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(54) Title: TRIARYL- AND TRIHETEROARYL- BENZENE MONOMERS AND POLYMERS

(57) Abstract: The invention relates to novel mono-, oligo- and polymeric compounds comprising substituted triaryl- and triheteroaryl benzene groups and their copolymers. The invention further relates to the methods of their synthesis, to organic semiconducting materials and blends, formulations and layers comprising them, and to electronic devices, like organic field effect transistors (OFETs) and organic photovoltaics (OPVs), comprising them.



Triaryl- and triheteroaryl- benzene Monomers and Polymers

Field of Invention

The invention relates to novel mono-, oligo- and polymeric compounds comprising substituted triaryl- and triheteroaryl benzene groups and their copolymers. The invention further relates to the methods of their synthesis, to organic semiconducting materials and blends, formulations and layers comprising them, and to electronic devices, like organic field effect transistors (OFETs) and organic photovoltaics (OPVs), comprising them.

Background

The use of organic polymers as the active layer in electronic and optoelectronic applications has been an area of recent growing interest. For example, organic semiconducting polymers have shown promise as the active layer in organic based thin film transistors and organic field effect transistors (TFT, OFET) (see for example de Boer, B. & Facchetti, A. Semiconducting polymeric materials. *Polymer Reviews* **48**, 423-431 (2008)). Potential applications include thin film transistor (TFT) backplanes for a variety of display modes including active matrix liquid crystal displays (AMLCD), flexible displays such as e-paper and disposable item level radio-frequency identity (RFID) tags. In addition semiconducting polymers have found use as the active layer in flexible solar cells and in cheap, disposable sensors. Much of the interest in semiconducting polymers arises from the fact that they are amenable to the fabrication of devices by solution-processing techniques such as spin casting, dip coating or ink jet printing enabling both significant cost savings over traditional manufacturing techniques and the ability to pattern flexible substrates with active electronics.

The performance of the transistor device 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 a high charge carrier mobility ($> 1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). In addition, it is extremely important that the semi-conducting material is relatively stable to oxidation i.e. it has a high ionisation potential, as oxidation leads to higher off currents and reduced device performance.

Several classes of conjugated organic polymers have been studied for use in FET devices. Amorphous polymers such as polyarylamines have demonstrated excellent ambient stability,

but with rather low mobilities of around $0.005 \text{ cm}^2/\text{Vs}$ and isotropic in-plane transport achieved in transistors with low work function electrodes and low K dielectrics, with minimal thermal annealing of the semiconductor required. Regioregular head-to-tail poly(3-hexylthiophene) (P3HT) has been reported with charge carrier mobilities up to $0.2 \text{ cm}^2/\text{Vs}$,
5 but with a rather low current on/off ratio between 10 and 10^3 . The high regioregularity of the backbone leads improved packing and optimised microstructure, which in turn leads to high charge carrier mobilities (see H. Sirringhaus et al., *Science*, 1998, **280**, 1741-1744; H. Sirringhaus et al., *Nature*, 1999, **401**, 685-688). This low on/off ratio is due in part to the low ionisation potential of the polymer, which can lead to oxygen doping of the polymer under
10 ambient conditions, and a subsequent high off current (see H. Sirringhaus et al., *Adv. Solid State Phys.*, 1999, **39**, 101).

Alternative thiophene based polymers have been developed which exhibit increased ionisation potentials and therefore have less tendency to dope under ambient conditions, whilst
15 maintaining high crystallinity and charge carrier mobility. Although the ambient stability is improved for these materials, changes in devices characteristics still occur over time, particularly in ambient air of relatively high humidity. In addition these polymers require a high temperature annealing step to afford devices of high mobility.

Polyfluorenes are rigid rod polymers which can be rendered soluble in organic solvents by appropriate substitution at the bridging C9 position. Alkyl substituted polyfluorenes can exhibit high temperature liquid crystalline phases which can be exploited to achieve the optimal microstructure in transistor devices. This class of polymer has very low lying HOMO energy levels, leading to poor charge injection in FET devices and poor charge transport, most
20 likely due to the poor backbone packing attributed to the non planar projection of the alkyl groups at the bridging position of the fluorene unit. Incorporation of a bithiophene unit to form the alternating copolymer poly(9,9-dioctylfluorene-co-bithiophene) (F8T2) resulted in an increase in both HOMO energy level (from -5.8eV to -5.4eV) and improved charge transport. Orientation of the polymer backbones can be achieved by a thermal annealing step
25 at the mesophase temperature utilising a rubbed polyimide alignment layer as substrate. Mobilities of up to $0.02 \text{ cm}^2/\text{Vs}$ have been reported for this polymer, with good ambient stability. Although the ambient stability of fluorene based polymers is reasonable, stability problems have been reported during device operation, particularly for devices with a high
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current density, such as OLEDs. A source of such instability is thought to be oxidation of the bridging carbon atom 9 position, by cleavage of the alkyl sidechains. Improved stability has been demonstrated by substitution of the carbon bridging unit, by (dialkyl)silicon, which is less prone to oxidation. Additionally, the silicon – carbon bond is larger than a carbon – carbon bond, which results in a slight perturbation to the coplanarity of the fluorene unit, and subsequent reduction in conjugation. This perturbation results in a lowering of the highest occupied molecular orbital energy which provides enhanced stability to electrochemical oxidation in ambient conditions.

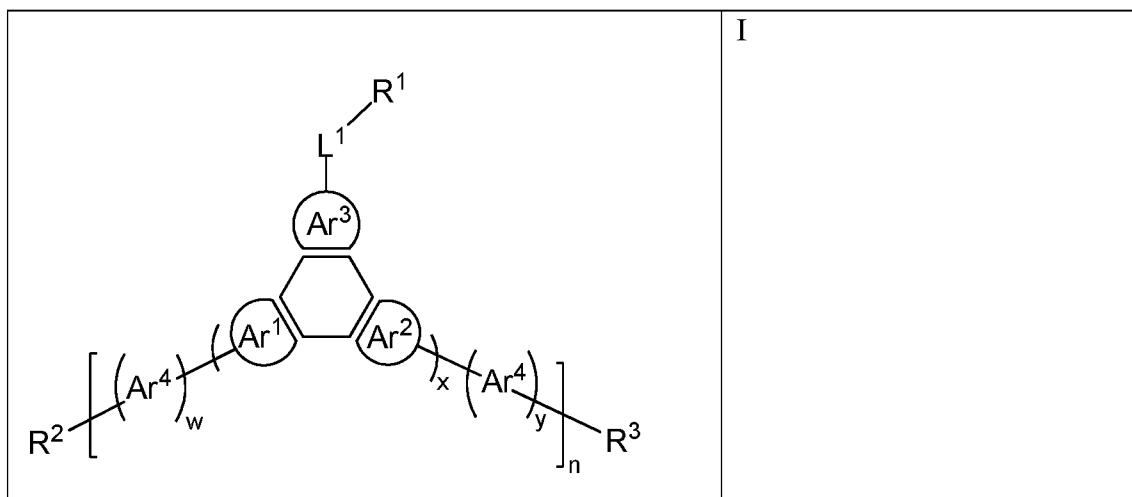
An aim of this invention is to provide a semiconducting polymer which can function as an active binder in a blend formulation with small molecule semiconductors, for use in thin film organic transistor devices. The binder polymer controls crystallisation and film forming properties of the small molecule, as well as in some instances optimising the charge injection from the transistor electrodes. The binder film can also provide improved ambient stability.

Another aim of the present invention to provide new and improved materials for use as semiconductors or charge transport materials, especially for use in OFET and OPV devices, which do not have the disadvantages as mentioned above, and are easy to synthesize, have high charge mobility, good processability and oxidative stability. Another aim of the invention is to provide new semiconductor and charge transport components, and new and improved electro-optical, electronic and luminescent devices comprising these components. Other aims of the invention are immediately evident to those skilled in the art from the following description.

The inventors of the present invention have found that these aims can be achieved by providing materials triaryl- and triheteroaryl-benzene units as described hereinafter.

Summary of the Invention

The invention relates to a compound which may be a monomer, dimer, trimer or polymer, wherein the compound is of formula I:



wherein:

R^1 at each occurrence is independently selected from H, halogen, aryl, heteroaryl, -C(=O) R^0 , -C(OR⁰)₂R⁰⁰, -CN, -NC, -NCO, -NCS, -OCN, -SCN, -C(=O)NR⁰R⁰⁰, -C(=O)X⁰, -NH₂, -NR⁰R⁰⁰, -SH, -SR⁰, -SO₃H, -SO₂R⁰, -OH, -NO₂, -CF₃, -SF₅, optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms,

R^{2-3} are independently of each other identical or different groups selected from H, halogen, aryl, heteroaryl, -C(=O) R^0 , -CN, -NC, -NCO, -NCS, -OCN, -SCN, -C(=O)NR⁰R⁰⁰, -C(=O)X⁰, -NH₂, -NR⁰R⁰⁰, -SH, -SR⁰, -SO₃H, -SO₂R⁰, -OSO₂R⁰, -OH, -NO₂, -CF₃, -SF₅, -CH₂Cl, -CHO, -CH=CH₂, -C(R⁰)=CR⁰R⁰⁰, C≡CH, -SiR⁰R⁰⁰R⁰⁰⁰, -SiR⁰R⁰⁰X⁰, -SiR⁰(X⁰)₂, -Si(X⁰)₃, -SnR⁰R⁰⁰R⁰⁰⁰, -BR⁰R⁰⁰, -B(OR⁰)(OR⁰⁰), -B(OH)₂, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms,

L^1 is a single bond, -C(=O)-, an imine, a hemiacetal or an acetal,

X^0 is halogen,

n is an integer ≥ 1 ,

R^0 , R^{00} and R^{000} are independently selected from H or an optionally substituted aliphatic or aromatic hydrocarbyl group having 1 to 20 C atoms, or R^0 and R^{00} may also form a ring together with the hetero atom to which they are attached,

each occurrence of w is independently an integer ≥ 0 ,

each occurrence of x is independently an integer ≥ 1 ,

each occurrence of y is independently an integer ≥ 0 ,

Ar^{1-3} in case of multiple occurrences are independently selected from mono- or polynuclear aryl or heteroaryl that is optionally substituted,

Ar⁴ in case of multiple occurrences is independently selected from -CY¹=CY²-, -C≡C- or mono- or polynuclear aryl or heteroaryl that is optionally substituted, or Ar⁴ has the formula:



wherein

- 5 m is 1, 2 or 3,
 Ar⁵ is independently selected from mono- or polynuclear aryl or heteroaryl that is optionally substituted, and
 Y¹ and Y² are independently selected from hydrogen, halogen or -CN.

- 10 It will be appreciated that the values of w, x, y and n can be varied in order to produce monomers and polymers with different structures. The skilled person will understand that formula I is intended to encompass homopolymers, for example, when w and y are both 0 and all instances of the macrocycle which encompasses the groups Ar¹⁻³, L¹ and R¹ are identical. The value of n will then determine the molecular weight of the homopolymer. The skilled
 15 person will also appreciate that formula I is intended to encompass copolymers, including statistical copolymers, alternating copolymers and block copolymers. In certain copolymers, w is 0 and x and y both equal 1, or w, x and y all equal 1. In certain block copolymers and random block copolymers, w is 0 and x and y are both > 1 or w, x and y are all > 1.
- 20 In certain embodiments, n(w + x + y) is an integer selected from 5 to 10,000. In preferred embodiments, n(w + x + y) is 10 to 5,000, more preferably 15 to 1,000.

- 25 The invention further relates to a polymer blend comprising one or more polymers according to the present invention and one or more further polymers, preferably selected from polymers having semiconducting, charge transport, hole/electron transport, hole/electron blocking, electrically conducting, photoconducting or light emitting properties. Preferred further polymers include polythiophenes, polyfluorenes, polydiketopyrrolopyrroles, polydithienobenzenes etc.

The invention further relates to a formulation comprising one or more polymers or polymer blends according to the present invention and one or more solvents, preferably selected from organic solvents. Preferred solvents include dichloromethane, trichloromethane, monochlorobenzene, o-dichlorobenzene, tetrahydrofuran, anisole, morpholine, toluene, xylene, 1,4-dioxane, acetone, methylethylketone, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, ethyl acetate, n-butyl acetate, dimethylformamide, dimethylacetamide, dimethylsulfoxide, tetraline, decaline, indane, methyl benzoate, ethyl benzoate, mesitylene and/or mixtures thereof.

The invention further relates to the use of polymers, polymer blends and formulations according to the present invention as charge transport, semiconducting, electrically conducting, photoconducting or light emitting material in optical, electrooptical, electronic, electroluminescent or photoluminescent components or devices.

The invention further relates to a charge transport, semiconducting, electrically conducting, photoconducting or light emitting material or component comprising one or more polymers, polymer blends or formulations according to the present invention.

The invention further relates to an optical, electrooptical or electronic component or device comprising one or more polymers, polymer blends, formulations, components or materials according to the present invention.

The optical, electrooptical, electronic electroluminescent and photoluminescent components or devices include, without limitation, organic field effect transistors (OFET), thin film transistors (TFT), integrated circuits (IC), logic circuits, capacitors, radio frequency identification (RFID) tags, devices or components, organic light emitting diodes (OLED), organic light emitting transistors (OLET), flat panel displays, backlights of displays, organic photovoltaic devices (OPV), solar cells, laser diodes, photoconductors, photodetectors, electrophotographic devices, electrophotographic recording devices, organic memory devices, sensor devices, charge injection layers, Schottky diodes, planarising layers, antistatic films, conducting substrates, conducting patterns, electrode materials in batteries, alignment layers, biosensors, biochips, security markings, security devices, and components or devices for detecting and discriminating DNA sequences.

Description of the Figures

Figure 1 shows the appearance of the ketone C=O stretch at 1664 cm^{-1} upon heating of a thin film of polymer **P2** indicating conversion to polymer **P1**. P1 and P2 are as described in examples 1 and 2.

Figure 2 shows a TGA confirming weight loss when heating polymer **P2** above 250°C indicating the conversion to polymer **P1**. P1 and P2 are as described in examples 1 and 2.

Figure 3 shows J–V characteristics (top) and external quantum efficiencies (bottom) of OPV devices described in Example 7.

Detailed Description of the Invention

The term "polymer" includes homopolymers and copolymers, e.g. random, statistical, alternating or block copolymers.

A polymer of the invention may be a conjugated polymer. The term "conjugated polymer" means a polymer containing in its backbone (or main chain) mainly C atoms with sp^2 -hybridisation, or optionally also sp -hybridisation, which may also be replaced by hetero atoms such as N, O, P, and S. In the simplest case this is for example a backbone with alternating C–C single and double, or triple, bonds, but does also include polymers with units like 1,3-phenylene. "Mainly" means in this connection that a polymer with naturally (spontaneously) occurring defects, which may lead to interruption of the conjugation, is still regarded as a conjugated polymer. Also included in this meaning are polymers wherein the backbone comprises for example units like aryl amines, aryl phosphines and/or certain heterocycles (i.e. conjugation via N-, O-, P- or S-atoms) and/or metal organic complexes (i.e. conjugation via a metal atom). By virtue of the fused Ar^{1-3} groups, the central six-membered ring shown in formula I comprises sp^2 ring carbon atoms.

The term "charge/hole/electron transport property" refers to a material capable of transporting charges, holes (i.e. positive charges) or electrons (i.e. negative charges) injected from a charge/hole/electron injecting material or an electrode (anode in case of holes and cathode in case of electrons). The term "light emitting property" refers to a material which, upon

receiving excitonic energy by energy transfer from other units, or by forming an exciton either electrically or optically, undergoes radiative decay to emit light. The term "hole/electron blocking property" refers to a material which, if coated adjacent to a hole/electron transporting layer in a multilayer structure, prevents the hole/electron flowing through.

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Unless stated otherwise, the molecular weight is given as the number average molecular weight M_n determined by gel permeation chromatography (GPC) against polystyrene standards. The degree of polymerization (n) means the number average degree of polymerization, given as $n = M_n/M_U$, wherein M_U is the molecular weight of the single repeating unit (usually without considering the end groups of the polymer which are not part of the repeating unit). A polymer of the invention preferably has a M_n of at least 5 kDa, more preferably at least 9 kDa.

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Unless stated otherwise, groups or indices like Ar, R^{1-4} , n etc. in case of multiple occurrences are selected independently from each other and may be identical or different from each other. Thus several different groups may be represented by a single label like " R^1 ".

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The term "unit" means a monomer unit or a repeating unit in a polymer or copolymer.

The term "aliphatic" includes both saturated and unsaturated, nonaromatic, straight chain (*i.e.*, unbranched), branched, acyclic, and cyclic (*i.e.*, carbocyclic) hydrocarbons, which are optionally substituted with one or more functional groups. As will be appreciated by one of ordinary skill in the art, "aliphatic" is intended herein to include, but is not limited to, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, and cycloalkynyl moieties containing from 1 to 40 carbon atoms, preferably 1 to 20 carbon atoms. Heteroaliphatic is an aliphatic group where one or more carbon atoms are replaced with a heteroatom, such as O, N, S, P etc.

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The term 'alkyl', 'aryl', 'heteroaryl' etc also include multivalent species, for example alkylene, arylene, 'heteroarylene' etc.

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The term "carbonyl group" as used above and below denotes any monovalent or multivalent organic radical moiety which comprises at least one carbon atom either without any non-carbon atoms (like for example $-C\equiv C-$), or optionally combined with at least one non-carbon

atom such as N, O, S, P, Si, Se, As, Te or Ge (for example carbonyl etc.). The term "hydrocarbyl group" denotes a carbyl group that does additionally contain one or more H atoms and optionally contains one or more hetero atoms like for example N, O, S, P, Si, Se, As, Te or Ge.

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A carbyl or hydrocarbyl group comprising a chain of 3 or more C atoms may also be linear, branched and/or cyclic, including spiro and/or fused rings.

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Preferred carbyl and hydrocarbyl groups include alkyl, alkenyl, alkynyl, alkoxy, alkylcarbonyl, alkoxy carbonyl, alkylcarbonyloxy and alkoxy carbonyloxy, each of which is optionally substituted and has 1 to 40, preferably 1 to 25, more preferably 1 to 20 or 1 to 18 C atoms, and optionally substituted aryl, arylalkyl, alkylaryl, or aryloxy having 5 to 40, preferably 5 to 25 C atoms, alkylaryloxy, arylcarbonyl, aryloxy carbonyl, arylcarbonyloxy and aryloxy carbonyloxy, each of which is optionally substituted and has 5 to 40, preferably 5 to

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The carbyl or hydrocarbyl group may be a saturated or unsaturated acyclic group, or a saturated or unsaturated cyclic group. Unsaturated acyclic or cyclic groups are preferred, especially aryl, alkenyl and alkynyl groups (especially ethynyl). Where the C₁-C₄₀ carbyl or hydrocarbyl group is acyclic, the group may be linear or branched.

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The C₁-C₄₀ carbyl or hydrocarbyl group includes for example: a C₁-C₄₀ alkyl group, a C₂-C₄₀ alkenyl group, a C₂-C₄₀ alkynyl group, a C₃-C₄₀ allyl group, a C₄-C₄₀ alkyldienyl group, a C₄-C₄₀ polyenyl group, a C₆-C₁₈ aryl group, a C₆-C₄₀ alkylaryl group, a C₆-C₄₀ arylalkyl group, a C₄-C₄₀ cycloalkyl group, a C₄-C₄₀ cycloalkenyl group, and the like. Preferred among the foregoing groups are a C₁-C₂₀ alkyl group, a C₂-C₂₀ alkenyl group, a C₂-C₂₀ alkynyl group, a C₃-C₂₀ allyl group, a C₄-C₂₀ alkyldienyl group, a C₅-C₁₂ aryl group, a C₆-C₂₀ arylalkyl group, a 5 to 20 membered heteroaryl and a C₄-C₂₀ 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.

