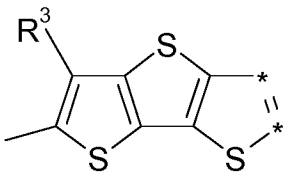
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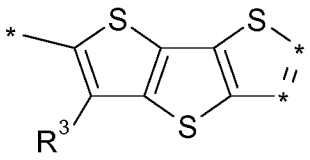
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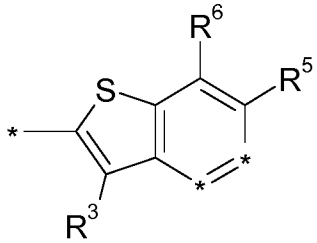
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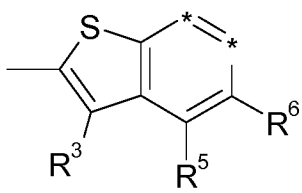
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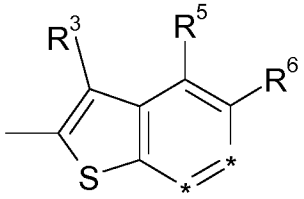
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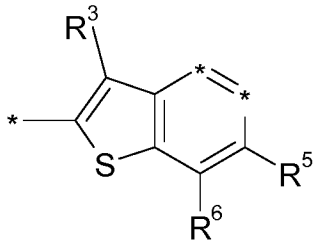
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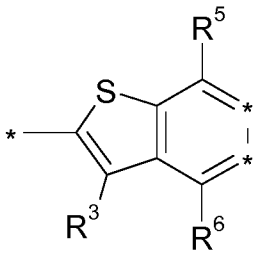
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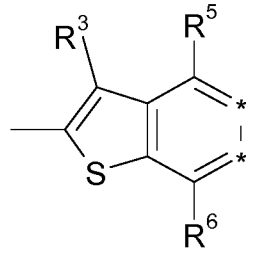
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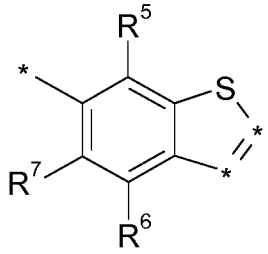
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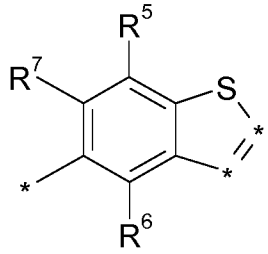
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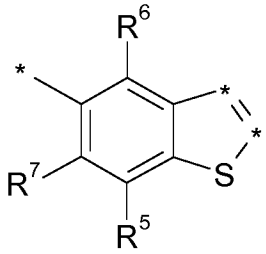
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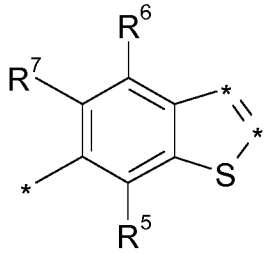
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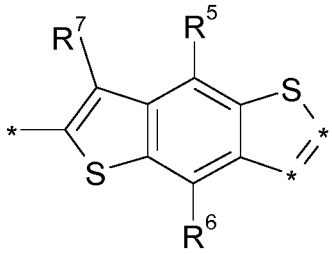
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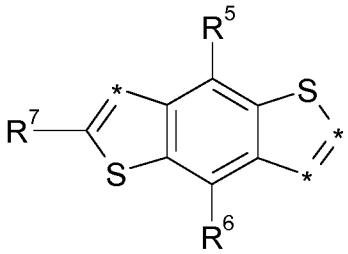
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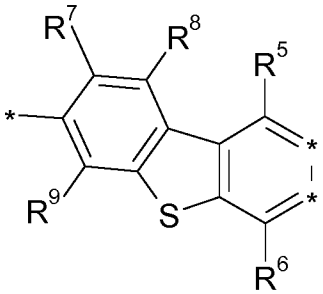
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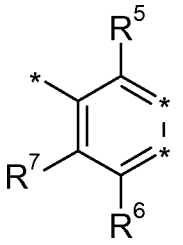
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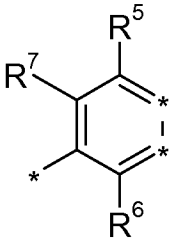
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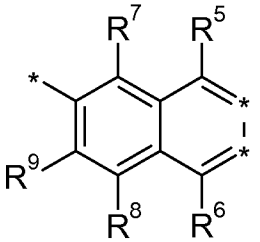
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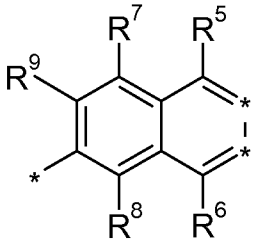
A4u



A4v



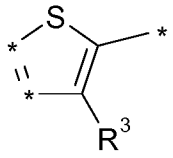
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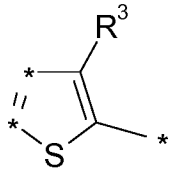
A4x

wherein R^{3-9} have the meanings given in claim 1.

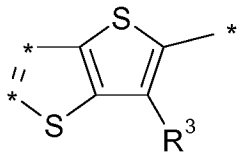
5. The compound according to any of claims 1 to 4, characterized in that the groups Ar^5 are on each occurrence identically or differently selected from the following formulae and their mirror images



