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(54) Title: ORGANIC SEMICONDUCTING POLYMERS

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



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Organic Semiconducting Polymers

Technical Field

5 The invention relates to novel photo-crosslinkable organic semiconducting (OSC) polymers, to methods for their preparation and educts or intermediates used therein, to compositions and formulations containing them, to the use of the polymers and compositions as organic
10 semiconductors in, or for the preparation of, organic electronic (OE) devices, especially organic photovoltaic (OPV) devices, perovskite-based solar cell (PSC) devices, organic photo-detectors (OPD), organic field effect transistors (OFET) and organic light emitting diodes (OLED), and to OE, OPV, PSC, OPD, OFET and OLED devices comprising these polymers or compositions.

15

Background

Carbon-based organic semiconducting materials (OSC) have attracted remarkable attention for more than two decades due to their commercial
20 prospects for use in organic electronics. In contrast to traditional silicon based semiconductors, OSCs are solution processable. Consequently, organic electronic devices can be made flexible, unbreakable, stretchable, thin and light weight. They can also be manufactured in large area by cost effective roll-to-roll printing techniques at low temperature. It is particularly
25 encouraging that some state-of-the-art application processes, such as electrophoretic display devices (EPD) driven by organic thin film transistor (OTFT) backplanes, and all organic liquid crystal display panels (OLCD), have been demonstrated and the transfer from laboratories to manufacturing plants has been underway.

30

Organic electronic devices in which OSCs are used as actives materials are, in general, multi-layered sandwich structures. An OTFT device, e.g., is composed of minimum four layers, namely, the source and drain electrodes layer, the OSC active layer, the gate insulator/dielectric layer
35 and the gate electrode. In practice, optimised devices have more layers such as surface modification and passivation layers. For bulk

heterojunction OPV and OPD devices, although the donor and acceptor OSCs are mixed in the same layer, both electron and hole transporting layers are normally required in addition to the electrodes leading to multi-layer stacks. A state-of-the-art flexible OLED device, however, consists of
5 even more layer in the stack than the other devices mentioned above.

Multi-layered architectures of organic electronic devices are normally fabricated through a layer-by-layer deposition process. Metal electrodes are in most of the cases deposited by vapour evaporation under high
10 vacuum although printed electrodes, subjected to further improvement, may also be possible. OSC layers, particularly polymeric, are mostly solution processed, which means that OSCs materials should be soluble in organic solvent to obtain uniformed solutions. The solvent should ideally be nontoxic to humans and animals, noncorrosive to the manufacturing
15 tools and benign to the environment.

Furthermore, it is crucial that the solvents for different functional layers need to be “orthogonal”, which means the solvent of the layer being deposited should not dissolve or ingress into the previous layer directly
20 underneath it. Otherwise, the previous layer will be removed, or the interface between these two layers will be damaged, or the morphology of the previous layer will be altered. In whichever case, the device performances will be negatively impacted, even stop functioning. However, finding orthogonal solvents is extremely challenging.

25 In this context, an alternative solution is to crosslink the OSC molecules in the films through chemical bonds after deposition, so that the material of the OSC layer is insolubilised to the solvent being used for the next layer of deposition. Hence, a photo-crosslinking process will enable fabrication
30 of top-gate OTFTs with fewer restrictions on gate dielectric materials, reduce leakage, cross-talks and off-current. In OPV devices, a cross-linked active layer will minimise the migration of active molecules such as fullerenes, achieving additional thermal stability of morphology.

35 As an immediate consequence of photo-crosslinking reactions, direct photo-patterning of photosensitive organic semiconducting polymers can

be made possible. These polymers can be processed exactly like negative photoresists, which, as a result, give rise to single pixels or patterns of arbitrary size and shape. Although printing processes are the ultimate goal for mass production of organic electronic devices, many obstacles, such as registration accuracy, cross-talks with neighbouring pixels, device performances and so on, must be overcome prior to commercialisation. More than often, the devices still need to be printed into pre-patterned bank structures on the substrates. Although conventional photolithography technique could be used to pattern organic semiconductor films, the process of applying, developing and striping photoresists would usually cause re-dissolution, solvent infiltration as well as contamination.

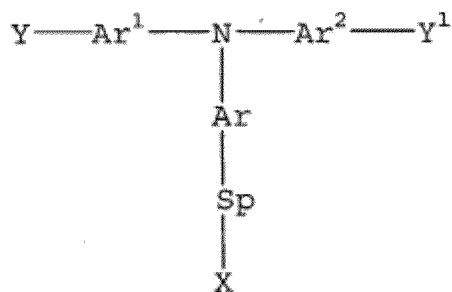
Several different photoreaction functional groups have been investigated and disclosed for direct patterning of conjugated oligomers and polymers upon exposure to UV light, such as acrylates, methacrylates, cinnamates, oxetanes, azides and thiol-ene photo-clicking groups. However, most of these cross-linking technologies require additives like photoinitiators, photoacid generators (PAG) and/or crosslinkers. These additives can result in side reactions and side-products which remain in the materials matrix to become charge traps.

US6107452 discloses a class of photo-crosslinkable conjugated and non-conjugated polymers where the photo active vinyl groups are the end-capping terminal groups. However, as there are only two crosslinkable groups per polymer chain, these concepts would be insufficient to render the semiconducting polymers insoluble to achieve micrometre sized patterns, particularly, when molecular weights are high.

WO0210129A2 discloses photo-crosslinkable electroluminescent spirofluorene copolymers, using oxetane functional groups attached to the fluorene monomer units. However, this type of unsymmetrical substitution lead to disorder and eventually poor packing of the polymer molecules, which is particularly unfavourable to OTFT applications, where packing of the OSC molecules is of crucial to achieve high charge mobilities. This type of strategy was later proved to be harmful to OTFT performances by A. Charas, *et al*, (*Chem. Phys. Lett.*, **2008**, **455**, 189–191).

WO2006043087A1 discloses a class of photo-crosslinkable polymers, where the photoreacting groups, preferably styrene groups, are attached through a spacer moiety to a nitrogen atom forming triarylamine polymers.

5 The general formula of the monomers is claimed as follows:



10 , in which X is the cross-linkable group.

15 C. B. Nielsen, *et al*, (*J. Am. Chem. Soc.*, **2008**, 130 (30), pp 9734–9746) demonstrate using acrylate groups to pattern oligothiophene films. E. Scheler and P. Strohriegl (*Chem. Mater.*, **2010**, 22, 1410–1419) and F.-J. Kahle, *et al*, (*J. Polym. Sci., Pt B, Polym. Phys.*, **2017**, 55(1), 112-120)

20 report using acrylate groups to pattern fluorene oligomers and polymers. T. Ube, *et al*, (*J. Mater. Chem. C*, **2017**, 5, 1414–1419) use cinnamate group to photo cross-link poly(3-alkylthiophene)s. However, these ester groups are thermal reactive as well, which is harmful to the stability and hence compromise the shelf life of OSC formulations. In addition,

25 undesirable thermal cross-linking should be avoided during the manufacturing process where thermal annealing is normally involved.

In addition to the above-mentioned photo-cross-linking methods, diene (WO2004093154A2), thiol-ene clicking (*Macromolecules*, **2015**, 48 (6), 1711–1722) and azide (*Nature Materials*, **2010**, 9, 152–158) have also

30 been disclosed to photo-crosslink semiconducting polymers. However, these functional groups require either crosslinkers or photo initiators for curing. While the addition of such compounds may in some cases be tolerable by OLED, OPV, OPD and dielectrics applications, in case high mobility semiconducting materials for OTFTs, which are sensitive to

35 defects, these reaction residues may induce additional trapping states for charge transport. Charge carriers travelling through the device will be

captured easily resulting in reduced charge mobilities.

5 Therefore there is still a need for photo-crosslinkable semiconducting polymers which do not have the drawbacks as described above and show advantageous properties, especially one or more of a good processability from solution, a high solubility in organic solvents, especially in nontoxic, noncorrosive, environment-friendly and/or orthogonal solvents, a good structural organization, good film-forming properties, being applicable for example by printing methods, being processable like negative
10 photoresists, and enabling direct photo-patterning. In addition, they should be easy to synthesize, especially by methods suitable for mass production.

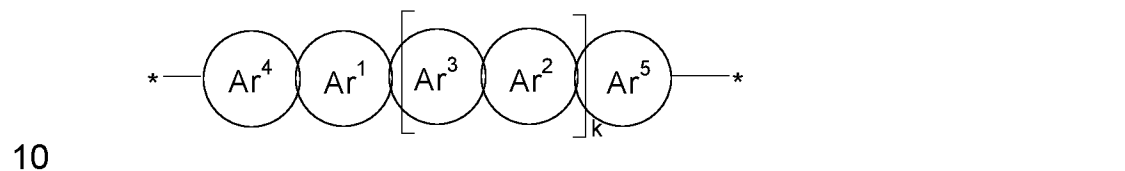
15 It was an aim of the present invention to provide new photo-crosslinkable semiconducting polymers, which can overcome the drawbacks of the polymers known from prior art and provide one or more of the above-mentioned advantageous properties. Another aim of the invention was to extend the pool of photo-crosslinkable semiconducting polymers available to the expert. Other aims of the present invention are immediately evident
20 to the expert from the following detailed description.

The inventors of the present invention have surprisingly found that one or more of the above aims can be achieved by providing polymers as disclosed and claimed hereinafter. These polymers represent a novel
25 class of photo-crosslinkable and photo-patternable semiconducting polymers comprising maleimide, for example 2,3-dimethylmaleimide (DMMI), as photoreactive groups, which can be directly crosslinked under UV radiation without the presence of photo-initiators or photo-crosslinkers.

30 These polymers can be used as the active materials in organic electronic devices such as semiconducting layer in organic thin film transistors (OTFT), donor or acceptor component in organic photovoltaic cells (OPV) and organic photodetectors (OPD), and emissive or charge transporting layers in organic light emitting diodes (OLED). In another aspect, the
35 present application also provides synthetic methods to incorporate pendent maleimide or DMMI groups to conjugated polymer main chains.

Summary

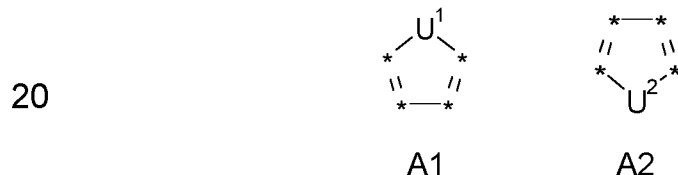
5 The invention relates to a conjugated polymer comprising one or more repeating units of formula I



and/or one or more divalent repeating units Ar⁶,

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

Ar¹, Ar² a group selected from the following formulae



U¹, U² CR¹R², SiR¹R², GeR¹R², C=CR¹R² or NR¹,

25 Ar³, Ar⁴, Ar⁵ fused aryl or heteroaryl ring which has from 5 to 20 ring atoms, is mono- or polycyclic, optionally contains fused rings, and is unsubstituted or substituted by one or more identical or different groups L,

30 Ar⁶ arylene or heteroarylene which has from 5 to 20 ring atoms, is mono- or polycyclic, optionally contains fused rings, and is unsubstituted or substituted by one or more identical or different groups L or R¹,

35 R¹, R² H, F, Cl, CN, -Sp-R^C, or straight-chain, branched or cyclic alkyl with 1 to 30, preferably 1 to 20, C atoms, in which one

- 5 or more CH₂ groups are each optionally replaced by -O-, -S-, -C(=O)-, -C(=S)-, -C(=O)-O-, -O-C(=O)-, -NR⁰-, -SiR⁰R⁰⁰-, -CF₂-, -CR⁰=CR⁰⁰-, -CY¹=CY²- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, and in which one or more H atoms are each optionally replaced by F, Cl, Br, I or CN, and in which one or more CH₂ or CH₃ groups are each optionally replaced by a cationic or anionic group, or aryl, heteroaryl, arylalkyl, heteroarylalkyl, aryloxy or heteroaryloxy, wherein each of the aforementioned
- 10 cyclic groups has 5 to 20 ring atoms, is mono- or polycyclic, optionally contains fused rings, and is unsubstituted or substituted by one or more identical or different groups L,
- 15 and the pair of R¹ and R², together with the C, Si or Ge atom to which they are attached, may also form a spiro group with 5 to 20 ring atoms which is mono- or polycyclic, optionally contains fused rings, and is unsubstituted or substituted by one or more identical or different groups L,
- 20 Sp a spacer group,
- R^C a maleimide or maleimide containing group that is unsubstituted or substituted, preferably by C₁₋₄ alkyl, very preferably by methyl,
- 25 L F, Cl, -NO₂, -CN, -NC, -NCO, -NCS, -OCN, -SCN, R⁰, OR⁰, SR⁰, -C(=O)X⁰, -C(=O)R⁰, -C(=O)-OR⁰, -O-C(=O)-R⁰, -NH₂, -NHR⁰, -NR⁰R⁰⁰, -C(=O)NHR⁰, -C(=O)NR⁰R⁰⁰, -SO₃R⁰, -SO₂R⁰, -OH, -CF₃, -SF₅, or optionally substituted silyl, or
- 30 carbyl or hydrocarbyl with 1 to 30, preferably 1 to 20 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, preferably F, -CN, R⁰, -OR⁰, -SR⁰, -C(=O)-R⁰, -C(=O)-OR⁰, -O-C(=O)-R⁰, -O-C(=O)-OR⁰, -C(=O)-NHR⁰, or -C(=O)-NR⁰R⁰⁰,
- 35

R^0, R^{00} H or straight-chain or branched alkyl with 1 to 20, preferably 1 to 12, C atoms that is optionally fluorinated,

X^0 halogen, preferably F or Cl,

k 0 or an integer from 1 to 10, preferably 0, 1, 2, 3, 4, 5, 6 or 7, very preferably 0, 1, 2 or 3, most preferably 1,

wherein the conjugated polymer comprises

a) at least one unit of formula I wherein at least two groups R^1 and R^2 that are attached to the same C, Si or Ge atom denote each $-Sp-R^C$, or wherein at least one group R^1 that is attached to an N atom denotes $-Sp-R^C$, or

b) at least one unit Ar^6 which is substituted by at least one group R^1 that denotes $-Sp-R^C$,

or both a) and b).

The invention further relates to a polymer as described above and below wherein the groups R^C are crosslinked.

The invention further relates to a pattern or patterned film comprising a polymer as described above and below wherein the groups R^C are crosslinked.

The invention further relates to a monomer comprising a divalent unit of formula I or its subformulae which are at least monosubstituted by R^C , optionally further comprising one or more additional arylene or heteroarylene units, and further comprising one or more reactive groups which can be reacted to form a polymer according to the present invention as described above and below.

The invention further relates to novel synthesis methods for preparing repeating units of formula I that are at least monosubstituted by R^C and

monomers and polymers comprising them, and novel intermediates used therein.