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Further preferred carbyl and hydrocarbyl groups include straight-chain, branched or cyclic alkyl with 1 to 40, preferably 1 to 25 C-atoms, which is unsubstituted, mono- or polysubstituted by F, Cl, Br, I or CN, and wherein one or more non-adjacent CH₂ groups are optionally replaced, in each case independently from one another, by -O-, -S-, -NH-, -NR⁰-, -SiR⁰R⁰⁰-, -CO-, -COO-, -OCO-, -O-CO-O-, -S-CO-, -CO-S-, -SO₂-, -CO-NR⁰-, -NR⁰-CO-, -NR⁰-CO-NR⁰⁰-, -CY¹=CY²- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, wherein Y¹ and Y² are independently of each other H, F, Cl, Br, I or CN, and R⁰ and R⁰⁰ are independently of each other H or an optionally substituted aliphatic or aromatic hydrocarbon with 1 to 20 C atoms. Preferred carbyl and hydrocarbyl groups are aliphatic and heteroaliphatic groups.

Halogen is F, Cl, Br or I.

As used herein, an alkyl group is a straight chain or branched, cyclic or acyclic, substituted or unsubstituted group containing from 1 to 40 carbon atoms, from 1 to 25 carbon atoms, from 1 to 20 carbon atoms, from 1 to 18 carbon atoms or from 1 to 12 carbon atoms, inclusive. An alkyl group may optionally be substituted at any position.

Preferred alkyl groups include, without limitation, methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, 2-methylbutyl, n-pentyl, s-pentyl, cyclopentyl, n-hexyl, cyclohexyl, 2-ethylhexyl, n-heptyl, cycloheptyl, n-octyl, cyclooctyl, dodecanyl, tetradecyl, hexadecyl, trifluoromethyl, perfluoro-n-butyl, 2,2,2-trifluoroethyl, perfluorooctyl, perfluorohexyl etc.

Preferred alkenyl groups include, without limitation, ethenyl, propenyl, butenyl, pentenyl, cyclopentenyl, hexenyl, cyclohexenyl, heptenyl, cycloheptenyl, octenyl, cyclooctenyl etc.

Preferred alkynyl groups include, without limitation, ethynyl, propynyl, butynyl, pentynyl, hexynyl, octynyl etc.

Preferred alkoxy groups include, without limitation, methoxy, ethoxy, 2-methoxyethoxy, n-propoxy, i-propoxy, n-butoxy, i-butoxy, s-butoxy, t-butoxy, 2-methylbutoxy, n-pentoxy, n-hexoxy, n-heptoxy, n-octoxy etc.

Preferred amino groups include, without limitation, dimethylamino, methylamino, methylphenylamino, phenylamino, etc.

5 Aryl and heteroaryl groups may be mononuclear, i.e. having only one aromatic ring (like for example phenyl or phenylene), or polynuclear, i.e. having two or more aromatic rings which may be fused (like for example naphthyl or naphthylene), individually covalently linked (like for example biphenyl), and/or a combination of both fused and individually linked aromatic rings. Preferably the aryl or heteroaryl group is an aromatic group which is substantially conjugated over substantially the whole group. Aryl groups may contain from 5 to 40 carbon
10 atoms, from 5 to 25 carbon atoms, from 5 to 20 carbon atoms, or from 5 to 12 carbon atoms. Heteroaryl groups may be from 5 to 40 membered, from 5 to 25 membered, from 5 to 20 membered or from 5 to 12 membered rings. Heteroaryl groups may contain from 1 to 4 heteroatoms selected from N, O, S and P.

15 Aryl and heteroaryl preferably denote a mono-, bi- or tricyclic aromatic or heteroaromatic group with up to 25 C atoms that may also comprise condensed rings and is optionally substituted.

Preferred aryl groups include, without limitation, benzene, biphenylene, triphenylene,
20 [1,1':3',1'']terphenyl-2'-ylene, naphthalene, anthracene, binaphthylene, phenanthrene, pyrene, dihydropyrene, chrysene, perylene, tetracene, pentacene, benzpyrene, fluorene, indene, indenofluorene, spirobifluorene, etc.

Preferred heteroaryl groups include, without limitation, 5-membered rings like pyrrole,
25 pyrazole, silole, imidazole, 1,2,3-triazole, 1,2,4-triazole, tetrazole, furan, thiophene, selenophene, oxazole, isoxazole, 1,2-thiazole, 1,3-thiazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,3,4-thiadiazole, 6-membered rings like pyridine, pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, 1,2,4,5-tetrazine, 1,2,3,4-tetrazine,
30 1,2,3,5-tetrazine, and fused systems like carbazole, indole, isoindole, indolizine, indazole, benzimidazole, benzotriazole, purine, naphthimidazole, phenanthrimidazole, pyridimidazole, pyrazinimidazole, quinoxalinimidazole, benzoxazole, naphthoxazole, anthroxazole, phenanthroxazole, isoxazole, benzothiazole, benzofuran, isobenzofuran, dibenzofuran,

quinoline, isoquinoline, pteridine, benzo-5,6-quinoline, benzo-6,7-quinoline, benzo-7,8-quinoline, benzoisoquinoline, acridine, phenothiazine, phenoxazine, benzopyridazine, benzopyrimidine, quinoxaline, phenazine, naphthyridine, azacarbazole, benzocarboline, phenanthridine, phenanthroline, thieno[2,3b]thiophene, thieno[3,2b]thiophene, dithienothiophene, dithienopyridine, isobenzothiophene, dibenzothiophene, benzothiadiazothiophene, or combinations thereof. The heteroaryl groups may be substituted with alkyl, alkoxy, thioalkyl, fluoro, fluoroalkyl or further aryl or heteroaryl substituents.

Preferred arylalkyl groups include, without limitation, 2-tolyl, 3-tolyl, 4-tolyl, 2,6-dimethylphenyl, 2,6-diethylphenyl, 2,6-di-i-propylphenyl, 2,6-di-t-butylphenyl, o-t-butylphenyl, m-t-butylphenyl, p-t-butylphenyl, 4-phenoxyphenyl, 4-fluorophenyl, 3-carbomethoxyphenyl, 4-carbomethoxyphenyl etc.

Preferred alkylaryl groups include, without limitation, benzyl, ethylphenyl, 2-phenoxyethyl, propylphenyl, diphenylmethyl, triphenylmethyl or naphthalinylmethyl.

Preferred aryloxy groups include, without limitation, phenoxy, naphthoxy, 4-phenylphenoxy, 4-methylphenoxy, biphenyloxy, anthracenyloxy, phenanthrenyloxy etc.

Any of the above groups (including aryl, heteroaryl, carbyl and hydrocarbyl groups) may optionally comprise one or more substituents, preferably selected from silyl, sulfo, sulphonyl, formyl, amino, imino, nitrilo, mercapto, cyano, nitro, halogen, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-NR^0R^{00}$, C_{1-12} alkyl, C_{1-12} alkenyl, C_{1-12} alkynyl, C_{6-12} aryl, heteroaryl having 5 to 12 ring atoms, C_{1-12} alkoxy, hydroxy, C_{1-12} alkylcarbonyl, C_{1-12} alkoxy-carbonyl, C_{1-12} alkylcarbonlyoxy or C_{1-12} alkoxycarbonyloxy wherein one or more H atoms are optionally replaced by F or Cl and/or combinations thereof. The optional substituents may comprise all chemically possible combinations in the same group and/or a plurality (preferably two) of the aforementioned groups (for example amino and sulphonyl if directly attached to each other represent a sulphamoyl radical).

Especially preferred substituents are selected from alkyl, alkoxy, alkenyl, thioalkyl, fluoroalkyl and fluoroalkoxy groups as defined for the preferred groups $R^{1,2,3}$ below.

If $R^{1,2,3}$ is an alkyl or alkoxy radical, i.e. where the alkyl is attached to the parent molecular moiety through an oxygen atom, this may be straight-chain or branched. It is preferably straight-chain, has 2 to 8 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, ethoxy, propoxy, butoxy, pentoxy, hexyloxy, heptoxy, or octoxy, furthermore methyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradecoxy, for example. Especially preferred are n-hexyl and n-dodecyl.

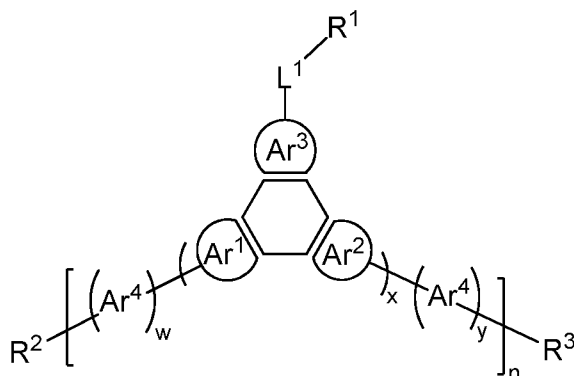
If $R^{1,2,3}$ is an alkenyl group (i.e. an alkyl group wherein one or more $-CH_2-CH_2-$ groups are replaced by $-CH=CH-$), this may be straight-chain or branched. It is preferably straight-chain, has 2 to 12 C-atoms and accordingly is preferably vinyl, prop-1-, or prop-2-enyl, but-1-, 2- or but-3-enyl, 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, undec-1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9- or undec-10-enyl, dodec-1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10 or undec-11-enyl. The alkenyl group may comprise C=C-bonds with E- or Z-configuration or a mixture thereof.

If $R^{1,2,3}$ is oxaalkyl, i.e. where one CH_2 group is replaced by $-O-$, is preferably straight-chain 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.

If $R^{1,2,3}$ is thioalkyl, 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-(thiododecyl), 1-(thioundecyl) or 1-(thiododecyl), wherein preferably the CH_2 group adjacent to the sp^2 hybridised vinyl carbon atom is replaced.

If $R^{1,2,3}$ is fluoroalkyl or fluoroalkoxy, it is preferably a straight-chain group $(O)C_iF_{2i+1}$, 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 the corresponding fluoroalkoxy group.

In one embodiment, the invention relates to a compound, which may be a monomer, dimer, trimer, or polymer, where the compound is of formula I:



wherein

- 5 R^1 at each occurrence is independently selected from H, halogen, aryl, heteroaryl, -C(=O) R^0 , -C(OR⁰)₂ R^{00} , -CN, -NC, -NCO, -NCS, -OCN, -SCN, -C(=O)NR⁰ R^{00} , -C(=O)X⁰, -NH₂, -NR⁰ R^{00} , -SH, -SR⁰, -SO₃H, -SO₂ R^0 , -OH, -NO₂, -CF₃, -SF₅, optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms,
- 10 R^{2-3} are independently of each other identical or different groups selected from H, halogen, aryl, heteroaryl, -C(=O) R^0 , -CN, -NC, -NCO, -NCS, -OCN, -SCN, -C(=O)NR⁰ R^{00} , -C(=O)X⁰, -NH₂, -NR⁰ R^{00} , -SH, -SR⁰, -SO₃H, -SO₂ R^0 , -OSO₂ R^0 , -OH, -NO₂, -CF₃, -SF₅, -CH₂Cl, -CHO, -CH=CH₂, -C(R⁰)=CR⁰ R^{00} , C≡CH, -SiR⁰ R^{00} R^{000} , -SiR⁰ R^{00} X⁰, -SiR⁰(X⁰)₂, -Si(X⁰)₃, -SnR⁰ R^{00} R^{000} , -BR⁰ R^{00} , -B(OR⁰)(OR⁰⁰), -B(OH)₂, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms,
- 15 L^1 is a single bond, -C(=O)-, an imine, a hemiacetal or an acetal,
 X^0 is halogen,
 n is an integer ≥ 1 ,
- 20 R^0 , R^{00} and R^{000} are independently selected from H or an optionally substituted aliphatic or aromatic hydrocarbyl group having 1 to 20 C atoms, or R^0 and R^{00} may also form a ring together with the hetero atom to which they are attached,
 each occurrence of w is independently an integer ≥ 0 ,
 each occurrence of x is independently an integer ≥ 1 ,
- 25 each occurrence of y is independently an integer ≥ 0 ,
 Ar^{1-3} in case of multiple occurrences are independently selected from mono- or polynuclear aryl or heteroaryl that is optionally substituted,

Ar⁴ in case of multiple occurrences is independently selected from -CY¹=CY²-, -C≡C- or mono- or polynuclear aryl or heteroaryl that is optionally substituted, or Ar⁴ has the formula:



wherein

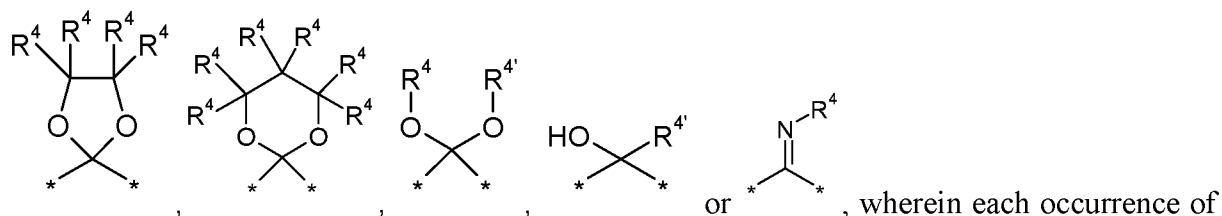
- 5 m is 1, 2 or 3,
 Ar⁵ is independently selected from mono- or polynuclear aryl or heteroaryl that is optionally substituted, and
 Y¹ and Y² are independently selected from hydrogen, halogen or -CN.

- 10 Preferably, R²⁻³ are independently of each other identical or different groups selected from H, halogen, aryl, heteroaryl, -C(=O)R⁰, -CN, -NC, -NCO, -NCS, -OCN, -SCN, -C(=O)NR⁰R⁰⁰, -C(=O)X⁰, -NH₂, -NR⁰R⁰⁰, -SH, -SR⁰, -SO₃H, -SO₂R⁰, -OH, -NO₂, -CF₃, -SF₅, -CH₂Cl, -CHO, -CH=CH₂, -C≡CH, -SiR⁰R⁰⁰R⁰⁰⁰, -SnR⁰R⁰⁰R⁰⁰⁰, -BR⁰R⁰⁰, -B(OR⁰)(OR⁰⁰), -B(OH)₂, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises
 15 one or more hetero atoms.

- Preferably, where there is more than one occurrence of the macrocyclic group encompassing Ar¹⁻³, L¹ and R¹, (for example when x is 2 or more), the macrocyclic group encompassing Ar¹⁻³ and L¹ and R¹ is identical at each occurrence. In some embodiments, each occurrence of
 20 Ar¹⁻³ is identical, preferably Ar¹⁻³ are each thiophene.

- R¹ is preferably selected from, straight-chain or branched, C₁-C₂₀-alkyl, C₁-C₂₀-alkoxy, C₂-C₂₀-alkenyl, C₂-C₂₀-alkynyl, C₁-C₂₀-thioalkyl, C₁-C₂₀-silyl, C₁-C₂₀-ester, C₁-C₂₀-ketone, C₁-C₂₀-acetal, C₁-C₂₀-alkylamino or C₁-C₂₀- dialkylamino, C₁-C₂₀-fluoroalkyl, and optionally
 25 substituted aryl or heteroaryl. More preferably, R¹ is straight-chain or branched, C₁-C₂₀-alkyl, C₁-C₂₀-alkoxy, C₂-C₂₀-alkenyl, C₂-C₂₀-alkynyl, C₁-C₂₀-thioalkyl, C₁-C₂₀-silyl, C₁-C₂₀-alkylamino or C₁-C₂₀- dialkylamino, C₁-C₂₀-fluoroalkyl, and optionally substituted aryl or heteroaryl.

L^1 is a single bond, $-C(=O)-$, an imine or an acetal. The imine, hemiacetal or acetal are preferably of the formula:



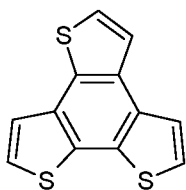
R^4 is independently selected from hydrogen or alkyl having from 1 to 6 carbon atoms and each occurrence of $R^{4'}$ is independently selected from alkyl having from 1 to 6 carbon atoms.

R^2 and R^3 are preferably hydrogen, alkyl, aryl, halogen and boronate-containing groups or tin-containing groups such as $SnR^0R^{00}R^{000}$, $-BR^0R^{00}$, $-B(OR^0)(OR^{00})$ and $-B(OH)_2$.

R^0 and R^{00} are preferably selected from H, straight-chain or branched alkyl with 1 to 18 C atoms or aryl with 6 to 12 C atoms.

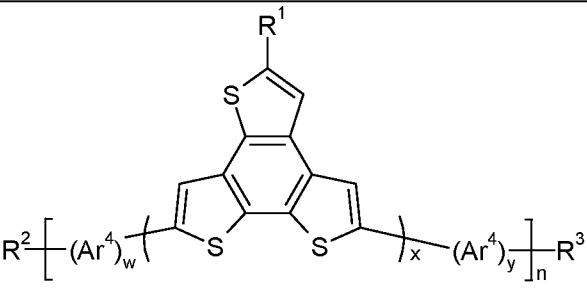
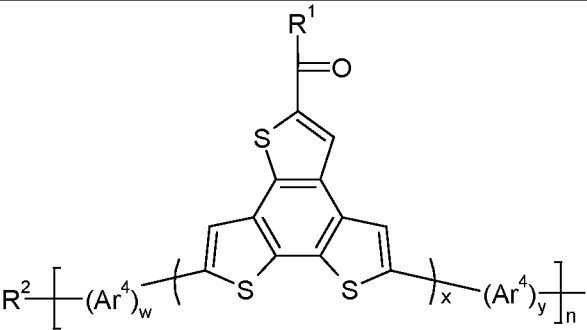
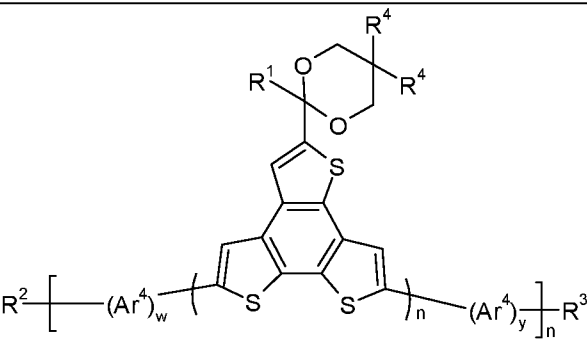
$-CY^1=CY^2-$ is preferably $-CH=CH-$, $-CF=CF-$ or $-CH=C(CN)-$.

Ar^{1-3} may be the same or different and are independently selected from mono- or polynuclear aryl with 5 to 20, preferably 6 to 12 carbon atoms, or mono- or polynuclear heteroaryl with 5 to 20, preferably 6 to 12 ring atoms. In certain embodiments, all occurrences of Ar^{1-3} are identical. In other embodiments, each occurrence of Ar^{1-3} is heteroaryl. In preferred embodiments, each occurrence of Ar^{1-3} is thiophene, preferably the arrangement of each thiophene in the macrocycle encompassing Ar^{1-3} is as follows:



It has been found that the above arrangement of the thiophene moieties allows for a direct conjugation pathway between the two free α -positions. It is believed that the extended aromatic core is advantageous for intermolecular π -stacking and charge transport.

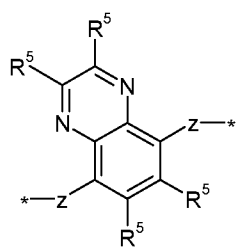
Particularly preferred polymers of formula I are the following:

	I1
	I2
	I3

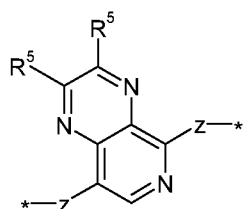
wherein R^{1-3} , Ar^4 , w , x , y and n are as defined in formula I, R^4 is preferably alkyl having 1 to 6 carbon atoms or H.