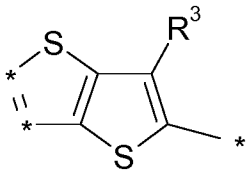
A5a1



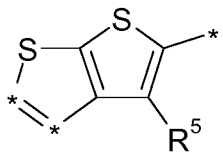
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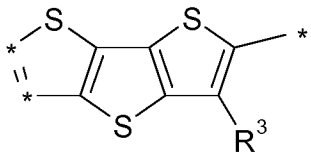
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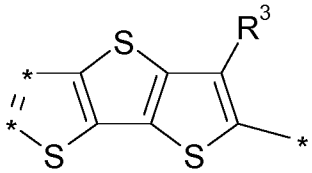
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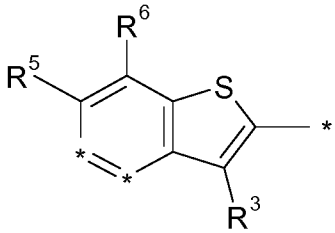
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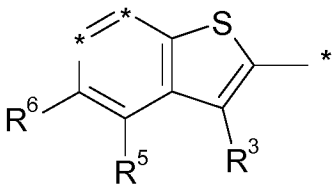
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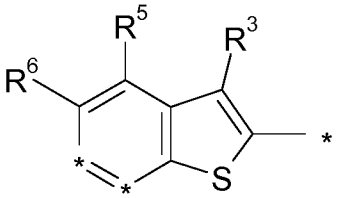
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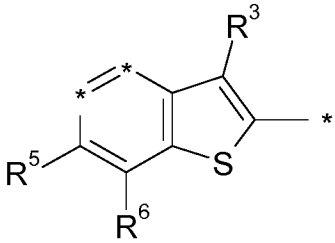
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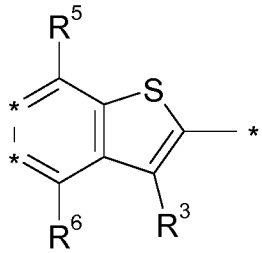
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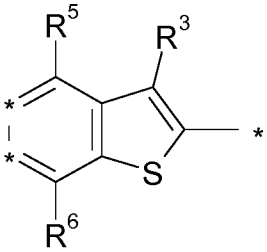
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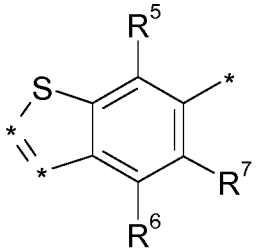
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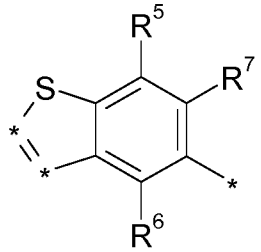
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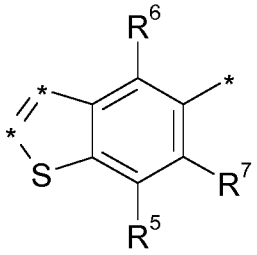
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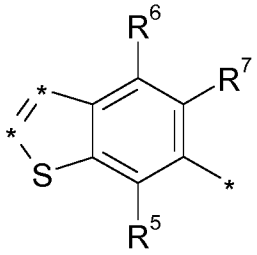
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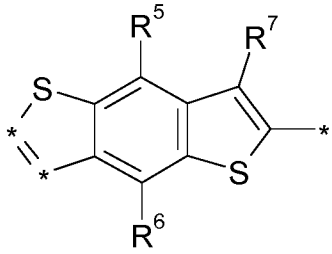
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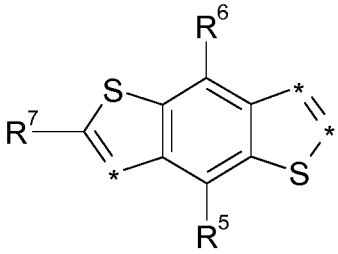
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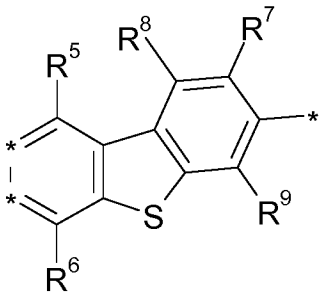
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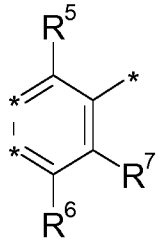
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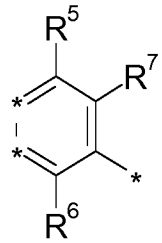
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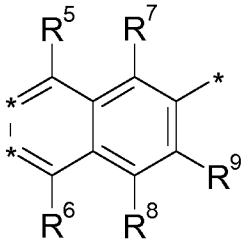
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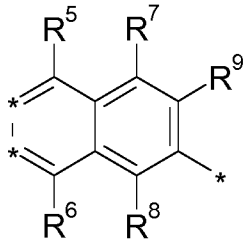
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A5v1



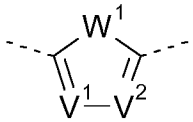
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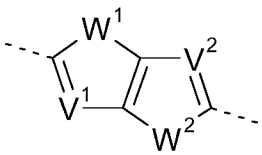


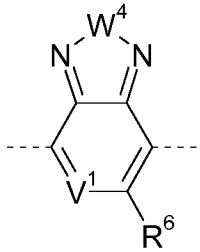
A5x1

wherein R^{3-9} have the meanings given above and below.

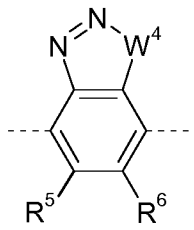
6. The compound according to one or more of claims 1 to 5, characterized in that the groups Ar^6 and Ar^7 are on each occurrence identically or differently selected from the following formulae and their mirror images

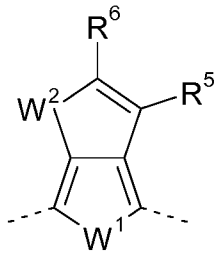


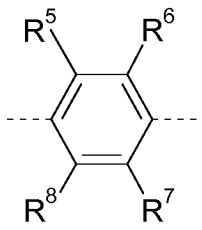




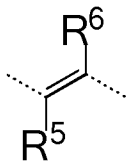
AR1 AR2 AR3







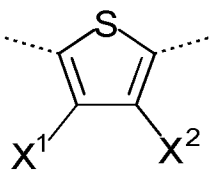
AR4 AR5 AR6

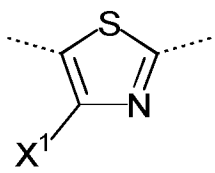


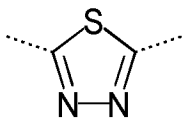
AR7

wherein, independently of each other and on each occurrence identically or differently, V^2 is CR^4 or N, R^4 has one of the meanings given for R^3 in claim 1, and V^1, W^1, W^2, W^4, R^{5-9} are as defined in claim 1.