5 The invention further relates to the use of the polymers according to the present invention as electron donor or p-type semiconductor.

The invention further relates to the use of the polymers according to the present invention as electron acceptor or n-type semiconductor.

10 The invention further relates to the use of a polymer according to the present invention in a semiconducting material, formulation, polymer blend, device or component of a device.

15 The invention further relates to a semiconducting material, formulation, polymer blend, device or component of a device comprising a polymer according to the present invention, and preferably further comprising one or more compounds having electron donor or electron acceptor properties.

20 The invention further relates to a composition, which may also be a polymer blend, comprising one or more polymers according to the present invention, and further comprising one or more additional compounds selected from compounds having one or more of semiconducting, charge transport, hole or electron transport, hole or electron blocking, electrically conducting, photoconducting or light emitting properties.

25 The invention further relates to a composition comprising an n-type semiconductor which is a polymer according to the present invention, and further comprising one or more p-type organic semiconductors, preferably selected from conjugated polymers.

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

35

The invention further relates to a formulation comprising one or more polymers or a composition according to the present invention, and further comprising one or more solvents, preferably selected from organic solvents.

5

The invention further relates to an organic semiconducting formulation comprising one or more polymers according to the present invention, and further comprising one or more organic binders or precursors thereof, preferably having a permittivity ϵ at 1,000 Hz and 20°C of 3.3 or less, and optionally one or more solvents preferably selected from organic solvents.

10

The invention further relates to an optical, electronic, optoelectronic, electroluminescent or photoluminescent device, or a component thereof, or an assembly comprising it, which is prepared using a formulation according to the present invention.

15

The invention further relates to the use of a polymer or composition according to the present invention as semiconducting, charge transport, electrically conducting, photoconducting or light emitting material, or in an optical, electronic, optoelectronic, electroluminescent or photoluminescent device, or in a component of such a device or in an assembly comprising such a device or component.

20

The invention further relates to a semiconducting, charge transport, electrically conducting, photoconducting or light emitting material comprising a polymer or composition according to the present invention.

25

The invention further relates to an optical, electronic, optoelectronic, electroluminescent or photoluminescent device, or a component thereof, or an assembly comprising it, which comprises a polymer, composition pattern or patterned film according to the present invention, or comprises a semiconducting, charge transport, electrically conducting, photoconducting or light emitting material according to the present invention.

30

The optical, electronic, optoelectronic, electroluminescent and photoluminescent devices include, without limitation, organic field effect

35

transistors (OFET), organic thin film transistors (OTFT), organic light emitting diodes (OLED), organic light emitting transistors (OLET), organic photovoltaic devices (OPV), organic photodetectors (OPD), organic solar cells, dye-sensitized solar cells (DSSC), perovskite-based solar cells (PSC), laser diodes, Schottky diodes, photoconductors and photodetectors.

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

Further preferred is the use of a polymer or composition according to the present invention as dye in a DSSC or a PSC. Further preferred is a DSSC or PSC comprising a polymer or composition according to the present invention.

The component of the above devices includes, without limitation, charge injection layers, charge transport layers, interlayers, planarising layers, antistatic films, polymer electrolyte membranes (PEM), conducting substrates and conducting patterns.

The assembly comprising such a device or component includes, without limitation, integrated circuits (IC), radio frequency identification (RFID) tags or security markings or security devices containing them, flat panel displays or backlights thereof, electrophotographic devices, electrophotographic recording devices, organic memory devices, sensor devices, biosensors and biochips.

In addition, the polymers, compositions and formulations of the present invention can be used as electrode materials in batteries and in components or devices for detecting and discriminating DNA sequences.

The invention further relates to a bulk heterojunction which comprises, or is being formed from, a composition comprising one or more polymers according to the present invention.

The invention further relates to a bulk heterojunction (BHJ) OPV or OPD device or inverted BHJ OPV or OPD device, comprising such a bulk heterojunction.

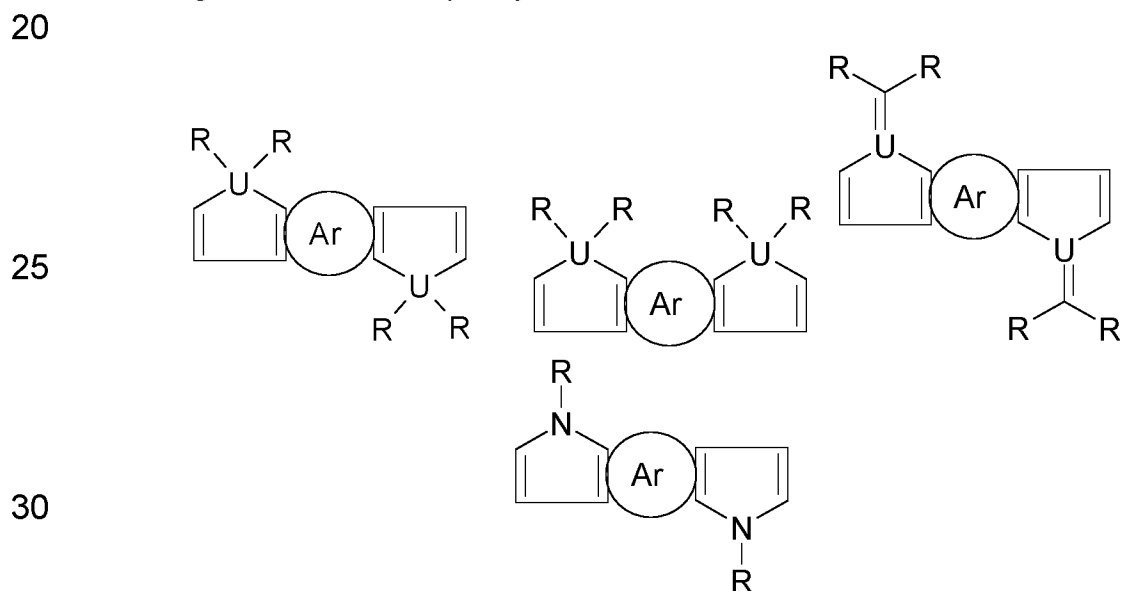
5 Brief Description of the Drawings

Fig. 1 shows the transistor characteristics for a top gate bottom contact field effect transistor according to Use Example 1.

10 **Fig. 2** shows a microscopic image of a directly patterned polymer film according to Use Example 2.

Terms and Definitions

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

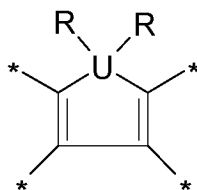


wherein U is e.g. C, Si or Ge and R is a carbyl or hydrocarbyl group.

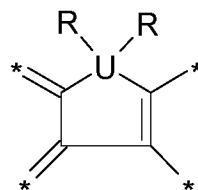
35 In the units of formula I adjacent rings Ar¹⁻⁵ are understood to be fused, i.e.

having at least two atoms and one covalent bond in common. In the rings Ar¹ and Ar² of formula A1 and A2 the pi-electrons may also be delocalised into adjacent rings Ar³, Ar⁴ or Ar⁵, so that for example a ring

5



may also include for example its mesomer



10

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

20

25

As used herein, the term "donor unit" will be understood to mean a unit, preferably a conjugated arylene or heteroarylene unit, which has an electron donating or electron pushing property towards a neighboured conjugated unit. The term "acceptor unit" will be understood to mean a unit, preferably a conjugated arylene or heteroarylene unit, which has an electron accepting or electron withdrawing property towards a neighboured conjugated unit. The term "spacer unit" will be understood to mean a unit which can be conjugated or non-conjugated and is located between a donor and an acceptor unit, and is preferably selected such that it does not have electron accepting property towards a neighboured donor unit.

30

35

As used herein, the term "spacer unit" will be understood to mean a unit, preferably a conjugated arylene or heteroarylene unit, which is located between two donor units, or between two acceptor units, or between an acceptor unit and a donor unit, such that said donor and acceptor units are

not connected directly with each other.

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

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

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

Further, as used herein, the term "polymer" will be understood to mean a

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

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

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

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

35 As used herein, a "terminal group" will be understood to mean a group that terminates a polymer backbone. The expression "in terminal position in the backbone" will be understood to mean a divalent unit or repeat unit that is linked at one side to such a terminal group and at the other side to another repeat unit. Such terminal groups include endcap groups, or reactive

groups that are attached to a monomer forming the polymer backbone which did not participate in the polymerization reaction, like for example a group having the meaning of R^{31} or R^{32} as defined below.

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

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

As used herein, the term "leaving group" will be understood to mean an atom or group (which may be charged or uncharged) that becomes detached from an atom in what is considered to be the residual or main
30 part of the molecule taking part in a specified reaction (see also *Pure Appl. Chem.*, **1994**, 66, 1134).

As used herein, unless stated otherwise the molecular weight is given as the number average molecular weight M_n or weight average molecular
35 weight M_w , which is determined by gel permeation chromatography (GPC) against polystyrene standards in eluent solvents such as tetrahydrofuran,

- trichloromethane (TCM, chloroform), chlorobenzene or 1,2,4-trichlorobenzene. Unless stated otherwise, chlorobenzene is used as solvent. The degree of polymerization, also referred to as total number of repeat units, n , will be understood to mean the number average degree of polymerization given as $n = M_n/M_U$, wherein M_n is the number average molecular weight and M_U is the molecular weight of the single repeat unit, see J. M. G. Cowie, *Polymers: Chemistry & Physics of Modern Materials*, Blackie, Glasgow, 1991.
- 10 As used herein, the term "carbonyl group" will be understood to mean any monovalent or multivalent organic moiety which comprises at least one carbon atom either without any non-carbon atoms (like for example $-C\equiv C-$), or optionally combined with at least one non-carbon atom such as B, N, O, S, P, Si, Se, As, Te or Ge (for example carbonyl etc.).
- 15 As used herein, the term "hydrocarbonyl group" will be understood to mean a carbonyl group that does additionally contain one or more H atoms and optionally contains one or more hetero atoms like for example B, N, O, S, P, Si, Se, As, Te or Ge.
- 20 As used herein, the term "hetero atom" will be understood to mean an atom in an organic compound that is not a H- or C-atom, and preferably will be understood to mean B, N, O, S, P, Si, Se, Sn, As, Te or Ge.
- 25 A carbonyl or hydrocarbonyl group comprising a chain of 3 or more C atoms may be straight-chain, branched and/or cyclic, and may include spiro-connected and/or fused rings.
- 30 Preferred carbonyl and hydrocarbonyl groups include alkyl, alkoxy, thioalkyl, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy and alkoxycarbonyloxy, each of which is optionally substituted and has up to 40, preferably up to 25, very preferably up to 18 C atoms, furthermore optionally substituted aryl or aryloxy having 6 to 40, preferably 6 to 25 C atoms, furthermore alkylaryloxy, arylcarbonyl, aryloxy, arylcarbonyloxy and
- 35 aryloxy, each of which is optionally substituted and has 1 to 40, preferably 6 to 40 C atoms, wherein each of these groups optionally

contains one or more hetero atoms, preferably selected from B, N, O, S, P, Si, Se, As, Te and Ge.

5 Further preferred carbyl and hydrocarbyl group include for example: a C₁-C₄₀ alkyl group, a C₁-C₄₀ fluoroalkyl group, a C₁-C₄₀ alkoxy or oxaalkyl 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 C₂-C₄₀ ketone group, a C₂-C₄₀ ester 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 C₁-C₂₀ fluoroalkyl group, a C₂-C₂₀ alkenyl group, a C₂-C₂₀ alkynyl group, a C₃-C₂₀ allyl group, a C₄-C₂₀ alkyldienyl group, a C₂-C₂₀ ketone group, a C₂-C₂₀ ester group, a C₆-C₁₂ aryl group, and a C₄-C₂₀ polyenyl group, respectively.

15 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.

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

25 A non-aromatic carbocyclic group as referred to above and below is saturated or unsaturated and preferably has 4 to 30 ring C atoms. A non-aromatic heterocyclic group as referred to above and below preferably has 4 to 30 ring C atoms, wherein one or more of the C ring atoms are each optionally replaced by a hetero atom, preferably selected from N, O, P, S, Si and Se, or by a -S(O)- or -S(O)₂- group. The non-aromatic carbo- and heterocyclic groups are mono- or polycyclic, may also contain fused rings, preferably contain 1, 2, 3 or 4 fused or unfused rings, and are optionally substituted with one or more groups L.

35

5 L is selected from F, Cl, -CN, -NO₂, -NC, -NCO, -NCS, -OCN, -SCN, -R⁰, -OR⁰, -SR⁰, -C(=O)X⁰, -C(=O)R⁰, -C(=O)-OR⁰, -O-C(=O)-R⁰, -NH₂, -NHR⁰, -NR⁰R⁰⁰, -C(=O)NHR⁰, -C(=O)NR⁰R⁰⁰, -SO₃R⁰, -SO₂R⁰, -OH, -CF₃, -SF₅, or optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 30, preferably 1 to 20 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, wherein X⁰ is halogen, preferably F or Cl, and R⁰, R⁰⁰ each independently denote H or straight-chain or branched alkyl with 1 to 20, preferably 1 to 12 C atoms that is optionally fluorinated.

10 Preferably L is selected from F, -CN, R⁰, -OR⁰, -SR⁰, -C(=O)-R⁰, -C(=O)-OR⁰, -O-C(=O)-R⁰, -O-C(=O)-OR⁰, -C(=O)-NHR⁰ and -C(=O)-NR⁰R⁰⁰.

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

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

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

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

35 An arylalkyl or heteroarylalkyl group as referred to above and below preferably denotes -(CH₂)_a-aryl or -(CH₂)_a-heteroaryl, wherein a is an integer from 1 to 6, preferably 1, and "aryl" and "heteroaryl" have the

meanings given above and below. A preferred arylalkyl group is benzyl which is optionally substituted by L.

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

10 Preferred aryl and heteroaryl groups are phenyl in which, in addition, one or more CH groups may each be replaced by N, naphthalene, thiophene, selenophene, thienothiophene, dithienothiophene, fluorene and oxazole, all of which can be unsubstituted, mono- or polysubstituted with L as defined above. Very preferred aryl and heteroaryl groups are selected from phenyl, pyrrole, preferably N-pyrrole, furan, pyridine, preferably 2- or
15 3-pyridine, pyrimidine, pyridazine, pyrazine, triazole, tetrazole, pyrazole, imidazole, isothiazole, thiazole, thiadiazole, isoxazole, oxazole, oxadiazole, thiophene, preferably 2-thiophene, selenophene, preferably 2-selenophene, 2,5-dithiophene-2',5'-diyl, thieno[3,2-b]thiophene, thieno[2,3-b]thiophene, furo[3,2-b]furan, furo[2,3-b]furan, seleno[3,2-b]selenophene, seleno[2,3-b]selenophene, thieno[3,2-b]selenophene, thieno[3,2-b]furan,
20 indole, isoindole, benzo[b]furan, benzo[b]thiophene, benzo[1,2-b;4,5-b']dithiophene, benzo[2,1-b;3,4-b']dithiophene, quinole, 2-methylquinole, isoquinole, quinoxaline, quinazoline, benzotriazole, benzimidazole, benzothiazole, benzisothiazole, benzisoxazole, benzoxadiazole,
25 benzoxazole, benzothiadiazole, 4H-cyclopenta[2,1-b;3,4-b']dithiophene, 7H-3,4-dithia-7-sila-cyclopenta[a]pentalene, all of which can be unsubstituted, mono- or polysubstituted with L as defined above. Further examples of aryl and heteroaryl groups are those selected from the groups shown hereinafter.