5

Preferred definitions of Ar^4 are as follows:



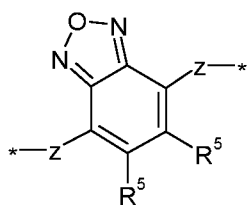
III1



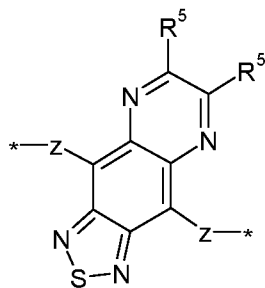
III2



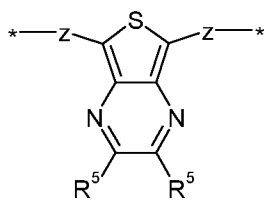
III3



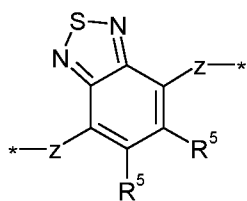
IV1



IV2



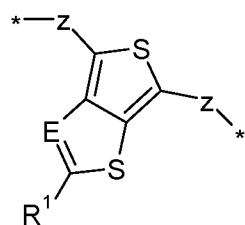
IV3



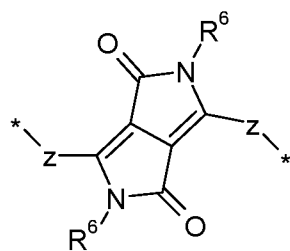
V1



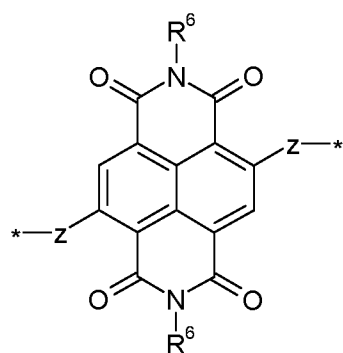
V2



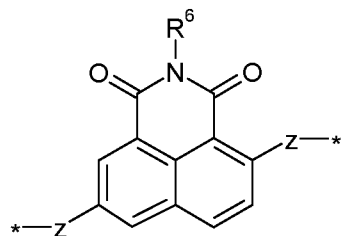
V3



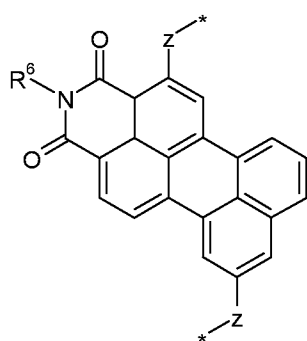
VII1



VI2

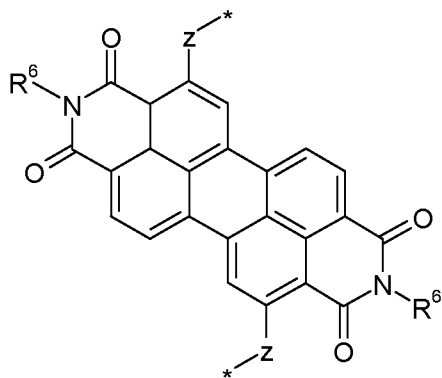


VI3

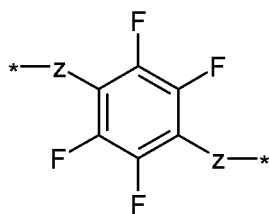


VIII1

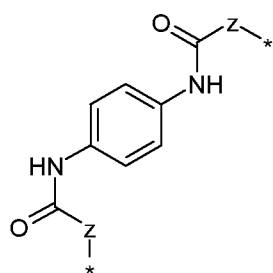
VII2



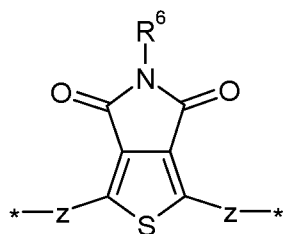
VII3



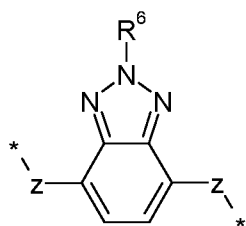
VIII1



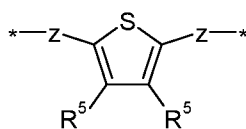
VIII2

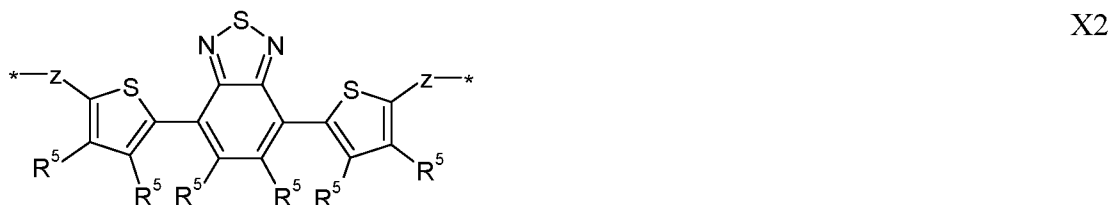


IX1



X1





wherein

R^5 is H, halogen, aryl, heteroaryl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, -C(=O)NR⁰R⁰⁰, -C(=O)X⁰, -C(=O)R⁰, -NH₂, -NR⁰R⁰⁰, -SH, -SR⁰, -SO₃H, -SO₂R⁰, -OH, -NO₂, -CF₃, -SF₅, , optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, and is preferably H, alkyl, halogen, branched alkyl, aryl, perfluoroalkyl, thioalkyl, cyano, alkoxy, heteroaryl, alkylaryl, or arylalkyl,

R^6 is hydrogen, alkyl, halogen, branched alkyl, aryl, perfluoroalkyl, thioalkyl, alkoxy, heteroaryl, alkylaryl, or arylalkyl,

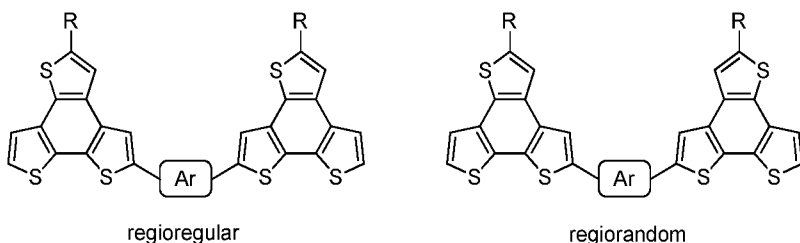
E is optionally N, CH, O, S, P, Si, Se, As, Te, Ge, P=O, PF₂, P=S, As, C-F, As=O, As=S, Sb, Sb=O or Sb=S, preferably N or CH,

z which may be the same or different, denote, independently if in different repeat units, an optionally substituted mononuclear or polynuclear aryl group, heteroaryl, fluorene, alkene, or arylalkyl, or z may be absent,

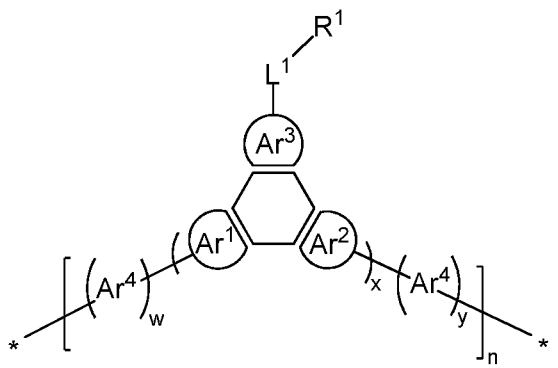
* represents the point of attachment within the compound.

The polymers of the present invention may be homopolymers, statistical or random copolymers, alternating or regioregular copolymers, block copolymers or combinations thereof. Copolymers of the invention may comprise two, three or more distinct monomer units. Thus, although for convenience the polymers of the invention may be illustrated herein in a regular fashion, it will be appreciated that the repeating units making up the polymers

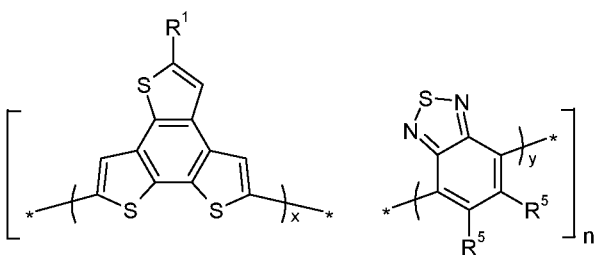
may be connected in a random fashion. Although polymers of the invention may be illustrated herein in a regioregular fashion for simplicity, where the Ar^{1-3} containing core is non-centrosymmetric, for example where the core comprises benzo[1,2-b:3,4-b':5,6-d'']trithiophene (BTT) and has an asymmetric thiophene unit, polymers and copolymers may be regiorandomly connected as illustrated below:



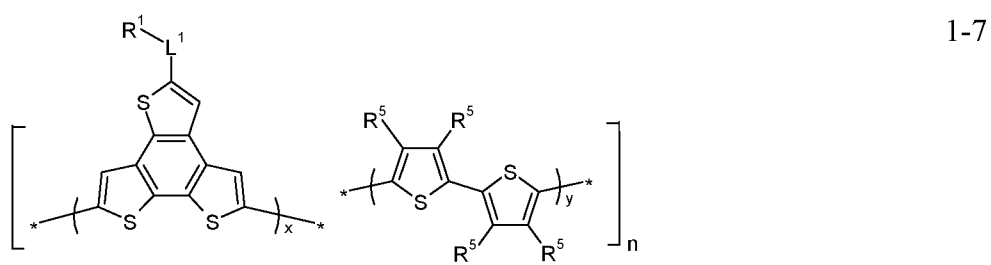
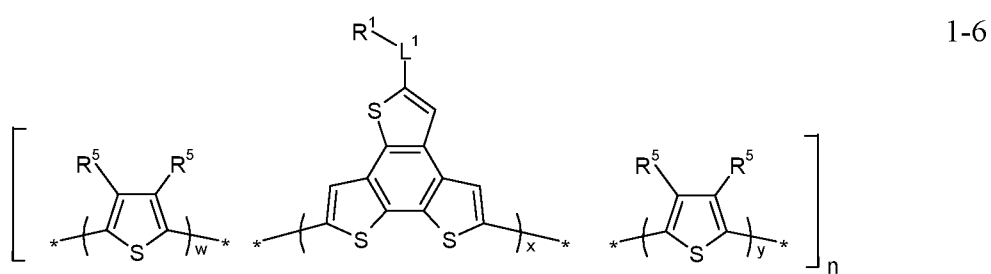
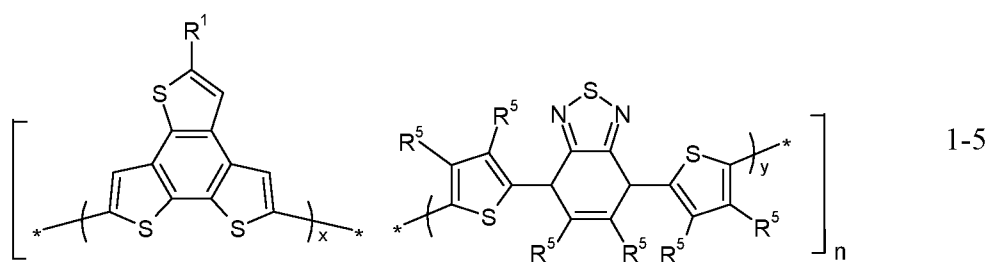
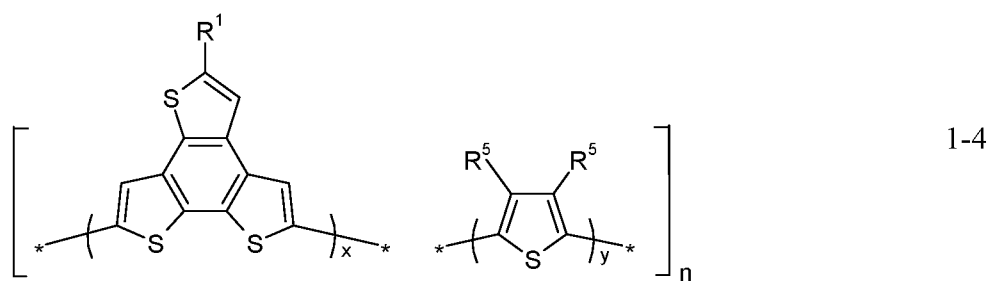
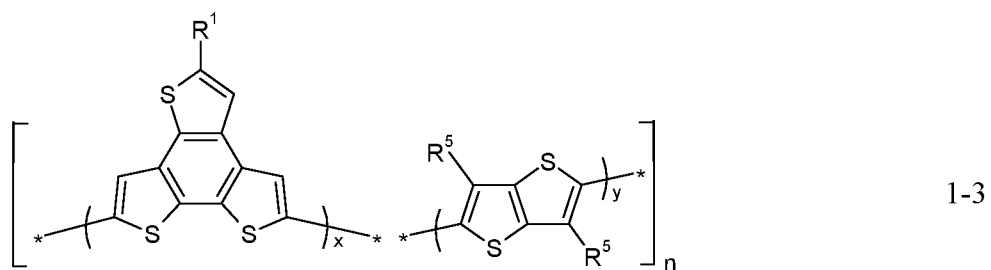
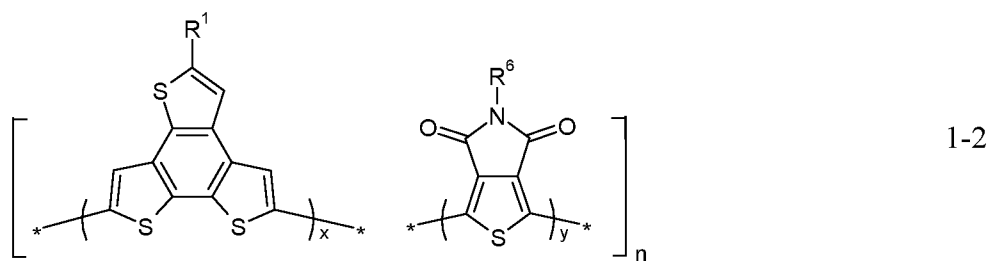
The symbol * is used herein to represent the point of attachment of repeat units within a compound. Terminating groups may be as defined for R^2 and R^3 in formula I. The terminating group may depend on the reactive groups used in the formation of the polymers and their nature may be varied. Thus, a compound of the invention may be any compound containing the repeat units defined herein, as represented by:

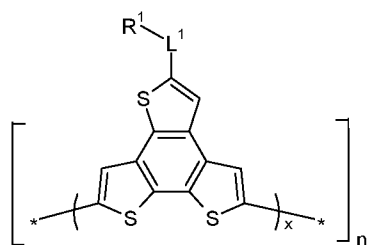


Preferred compounds of formula 1 comprise units as illustrated below. Accordingly, a compound (preferably a polymer) may be selected from the following subformulae:

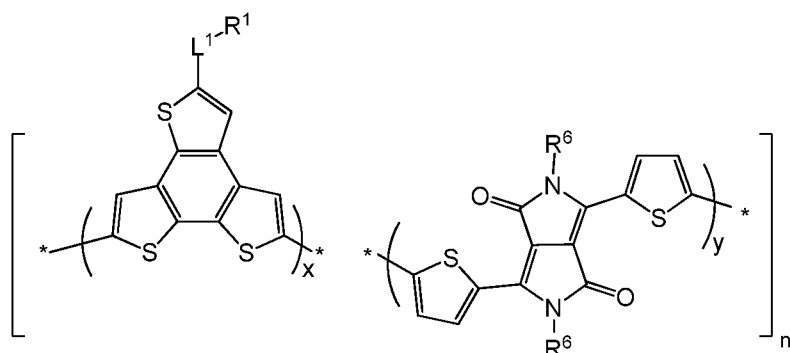


1-1





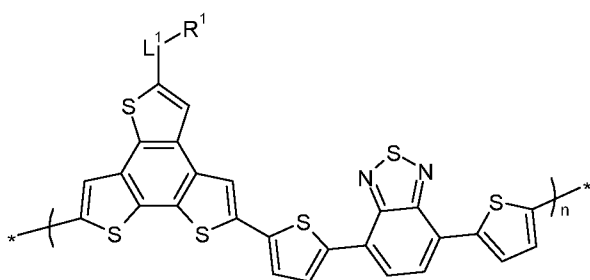
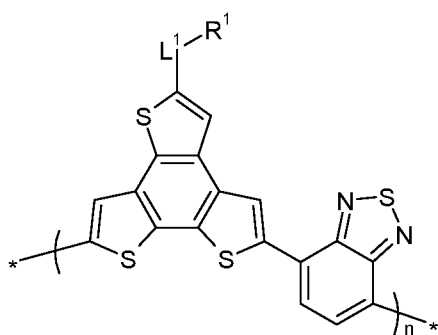
1-8

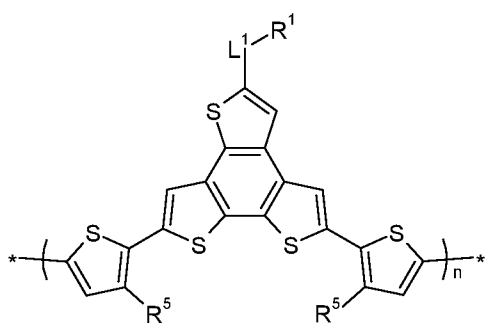
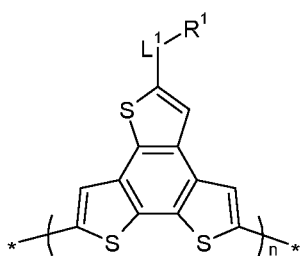
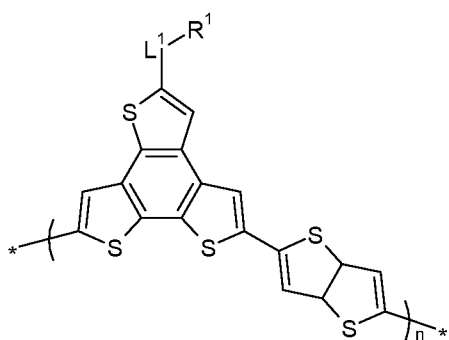
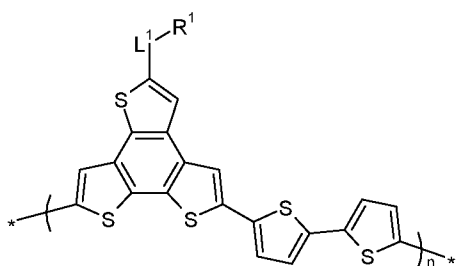
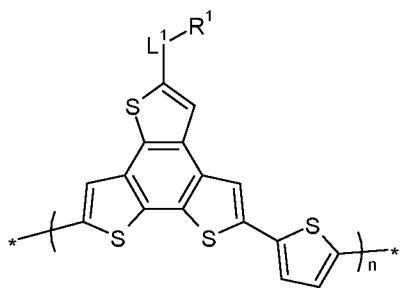


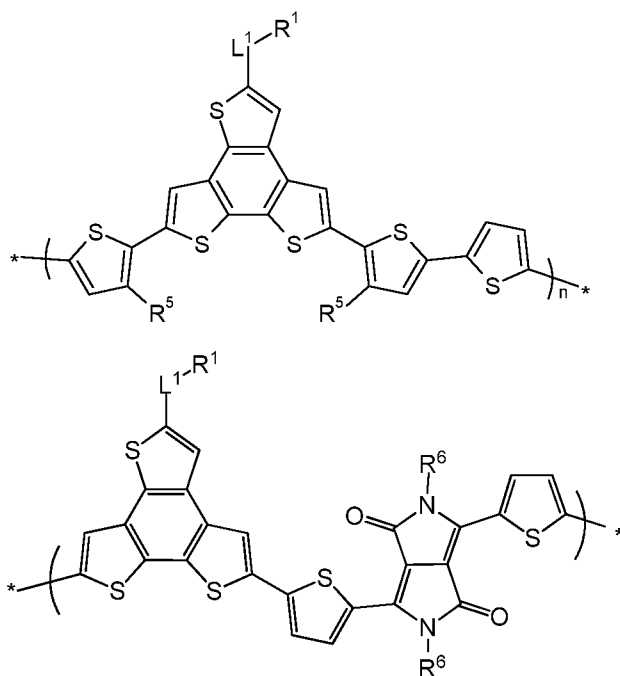
1-9

wherein R^1 , R^5 , R^6 , L^1 , w , x , y and n are as defined above and *represents the point of attachment within the compound.