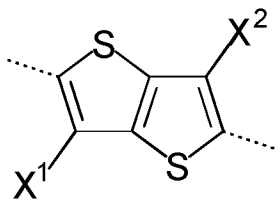
7. The compound according to one or more of claims 1 to 6, characterized in that the groups Ar^6 and Ar^7 are on each occurrence identically or differently selected from the following formulae and their mirror images



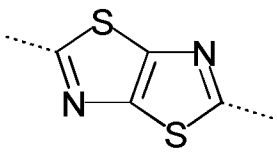




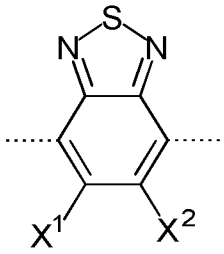
AR1-1 AR1-2 AR1-3



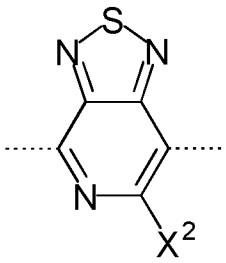
AR2-1



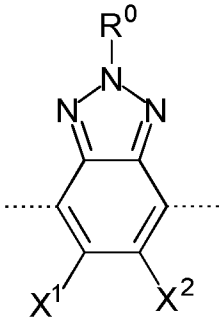
AR2-2



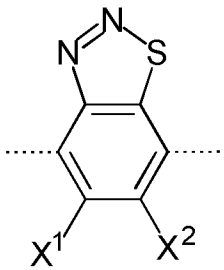
AR3-1



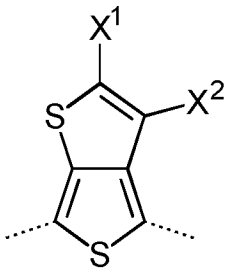
AR3-2



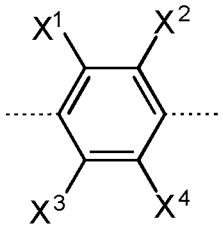
AR3-3



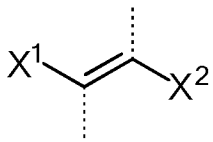
AR4-1



AR5-1



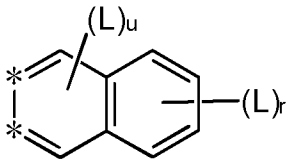
AR6-1



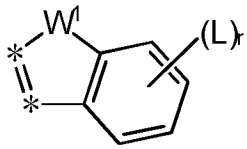
AR7-1

wherein X^1, X^2, X^3 and X^4 have one of the meanings given for R^1 in claim 1, and preferably denote H, F, Cl, -CN, R^0, OR^0 or $C(=O)OR^0$, and R^0 is as defined in claim 1.

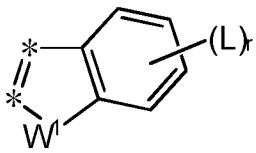
8. The compound according to one or more of claims 1 to 7, characterized in that group Ar^8 in formula TG is on each occurrence identically or differently selected from the following formulae and their mirror images