30 An alkyl group or an alkoxy group, *i.e.*, where the terminal CH₂ group is replaced by -O-, can be straight-chain or branched. Particularly preferred straight-chains have 2, 3, 4, 5, 6, 7, 8, 12 or 16 carbon atoms and accordingly denote preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl,
35 octyl, dodecyl or hexadecyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, octoxy, dodecoxy or hexadecoxy, furthermore methyl, nonyl,

decyl, undecyl, tridecyl, tetradecyl, pentadecyl, nonoxy, decoxy, undecoxy, tridecoxy or tetradecoxy, for example.

5 An alkenyl group, *i.e.*, wherein one or more CH₂ groups are each replaced by -CH=CH- can be straight-chain or branched. It is preferably straight-chain, has 2 to 10 C atoms and accordingly is preferably vinyl, prop-1-, or prop-2-enyl, but-1-, 2- or but-3-enyl, pent-1-, 2-, 3- or pent-4-enyl, hex-1-, 2-, 3-, 4- or hex-5-enyl, hept-1-, 2-, 3-, 4-, 5- or hept-6-enyl, oct-1-, 2-, 3-, 4-, 5-, 6- or oct-7-enyl, non-1-, 2-, 3-, 4-, 5-, 6-, 7- or non-8-enyl, dec-1-, 2-, 3-, 4-, 5-, 6-, 7-, 8- or dec-9-enyl.

Especially preferred alkenyl groups are C₂-C₇-1E-alkenyl, C₄-C₇-3E-alkenyl, C₅-C₇-4-alkenyl, C₆-C₇-5-alkenyl and C₇-6-alkenyl, in particular C₂-C₇-1E-alkenyl, C₄-C₇-3E-alkenyl and C₅-C₇-4-alkenyl. Examples for particularly preferred alkenyl groups are vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 1E-heptenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-heptenyl, 4-pentenyl, 4Z-hexenyl, 4E-hexenyl, 4Z-heptenyl, 5-hexenyl, 6-heptenyl and the like. Groups having up to 5 C atoms are generally preferred.

20 An oxaalkyl group, *i.e.*, where one CH₂ group is replaced by -O-, can be straight-chain. Particularly preferred straight-chains are 2-oxapropyl (=methoxymethyl), 2- (=ethoxymethyl) or 3-oxabutyl (=2-methoxyethyl), 2-, 3-, or 4-oxapentyl, 2-, 3-, 4-, or 5-oxahexyl, 2-, 3-, 4-, 5-, or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl, for example.

In an alkyl group wherein one CH₂ group is replaced by -O- and one CH₂ group is replaced by -C(O)-, these radicals are preferably neighbored. Accordingly, these radicals together form a carbonyloxy group -C(O)-O- or an oxycarbonyl group -O-C(O)-. Preferably this group is straight-chain and has 2 to 6 C atoms. It is accordingly preferably acetyloxy, propionyloxy, butyryloxy, pentanoyloxy, hexanoyloxy, acetyloxymethyl, propionyloxymethyl, butyryloxymethyl, pentanoyloxymethyl, 2-acetyloxyethyl, 2-propionyloxyethyl, 2-butyryloxyethyl, 3-acetyloxypropyl, 3-propionyloxypropyl, 4-acetyloxybutyl, methoxycarbonyl, ethoxycarbonyl,

propoxycarbonyl, butoxycarbonyl, pentoxycarbonyl,
methoxycarbonylmethyl, ethoxycarbonylmethyl, propoxycarbonylmethyl,
butoxycarbonylmethyl, 2-(methoxycarbonyl)ethyl, 2-(ethoxycarbonyl)ethyl,
2-(propoxycarbonyl)ethyl, 3-(methoxycarbonyl)propyl,
5 3-(ethoxycarbonyl)propyl or 4-(methoxycarbonyl)-butyl.

An alkyl group wherein two or more CH₂ groups are replaced by -O-
and/or -C(O)O- can be straight-chain or branched. It is preferably straight-
chain and has 3 to 12 C atoms. Accordingly, it is preferably bis-carboxy-
10 methyl, 2,2-bis-carboxy-ethyl, 3,3-bis-carboxy-propyl, 4,4-bis-carboxy-
butyl, 5,5-bis-carboxy-pentyl, 6,6-bis-carboxy-hexyl, 7,7-bis-carboxy-
heptyl, 8,8-bis-carboxy-octyl, 9,9-bis-carboxy-nonyl, 10,10-bis-carboxy-
decyl, bis-(methoxycarbonyl)-methyl, 2,2-bis-(methoxycarbonyl)-ethyl,
3,3-bis-(methoxycarbonyl)-propyl, 4,4-bis-(methoxycarbonyl)-butyl, 5,5-bis-
15 (methoxycarbonyl)-pentyl, 6,6-bis-(methoxycarbonyl)-hexyl, 7,7-bis-
(methoxycarbonyl)-heptyl, 8,8-bis-(methoxycarbonyl)-octyl, bis-
(ethoxycarbonyl)-methyl, 2,2-bis-(ethoxycarbonyl)-ethyl, 3,3-bis-
(ethoxycarbonyl)-propyl, 4,4-bis-(ethoxycarbonyl)-butyl or 5,5-bis-
(ethoxycarbonyl)-hexyl.

20 A thioalkyl group, *i.e.*, where one CH₂ group is replaced by -S-, is
preferably straight-chain thiomethyl (-SCH₃), 1-thioethyl (-SCH₂CH₃),
1-thiopropyl (= -SCH₂CH₂CH₃), 1- (thiobutyl), 1-(thiopentyl), 1-(thiohexyl),
1-(thioheptyl), 1-(thiooctyl), 1-(thiononyl), 1-(thiodecyl), 1-(thioundecyl) or
25 1-(thiododecyl), wherein preferably the CH₂ group adjacent to the sp²
hybridized vinyl carbon atom is replaced.

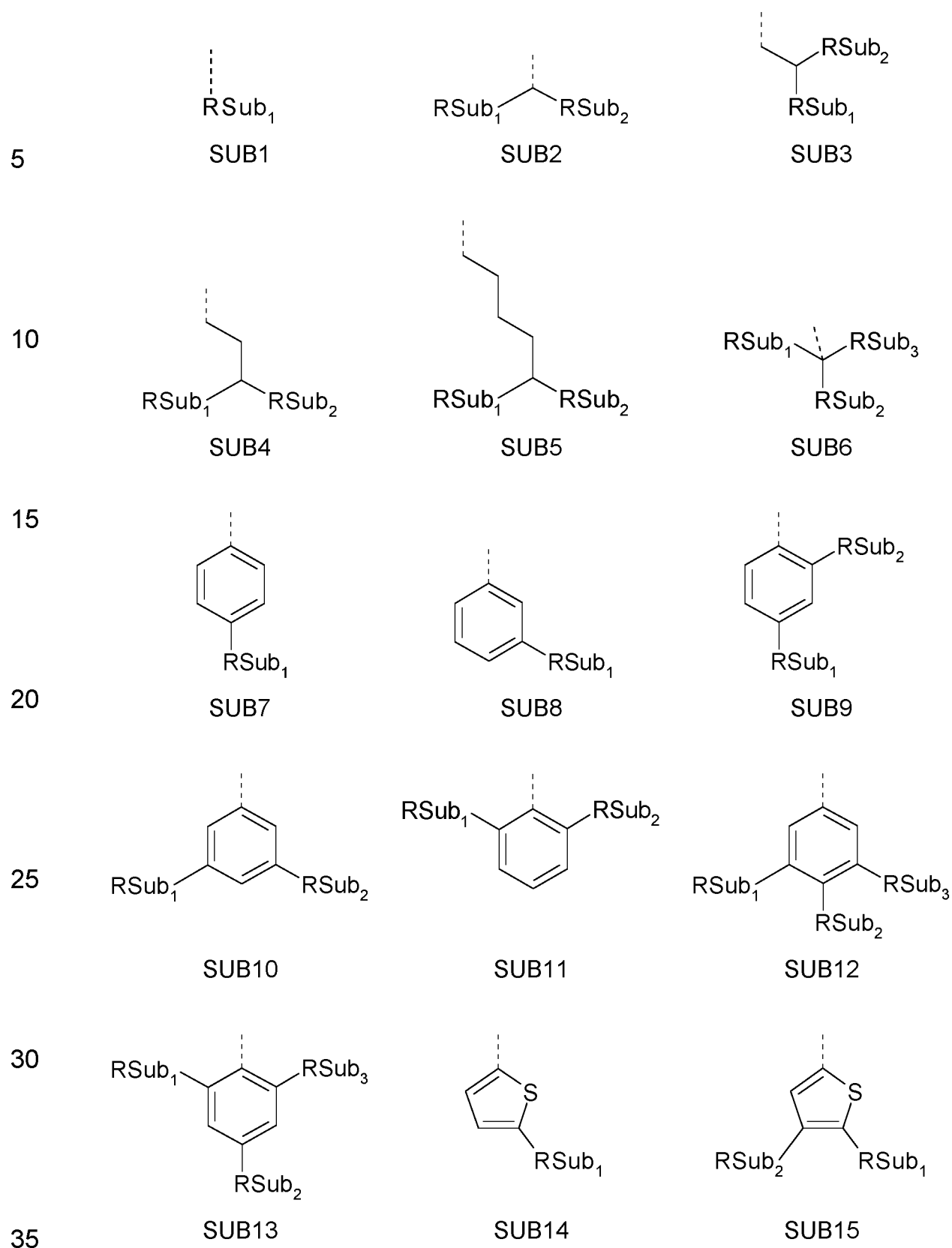
A fluoroalkyl group can be perfluoroalkyl C_iF_{2i+1}, wherein i is an integer
from 1 to 15, in particular CF₃, C₂F₅, C₃F₇, C₄F₉, C₅F₁₁, C₆F₁₃, C₇F₁₅ or
30 C₈F₁₇, very preferably C₆F₁₃, or partially fluorinated alkyl, preferably with 1
to 15 C atoms, in particular 1,1-difluoroalkyl, all of the aforementioned
being straight-chain or branched.

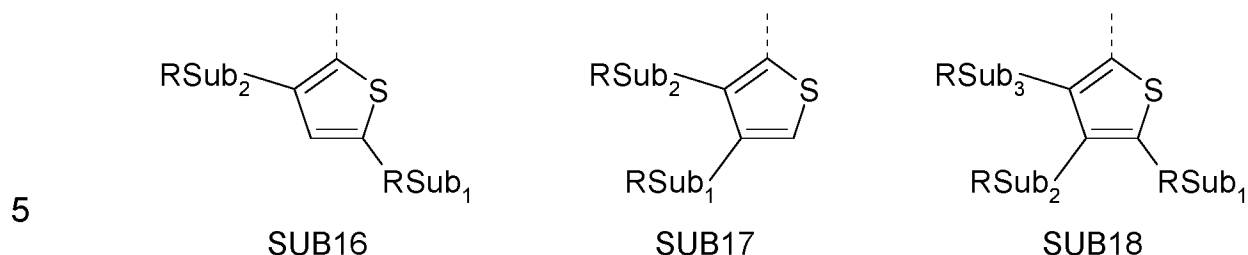
35 Preferably "fluoroalkyl" means a partially fluorinated (*i.e.* not
perfluorinated) alkyl group.

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

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

In a preferred embodiment, the substituents on an aryl or heteroaryl ring are independently of each other selected from primary, secondary or tertiary alkyl, alkoxy, oxaalkyl, thioalkyl, alkylcarbonyl or alkoxy carbonyl with 1 to 30 C atoms, wherein one or more H atoms are each optionally replaced by F, or aryl, aryloxy, heteroaryl or heteroaryloxy that is optionally alkylated, alkoxyated, alkylthiolated or esterified and has 4 to 30, preferably 5 to 20, ring atoms. Further preferred substituents are selected from the group consisting of the following formulae





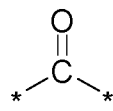
10 wherein RSub₁₋₃ each denote L as defined above and below and where at least, preferably all, of RSub₁₋₃ is alkyl, alkoxy, oxaalkyl, thioalkyl, alkyl-carbonyl or alkoxy carbonyl with up to 24 C atoms, preferably up to 20 C atoms, that is optionally fluorinated, and wherein the dashed line denotes the link to the ring to which these groups are attached. Very preferred among these substituents are those wherein all RSub₁₋₃ subgroups are identical.

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

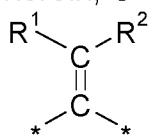
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Above and below, Y¹ and Y² are independently of each other H, F, Cl or CN.

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



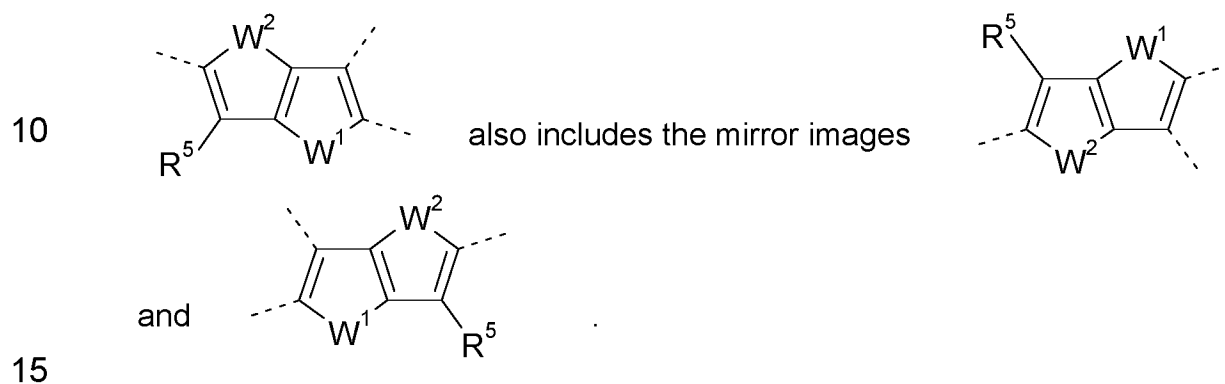
30 As used herein, C=CR¹R² will be understood to mean a group having the structure



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

in a monomer or an intermediate is preferably Br or I.