- 5 In certain embodiments, the compounds of the invention comprise units as illustrated below. Accordingly, a compound (preferably a polymer) may have the following formulae:

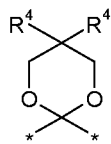






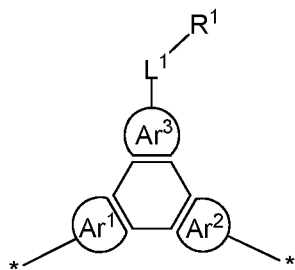
wherein L^1 , R^1 , R^5 , R^6 and n are as defined above and $*$ represents the point of attachment within the compound.

In preferred embodiments of a compound of the invention, R^5 is hydrogen, halogen, aryl, heteroaryl, $-\text{CN}$, $-\text{NO}_2$, $-\text{OH}$, $-\text{NH}_2$, alkyl, alkenyl or alkynyl. More preferably, R^5 is a branched or unbranched alkyl having from 1 to 12 carbon atoms (for example $-\text{C}_6\text{H}_{13}$). In preferred embodiments, R^6 is a branched or unbranched alkyl having from 1 to 40, preferably 1 to 25 carbon atoms (for example $-\text{CH}_2\text{CH}(\text{C}_{10}\text{H}_{21})(\text{C}_8\text{H}_{17})$). In some preferred embodiments, L^1 is a single bond and R^1 is branched or unbranched alkyl having from 1 to 25 carbon atoms (for example $-\text{C}(\text{C}_8\text{H}_{17})_2$), or L^1 is $-\text{C}(=\text{O})-$ or an acetal and R^1 is a branched or unbranched alkyl having from 1 to 25 carbon atoms (for example, $-\text{C}_{15}\text{H}_{31}$). Preferably, the

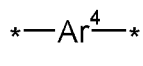


acetal has the formula R^4 , wherein R^4 is as defined above.

In certain embodiments, the compound of the invention is a copolymer comprising at least two structurally distinct macrocyclic units:



and/or at least two structurally distinct units:

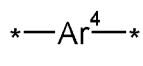


wherein R^1 , L^1 and Ar^{1-4} are as defined for formula I.

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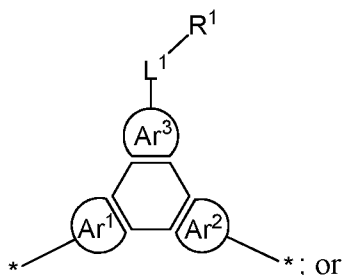
Preferably, the copolymer is a random copolymer. The random copolymer may be a terpolymer comprising:

a) two structurally distinct repeating units of structure:



10

and a repeating unit of structure:

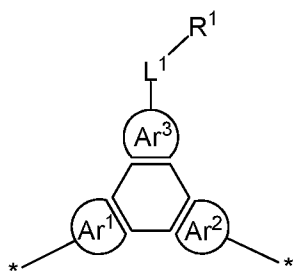


b) a repeating unit of structure:



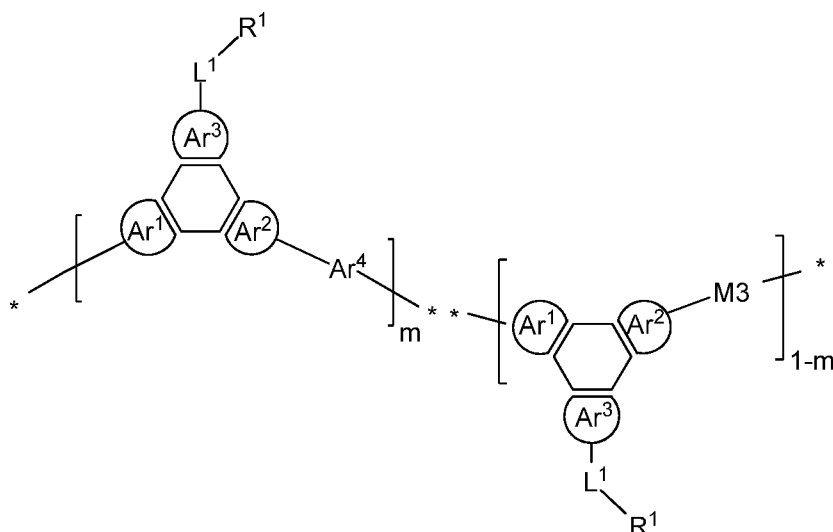
and two structurally distinct repeating units of structure:

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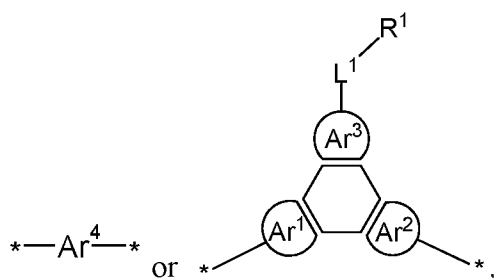


wherein R^1 , L^1 and Ar^{1-4} are as defined above.

Accordingly, the random terpolymer can be represented by



wherein M3 is a structurally distinct third monomer unit of formula

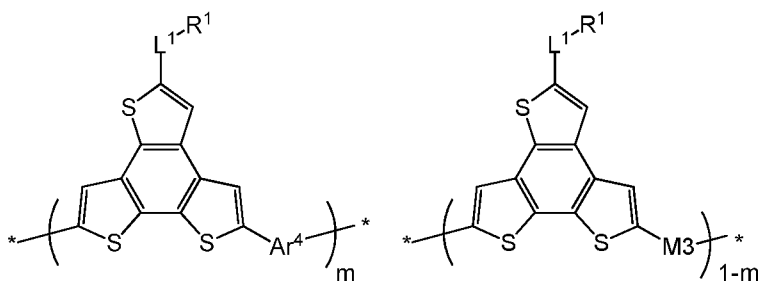


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wherein m and 1-m represent the molar proportions of the repeat units. Preferably, m is 0.05-0.95, more preferably 0.2-0.8, even more preferably 0.25-0.75. A terpolymer as defined above is formed from three repeating monomer units. Where M3 is Ar⁴, there will be two structurally distinct repeating Ar⁴ groups and one repeating macrocyclic group encompassing Ar¹⁻³, L¹ and R¹. Where M3 is a macrocyclic group encompassing Ar¹⁻³, L¹ and R¹ there will be two structurally distinct repeating macrocyclic groups encompassing Ar¹⁻³, L¹ and R¹ and one repeating Ar⁴ group.

10

In some embodiments, the terpolymer comprises the repeat units:

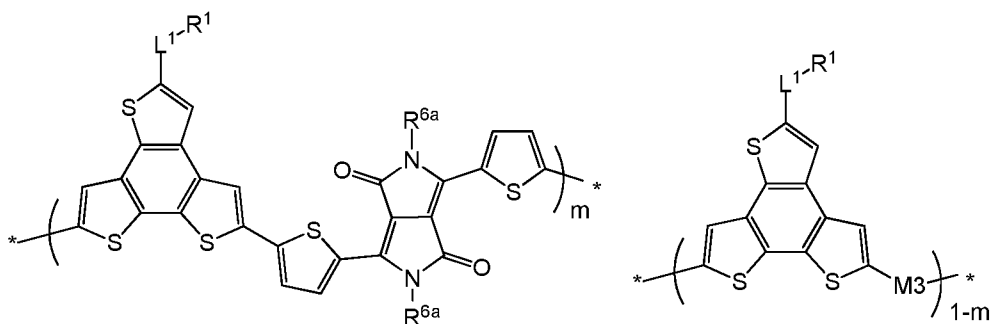


15

wherein R^1 , L^1 , Ar^4 , M3 and m are as defined above. In preferred embodiments, M3 may correspond to any of the structures illustrated herein for the macrocyclic group encompassing Ar^{1-3} , L^1 and R^1 or any of the structures illustrated herein for Ar^4 .

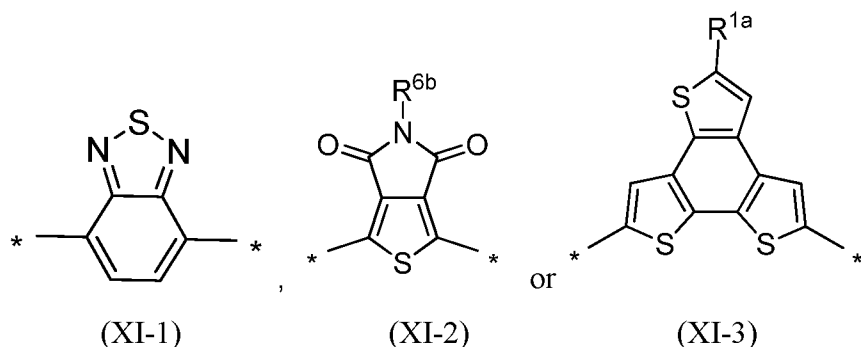
5

In a preferred embodiment, the terpolymer comprises the repeat units:



wherein R^1 , L^1 , M3 and m are as defined above and R^{6a} is as defined above for R^6 . In some embodiments R^{6a} is a branched or unbranched alkyl having from 1 to 40, preferably 1 to 25 carbon atoms (for example $-CH_2CH(C_{10}H_{21})(C_8H_{17})$). In some embodiments, M3 is:

10



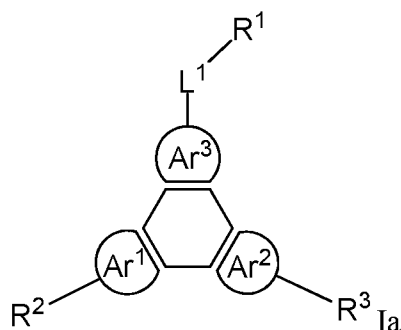
wherein R^{6b} is as defined herein for R^6 and R^{1a} is as defined for R^1 . In some embodiments R^{6b} is a branched or unbranched alkyl having from 1 to 40, preferably 1 to 25, more preferably 1 to 12 carbon atoms (for example $-C_8H_{17}$). In some embodiments R^{1a} is branched or unbranched alkyl having from 1 to 25 carbon atoms (for example $-C(C_8H_{17})_2$). In some embodiments, m is 0.6-0.9, preferably 0.7-0.8, for example about 0.75. In some embodiments, where M3 is (XI-3), m is 0.4-0.9, preferably 0.7-0.8 or 0.4-0.6, for example about 0.75 or about 0.5.

20

It will also be appreciated that formula I is intended to encompass monomers, dimers and trimers which can be used to produce the polymers of the invention. Therefore, in another aspect of the invention, for compounds of formula I, n is 1, x is 1, y is 1 or 0 and w is 1 or 0, preferably w is 0 and y is 1 or 0, or w and y are both 0. In such monomers, dimers and

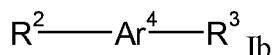
trimers, the groups represented by R^2 and R^3 are preferably selected from Cl, Br, I, O-tosylate, O-triflate, O-mesylate, O-nonaflate, SiMe_2F , SiMeF_2 , $\text{O-SO}_2\text{Z}$, $\text{B}(\text{OZ}^1)_2$, $-\text{CZ}^2=\text{C}(\text{Z}^2)_2$, $-\text{C}\equiv\text{CH}$ and $\text{Sn}(\text{Z}^3)_3$, wherein Z and Z^{1-3} are selected from the group consisting of hydrogen, alkyl and aryl, each being optionally substituted, and two groups Z^1 may also form a cyclic group.

When n is 1, x is 1, y is 0 and w is 0, the compound of the invention is a monomer of formula Ia:



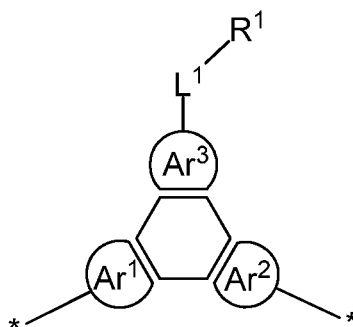
wherein R^{1-3} , Ar^{1-3} and L^1 are as defined for formula I.

A polymer of the invention can be prepared from one or more monomers of formula Ia and optionally also one or more monomers of formula Ib:



wherein R^{2-3} and Ar^4 are as defined for formula I.

Thus, it will be appreciated that a polymer of the invention is a polymer comprising one or more of a monomer repeat unit:



and optionally also one or more of:

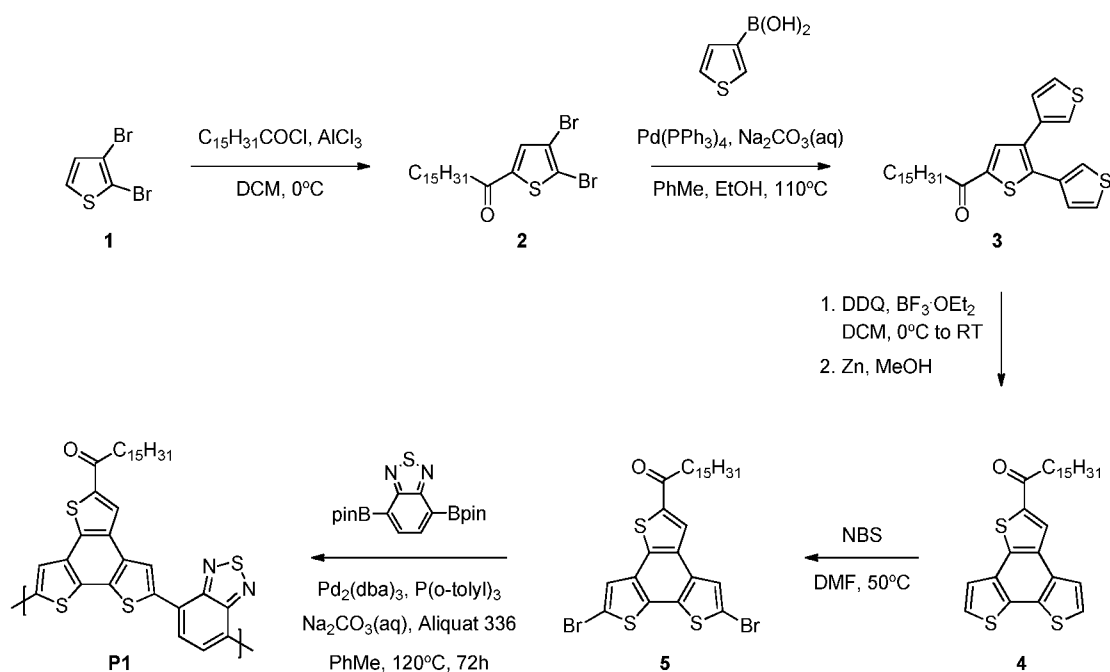


wherein R^1 , Ar^{1-4} and L^1 are as defined for formula I.

It will be appreciated that any of the various repeat units described herein can be used in combination in a compound of the invention.

- 5 The polymers of the present invention may be prepared by any suitable method. For example, they can be suitably prepared by aryl-aryl coupling reactions, such as Yamamoto coupling, Suzuki coupling, Stille coupling, Sonogashira coupling or Heck coupling. Suzuki, Stille and Yamamoto coupling are especially preferred.
- 10 The synthetic scheme shown below (scheme 1) illustrates the preparation of a Benzo[1,2-b:3,4-b':5,6-d'']trithiophene (BTT) core and the provision of an example polymer.

Scheme 1:



Another aspect of the invention is a process for preparing a polymer by coupling one or more monomers based on a unit of formula I with one or more monomers based on a unit selected from formulae III1 to X4, and optionally with further units, in a polymerisation reaction.

Preferred methods for polymerisation are those leading to C-C-coupling or C-N-coupling, like Suzuki polymerisation, as described for example in WO 00/53656, Yamamoto polymerisation, as described in for example in T. Yamamoto et al., Progress in Polymer Science 1993, 17, 1153-1205 or in WO 2004/022626 A 1, and Stille coupling. For example, when synthesizing a linear polymer by Yamamoto polymerisation, a monomer as described *above* having two reactive halide groups is preferably used. When synthesizing a linear polymer by Suzuki polymerisation, preferably a monomer as described *above* is used wherein at least one reactive group is a boron derivative group.

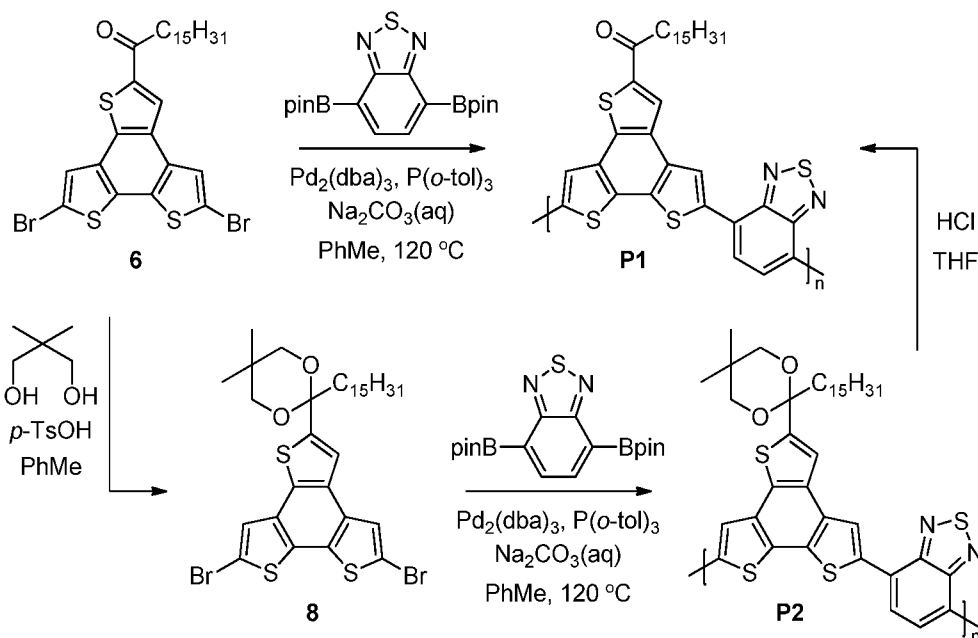
Suzuki polymerisation may be used to prepare regioregular, block and random copolymers. In particular, random copolymers may be prepared from the *above* monomers wherein one reactive group is halogen and the other reactive group is a boron *derivative* group. Alternatively, block or regioregular copolymers, in particular AB copolymers, may be prepared from a first and a second of the *above* monomers wherein both reactive groups of the first monomer are boron and both reactive groups of the second monomer are halide. The synthesis of block copolymers is described in detail for example in WO 2005/014688 A2.

Suzuki polymerisation employs a Pd(O) complex or a Pd(II) salt. Preferred Pd(O) complexes are those bearing at least one phosphine ligand such as Pd(Ph₃P)₄. Another preferred phosphine ligand is tris(*orthotolyl*) phosphine, i.e. Pd(o-Tol)₄. Preferred Pd(II) salts include palladium acetate, i.e. Pd(OAc)₂. Suzuki polymerisation is performed in the presence of a base, for example sodium carbonate, potassium phosphate or an organic base such as tetraethylammonium carbonate. Yamamoto polymerisation employs a Ni(O) complex, for example bis(1,5-cyclooctadienyl) nickel(O).

As alternatives to halogens as described above, leaving groups of formula -O-SO₂Z can be used wherein Z is as described above. Particular examples of such leaving groups are tosylate, mesylate and triflate.

A further aspect of the invention is a process for converting an acetal group when it is present in the compounds of the invention, to an aldehyde or ketone.

Scheme 2:



Scheme 2 illustrates the conversion of acetal polymer **P2** to ketone polymer **P1**. The reaction conditions (HCl , THF) are for the conversion in solution. The acetal conversion can also be carried out in the solid state, such as upon heating of a thin film of the compound. It will also be appreciated that groups other than acetals, such as hemiacetals or imines can be converted by heating a compound containing these groups, for example above 250°C , preferably in a thin film. Figure 1 shows the FTIR spectra of polymer **P2** (containing an acetal group) before and after heating as thin film. The appearance of a ketone $\text{C}=\text{O}$ stretch at 1664cm^{-1} indicates that polymer **P2** is converted to polymer **P1** using this method. Polymer **P2** was heated in air and in N_2 above 250°C . The TGA in figure 2 shows that polymer **P2** is converted to polymer **P1** on heating in both air and N_2 .