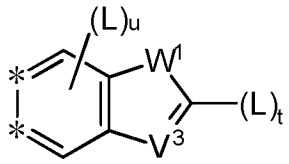
A8-1



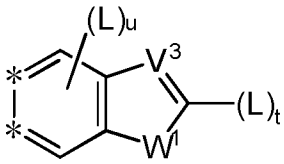
A8-2



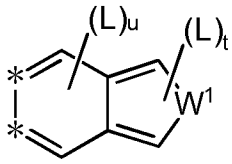
A8-3



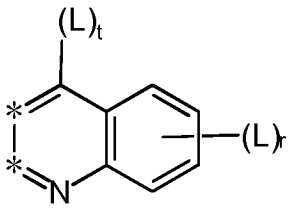
A8-4



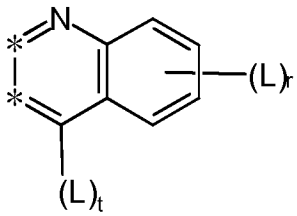
A8-5



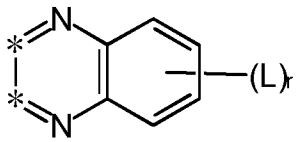
A8-6



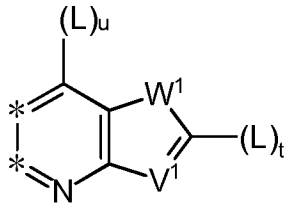
A8-7



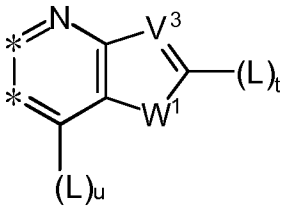
A8-8



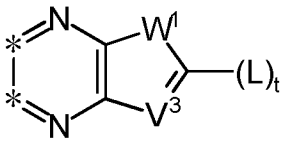
A8-9



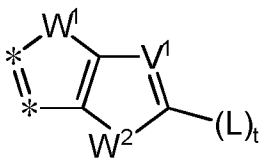
A8-10



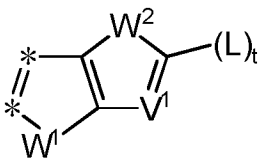
A8-11



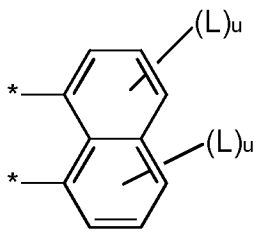
A8-12



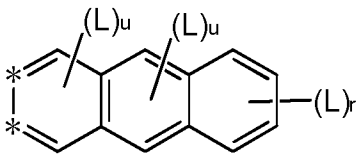
A8-13



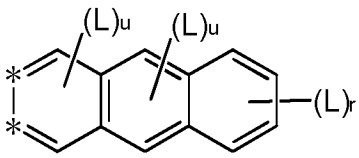
A8-14



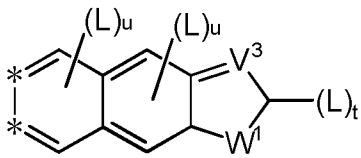
A8-15



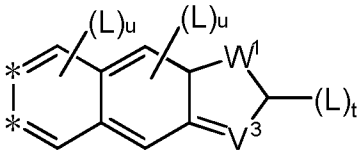
A8-16



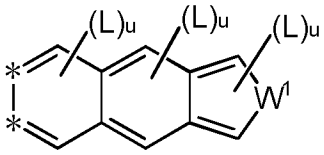
A8-17



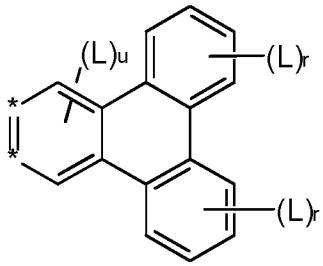
A8-18



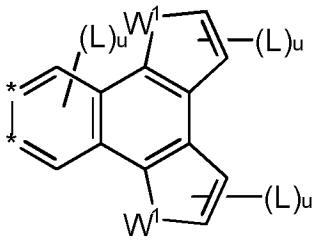
A8-19



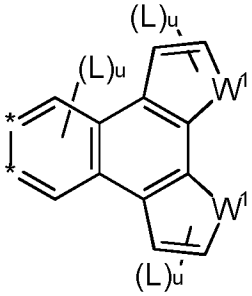
A8-20



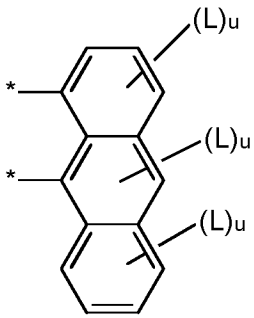
A8-21



A8-22



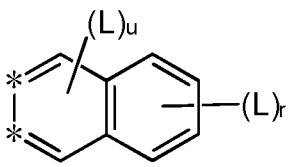
A8-23

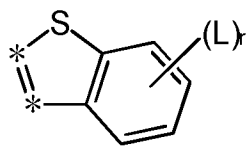


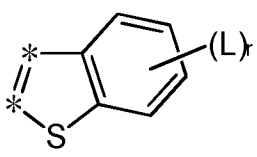
A8-24

wherein, independently of each other and on each occurrence identically or differently, W^1 and L have the meanings given in claim 1, V^3 is N or $C(L)_t$, r is 0, 1, 2, 3 or 4, u is 0, 1 or 2, and t is 0 or 1.

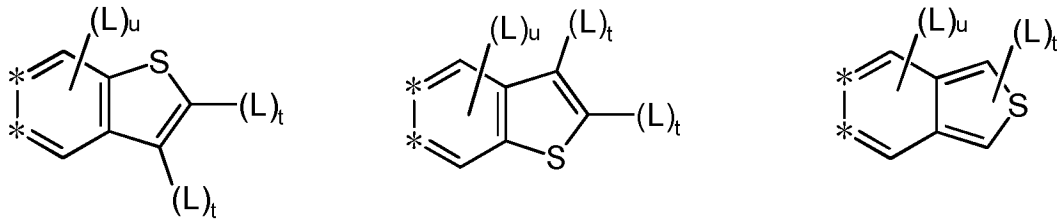
9. The compound according to one or more of claims 1 to 8, characterized in that group Ar^8 in formula TG is on each occurrence identically or differently selected from the following formulae and their mirror images







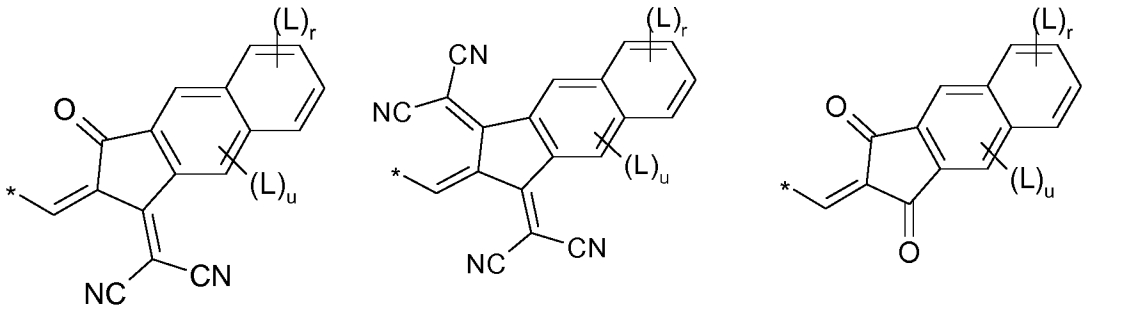
A8-1a A8-2a A8-3a



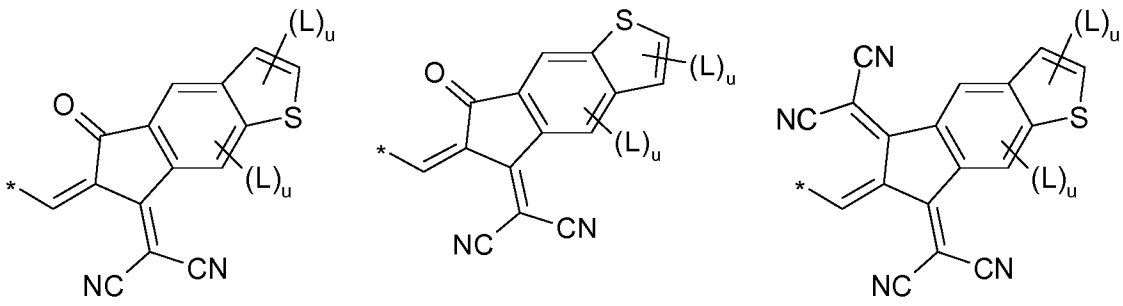
A8-4a A8-5a A8-6a

wherein L, r, t and u, independently of each other and on each occurrence identically or differently, have the meanings given in claim 8.

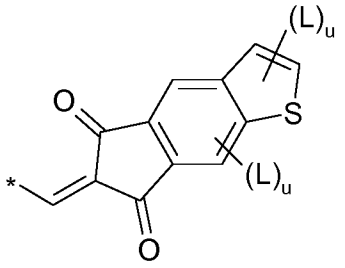
10. The compound according to one or more of claims 1 to 9, characterized in that R^{T1} and R^{T2} in formula I are selected from the following subformulae