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



Detailed Description

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

The polymers according to the present invention comprise maleimide groups as photo-active pendent group and can thus be advantageously used as photo-crosslinkable semiconducting polymers. They do not require additives like photo-initiators or photo-crosslinkers which can generally induce side-reactions and form side-products which, as a result, become additional trapping states and hence impact negatively on the charge mobilities.

Also, in contrast to photo-crosslinkable polyfluorenes as reported in prior art (*Chem. Phys. Lett.*, **2008**, 455, 189–191; *J. Polym. Sci., Pt B, Polym. Phys.*, **2017**, 55(1), 112-120), where the photoactive groups are attached in one of the two solubilising chains, the maleimide groups in the polymers

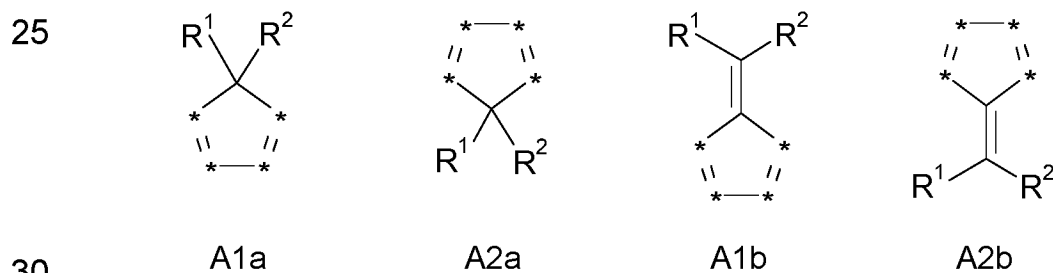
according to the present invention are introduced in a symmetrical pattern, which is of great benefit to the ordering of the polymer main chains and hence facilitates charge carrier mobilities in OTFT, OPV and OPD devices.

- 5 In another aspect of this invention, the semiconducting polymers can be directly patterned like a conventional negative photoresist.

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

15 Preferably the conjugated polymer comprises at least one unit of formula I wherein at least two groups R^1 and R^2 that are attached to the same C, Si or Ge atom denote each $-Sp-R^C$, or wherein at least one group R^1 that is attached to an N atom denotes $-Sp-R^C$, and optionally comprises at least one unit Ar^6 which is substituted by at least one group R^1 that denotes $-Sp-R^C$. Very preferably the conjugated polymer comprises at least one unit of formula I wherein U^1 and U^2 denote CR^1R^2 and at least two groups R^1 and R^2 that are attached to the same C atom denote each $-Sp-R^C$.

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

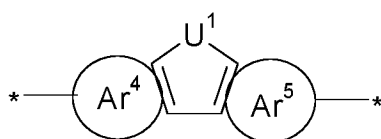


Especially preferred groups Ar^1 and Ar^2 are selected from formulae A1a and A2a.

35 A first preferred embodiment of the present invention relates to units of formula I wherein $k=0$.

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

5



I1

10

wherein U^1 , Ar^4 and Ar^5 , independently of each other and on each occurrence identically or differently, have the meanings given in formula I or one of the preferred meanings given above and below.

Preferred units of formula I1 are those wherein U^1 denotes CR^1R^2 .

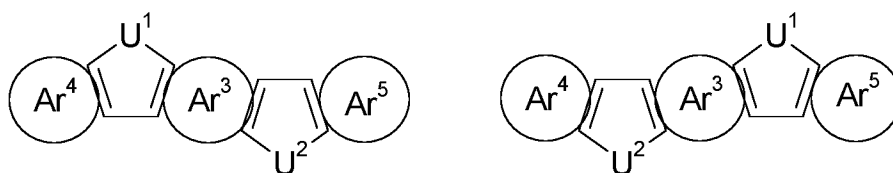
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In the units of formula I where $k > 1$ the groups Ar^1 and Ar^2 can be selected such that the resulting indaceno-type groups have trans- or cis-configuration.

20

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

25

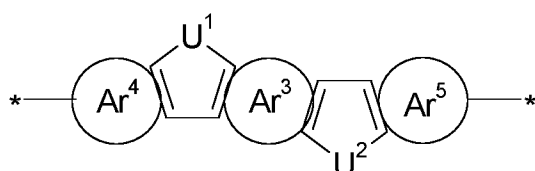


trans-configuration.

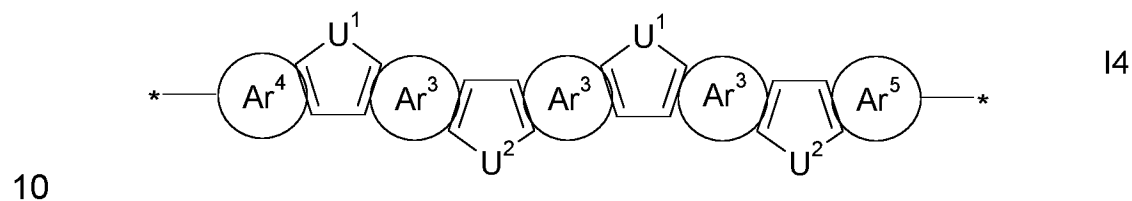
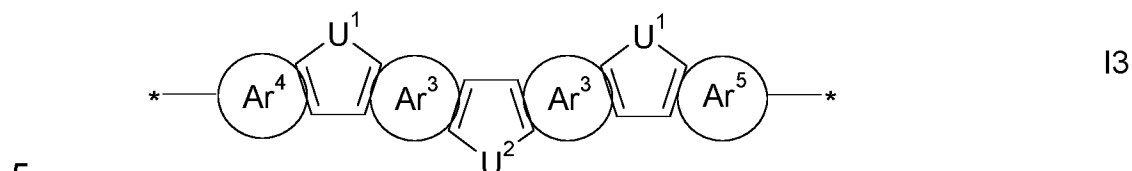
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Preferred units of formula I according to this second preferred embodiment are selected from the following subformulae

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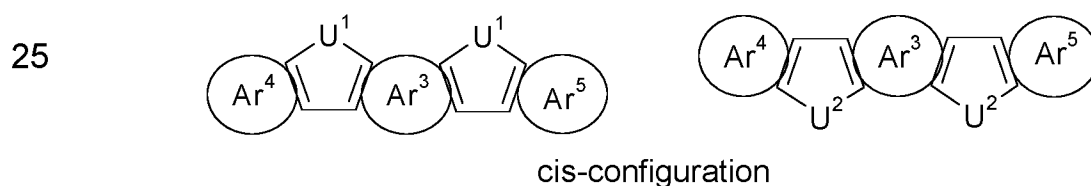
I2



wherein U^1 , U^2 , Ar^3 , Ar^4 and Ar^5 , independently of each other and on each occurrence identically or differently, have the meanings given in formula I or one of the preferred meanings given above and below.

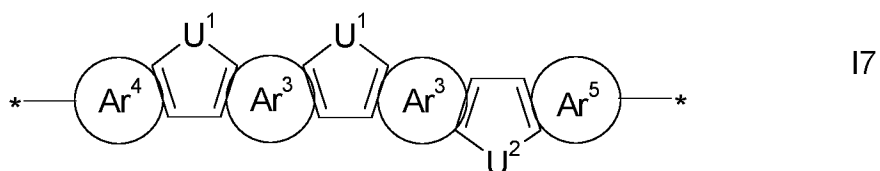
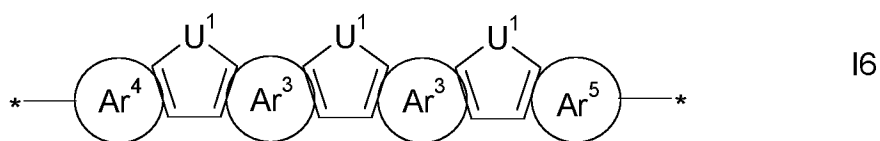
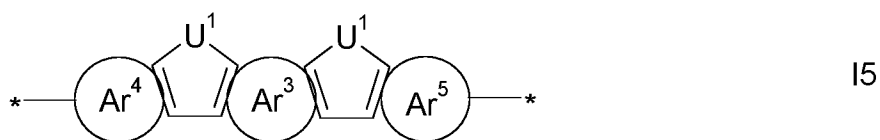
15 Preferred units of formula I2-I4 are those wherein all of the groups U^1 and U^2 denote CR^1R^2 .

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



30 This third preferred embodiment includes units of formula I having an "all-cis" configuration as exemplarily shown in formula I5 and I6 below, and units of formula I including both trans-configuration and cis-configuration, as exemplarily shown in formula I7 below.

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

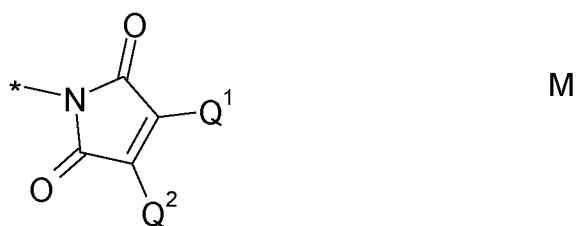


wherein U^1 , U^2 , Ar^3 , Ar^4 and Ar^5 , independently of each other and on each occurrence identically or differently, have the meanings given in formula I or one of the preferred meanings given above and below.

Preferred units of formula I5-I7 are those wherein all groups U^1 and U^2 denote CR^1R^2 .

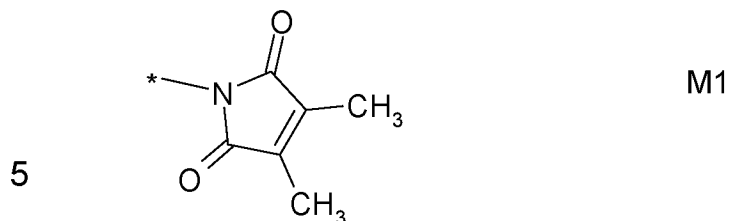
Especially preferred are units of formula I1, I2, I3 and I4, very preferred those of formula I1 and I2.

Preferred groups R^C in formula I are selected from formula M



wherein Q^1 and Q^2 are each independently from one another H, or C_nH_{2n+1} wherein n is an integer from 1 to 16, more preferably CH_3 , C_2H_5 , C_3H_7 or C_4H_9 , very preferably H or CH_3 , most preferably CH_3 .

Preferred groups R^C in formula I are selected from formula M1

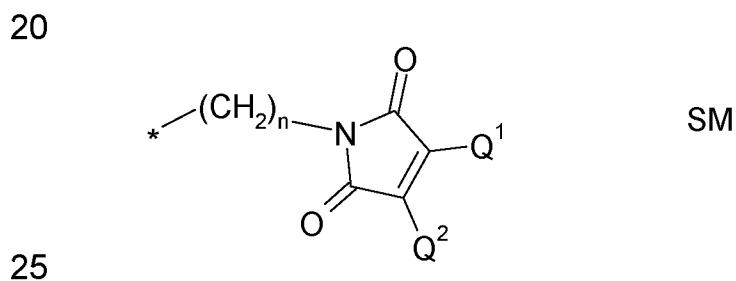


10 Preferred spacer groups Sp in formula I are selected from alkylene with 1 to 30, preferably 1 to 20, C atoms, wherein one or more, but not all, CH₂ groups are each optionally replaced by -O-, -S-, -C(=O)-, -C(=S)-, -C(=O)-O-, -O-C(=O)-, -NR⁰-, -SiR⁰R⁰⁰-, -CF₂-, -CR⁰=CR⁰⁰-, -CY¹=CY²- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, and in which one or more H atoms are each optionally replaced by F, Cl, Br, I or CN.

15

Very preferred spacer groups Sp are selected from alkylene with 1 to 20, preferably 5 to 20, more preferably 5 to 16 C atoms.

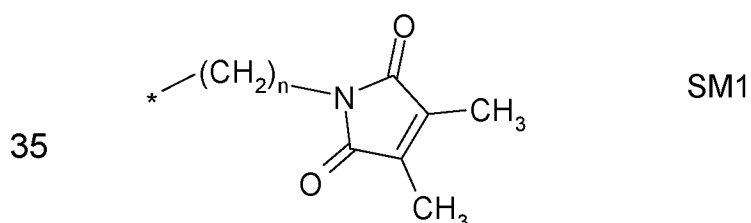
20 Preferred groups -Sp-R^C in formula I are selected from formula SM



wherein n is an integer from 1 to 20, preferably 5 to 20, very preferably 8 to 16, and Q¹ and Q² are each independently from one another H, CH₃, C₂H₅, C₃H₇ or C₄H₉, very preferably H or CH₃, most preferably CH₃.

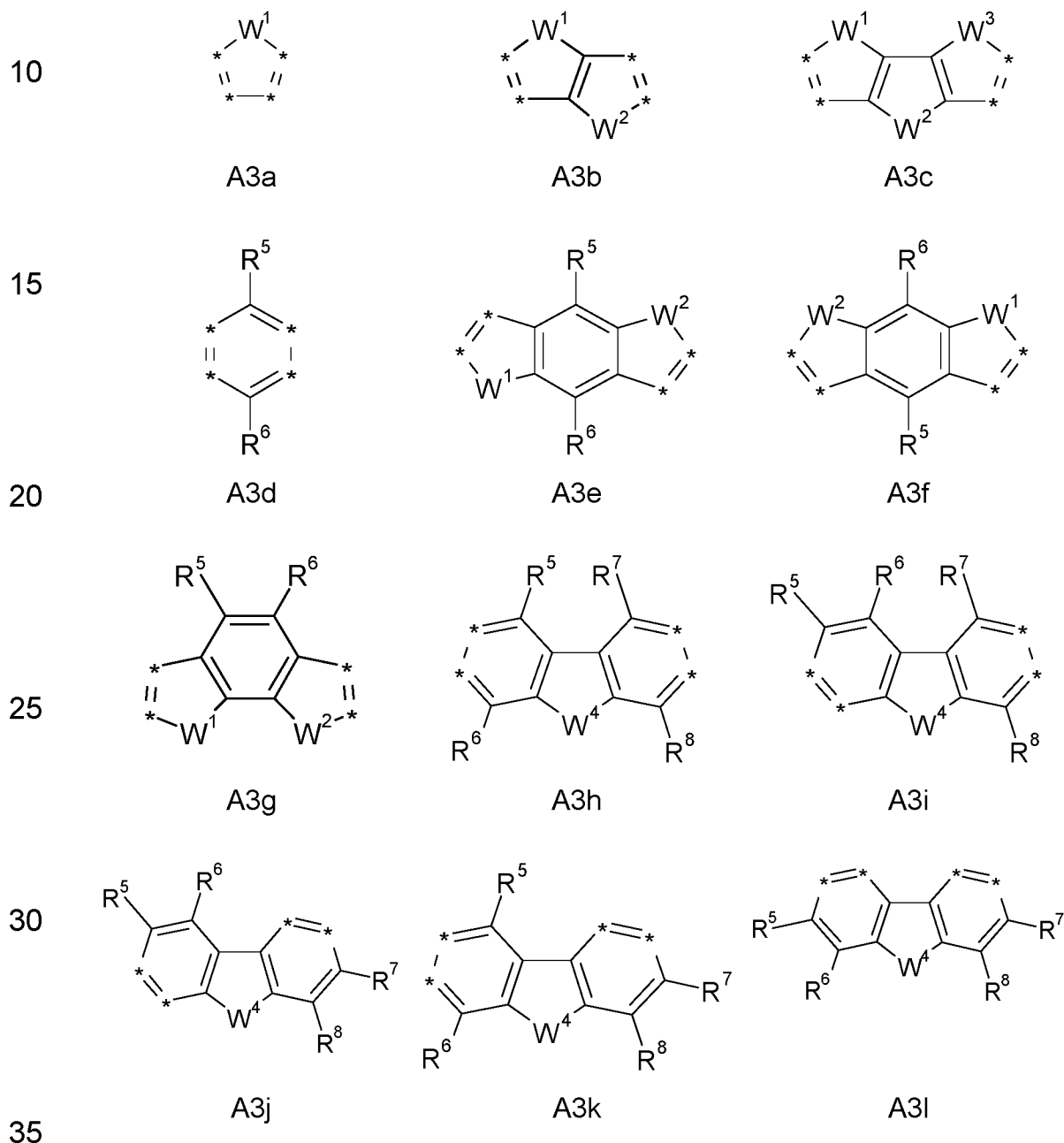
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Preferred groups -Sp-R^C in formula I are selected from formula SM1

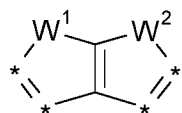


wherein n is an integer from 1 to 20, preferably 5 to 20, very preferably 8 to 16.