A further aspect of the present invention is an organic semiconductor material, layer or component comprising one or more polymers described above and below. A further aspect is the use of the polymers or materials as described above and below in an electronic or electrooptical component or device. A further aspect is an electronic component or device comprising a polymer or material as described above and below.

The electronic or electrooptical component or device is for example an organic field effect transistor (OFET), thin film transistor (TFT), integrated circuit (Ic), radio frequency identification (RFID) tag, photodetector, sensor, logic circuit, memory element, capacitor, organic photovoltaic (OPV) cell, charge injection layer, charge transport layer, Schottky

diode, planarising layer, antistatic film, polymer electrolyte membrane (PEM), conducting substrate or pattern, photoconductor, electrophotographic element, or organic light emitting diode (OLEO).

5 The polymers of the present invention are typically used as either binders or organic semiconductors in form of thin organic layers or films, preferably less than microns thick. Typically the semiconducting layer of the present invention is at most 1 micron (=1 μ m) thick, although it may be thicker if required. For various electronic device applications, the thickness may also be less than about 1 micron thick. For use in an OFET, the layer thickness
10 may typically be 500 nm or less, in an OLEOs be 100nm or less. The exact thickness of the layer will depend, for example, upon the requirements of the electronic device in which the layer is used.

For example, the active semiconductor channel between the drain and source in an OFET may
15 comprise a layer of the present invention. As another example, a hole injection or transport layer, and or an electron blocking layer in an OLED device may comprise a layer of the present invention.

An OFET device according to the present invention preferably comprises:

- 20 - a source electrode,
- a drain electrode,
- a gate electrode,
- a semiconducting layer,
- one or more gate insulator layers,
25 - optionally a substrate,
wherein the semiconductor layer preferably comprises one or more polymers as described above and below.

30 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.

Preferably the electronic device is an OFET comprising an insulator having a first side and a second side, a gate electrode located on the first side of the insulator, a layer comprising a polymer of the present invention located on the second side of the insulator, and a drain electrode and a source electrode located on the polymer layer.

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 WO 03/052841.

The gate insulator layer may comprise for example 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 Fe 43® (Acros, No. 12377).

Further preferred is an integrated circuit comprising a field effect transistor according to the present invention.

Further preferred is a photovoltaic cell comprising a polymer or layer according to the present invention.

Besides the devices mentioned above, the polymers of the present invention may also function as electron transporting components of an organic light emitting device (OLEO). In particular, it can be used as hole or electron transport, injection or blocking layer in PLEDs.

The polymers of the present invention may also be used in polymer electrolyte membranes, e.g. for fuel cells. A fuel cell using a polymer electrolyte membrane typically consists of a positive electrode layer and a negative electrode layer disposed on the front and rear sides of

the polymer electrolyte membrane (PEM). To generate electricity, hydrogen will be brought into contact with a catalyst in the negative electrode layer and oxygen into contact with a catalyst in the positive electrode layer. The PEM is responsible for the proton transport. The typically used method to make a PEM is through sulfonation and/or phosphonation.

5

Another aspect of the invention relates to a solution comprising one or more polymers as described above and below and one or more organic solvents.

10

Another aspect of the invention relates to a dispersion, wherein one or more polymers as described above and below are sulfonated or phosphonated and and formed a dispersion in water or one/more organic solvents. Suitable and preferred methods for sulfonation or phosphonation are described in Chemical Review 2004, Vol 104, 45687. Such dispersions are suitable for example for use in polymer electrolyte membranes (PEMs).

15

Examples of suitable and preferred organic solvents include, without limitation, dichloromethane, trichloromethane, monochlorobenzene, o-dichlorobenzene, tetrahydrofuran, anisole, 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, dimethylformamide, dimethylacetamide, dimethylsulfoxide, tetralin, decalin, indane and/or mixtures thereof.

20

The concentration of the polymers in the solution is preferably 0.1 to 10% by weight, more preferably 0.5 to 5% by weight.

25

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, 38, No 496,296 (1966)". 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

30

polymers of the present invention, although it is desirable to have at least one true solvent in a blend.

5 It is desirable to generate small structures or patterns in modern microelectronics to reduce cost (more devices/unit area), and power consumption. Patterning of the layer of the invention may be carried out by photolithography.

10 For use as semiconducting layer the polymers or solutions of the present invention may be deposited by any suitable method. Liquid coating of organic electronic devices such as field effect transistors is more desirable than vacuum deposition techniques. Solution deposition methods are especially preferred. Preferred deposition techniques include, without limitation, dip coating, spin coating, ink jet printing, letter-press printing, screen printing, doctor blade coating, roller printing, reverse-roller printing, offset lithography printing, flexographic printing, web printing, spray coating, brush coating or pad printing. Ink-jet printing is
15 particularly preferred as it allows high resolution displays to be prepared.

Selected solutions 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
20 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 TEE or single nozzle microdispensers such as those produced by Microdrop and Microfab may be used.

25 In order to be applied by ink jet printing or microdispensing, the polymers should be first dissolved in a suitable solvent. Solvents must fulfil the requirements stated above and must not have any detrimental effect on the chosen print head. Additionally, solvents should have boiling points $>100^{\circ}\text{C}$, preferably $>140^{\circ}\text{C}$ and more preferably $>150^{\circ}\text{C}$ in order to prevent operability problems caused by the solution drying out inside the print head. Apart from the
30 solvents mentioned above, suitable solvents include substituted and non-substituted xylene derivatives, di-C1_2-alkyl formamide, substituted and non-substituted anisoles and other phenolether derivatives, substituted heterocycles such as substituted pyridines, pyrazines,

pyrimidines, pyrrolidinones, substituted and non-substituted N,N-di-C1-2-alkylanilines and other fluorinated or chlorinated aromatics.

5 A preferred solvent for depositing a polymer according to the present invention 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 polymer, which
10 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, diethylbenzene. The solvent may be a solvent mixture, that is a combination of two or more solvents, each solvent preferably having a boiling point $>100^{\circ}\text{C}$, more preferably
15 $>140^{\circ}\text{C}$. 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 1-100mPa·s, more preferably 1-50mPa·s and most preferably 1-
20 30mPa·s.

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

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.

30 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).

It will be appreciated that many of the features described above, particularly of the preferred embodiments, are inventive in their own right and not just as part of an embodiment of the present invention. Independent protection may be sought for these features in addition to or alternative to any invention presently claimed.

Examples

Example 1 – Synthesis of Polymer P1

2,3-Dibromo-5-pentadecanoylthiophene (2). To an ice-cooled solution of 2,3-dibromothiophene (25.30 g, 104.6 mmol) and palmitoyl chloride (31.70 g, 115.3 mmol) in dichloromethane (200 mL) was added aluminium chloride (18.05 g, 135.4 mmol) portion-wise during 15 min. The reaction mixture was stirred for 2 h and then quenched with ice-cold hydrochloric acid (2 M, 400 mL). The quenched reaction mixture was extracted with diethyl ether and dried over anhydrous magnesium sulphate; removal of the solvent afforded the title compound (49.74 g, 103.6 mmol) as an oily yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.43 (s, 1H), 2.76 (t, 2H), 1.67 (m, 2H), 1.21 (m, 24H), 0.84 (t, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 191.71, 144.76, 133.63, 121.32, 115.03, 38.70, 32.10, 29.84, 29.77, 29.62, 29.54, 29.39, 24.60, 22.87, 14.30. MS: m/z 478 (M⁺), 282 (M-C₁₄H₂₈). HRMS (EI): m/z calcd for C₂₀H₃₂Br₂OS (M⁺) 478.0541 found 478.0535.

5-Pentadecanoyl-2,3-bis(3-thienyl)thiophene (3). A suspension of 2 (20.34 g, 42.35 mmol), thiophene-3-boronic acid (12.68 g, 99.09 mmol) and sodium carbonate (55.5 g, 0.524 mol) in toluene (140 mL), ethanol (140 mL) and water (140 mL) was degassed by bubbling with argon for 2 h. Then tetrakis(triphenylphosphine)palladium(0) (1.03 g, 0.891 mmol) was added and the reaction mixture was heated to reflux for 20 h. The reaction mixture was quenched with water, extracted with diethyl ether, dried over anhydrous magnesium sulphate and concentrated to afford the crude product. Purification by column chromatography (silica, toluene) and subsequent recrystallisation (toluene/methanol) afforded the title compound (9.99 g, 20.5 mmol) as a pale yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.66 (s, 1H), 7.30 (dd, J = 5.0, 3.0 Hz, 1H), 7.27 (m, 2H), 7.21 (dd, J = 3.0, 1.3 Hz, 1H), 6.99 (m, 2H), 2.86 (t, 2H), 1.74 (m, 2H), 1.24 (m, 24H), 0.86 (t, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 193.65, 141.55, 141.28, 136.25, 134.39, 134.09, 134.04, 128.20, 127.94, 126.35, 126.02, 124.59, 123.38, 39.32, 32.14, 29.90, 29.88, 29.85, 29.71, 29.65, 29.58, 25.14, 22.91, 14.35. MS: m/z 486 (M⁺), 290 (M-C₁₄H₂₈). HRMS (ESI-TOF): m/z calcd for C₂₈H₃₉OS₃ (MH⁺) 487.2163 found 487.2166.

2-Hexadecanoylbenzo[1,2-b:3,4-b':5,6-d'']trithiophene (4). To an ice-cooled solution of 3 (5.18 g, 10.6 mmol) in anhydrous dichloromethane (500 mL) was added boron trifluoride diethyl etherate (1.70 mL, 13.8 mmol) after which 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (2.90 g, 12.8 mmol) was added portion-wise during 10 min. The reaction mixture was allowed to warm to room temperature over night and was subsequently quenched by addition of zinc (7.0 g, 0.10 mol) and methanol (250 mL). After stirring over night, the reaction mixture was filtered, washed with water, dried over anhydrous magnesium sulphate and concentrated to afford the crude product. Purification by column chromatography (silica, toluene) and subsequent recrystallisation (ethanol) afforded the title compound (2.52 g, 5.20 mmol) as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 8.31 (s, 1H), 7.75 (d, J = 5.3 Hz, 1H), 7.63 (d, J = 5.4 Hz, 1H), 7.54 (d, J = 5.3 Hz, 1H), 7.52 (d, J = 5.4 Hz, 1H), 3.05 (t, 2H), 1.82 (m, 2H), 1.23 (m, 10H), 0.86 (t, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 194.69, 142.25, 136.36, 133.69, 133.41, 132.39, 131.81, 131.31, 127.25, 125.65, 125.45, 122.83, 122.67, 39.60, 32.13, 29.90, 29.87, 29.73, 29.70, 29.61, 29.57, 25.04, 22.90, 14.34. MS: m/z 484 (M⁺), 288 (M-C₁₄H₂₈). HRMS (ESI-TOF): m/z calcd for C₂₈H₃₇OS₃ (MH⁺) 485.2001 found 485.2029.

5,8-Dibromo-2-hexadecanoylbenzo[1,2-b:3,4-b':5,6-d'']trithiophene (**5**). A solution of **4** (1.61 g, 3.32 mmol) and N-bromosuccinimide (1.24 g, 6.97 mmol) in anhydrous N,N-dimethylformamide (150 mL) was stirred at 50 °C in the dark over night, after which the reaction mixture was quenched with water, extracted with chloroform, washed with aqueous sodium thiosulphate and water and finally dried over anhydrous magnesium sulphate and concentrated to afford the crude product. Purification by column chromatography (silica, toluene) and subsequent recrystallisation (toluene/methanol) afforded the title compound (1.17 g, 1.82 mmol) as a white solid. ¹H NMR (500 MHz, 323 K, CDCl₃): δ 8.12 (s, 1H), 7.66 (s, 1H), 7.52 (s, 1H), 3.01 (t, 2H), 1.82 (m, 2H), 1.44 (m, 2H), 1.26 (m, 22H), 0.87 (t, 3H). ¹³C NMR (100 MHz, 323 K, CDCl₃): δ 194.29, 143.34, 135.34, 133.43, 131.81, 131.78, 131.42, 126.58, 125.62, 125.54, 114.87, 114.72, 39.78, 32.17, 29.92, 29.87, 29.73, 29.67, 29.64, 29.57, 25.08, 22.90, 14.25. MS: m/z 640 (M⁺), 444 (M-C₁₄H₂₈). HRMS (EI): m/z calcd for C₂₈H₃₄Br₂OS₃ (M⁺) 640.0139 found 640.0130.

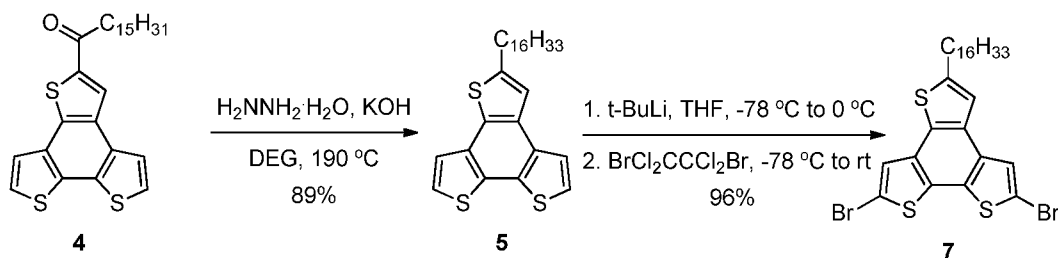
Poly[(2-hexadecanoylbenzo[1,2-b:3,4-b':5,6-d'']trithiophene-5,8-diyl)-alt-co-(2,1,3-benzothiadiazole-4,7-diyl)] (**P1**). A solution of **5** (172.33 mg, 0.2682 mmol), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (104.08 mg, 0.2682 mmol) and Aliquat 336 (one drop) in toluene (5 mL) was degassed by bubbling with argon for 1 h whereupon tris(dibenzylideneacetone)dipalladium (5.1 mg, 5.6 μmol), tris(o-tolyl)phosphine (6.7 mg, 22 μmol) and a degassed aqueous solution of sodium carbonate (1.0 M, 1.0 mL) were added and the reaction mixture was sealed and heated to 120 °C for 72 h. The reaction mixture was poured into HCl-acidic methanol and the crude polymer was isolated by filtration.

Example 2 – Synthesis of Polymer **P2** and Conversion to Polymer **P1**

Polymer **P2** was synthesised as illustrated in Scheme 2 above. Conversion of ketone (**6**) to the more soluble neopentyl ketal (**8**) allowed the preparation of **P1** from the ketal-derivative **P2**. It was also possible to increase solubility of the **P1** polymer prepared from (**6**) by converting it to polymer **P2**. **P1** was obtained by synthesis from the ketone with a number-average molecular weight, M_n, of 9.1 kDa. **P1** was obtained by forming ketal-derivative (**8**) with a M_n of 16.5 kDa.

Example 3 – Conversion of Acyl-functionalized Benzo[1,2-b:3,4-b':5,6-d'']trithiophene (BTT) core to corresponding alkyl-BTT

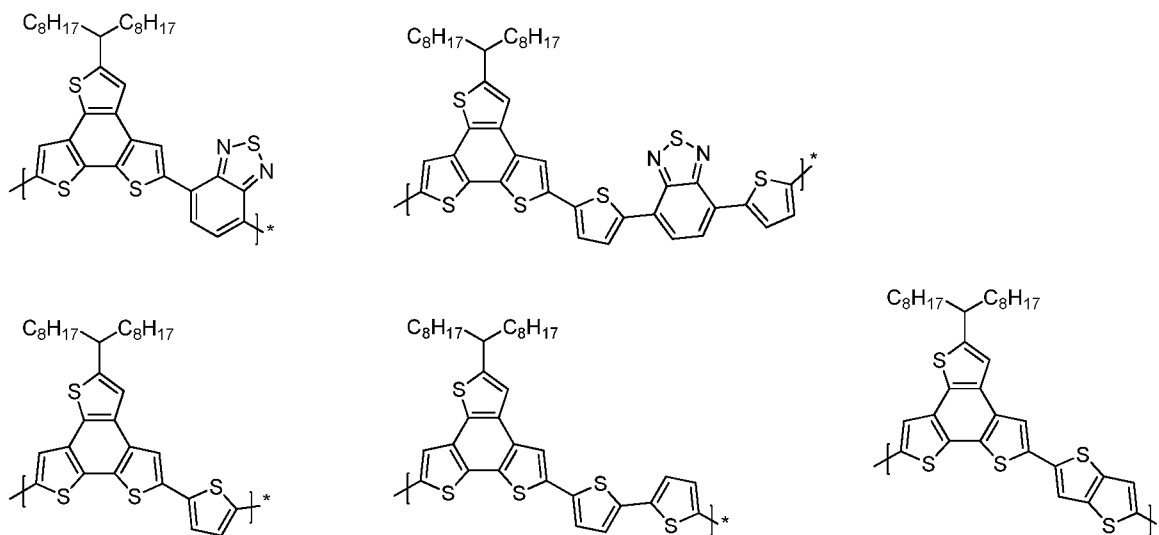
Scheme 3



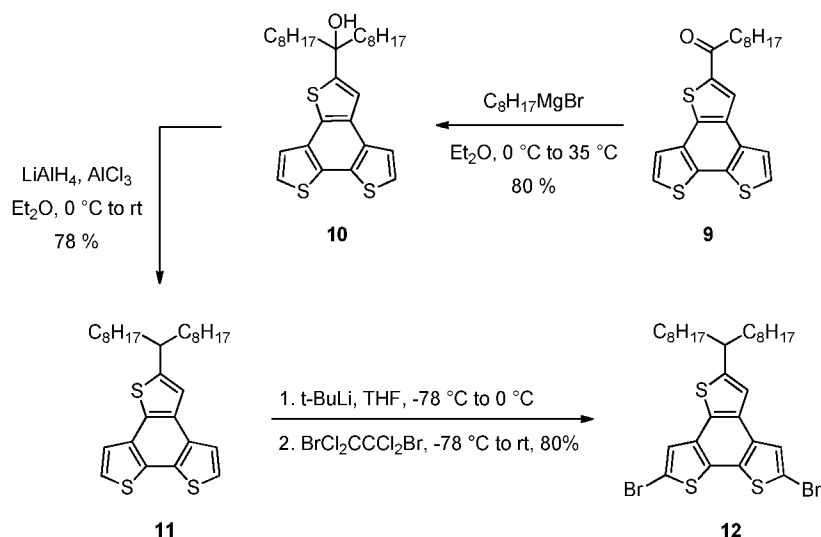
Acyl-functionalized BTT (4) is easily converted to the corresponding alkyl-BTT (5) using the Huang-Minlon modification of the Wolff-Kishner reduction. The bromination of 5 with NBS led to the formation of mono- and di-brominated species, including regioisomers. An alternative method for the synthesis of (7) involved forming the 2,8-dilithiated BTT selectively with *tert*-butyllithium and subsequently reacting the dilithiated species with 1,2-dibromotetrachloroethane to form the 2,8-dibrominated compound (7) very cleanly and in excellent yield.