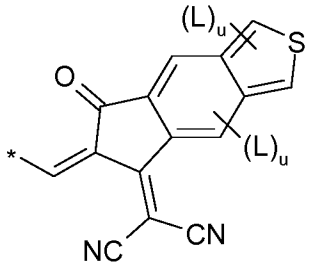
TG1 TG2 TG3



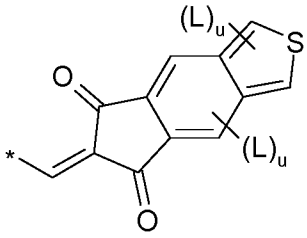
TG4 TG5 TG6



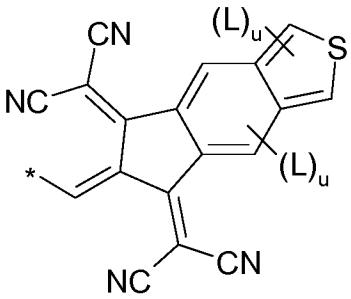
TG7



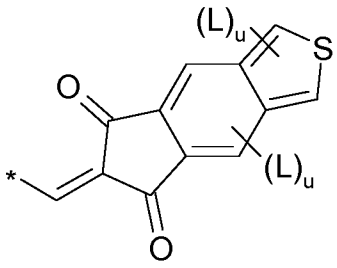
TG8



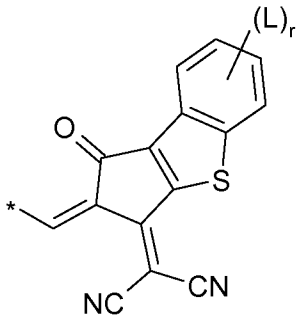
TG9



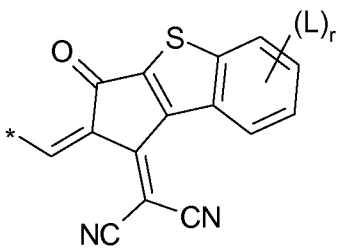
TG10



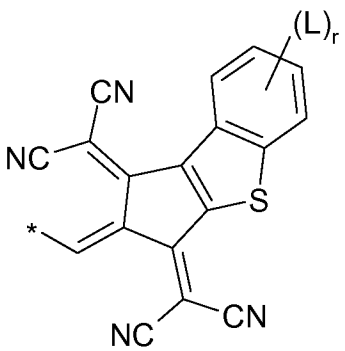
TG11



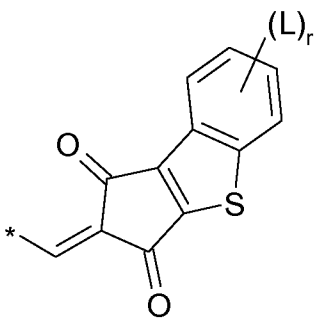
TG12



TG13



TG14

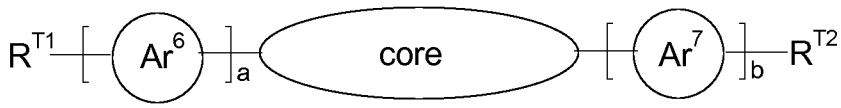


TG15

wherein L, u and r have the meanings given in claim 8.

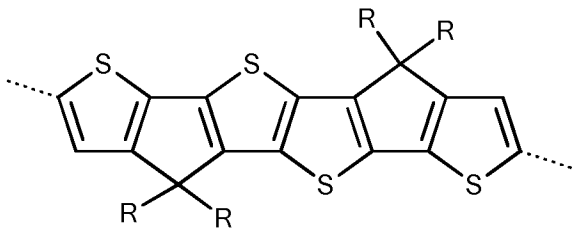
11. The compound according to one or more of claims 1 to 10, characterized in that both R^{T1} and R^{T2} are selected from formula TG as defined in claim 1.

12. The compound according to one or more of claims 1 to 11, characterized in that it is selected of the following subformula

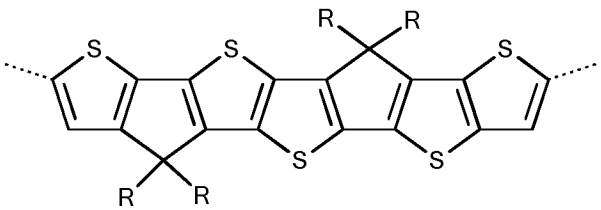


IA

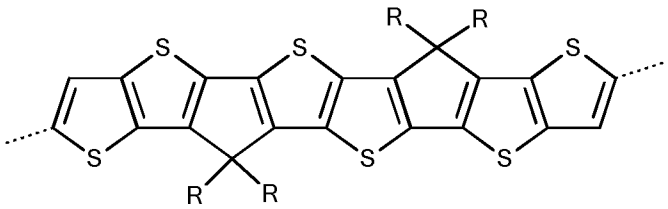
wherein Ar^6, Ar^7, R^{T1}, R^{T2}, a and b, independently of each other and on each occurrence identically or differently, have the meanings given in claim 1, and "Core" is, on each occurrence identically or differently, a polycyclic divalent group selected from the following formulae