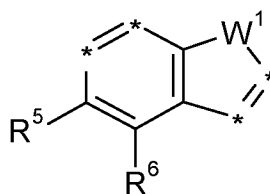
- 5 Preferred groups Ar³ in formula I, I2-I7 and their subformulae are on each occurrence identically or differently selected from the following formulae and their mirror images



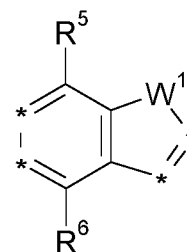
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A3m

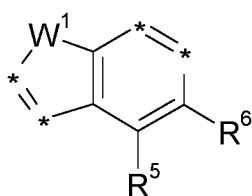


A3n

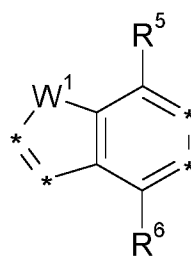


A3o

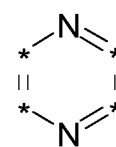
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A3p

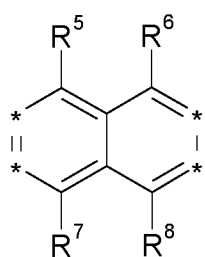


A3q

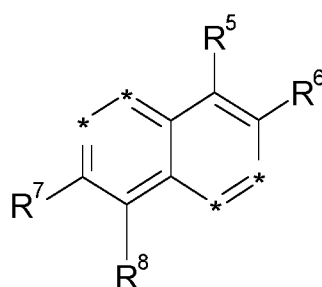


A3r

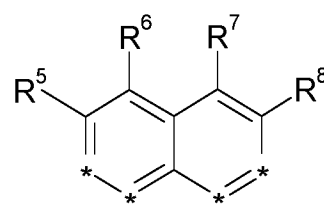
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A3s



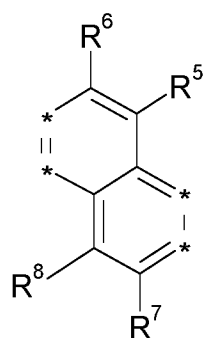
A3t



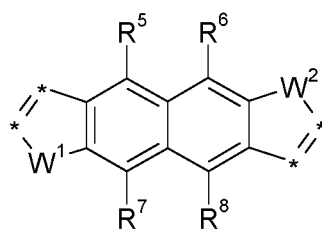
A3u

20

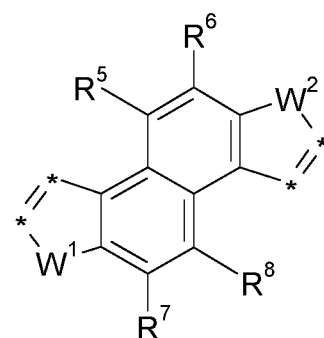
25



A3v



A3w



A3x

30

35

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

W^1, W^2, W^3 S, O, Se or C=O, preferably S,

W^4 S, O, Se, C=O or NR^5 ,

R^{5-8} one of the meanings given for R^1 above and below.

5

Preferred groups Ar^3 are selected from formulae A3b, A3d, A3f and A3t, very preferably from formulae A3b and A3d.

10

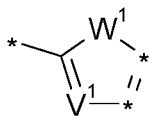
Further preferred groups Ar^3 are selected from formula A3d wherein R^5 and R^6 denote F.

Further preferred groups Ar^3 are selected from formulae A3e and A3f wherein R^5 and R^6 are different from H.

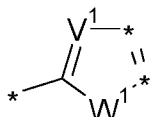
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Preferred groups Ar^4 in formula I, I1-I7 and their subformulae are on each occurrence identically or differently selected from the following formulae and their mirror images

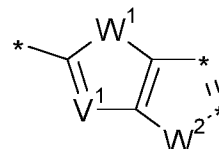
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A4a

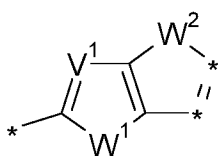


A4b

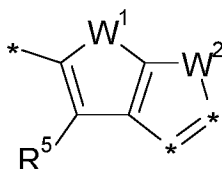


A4c

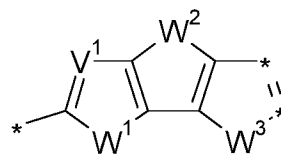
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A4d

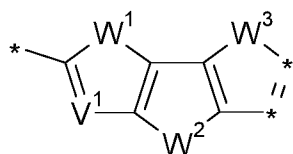


A4e

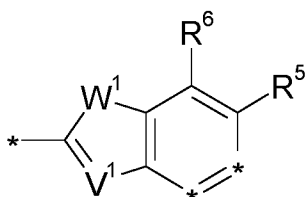


A4f

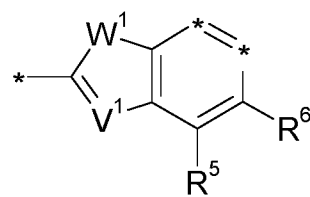
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A4g



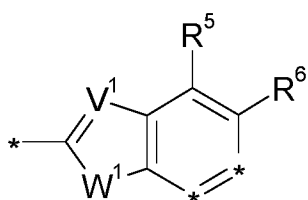
A4h



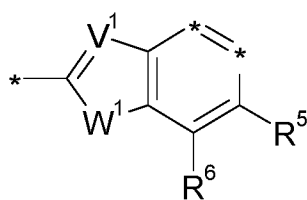
A4i

35

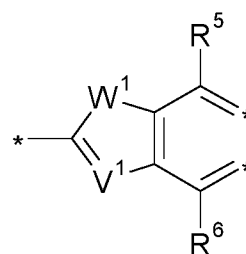
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A4j

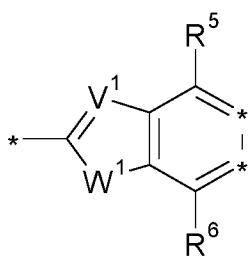


A4k

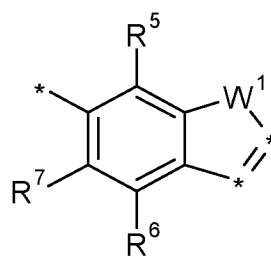


A4l

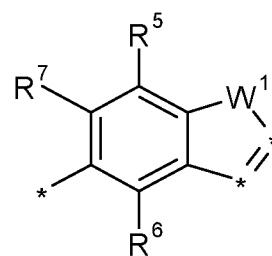
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A4m

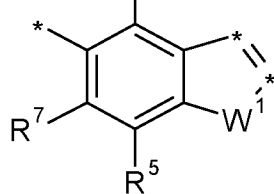


A4n

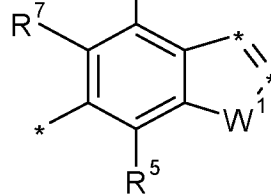


A4o

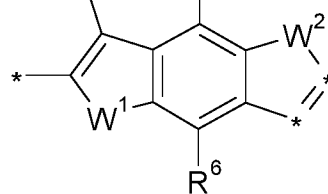
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A4p

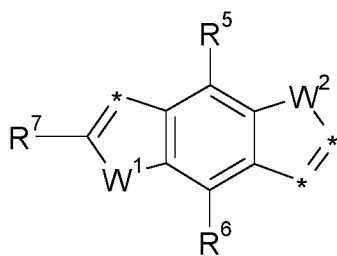


A4q

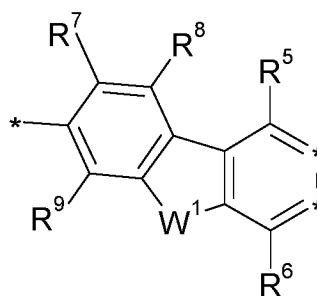


A4r

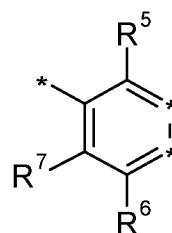
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A4s

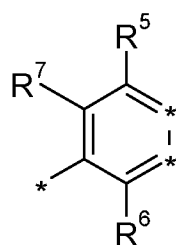


A4t

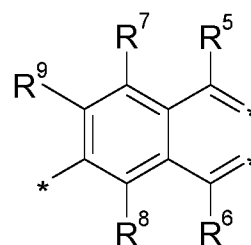
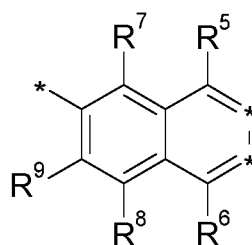


A4u

30



35



A4v

A4w

A4x

wherein W^1 , W^2 , W^3 and R^{5-8} have the meanings given above, V^1 denotes CR^5 or N, and R^9 has one of the meanings given for R^5 .

5

Preferred groups Ar^4 are selected from formulae A4a, A4b, A4c, A4d, A4f, A4g, A4h, A4i, A4k, A4l, A4m, A4n, A4o, A4p, A4q, A4u and A4v, very preferably from formula A4a, A4b, A4c, A4d, A4l, A4m, A4n, A4o, A4p, A4q, A4u and A4v.

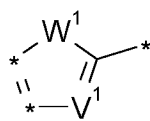
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Further preferred groups Ar^4 are selected from formulae A4r and A4s wherein R^5 and R^6 are different from H.

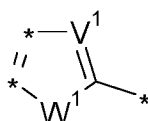
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Preferred groups Ar^5 in formula I, I1-I7 and their subformulae are on each occurrence identically or differently selected from the following formulae and their mirror images

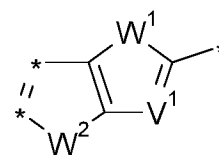
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A5a

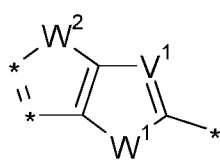


A5b

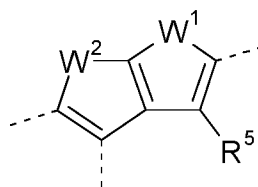


A5c

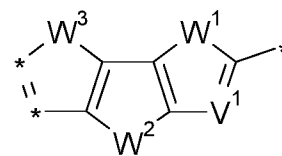
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A5d

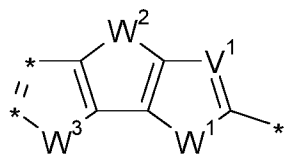


A5e

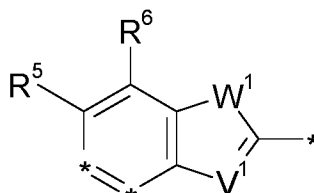


A5f

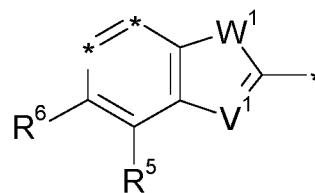
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A5g



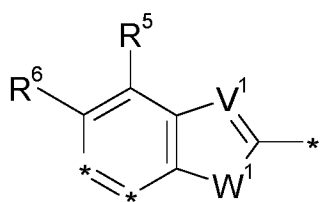
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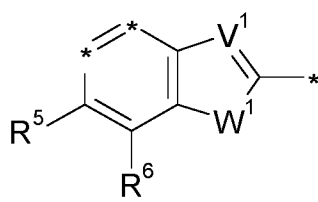
A5i

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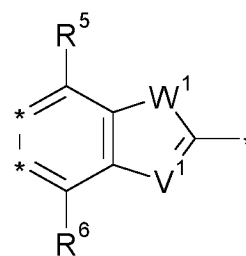
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A5j

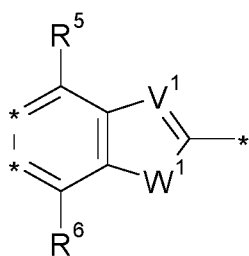


A5k

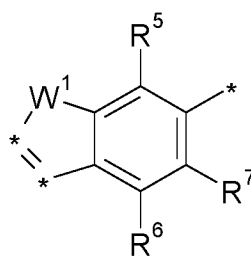


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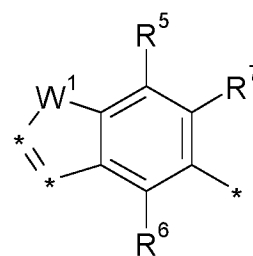
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A5m

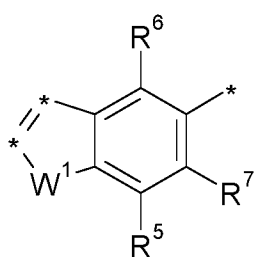


A5n

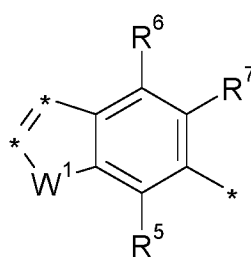


A5o

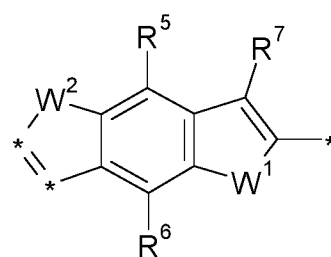
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A5p

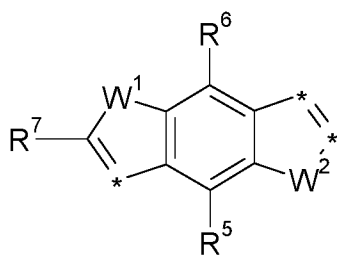


A5q

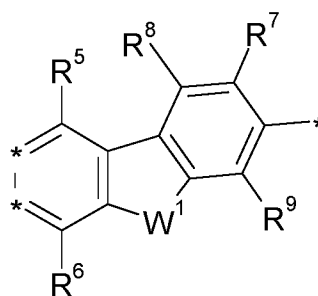


A5r

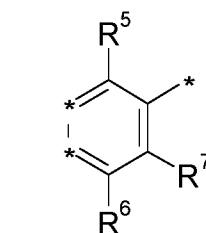
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A5s

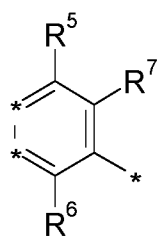


A5t

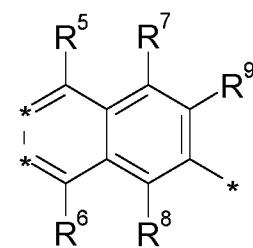
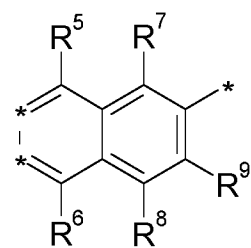


A5u

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35



A5v

A5w

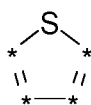
A5x

wherein W^1 , W^2 , W^3 , V^1 and R^{5-9} have the meanings given above,

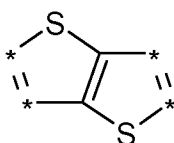
5 Preferred groups Ar^5 are selected from formulae A5a, A5b, A5c, A5d, A5f, A5g, A5h, A5i, A5k, A5l, A5m, A5n, A5o, A5p, A5q, A5u and A5v, very preferably from formula A5a, A5b, A5c, A5d, A5l, A5m, A5n, A5o, A5p, A5q, A5u and A5v.