Example 4 – Synthesis of Polymers based on a 5-Nonanoylbenzo[1,2-b:3,4-b':5,6-d'']trithiophene Core

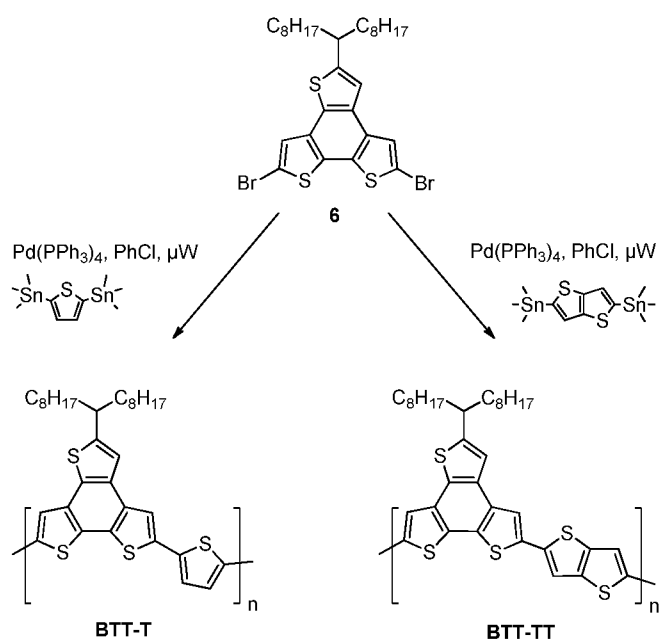
Polymers of the invention formed from the following repeating units were synthesised:



The 5-Nonanoylbenzo[1,2-b:3,4-b':5,6-d'']trithiophene monomer was synthesized according to Scheme 4:



Compound (9) was prepared as described in Example 1 for compound (4), but replacing $\text{C}_{15}\text{H}_{31}\text{COCl}$ with $\text{C}_8\text{H}_{17}\text{COCl}$. Polymers may be prepared as illustrated in Scheme 5:



Monomer 6 (150mg, 0.233mmol) was added together with 2,5-bis(trimethylstannyl)thiophene (96mg, 0.233mmol) and tetrakis(triphenylphosphine)palladium (13.49mg, 12 μ mol) to a microwave vial. The vial was sealed, 0.8mL of anhydrous chlorobenzene was added and the resulting solution was degassed with argon before subjecting to the following heating conditions in a microwave reactor: 100 °C for 2 minutes, 120 °C for 2 minutes, 140 °C for 10 minutes and finally 160 °C for 30 minutes. After reaction the crude polymer was precipitated in methanol and then further purified by Soxhlet extractions with acetone, cyclohexane, THF and chloroform, each for 24 hours. Remaining palladium residues were removed by treating a

polymeric chlorobenzene solution with an aqueous sodium diethyldithiocarbamate solution for 1 hour at 60 °C under vigorous stirring. Afterwards the organic phase was separated from the aqueous phase and washed several times with water. The polymeric solution was concentrated under reduced pressure and precipitated into methanol.

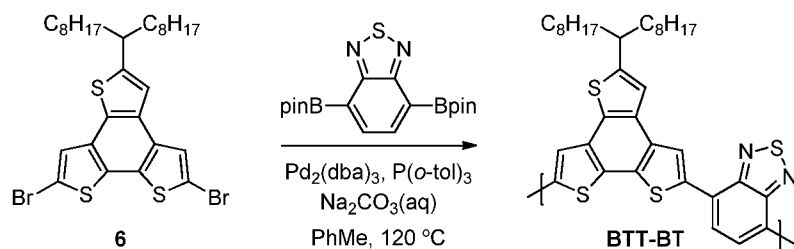
BTT-T (66mg, 0.11mmol) was recovered as a dark red solid. GPC (chlorobenzene): $M_n = 16.6$ kDa, $M_w = 48.2$ kDa, PDI = 2.90. ^1H NMR (500 MHz, $o\text{-C}_6\text{D}_4\text{Cl}_2$, 60 °C): δ 7.8-6.7 (br, 5H), 3.6-3.1 (br, 1H), 2.8-0.6 (br, 34H).

BTT-TT (75mg, 115 μ mol) was recovered as a dark red solid. GPC (chlorobenzene): $M_n = 6.2$ kDa, $M_w = 13.1$ kDa, PDI = 2.11. ^1H NMR (500 MHz, $o\text{-C}_6\text{D}_4\text{Cl}_2$, 60 °C): δ 8.2-6.7 (br, 5H), 3.7-3.0 (br s, 1H), 2.7-0.6 (br, 34H).

Inclusion in Field-Effect Transistor Devices.

Using a bottom-gate/top-contact transistor device architecture, the **BTT-T** and **BTT-TT** polymers were deposited onto octadecyltrichlorosilane-treated Si/SiO₂ substrates by spin-coating from chlorobenzene and Au electrodes were deposited on top by thermal evaporation. After annealing at 200 °C, the polymer films showed hole mobilities as high as 0.24 cm²/Vs for **BTT-T** (average of 0.21 for three devices, on/off ratio $\sim 10^6$) and 0.025 cm²/Vs for **BTT-TT** (average of 0.022 for three devices, on/off ratio $\sim 10^4$). With hole mobilities in the order of 10⁻¹ to 10⁻² cm²/Vs, these copolymers show very promising OFET performance, highlighting the potential of the BTT building block in semiconductor materials.

Polymer BTT-BT was prepared as illustrated in Scheme 6:



Inclusion of BTT-BT in Solar Cells

Bulk heterojunction solar cells were fabricated with a conventional device configuration consisting of ITO/PEDOT:PSS/**BTT-BT**:PCBM/Ca/Ag and tested under simulated 100 mW cm⁻² AM1.5G illumination. Measured photovoltaic properties of polymer solar cells using the fullerene PC₇₁BM are shown in the table below:

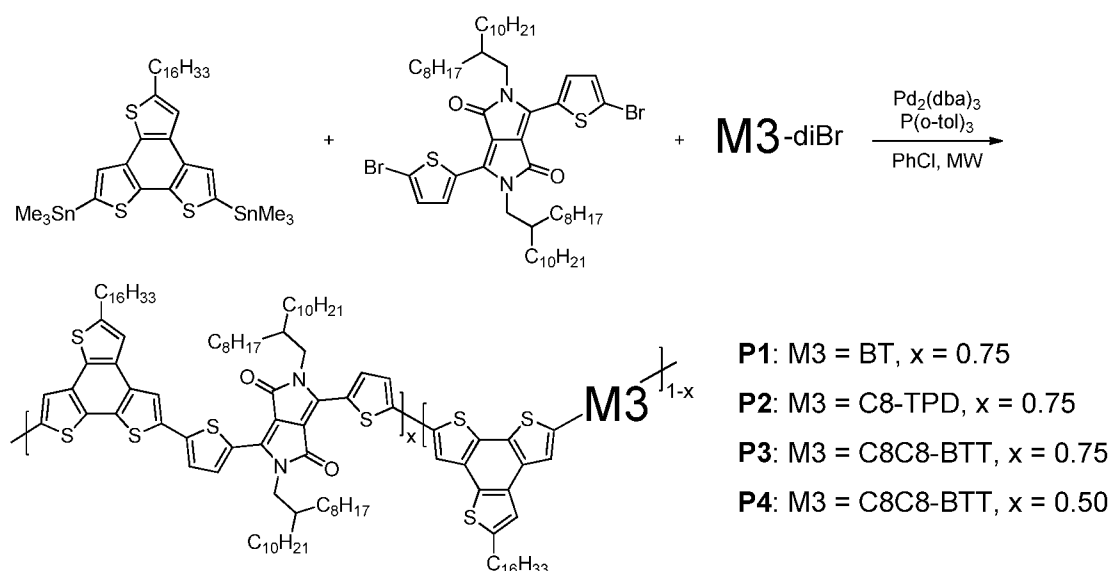
PCBM Thickness	V_{oc}	J_{sc}	FF	PCE	
(nm)	(V)	(mA/cm ²)		(%)	
C ₆₀	55	0.80	5.09	0.40	1.64
C ₇₀	45	0.81	6.07	0.44	2.18
C ₇₀	55	0.81	6.36	0.41	2.12

^a All devices made from chloroform:ODCB with a 1:2 ratio of **P1**:PCBM

The benzotrithiophene-containing D-A type copolymer provides a good compromise between a low band gap and a low-lying HOMO and shows promise for use as donor material in BHJ solar cells as manifested in a high V_{oc} (0.81 V) and a moderate PCE (2.2%).

Example 6 – Synthesis of Random Terpolymers

A series of BTT-containing terpolymers were synthesized as shown in Scheme 7:



Scheme 6: Synthesis of random BTT-containing copolymers (BT = 2,1,3-benzothiadiazole, C8-TPD = *N*-octylthienopyrrolo-dione, C8C8 = 1-octynonyl BTT).

2,8-Bis(trimethylstannyl)-5-hexadecylbenzo[1,2-b:3,4-b':5,6-d'']trithiophene (C16-BTT-ditin). 5-Hexadecylbenzo[1,2-b:3,4-b':5,6-d'']trithiophene (1.3 g, 2.8 mmol) was dissolved in 200 mL of anhydrous THF and cooled to -78°C. A 2.5 M solution of *n*-butyl lithium in hexanes (2.8 mL, 7.0 mmol) was added slowly to the reaction mixture. After two hours of

stirring at low temperature, trimethyltin chloride (7.2 mL, 7.2 mmol) in a 1 M THF solution was added and the reaction mixture was allowed to warm slowly to room temperature over night. The bright yellow solution was diluted with hexane and quenched with water. The organic layer was separated and dried with sodium sulphate. After solvent evaporation, a pale yellow oil was obtained, which was further purified by recycling gel permeation chromatography to yield pure 2,8-bis(trimethylstannyl)-5-hexadecylbenzo[1,2-b:3,4-b':5,6-d']trithiophene as a colourless oil (842 mg, 1.06 mmol). ^1H NMR (400 MHz, 298 K, $(\text{CD}_3)_2\text{CO}$): δ 7.99 (s, 1H), 7.73 (s, 1 H), 7.67 (s, 1H), 3.02 (t, 2H), 1.81 (quint, 2H), 1.47 – 1.21 (m, 26H), 0.87 (t, 3H), 0.49 (s, 1H), 0.48 (s, 1H). ^{13}C NMR (100 MHz, 298 K, $(\text{CD}_3)_2\text{CO}$): δ 145.90, 140.64, 139.40, 134.67, 133.62, 133.49, 132.17, 131.18, 131.07, 121.14, 206.26, 32.80, 32.42, 31.36, 30.54, 30.48, 29.88, 23.50, 15.77, 14.54, -8.01.

BTT-DPP. A degassed solution of C16-BTT-ditin (141.60 mg, 0.17780 mmol), C8C12-DPP-dibromide (181.19 mg, 0.17778 mmol), $\text{Pd}_2(\text{dba})_3$ (3.51 mg, 0.004 mmol) and $\text{P}(\text{o-tol})_3$ (4.42 mg, 0.015 mmol) in anhydrous chlorobenzene (2.5 mL) was stirred at 180°C for 30 minutes in a microwave reactor. The crude polymer was end-capped with bromobenzene (1.2 μL) and trimethyl(phenyl)tin (0.7 μL) and subsequently precipitated into methanol. Using a Soxhlet extractor, the crude polymer was washed with acetone and hexane and subsequently extracted with chloroform and precipitated into methanol to afford the title compound (126 mg) as a black solid. GPC: M_n = 25.8 kDa, M_w = 65.7 kDa, PDI = 2.55. ^1H NMR: δ (ppm) 9.0 (br s, 2H), 7.3 (br s, 5H), 4.0 (br s, 4H), 3.2 (br s, 2H), 1.3 (br m, 109H).

P1. Following the procedure for **BTT-DPP** using C16-BTT-ditin (65.07 mg, 0.08170 mmol), C8C12-DPP-dibromide (62.46 mg, 0.06128 mmol) and BT-dibromide (6.02 mg, 0.02048 mmol) to afford **P1** (54 mg, 57%) as a black solid. GPC: M_n = 108 kDa, M_w = 173 kDa, PDI = 1.60. ^1H NMR: δ (ppm) 9.0 (br s), 7.3 (br s), 3.2 (br s), 1.3 (br m).

P2. Following the procedure for **BTT-DPP** using C16-BTT-ditin (66.30 mg, 0.08325 mmol), C8C12-DPP-dibromide (63.63 mg, 0.06243 mmol) and C8-TPD-dibromide (8.81 mg, 0.02082 mmol) to afford **P2** (86 mg, 88%) as a black solid. GPC: M_n = 71 kDa, M_w = 100 kDa, PDI = 1.41. ^1H NMR: δ (ppm) 9.0 (br s), 7.3 (br s), 3.2 (br s), 1.3 (br m).

P3. Following the procedure for **BTT-DPP** using C16-BTT-ditin (94.87 mg, 0.1191 mmol), C8C12-DPP-dibromide (91.09 mg, 0.08937 mmol) and C8C8-BTT-dibromide (19.17 mg, 0.02983 mmol) to afford **P3** (63 mg, 43%) as a black solid. GPC: $M_n = 148$ kDa, $M_w = 279$ kDa, PDI = 1.89. $^1\text{H NMR}$: δ (ppm) 9.0 (br s), 7.3 (br s), 3.2 (br s), 1.3 (br m).

P4. Following the procedure for **BTT-DPP** using C16-BTT-ditin (73.37 mg, 0.09213 mmol), C8C12-DPP-dibromide (46.96 mg, 0.04608 mmol) and C8C8-BTT-dibromide (29.58 mg, 0.04603 mmol) to afford **P4** (65 mg, 62%) as a black solid. GPC: $M_n = 134$ kDa, $M_w = 243$ kDa, PDI = 1.81. $^1\text{H NMR}$: δ (ppm) 9.0 (br s), 7.3 (br s), 3.2 (br s), 1.3 (br m).

P4 and **P6** were synthesized by using BT and C8-TPD respectively as M3 with a DPP/M3 ratio of 3:1 in both cases. Random terpolymers **P7** (DPP/M3 ratio 3:1) and **P8** (DPP/M3 ratio 1:1) were obtained with C8C8-BTT as the third comonomer. Additionally, the alternating **BTT-DPP** copolymer was prepared from equimolar amounts of distannylated C16-BTT and dibrominated DPP using identical reaction conditions. Table 1 shows the molecular weights and thermal stability of the obtained polymers

Table 1 Molecular Weights and Thermal Stability of the Polymers

Polymer	M_n^a (kg/mol)	M_w^b (kg/mol)	PDI ^c	T_d^d (°C)
BTT-DPP	185	580	3.1	391
P1	130	280	2.1	415
P2	90	130	1.4	416
P3	190	520	2.7	420
P4	165	430	2.6	426

^a Number-average molecular weight. ^b Weight-average molecular weight. ^c M_w/M_n . ^d

Decomposition temperature (5% weight loss) determined by thermal gravimetric analysis under nitrogen.

Table 3 Photovoltaic Properties of the Polymers

Polymer	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
BTT-DPP	6.30	0.71	0.60	2.68
P1	10.95	0.68	0.69	5.14
P2	8.87	0.72	0.66	4.23
P3	11.10	0.68	0.61	4.58
P4	12.07	0.66	0.53	4.28

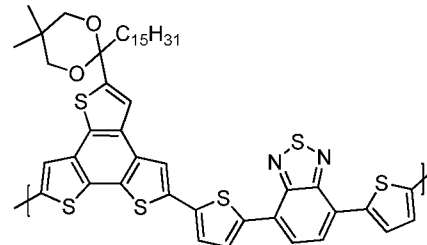
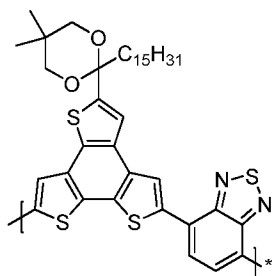
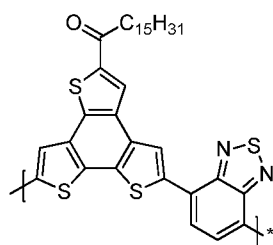
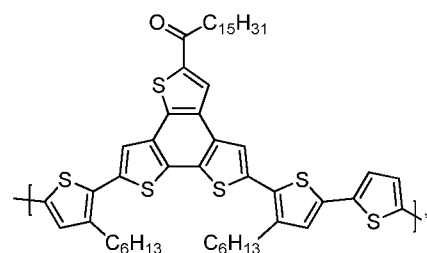
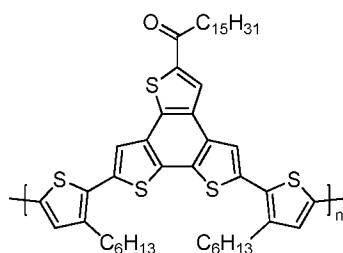
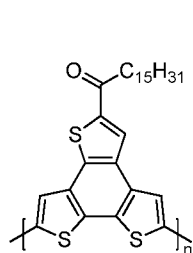
Photovoltaic properties of the polymers were assessed in solar cell devices (Figure 3 and Table 3), the alternating **BTT-DPP** polymer afforded an open-circuit voltage (V_{OC}) of 0.71 V and a fill factor (FF) of 0.60; values which are comparable to some of the best performing DPP-polymers. The short-circuit current (J_{SC}), was 6.30 mA/cm², thus causing an over-all power conversion efficiency (PCE) of 2.68%. Terpolymers **P1** and **P2** showed improved short-circuit currents and also significantly higher fill factors. **P2** moreover afforded a slightly higher V_{OC} (0.72 V versus 0.68 V for **P1**). Consequently, the PCE of the device with **P1** was nearly doubled to 5.14% while **P2** displayed a PCE of 4.23%. **P3** and **P4**, where increasing amounts of DPP is substituted with BTT (12.5% and 25% respectively), also showed improved OPV device performances.

The external quantum efficiencies (EQEs) are displayed in Figure 3 for five polymer : PC₇₁BM devices. The devices had a polymer:PC₇₁BM blend ratio of 1:2 processed from chloroform:*o*-dichlorobenzene (4:1). The device configuration used was ITO/PEDOT:PSS/polymer:PC₇₁BM/LiF/Al; tested under simulated 100 mW/cm² AM1.5G illumination. The **BTT-DPP** device exhibited a broad response from 350 nm extending beyond 800 nm, with a maximum EQE of 25% at 490 nm. **P1** and **P2** show higher EQEs with peak values of 41% and 42% respectively at 490 nm. **P3** and especially **P4** show improved photogeneration from polymer excitons as evident from the much larger EQE response in the 650 - 800 nm region. EQE values of 37% (490 nm) and 24% (750 nm) were measured for **P3**, while EQEs of 43% at 500 nm and 33% at 750 nm were found for **P4**. In conclusion, all presented terpolymers gave highly efficient OPV devices displaying high currents and high fill factors.

Example 7 – Additional Exemplary Polymers of the Invention

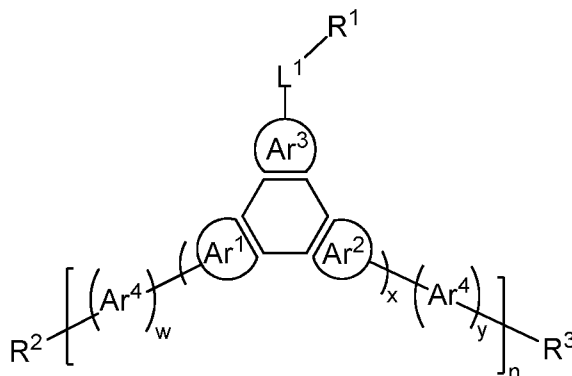
Additional polymers of the invention that have been synthesised include polymers formed from the following repeating units:

5



Claims

1. A compound of formula I:



(I)

wherein

R^1 is selected from H, halogen, aryl, heteroaryl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, -C(=O)NR⁰R⁰⁰, -C(=O)X⁰, -C(=O)R⁰, -C(OR⁰)₂R⁰⁰, -NH₂, -NR⁰R⁰⁰, -SH, -SR⁰, -SO₃H, -SO₂R⁰, -OH, -NO₂, -CF₃, -SF₅, optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms,

R^{2-3} are independently selected from H, halogen, aryl, heteroaryl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, -C(=O)NR⁰R⁰⁰, -C(=O)X⁰, -C(=O)R⁰, -NH₂, -NR⁰R⁰⁰, -SH, -SR⁰, -SO₃H, -SO₂R⁰, -OH, -NO₂, -CF₃, -SF₅, optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms -CH₂Cl, -CHO, -CH=CH₂, C≡CH, -SiR⁰R⁰⁰R⁰⁰⁰, -SnR⁰R⁰⁰R⁰⁰⁰, -BR⁰R⁰⁰, -B(OR⁰)(OR⁰⁰), -B(OH)₂, -OSO₂R⁰, -C(R⁰)=CR⁰R⁰⁰, -SiR⁰R⁰⁰X⁰, -SiR⁰(X⁰)₂, -Si(X⁰)₃,

L^1 is a single bond, -C(=O)-, an imine, a hemiacetal or an acetal group,

X^0 is halogen,

R^0 , R^{00} and R^{000} are independently of each other H or an optionally substituted aliphatic or aromatic hydrocarbyl group having 1 to 20 C atoms, or R^0 and R^{00} may also form a ring together with the hetero atom to which they are attached,

w at each occurrence is independently an integer ≥ 0 ,

x at each occurrence is independently an integer ≥ 1 ,

y at each occurrence is independently an integer ≥ 0 ,

n is an integer ≥ 1 ,

Ar¹⁻³ is in case of multiple occurrences independently selected from a mono- or polynuclear aryl or heteroaryl that is optionally substituted,

Ar⁴ is in case of multiple occurrences independently selected from -CY¹=CY², -C≡C- or mono- or polynuclear aryl or heteroaryl that is optionally substituted or Ar⁴ has the formula:



wherein

m is 1, 2 or 3,

Ar⁵ at each occurrence, is independently selected from a mono- or polynuclear aryl or heteroaryl that is optionally substituted, and

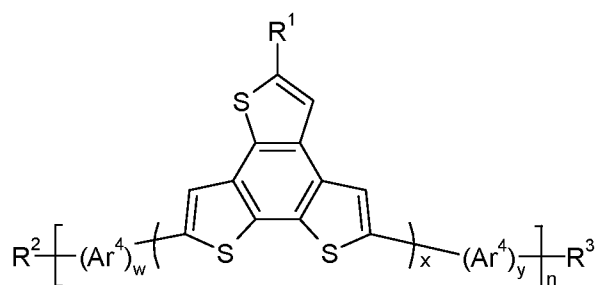
Y¹ and Y² are independently selected from hydrogen, halogen or -CN.