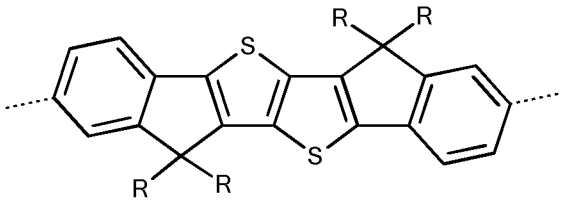
C1



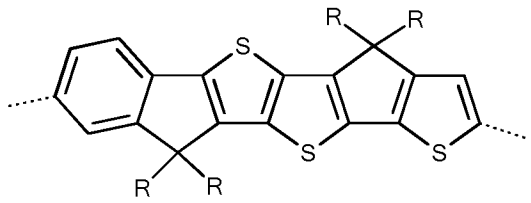
C2



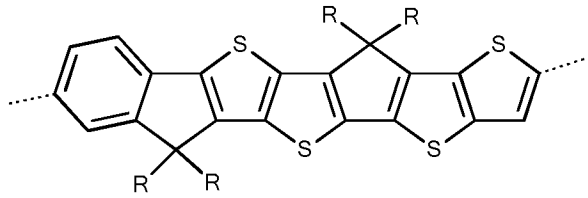
C3



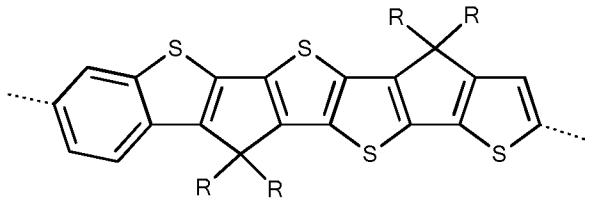
C4



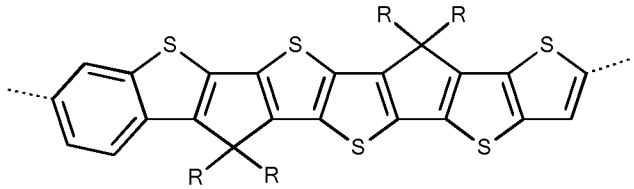
C5



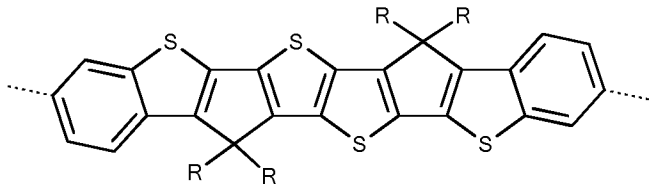
C6



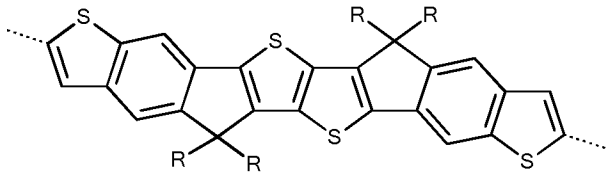
C7



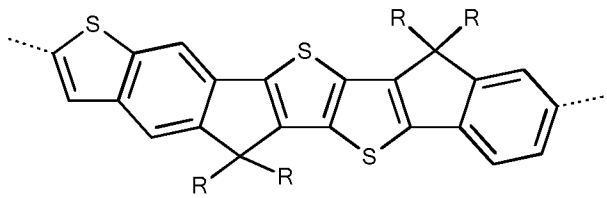
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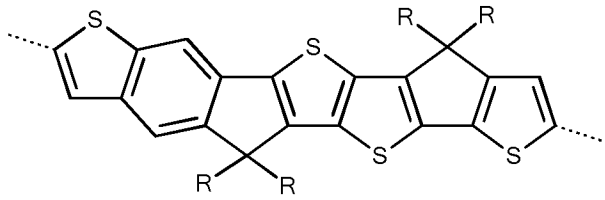
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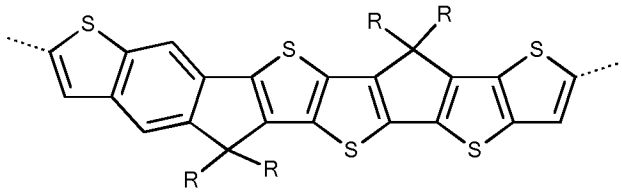
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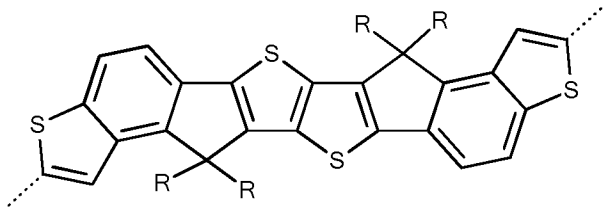
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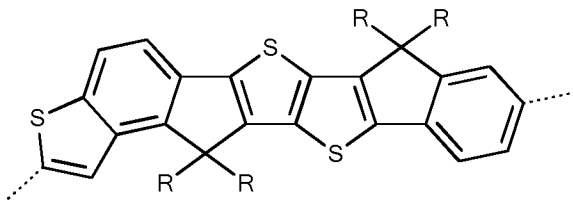
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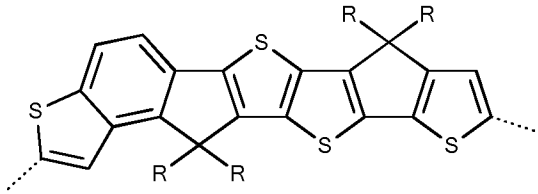
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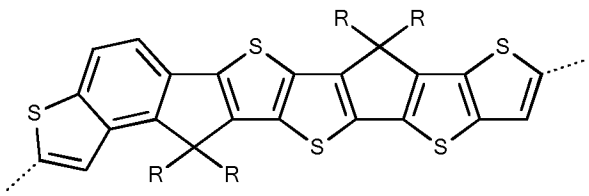
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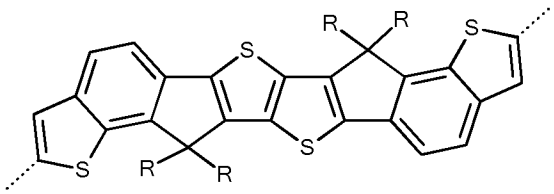
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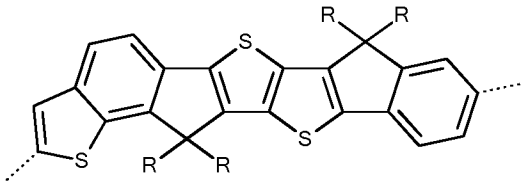
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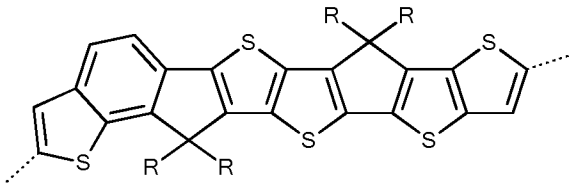
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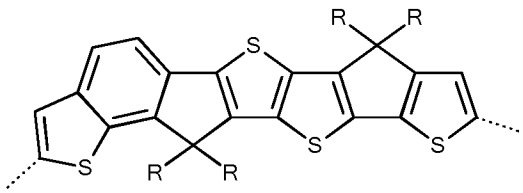
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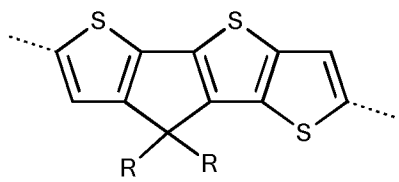
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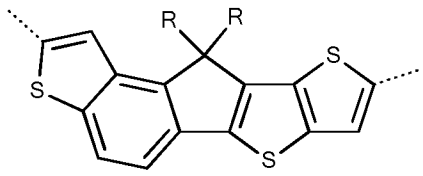
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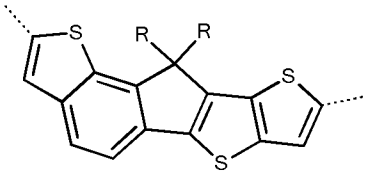
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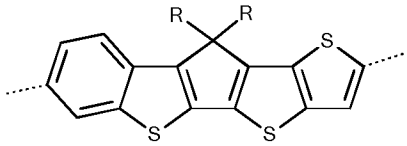
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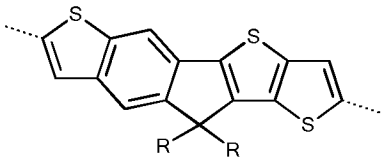
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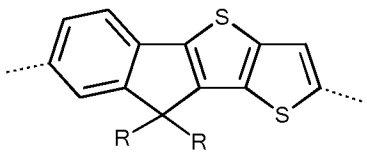
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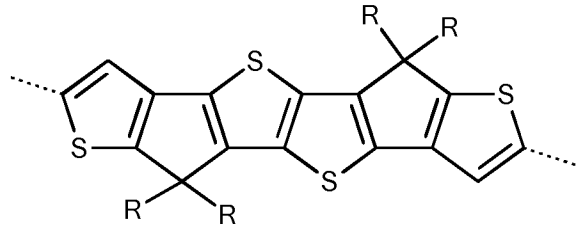
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C26