10 Further preferred groups Ar^5 are selected from formulae A5r and A5s wherein R^5 and R^6 are different from H.

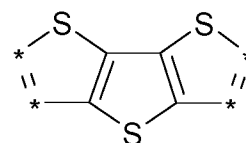
15 Very preferred groups Ar^3 in formula I and I2-I7 and their subformulae are on each occurrence identically or differently selected from the following formulae and their mirror images



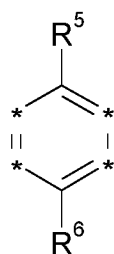
A3a1



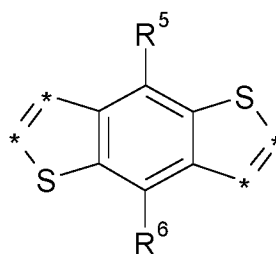
A3b1



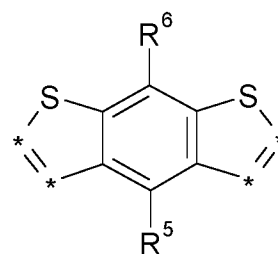
A3c1



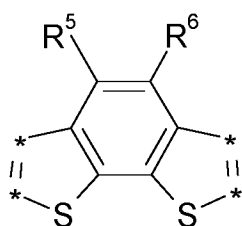
A3d1



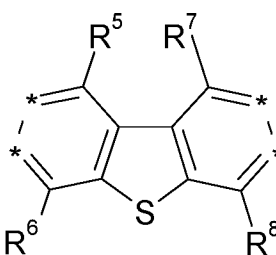
A3e1



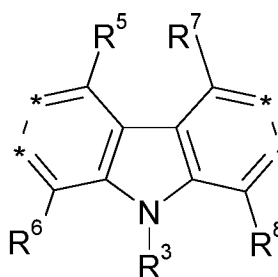
A3f1



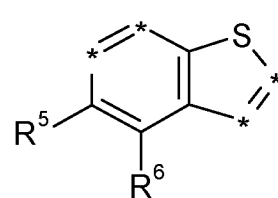
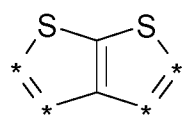
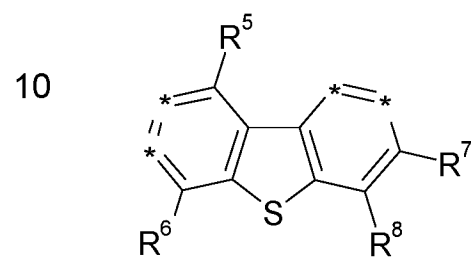
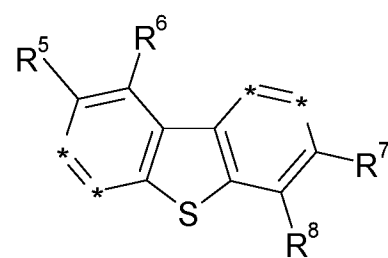
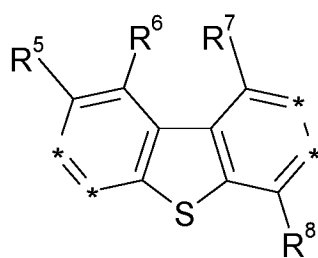
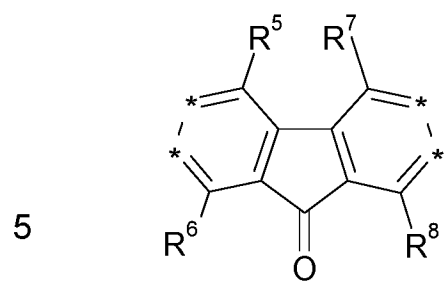
A3g1



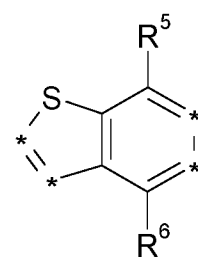
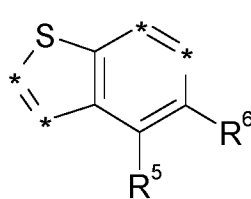
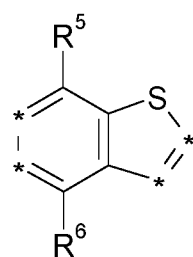
A3h1



A3h2

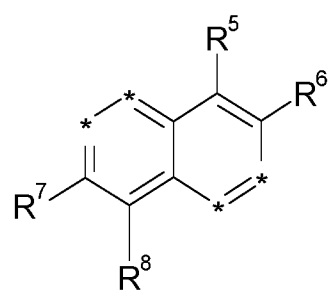
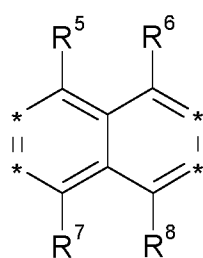
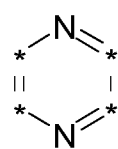


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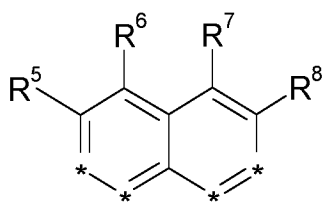
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A3u1

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

- 5 Very preferred groups Ar^3 are selected from formulae A3b1, A3d1, A3f1 and A3t1, very preferably from formulae A3b1 and A3d1.

Further preferred groups Ar^3 are selected from formula A3d1 wherein R^5 and R^6 denote F.

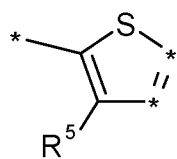
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Further preferred groups Ar^3 are selected from formulae A3e1 and A3f1 wherein R^5 and R^6 are different from H.

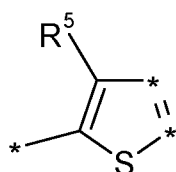
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Very preferred groups Ar^4 in formula I and I1-I7 and their subformulae are on each occurrence identically or differently selected from the following formulae and their mirror images

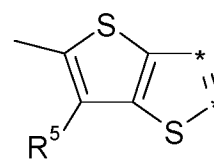
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A4a1

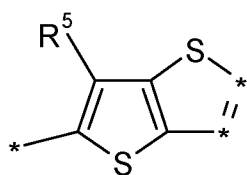


A4b1

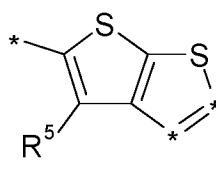


A4c1

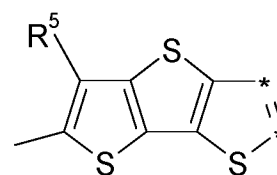
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A4d1

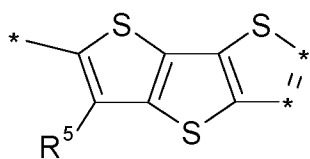


A4e1

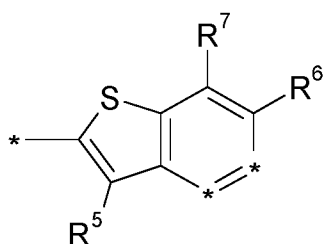


A4f1

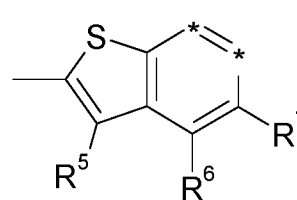
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A4g1



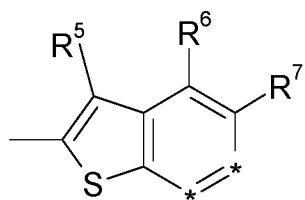
A4h1



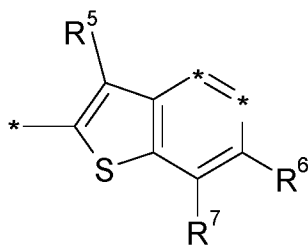
A4i1

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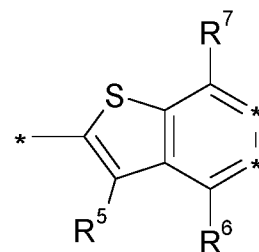
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A4j1

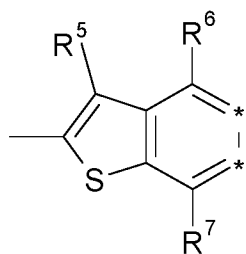


A4k1

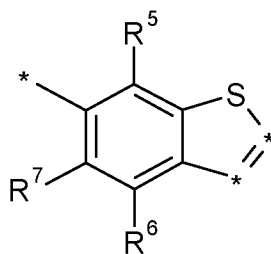


A4l1

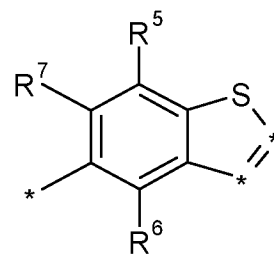
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A4m1

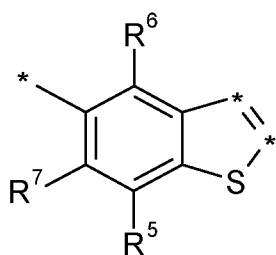


A4n1

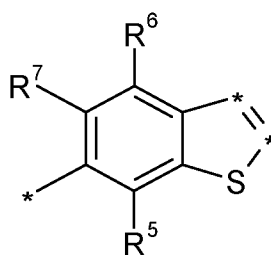


A4o1

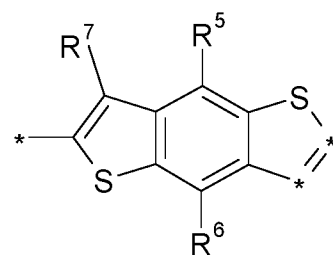
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A4p1

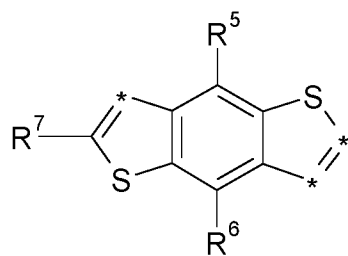


A4q1

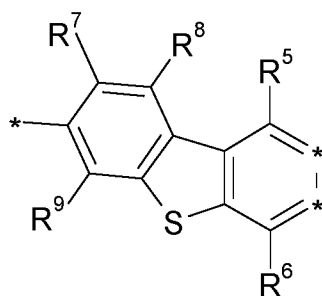


A4r1

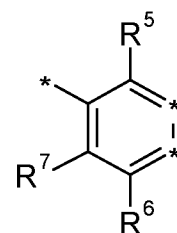
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A4s1

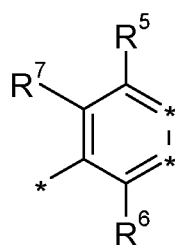


A4t1

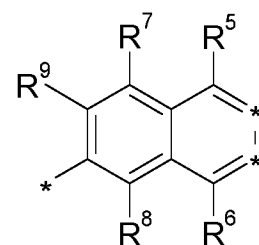
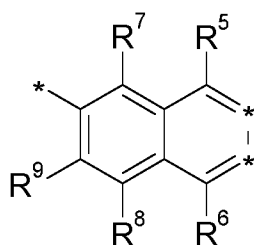


A4u1

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A4v1

A4w1

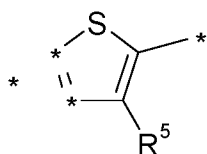
A4x1

wherein R^{5-9} have the meanings given above and below.

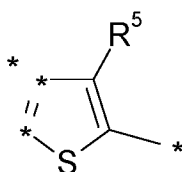
5 Very preferred groups Ar^4 are selected from formulae A4a1, A4b1, A4c1, A4d1, A4f1, A4g1, A4h1, A4i1, A4k1, A4l1, A4m1, A4n1, A4o1, A4p1, A4q1, A4u and A4v1, very preferably from formula A4a1, A4b1, A4c1, A4d1, A4l1, A4m1, A4n1, A4o1, A4p1, A4q1, A4u1 and A4v1.