2. The compound according to claim 1, wherein the macrocyclic group encompassing Ar¹⁻³, L¹ and R¹ is identical at each occurrence.

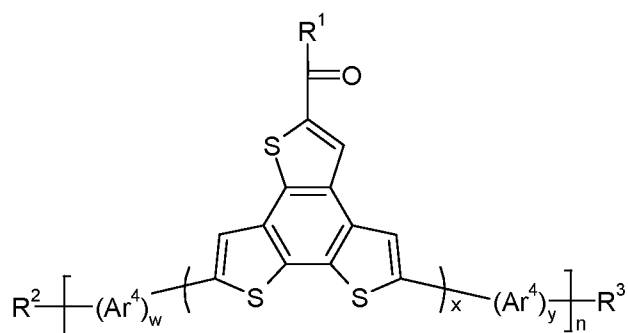
3. The compound according to claim 1 or 2, wherein Ar¹⁻³ are each thiophene.

4. The compound according to any preceding claim, wherein R¹ is selected from optionally substituted straight-chain or branched, C₁-C₂₀-alkyl, C₁-C₂₀-alkoxy, C₂-C₂₀-alkenyl, C₂-C₂₀-alkynyl, C₁-C₂₀-thioalkyl, C₁-C₂₀-silyl, C₁-C₂₀-ester, C₁-C₂₀-ketone, C₁-C₂₀-acetal, C₁-C₂₀-alkylamino or C₁-C₂₀-dialkylamino, C₁-C₂₀-fluoroalkyl, and optionally substituted aryl or heteroaryl.

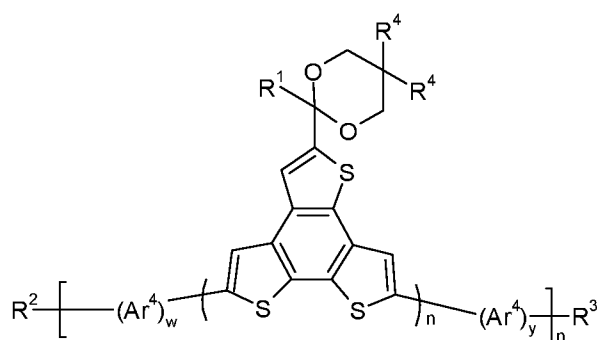
5. The compound according to any preceding claim, wherein formula I is selected from the following subformulae:



I1



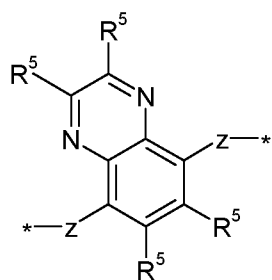
I2



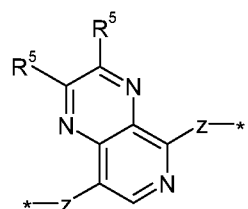
I3

wherein R^{1-3} , Ar^4 , w , x , y and n are as defined in any preceding claim and R^4 is hydrogen or alkyl.

- 5 6. The compound according to any preceding claim, characterised in that the unit Ar^4 is selected from the following formulae:



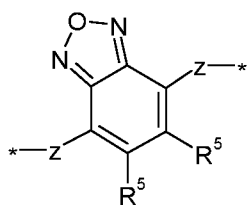
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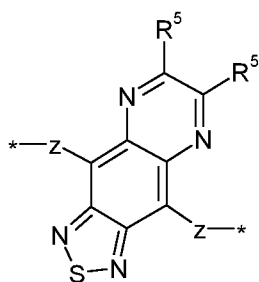
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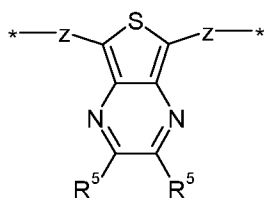
III3



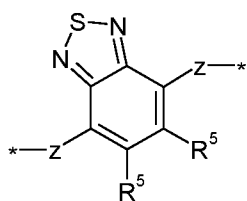
IV1



IV2



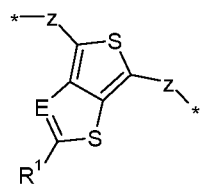
IV3



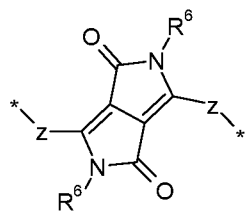
V1



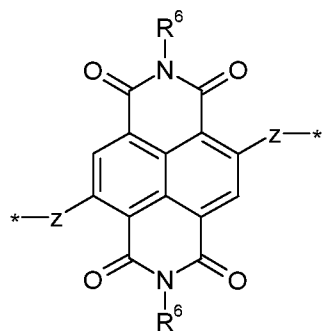
V2



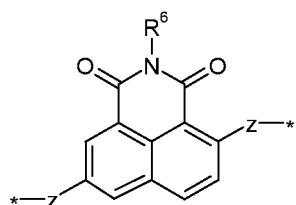
V3



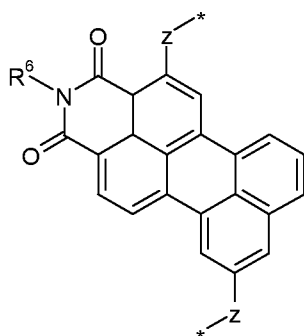
VI1



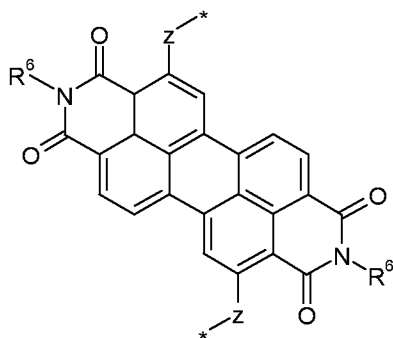
VI2



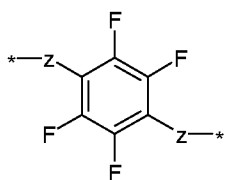
VI3



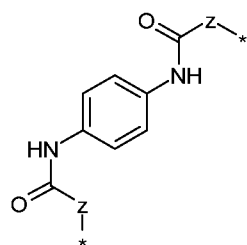
VII1



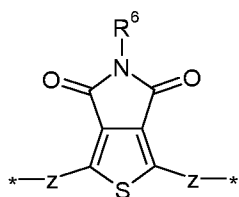
VII2



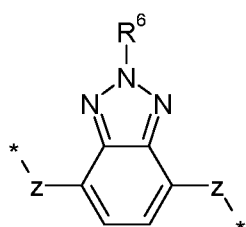
VII3



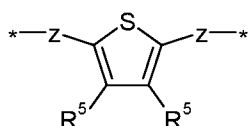
VIII1



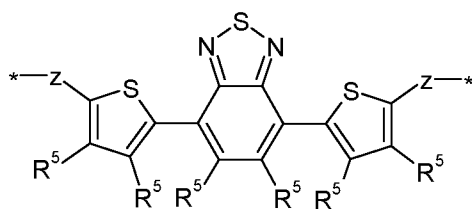
VIII2



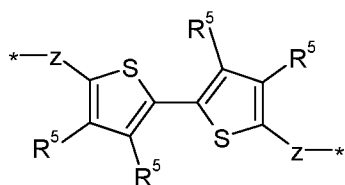
IX1



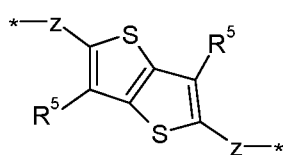
X1



X2



X3



X4

wherein

R^5 is H, halogen, aryl, heteroaryl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, -C(=O)NR⁰R⁰⁰, -C(=O)X⁰, -C(=O)R⁰, -NH₂, -NR⁰R⁰⁰, -SH, -SR⁰, -SO₃H, -SO₂R⁰, -OH, -NO₂, -CF₃, -SF₅, , optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 40

C atoms that is optionally substituted and optionally comprises one or more hetero atoms, preferably H, halogen, alkyl, aryl, perfluoroalkyl, thioalkyl, cyano, alkoxy, heteroaryl, alkylaryl, or arylalkyl,

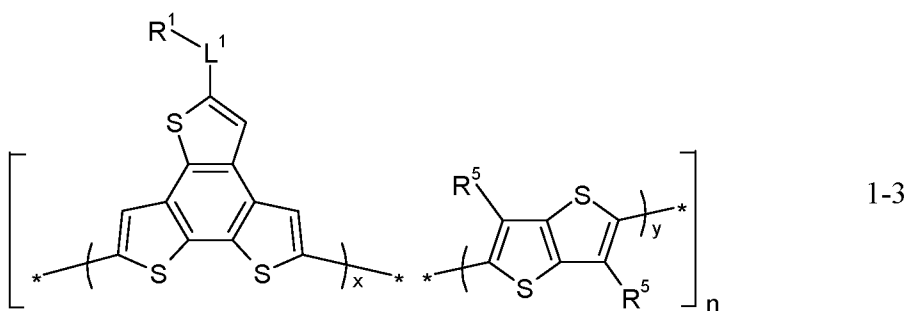
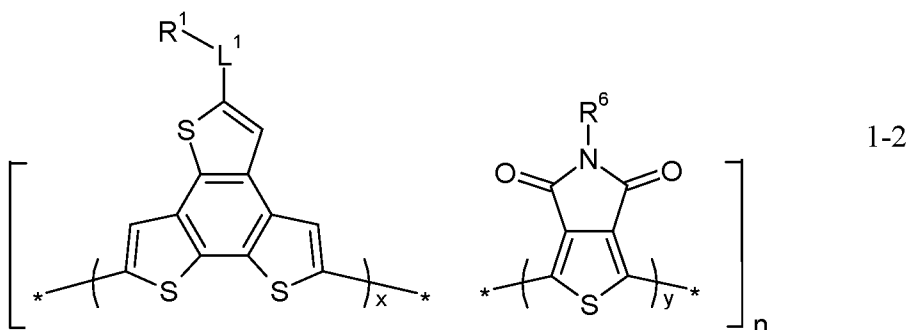
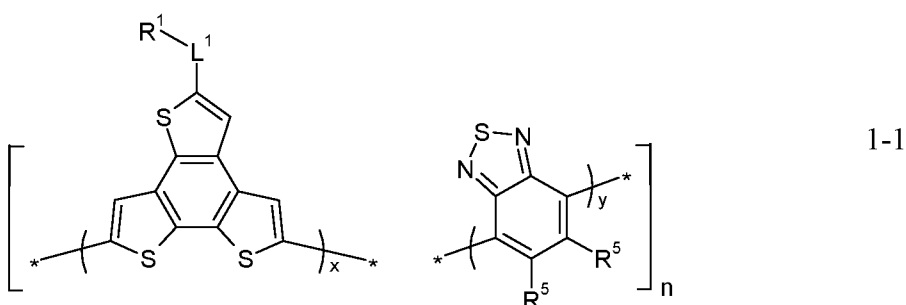
R^6 is hydrogen, alkyl, halogen, aryl, perfluoroalkyl, thioalkyl, alkoxy, heteroaryl, alkylaryl, or arylalkyl,

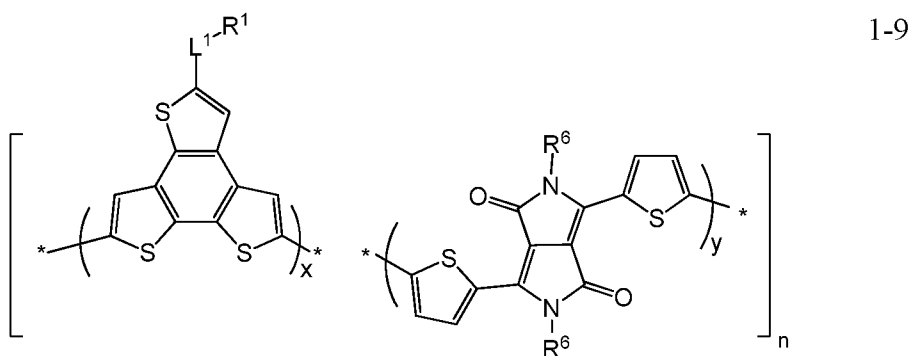
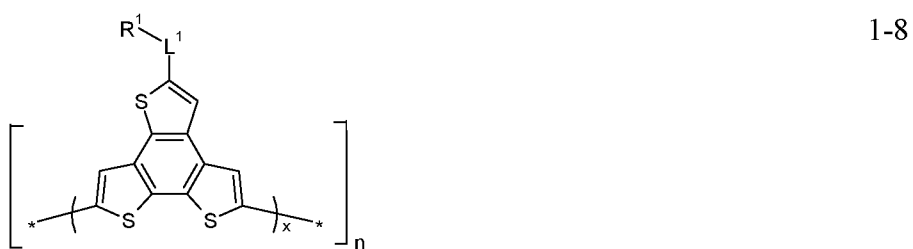
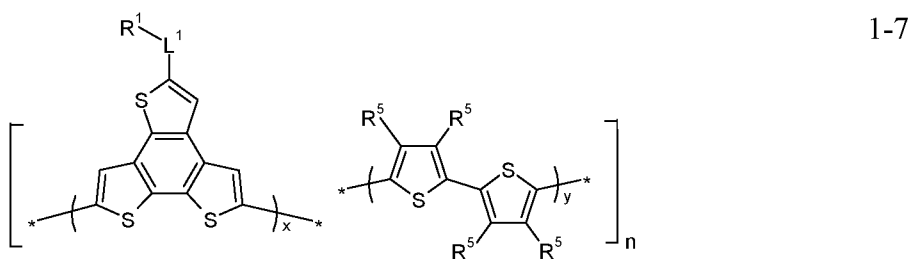
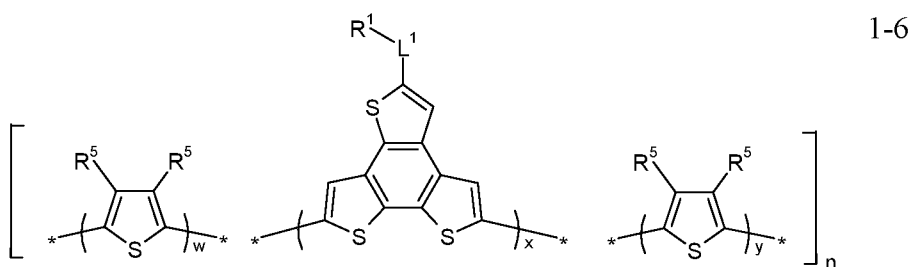
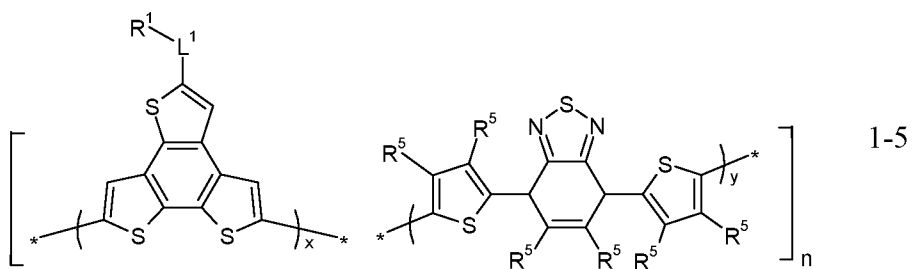
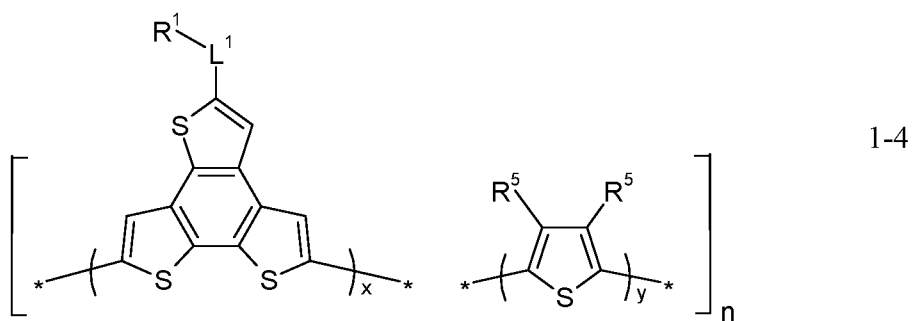
E is N, CH, O, S, P, Si, Se, As, Te, Ge, P=O, PF₂, P=S, As, As=O, As=S, Sb, Sb=O or Sb=S, preferably N or CH,

z which may be the same or different, denote, independently if in different repeat units, an optionally substituted mononuclear or polynuclear aryl group, heteroaryl, fluorenyl, alkenyl, or arylalkyl, or z is absent,

* represents the point of attachment within the compound.