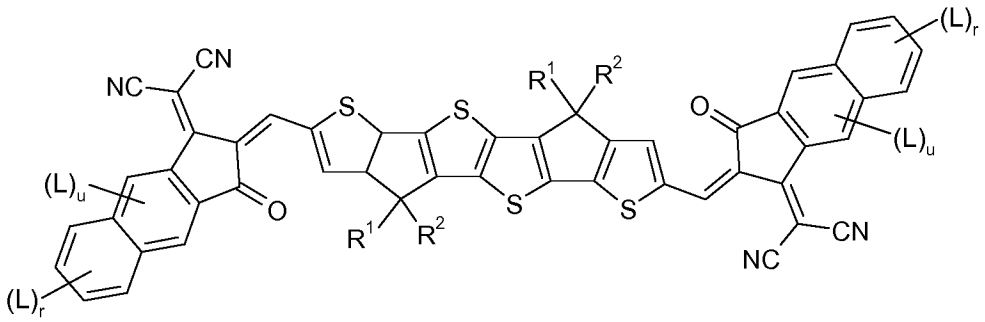
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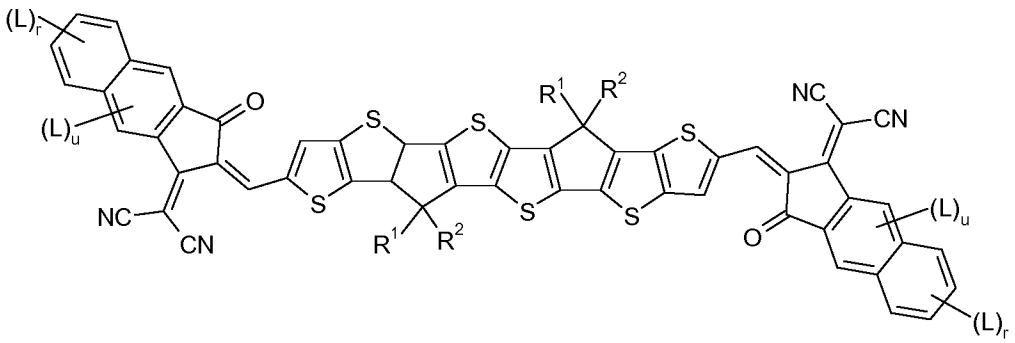
C28

wherein R has on each occurrence identically or differently one of the meanings of R^1 as given in claim 1.

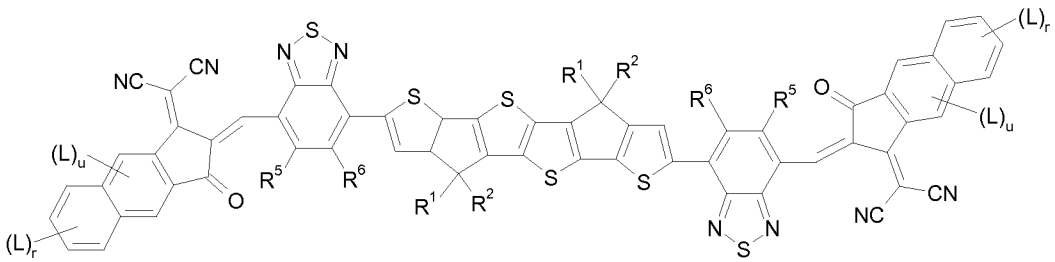
13. The compound according to one or more of claims 1 to 12, characterized in that it is selected from the following subformulae



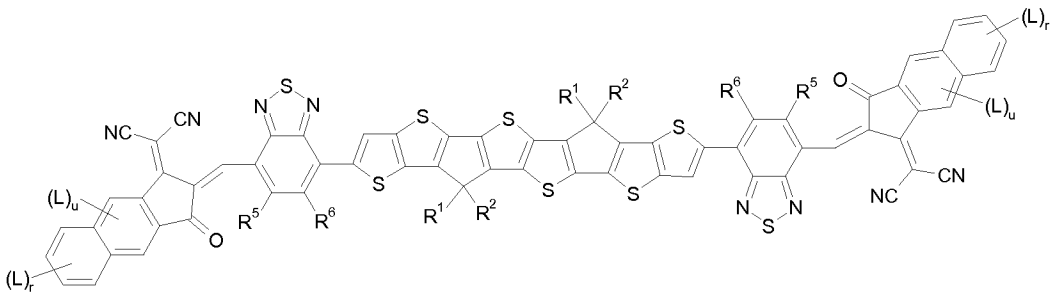
I1A1



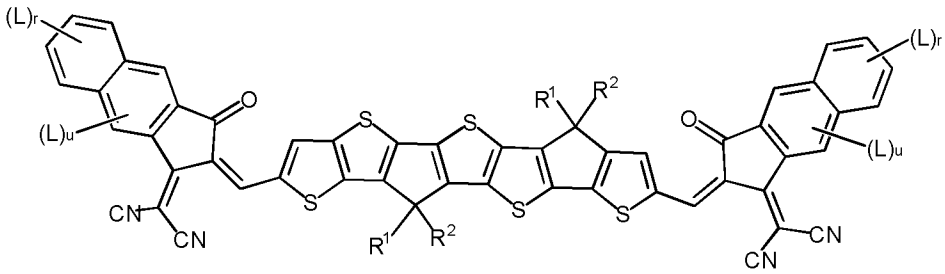
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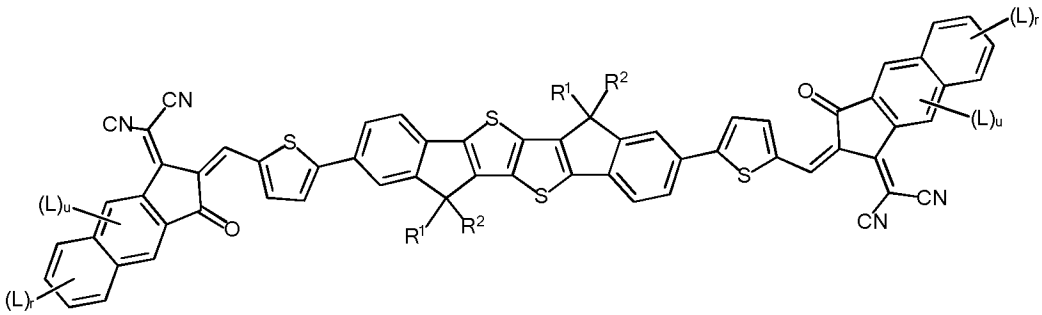
I1A3