10 Further preferred groups Ar^4 are selected from formula A4r1 and A4s1 wherein R^5 and R^6 are different from H.

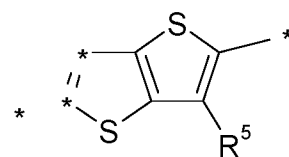
15 Very preferred groups Ar^5 in formula I and I1-I7 and their subformulae are on each occurrence identically or differently selected from the following formulae and their mirror images



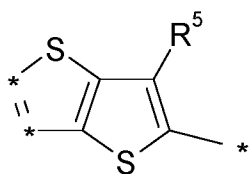
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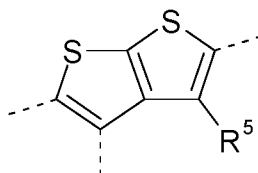
A5b1



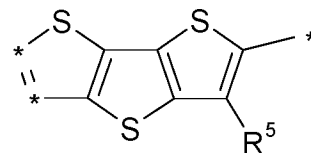
A5c1



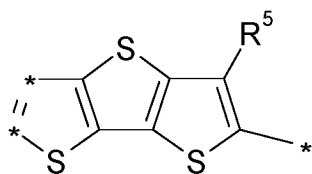
A5d1



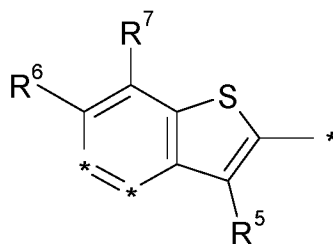
A5e1



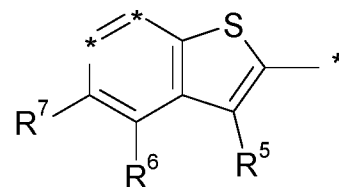
A5f1



A5g1

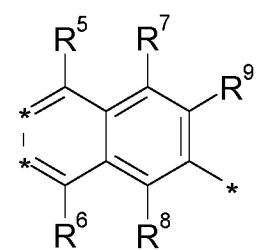
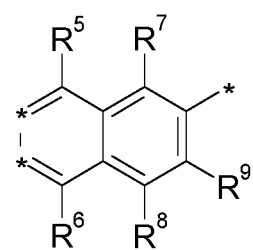
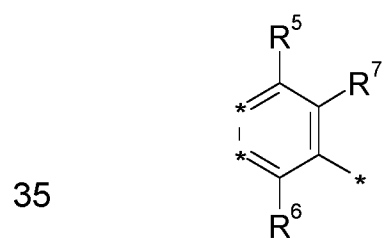
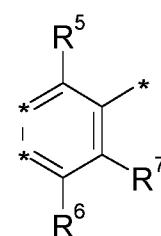
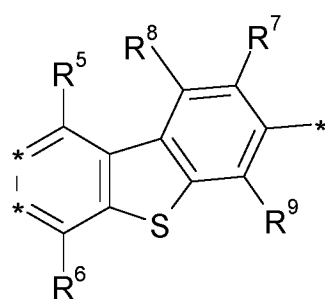
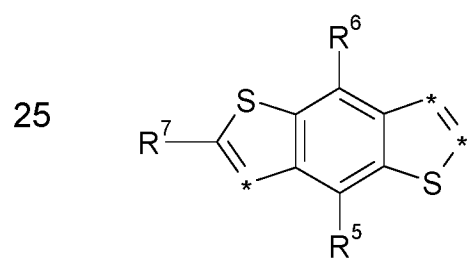
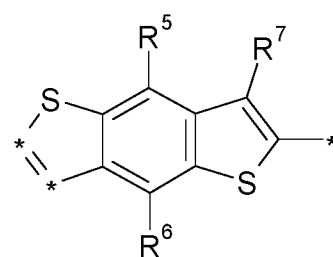
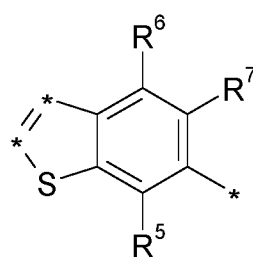
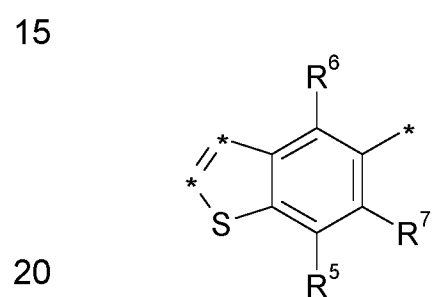
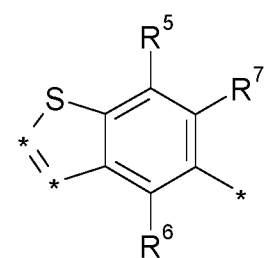
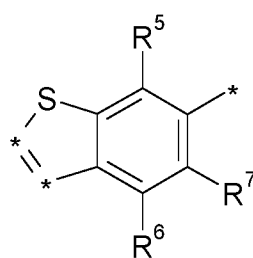
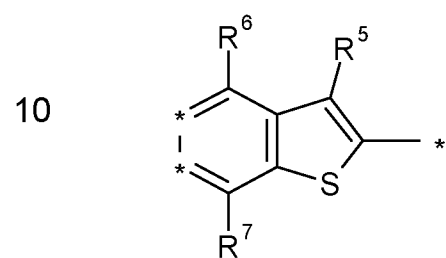
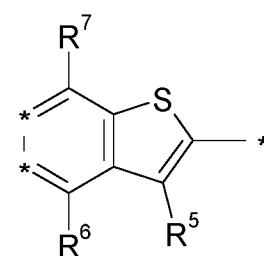
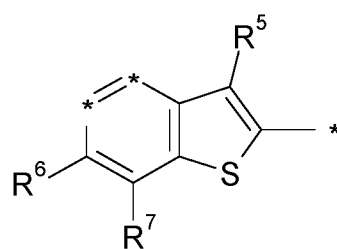
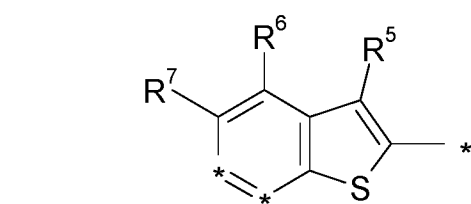


A5h1



A5i1

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A5v1

A5w1

A5x1

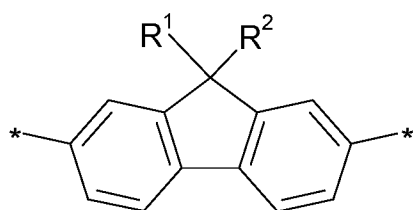
wherein R^{5-9} have the meanings given above and below.

5 Very preferred groups Ar^5 are selected from formulae A5a1, A5b1, A5c1, A5d1, A5f1, A5g1, A5h1, A5i1, A5k1, A5l1, A5m1, A5n1, A5o1, A5p1, A5q1, A5u and A5v1, very preferably from formula A5a1, A5b1, A5c1, A5d1, A5l1, A5m1, A5n1, A5o1, A5p1, A5q1, A5u1 and A5v1.

10 Further preferred groups Ar^5 are selected from formula A5r1 and A5s1 wherein R^5 and R^6 are different from H.

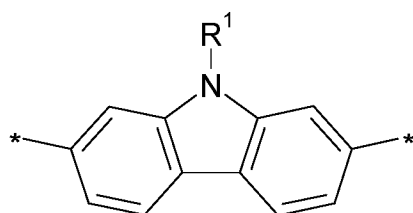
Preferred units of formula I and I1-17 are selected from the the group consisting of the following subformulae

15



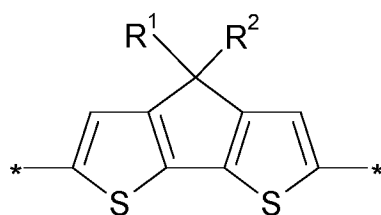
I1-1

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I1-2

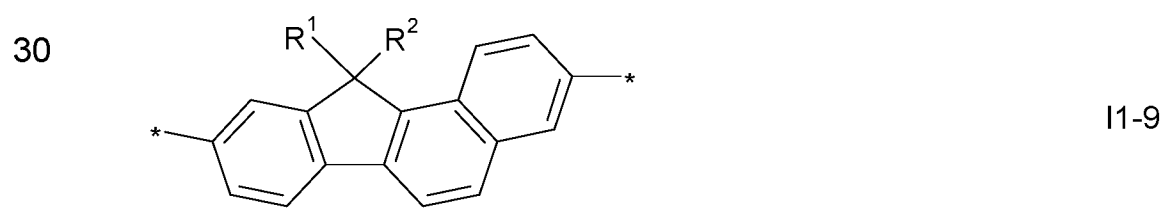
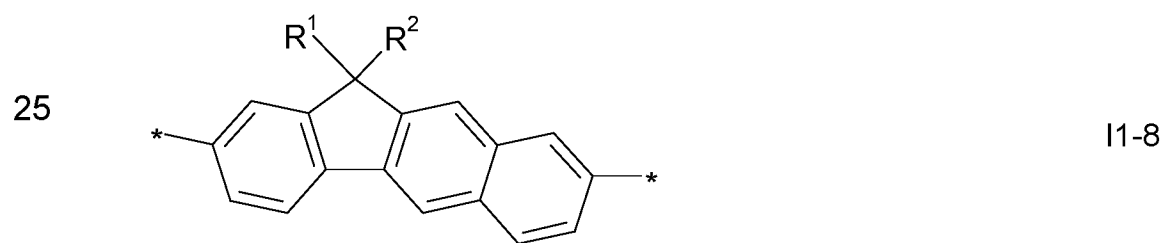
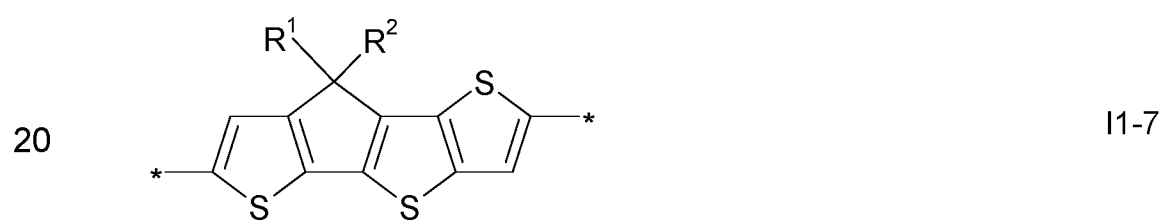
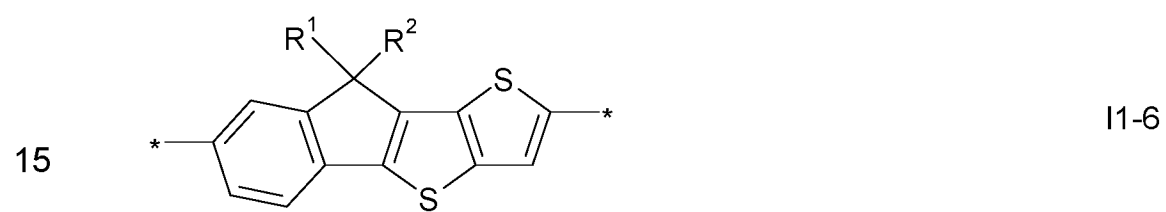
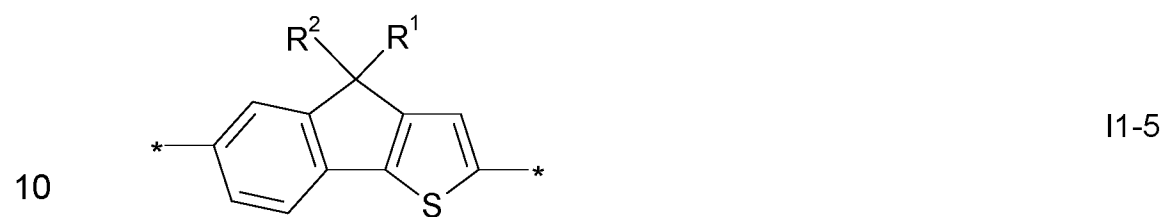
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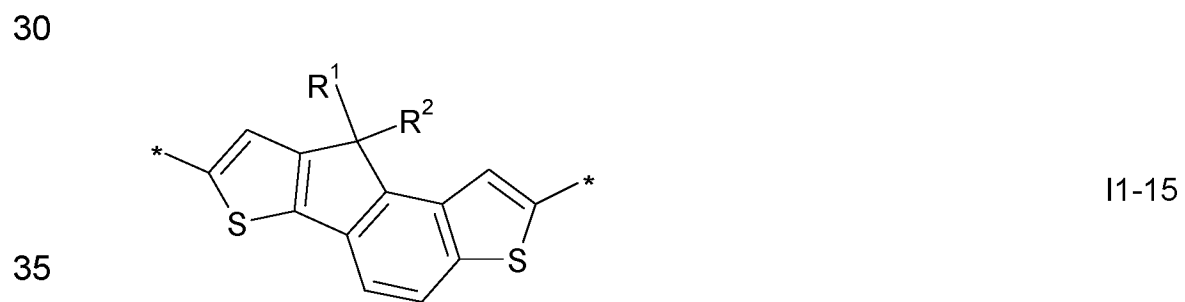
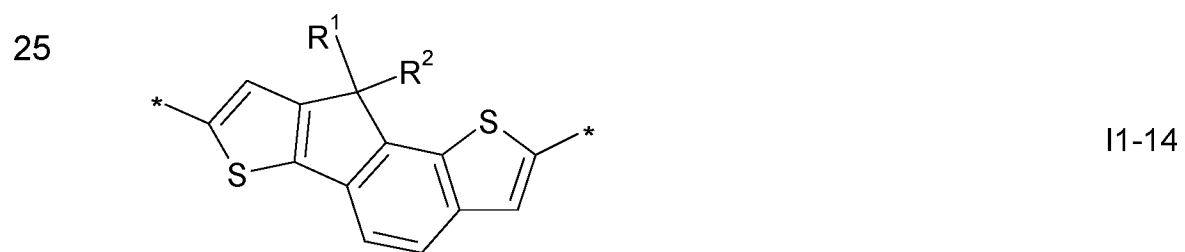
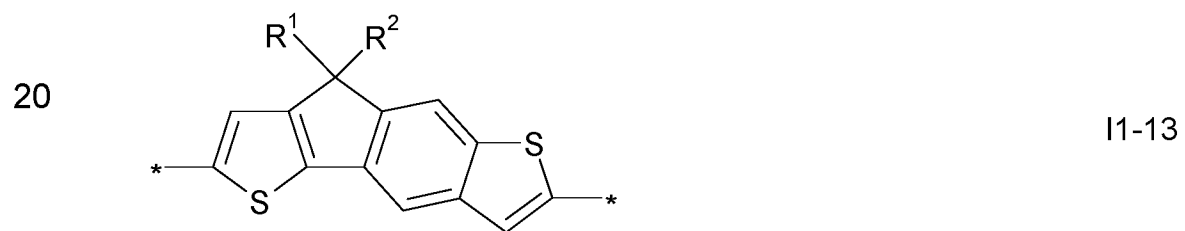
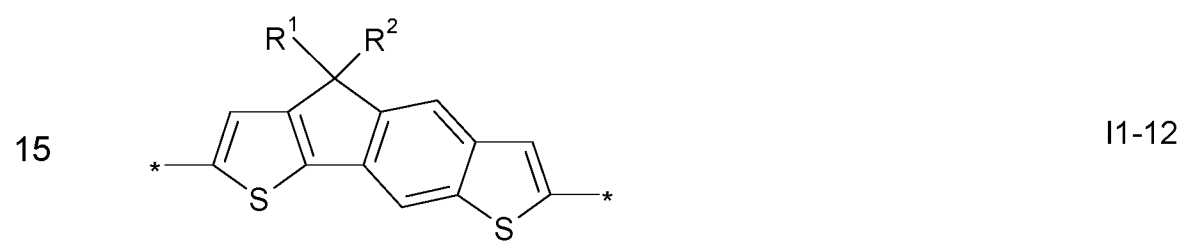
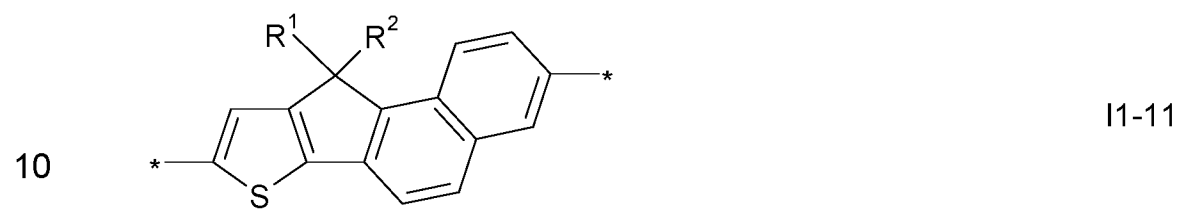
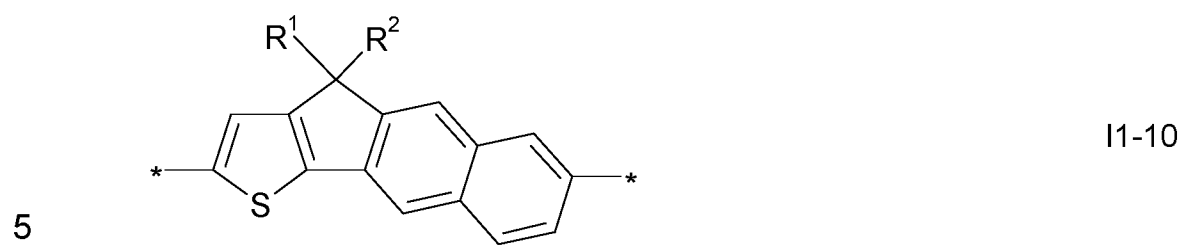
I1-3