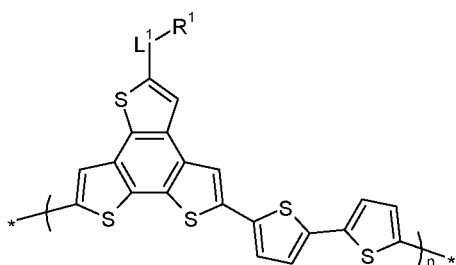
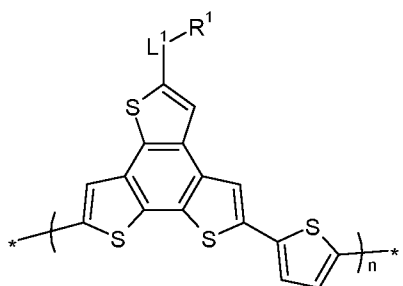
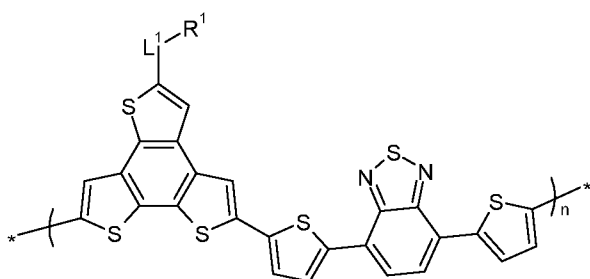
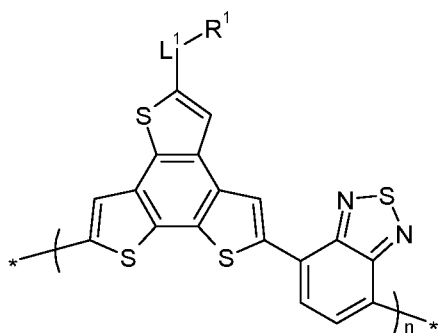
7. The compound according to any preceding claim, wherein the compound is selected from the following formulae

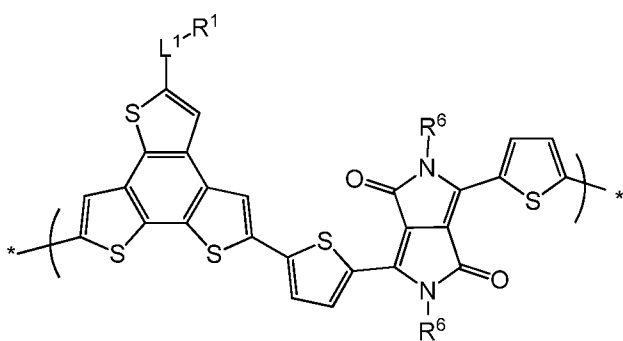
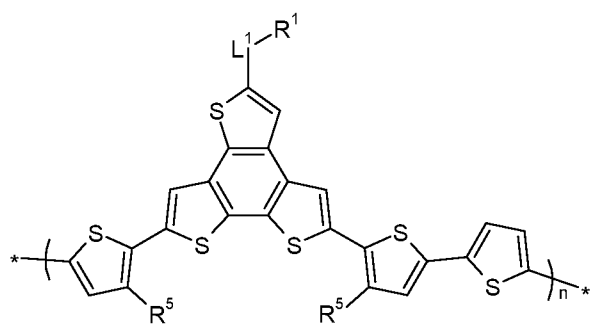
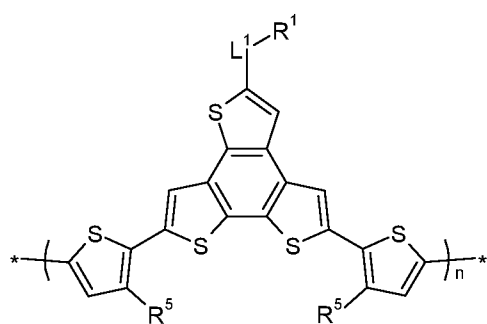
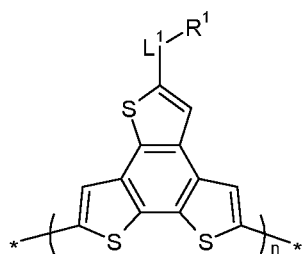
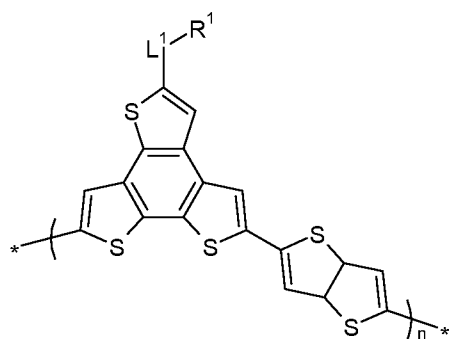




wherein R^1 , L^1 , w, x, y and n are as defined in any preceding claim.

8. The compound according to any preceding claim, wherein the compound is selected from the following formulae:

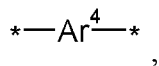




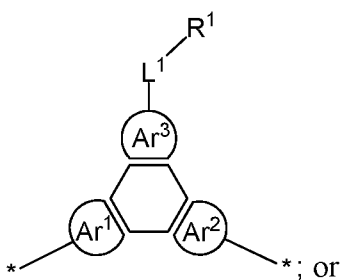
wherein L^1 , R^1 , R^5 and n are as defined in any preceding claim.

9. A compound according to any one of claims 1 to 7, wherein the compound is a random terpolymer comprising:

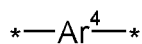
a) two structurally distinct repeating units of structure:



5 and a repeating unit of structure:

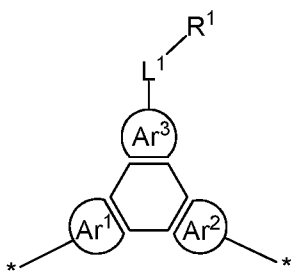


b) a repeating unit of structure:



and two structurally distinct repeating units of structure:

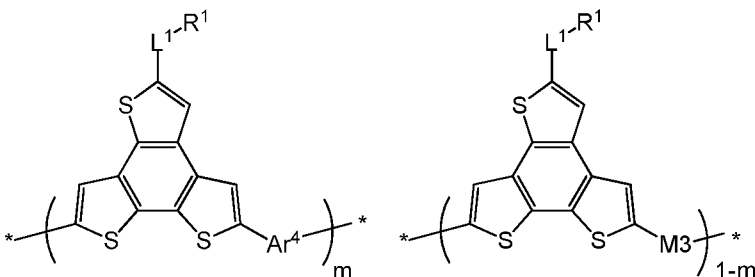
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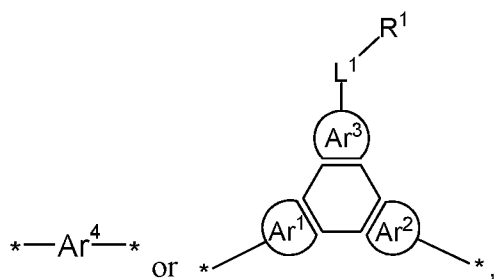
wherein R^1 , L^1 and Ar^{1-4} are as defined in any of claims 1 to 8.

15

10. A compound according to claim 9, wherein the compound is a terpolymer comprising the repeat units:

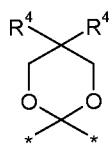


wherein M3 is a structurally distinct third monomer unit of formula



m and 1-m represent the molar proportions of the repeat units and R^1 , L^1 and Ar^4 are as defined in claim 9.

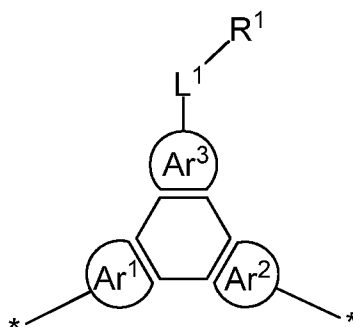
- 5 11. A compound of any preceding claim, wherein:
- a) R^5 is hydrogen, halogen, aryl, heteroaryl, -CN, -NO₂, -OH, -NH₂, alkyl, alkenyl or alkynyl, preferably a branched or unbranched alkyl having from 1 to 12 carbon atoms (for example, -C₆H₁₃); and/or
- b) R^6 is a branched or unbranched alkyl having from 1 to 40, preferably 1 to 25
 10 carbon atoms (for example -CH₂CH(C₁₀H₂₁)(C₈H₁₇)); and/or
- c) L^1 is a single bond and R^1 is branched or unbranched alkyl having from 1 to 25 carbon atoms (for example -C(C₈H₁₇)₂), or L^1 is -C(=O)- or an acetal and R^1 is a branched or unbranched alkyl having from 1 to 25 carbon atoms (for example, -C₁₅H₃₁), preferably



wherein the acetal has the formula $\text{*—C(R}^4\text{)}_2\text{—O—C(R}^4\text{)}_2\text{—O—*}$, wherein R^4 is as defined above.

15

12. A polymer comprising one or more of a monomer repeat unit:



and optionally also one or more of:



- 20 wherein R^1 , Ar^{1-4} and L^1 are as defined in any one of claims 1 to 11.

13. The compound according to any preceding claim, wherein the compound is a copolymer.

14. The compound according to claim 13, wherein the copolymer is a statistical
5 copolymer, an alternating copolymer or a block copolymer.

15. The compound according to any one of claims 1 to 8, wherein the compound is a homopolymer.

10 16. A process comprising providing a compound of formula I as defined in any one of claims 1 to 15, wherein L¹ is an imine, a hemiacetal or an acetal, and cleaving the imine, hemiacetal or acetal therefrom.

15 17. The process according to claim 16, wherein cleaving of the imine, hemiacetal or acetal is achieved by heating above 250°C.

18. The process according to claim 16 or 17, wherein the process comprises heating a thin film of the compound of formula I.

20 19. Organic semiconductor layer or component comprising a polymer according to any one of claims 1 to 15.

20. Electronic or electrooptical device comprising a polymer, layer or component according to at least one of claims 1 to 15 and 19.

25 21. Electronic or electrooptical device according to claim 19, which is an organic field effect transistor (OFET), thin film transistor (TFT), integrated circuit (IC), radio frequency identification (RFID) tag, photodetector, sensor, logic circuit, memory element, capacitor, organic photovoltaic (OPV) cell, charge injection layer, charge transport layer or interlayer in
30 polymer light emitting diodes (PLEDs), Schottky diode, planarising layer, antistatic film, polymer electrolyte membrane (PEM), conducting substrate or pattern, photoconductor, electrophotographic element or organic light emitting diode (OLED).

22. The compound of any of claims 1 to 8, wherein x is 1, y is 0 or 1, w is 1 or 0 and n is 1.

23. Process for preparing a polymer according to one or more of claims 1 to 15,
5 comprising the steps of coupling one or more monomers as defined in claim 22 optionally with one or more monomers based on a unit of claim 6, and optionally with further units, in a polymerisation reaction.

24. A copolymer comprising two different types of unit, one of which is selected of
10 formula I as defined in any of claims 1 to 15, and the other is selected of a unit having hole or electron transporting properties.

Figure 1

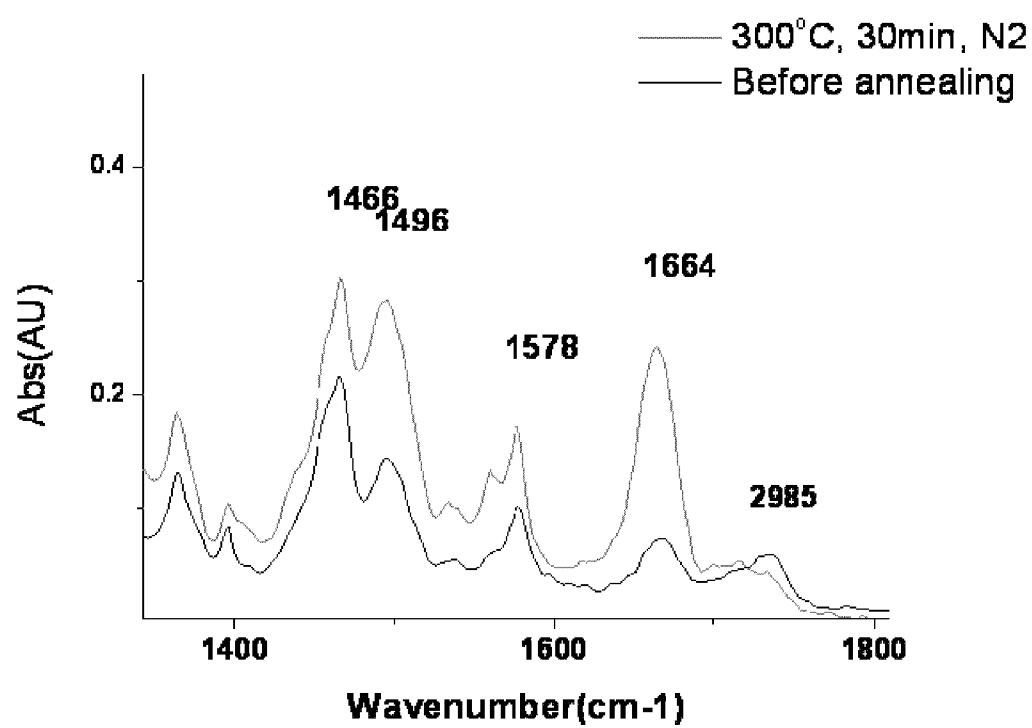


Figure 2

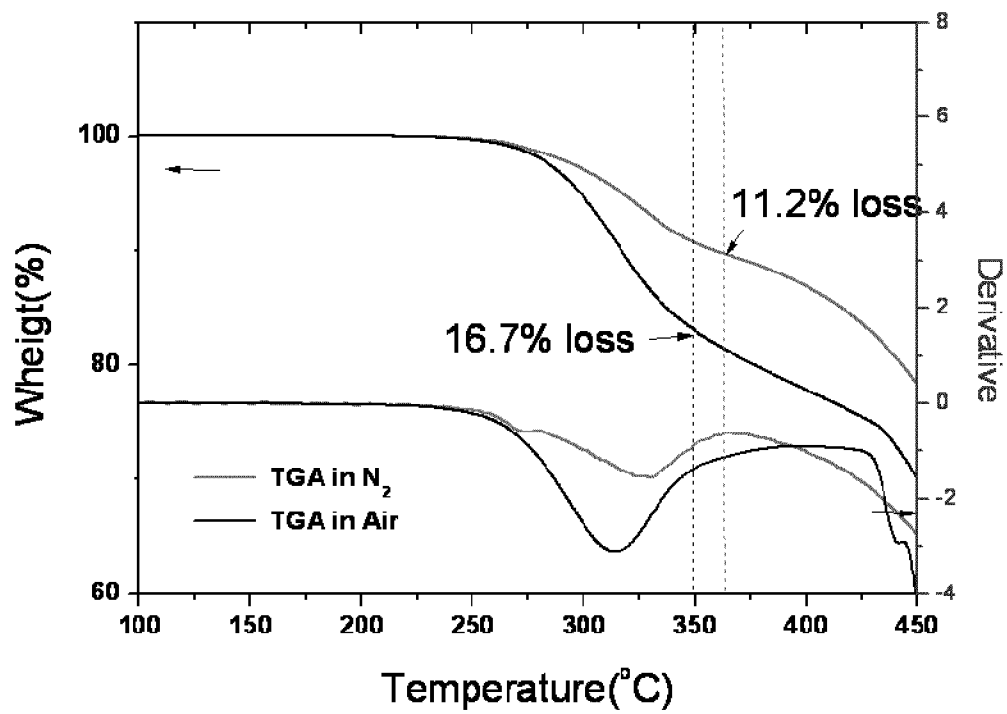
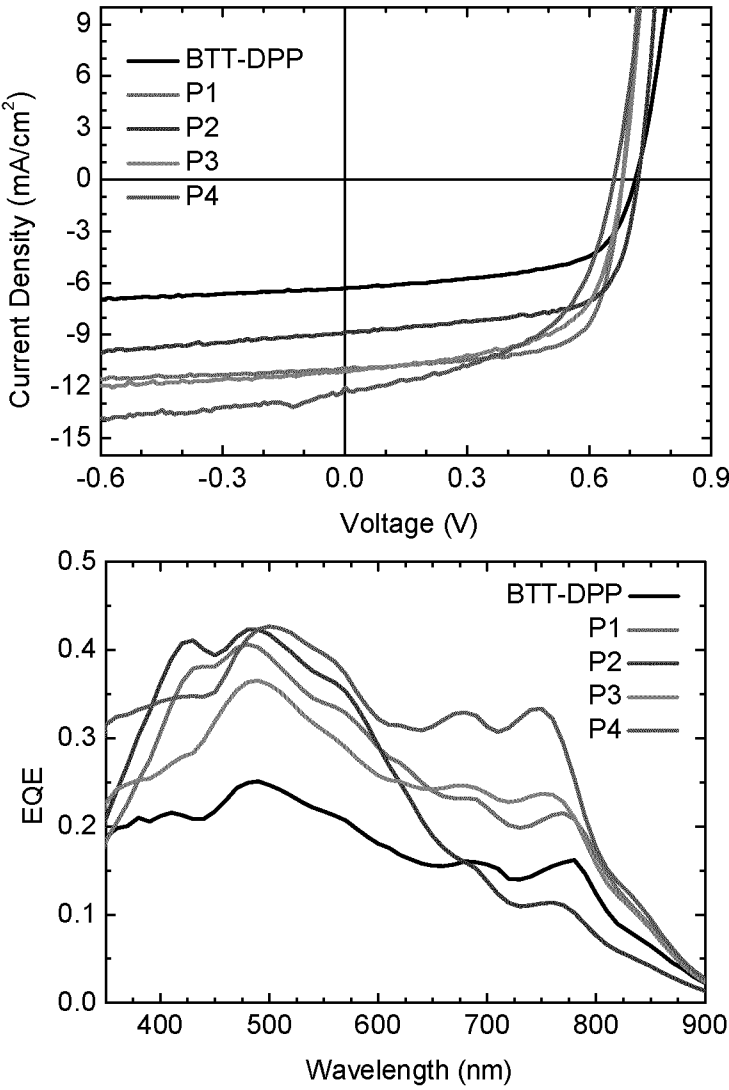


Figure 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/055911

A. CLASSIFICATION OF SUBJECT MATTER INV. C07D495/14 C07D519/00 A61K31/385 C08G61/12 H01L51/00 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) C07D C08B 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, CHEM ABS Data, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HUXING ZHOU ET AL.: "A weak donor-strong acceptor strategy to design ideal polymers for organic solar cells", APPLIED MATERIALS AND INTERFACES, vol. 2, no. 5, 2010, pages 1377-1383, XP002674729, the whole document -----	1,4,6, 11-15, 19-23
X	XIAO S ZHOU H ET AL: "Conjugated Polymers of Fused Bithiophenes with Enhanced pi-Electron Delocalization for Photovoltaic Applications", MACROMOLECULES, AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC; US, vol. 41, no. 15, 12 July 2008 (2008-07-12), pages 5688-5696, XP002612427, ISSN: 0024-9297, DOI: 10.1021/MA800776Q the whole document ----- -/-	1,2,4,9, 11-14
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "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 25 April 2012	Date of mailing of the international search report 14/05/2012	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Diederren, Jeroen	

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2012/055911

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DAHLMANN AND R NEIDLEIN U: "The diyne reaction of 3,3'-bis(phenylethynyl)-2,2'-bithiophene derivatives via rhodium complexes. A novel approach to condensed benzo[2,1-b:3,4-b']dithiophenes", HELVETICA CHIMICA ACTA, VERLAG HELVETICA CHIMICA ACTA, BASEL, CH, vol. 80, no. 1, 1 January 1997 (1997-01-01), pages 111-120, XP008139779, ISSN: 0018-019X the whole document	1-4
X	----- UWE DAHLMANN ET AL.: "Rhodium(I)-Mediated Synthesis of Benzo[2,1-b:3,4-b':5,6-c']trithiophenes and Naphtho[2,1-n:3,4-b']dithiophenes", SYNTHESIS, 1997, pages 1027-1033, XP002674730, the whole document	1-4
X	----- WO 2010/136353 A1 (BASF SE [DE]; DUEGGELI MATHIAS [CH]; AEBISCHER OLIVIER FREDERIC [CH];) 2 December 2010 (2010-12-02) compounds 50, 51, 52, 53, 54	1,4
X	----- CHANGSIK SONG ET AL.: "Reactive Conducting Thiophene Polymers", J. ORG. CHEM., vol. 75, 2010, pages 999-1005, XP002674731, compound 13 and polymer of 11 (Scheme 6); compound 15	1,4,9,11
X	----- NABIL KLEINHENZ ET AL.: "Low-Band-Gap Polymers That Utilize Quinoid Resonance Structure Stabilization by Thienothiophene: Fine-Tuning of HOMO level", MACROMOLECULES, vol. 44, 22 February 2011 (2011-02-22), pages 872-877, XP002674732, the whole document	1,4,6, 12-14
X	----- WO 2010/136401 A2 (BASF SE [DE]; KIRNER HANS JUERG [CH]; CHEBOTAREVA NATALIA [FR]; AEBISC) 2 December 2010 (2010-12-02) examples 25,26,27	1,4
X,P	----- WO 2011/156478 A2 (UNIV NORTH CAROLINA [US]; YOU WEI [US]) 15 December 2011 (2011-12-15) the whole document	1,4,6, 11-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/055911

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010136353 A1	02-12-2010	EP 2435500 A1 TW 201114800 A US 2012071617 A1 WO 2010136353 A1	04-04-2012 01-05-2011 22-03-2012 02-12-2010
WO 2010136401 A2	02-12-2010	EP 2435497 A2 WO 2010136401 A2	04-04-2012 02-12-2010
WO 2011156478 A2	15-12-2011	NONE	