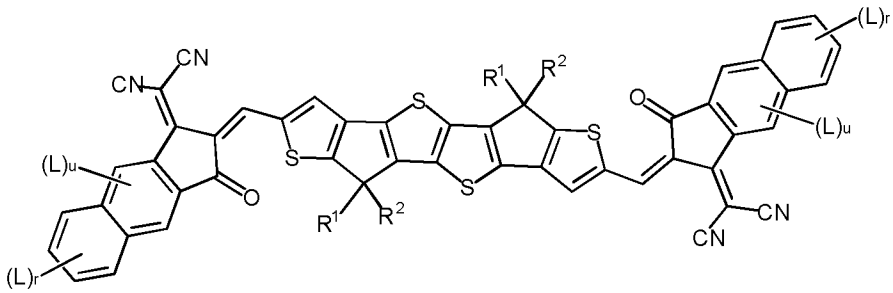
I1A4



I1A5



I1A6



I1A7

wherein R^1, R^2, R^5, R^6, L, r and u have the meanings given in claims 1 and 8.

14. The compound according to one or more of claims 1 to 13, characterized in that R^1 and R^2 are selected from F, Cl, CN, straight-chain or branched alkyl, alkoxy, sulfanylalkyl, sulfonylalkyl, alkyl-carbonyl, alkoxycarbonyl and alkylcarbonyloxy, each having 1 to 20 C atoms and being unsubstituted or substituted by one or more F atoms.

15. The compound according to one or more of claims 1 to 14, characterized in that R^1 and R^2 are selected from mono- or polycyclic aryl or heteroaryl, each of which is optionally substituted with one or more groups L^S as defined in claim 1 and has 5 to 20 ring atoms, and

wherein two or more rings may be fused to each other or connected with each other by a covalent bond.

16. The compound according to one or more of claims 1 to 15, characterized in that at least one of R^{3-8} is different from H, and is selected from F, Cl or straight-chain or branched alkyl, alkoxy, sulfanylalkyl, sulfonylalkyl, alkylcarbonyl, alkoxycarbonyl and alkylcarbonyloxy, each having 1 to 20 C atoms and being unsubstituted or substituted by one or more F atoms, without being perfluorinated.

17. A composition comprising one or more compounds according to one or more of claims 1 to 16, and further comprising one or more compounds having one or more of a semiconducting, hole or electron transporting, hole or electron blocking, electrically conducting, photoconducting, photoactive or light emitting property, and/or a binder.

18. The composition of claim 17, comprising one or more n-type semiconductors, at least one of which is a compound according to one or more of claims 1 to 16, and further comprising one or more p-type semiconductors, preferably selected from conjugated polymers.

19. The composition according to claim 17 or 18, comprising one or more n-type semiconductors selected from fullerenes or fullerene derivatives.

20. A bulk heterojunction (BHJ) formed from a composition according to one or more of claims 17 to 19.

21. Use of a compound according to one or more of claims 1 to 16, or of a composition according to one or more of claims 17 to 19, in an electronic or optoelectronic device, or in a component of such a device or in an assembly comprising such a device.

22. A formulation comprising one or more compounds according to one or more of claims 1 to 16, or a composition according to one or more

of claims 17 to 19, and further comprising one or more solvents selected from organic solvents.

23. An electronic or optoelectronic device, or a component thereof, or an assembly comprising it, which comprises a compound according to one or more of claims 1 to 16, or a composition according to one or more of claims 17 to 19.

24. The electronic or optoelectronic device according to claim 23, which is selected from organic field effect transistors (OFET), organic thin film transistors (OTFT), organic light emitting diodes (OLED), organic light emitting transistors (OLET), organic light emitting electro-chemical cells (OLEC), organic photovoltaic devices (OPV), organic photodetectors (OPD), organic solar cells, dye-sensitized solar cells (DSSC), perovskite-based solar cells (PSC), organic photoelectrochemical cells (OPEC),laser diodes, Schottky diodes, photoconductors, photodetectors, thermoelectric devices.

25. The component according to claim 23, which is selected from charge injection layers, charge transport layers, interlayers, planarizing layers, antistatic films, polymer electrolyte membranes (PEM), conducting substrates and conducting patterns.

26. The assembly according to claim 23, which is selected from integrated circuits (IC), radio frequency identification (RFID) tags, security markings, security devices, flat panel displays, LC windows, backlights of flat panel displays, electrophotographic devices, electrophotographic recording devices, organic memory devices, sensor devices, biosensors and biochips.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/057499

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L51/46
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	MA DANYANG ET AL: "The design of highly efficient polymer solar cells with outstanding short-circuit current density based on small band gap electron acceptor", DYES AND PIGMENTS, ELSEVIER APPLIED SCIENCE PUBLISHERS. BARKING, GB, vol. 150, 9 December 2017 (2017-12-09), pages 363-369, XP085352691, ISSN: 0143-7208, DOI: 10.1016/J.DYEPIG.2017.12.017 page 365, column 1, line 47 - column 2, line 9; figures 2,3; compounds TTIC, TTIC-M ----- -/--	1-26

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 June 2019	21/06/2019

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Fratiloiu, Silvia

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/057499

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	RENLONG LI ET AL: "Non-fullerene acceptors based on fused-ring oligomers for efficient polymer solar cells via complementary light-absorption", JOURNAL OF MATERIALS CHEMISTRY A, vol. 5, no. 45, 26 October 2017 (2017-10-26), pages 23926-23936, XP055596054, GB ISSN: 2050-7488, DOI: 10.1039/C7TA06631G figure Scheme 2; compounds IDT-N, IDT-T-N ----- WO 2019/052935 A1 (MERCK PATENT GMBH [DE]) 21 March 2019 (2019-03-21) page 60; example 6; compound 13 -----	1-26
X,P		1-26

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2019/057499

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2019052935 A1	21-03-2019	NONE	