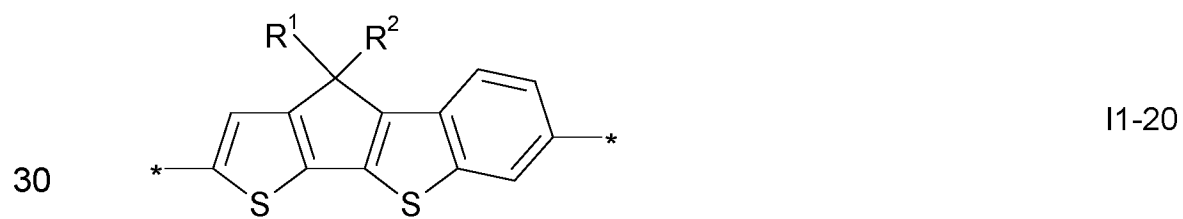
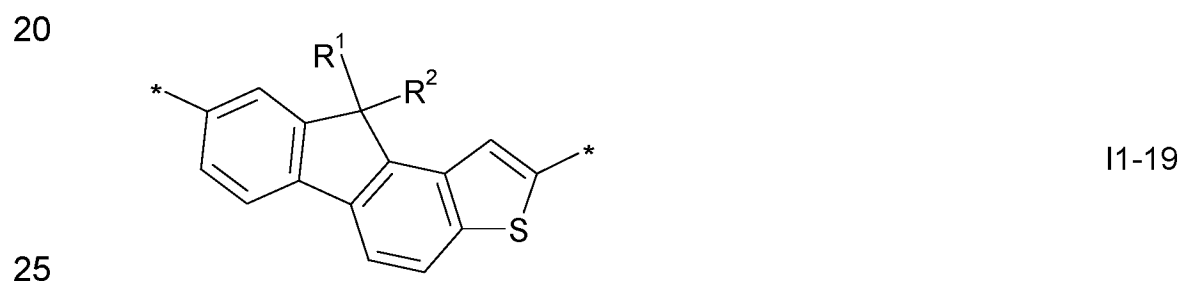
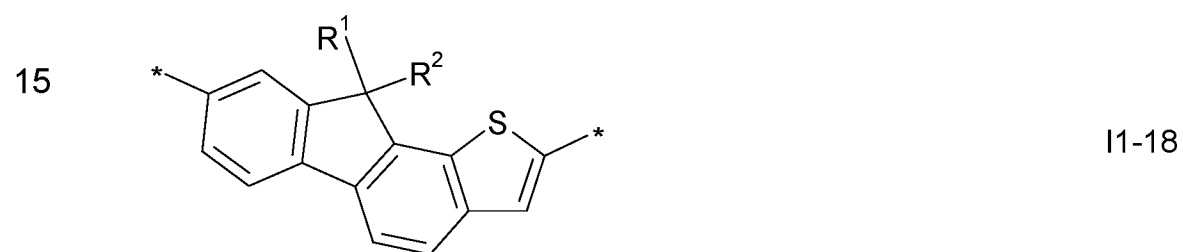
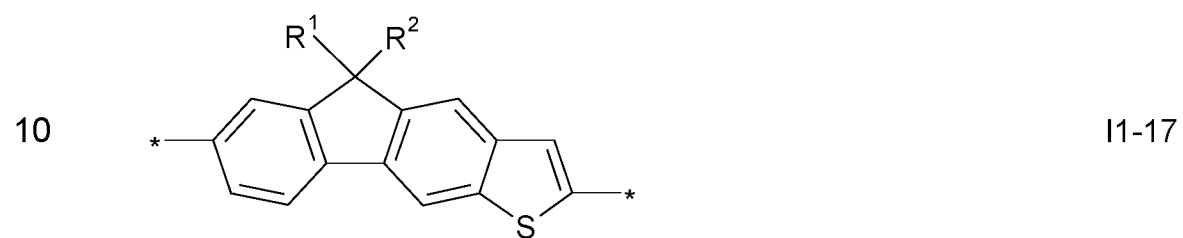
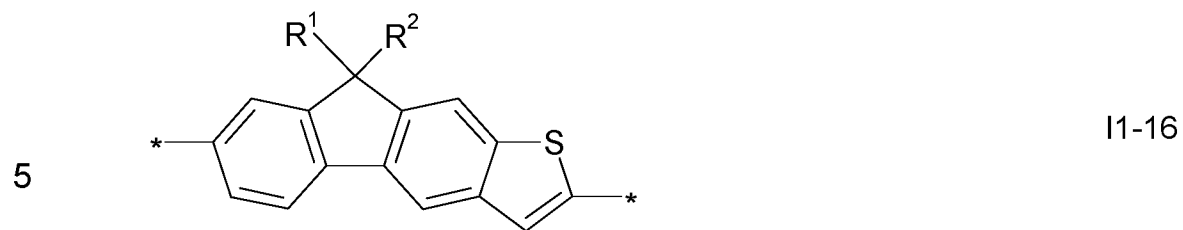
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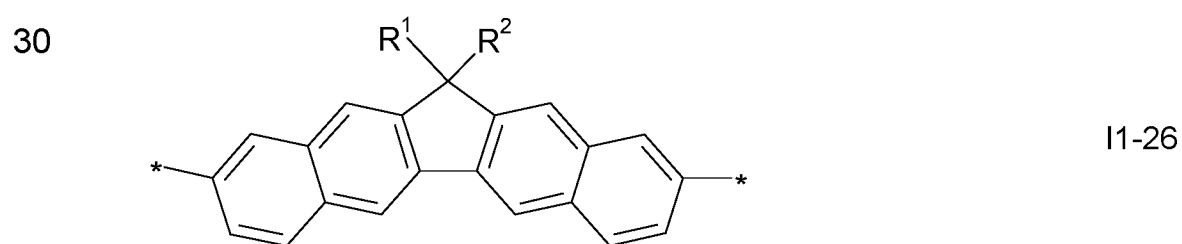
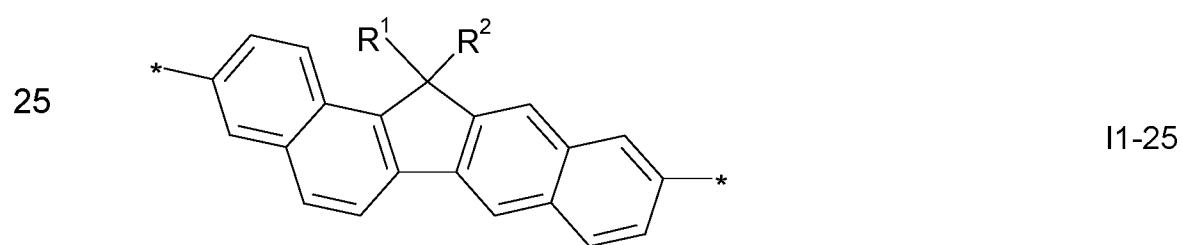
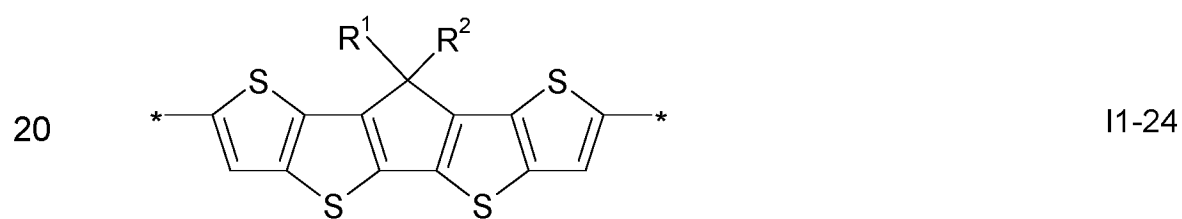
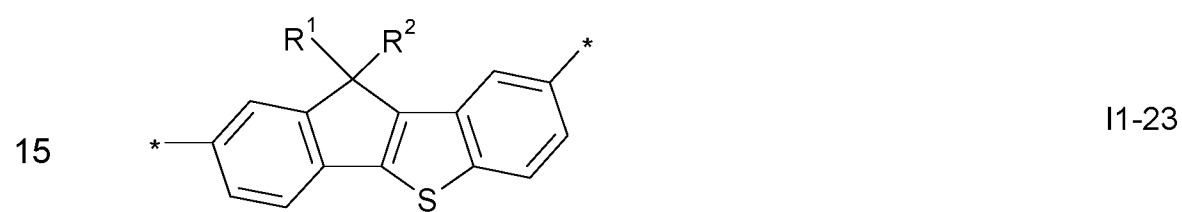
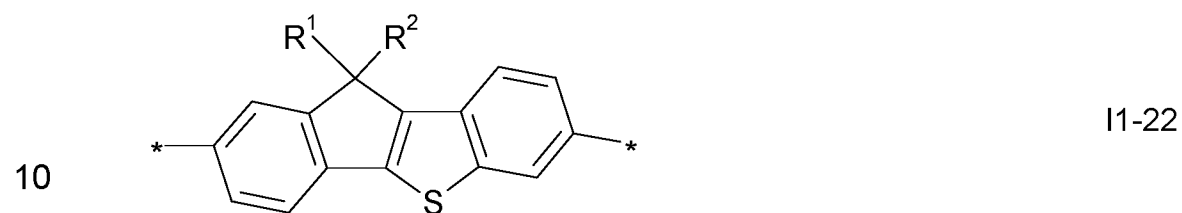
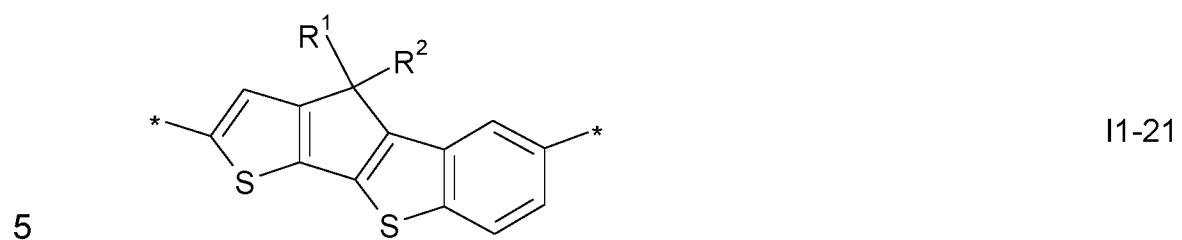
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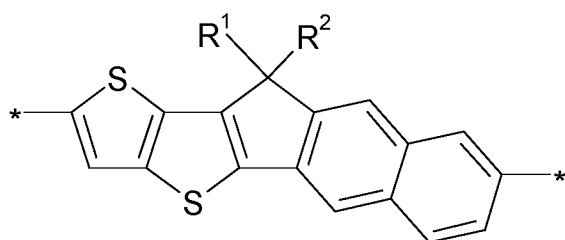






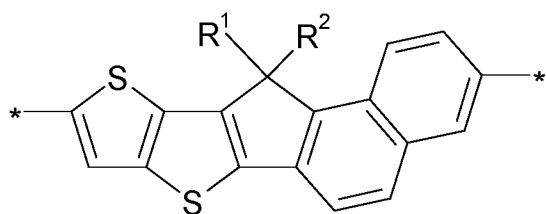
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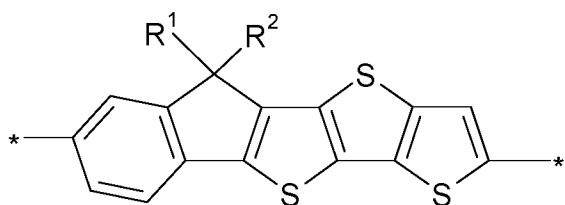
I1-27

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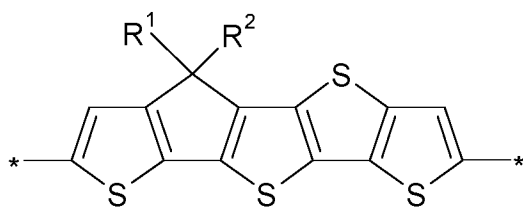
I1-28

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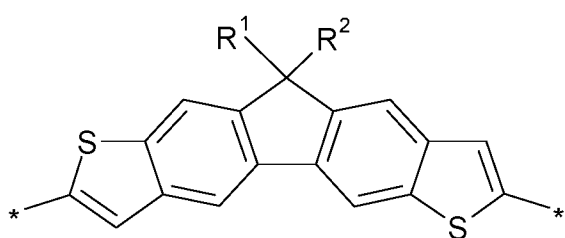
I1-29

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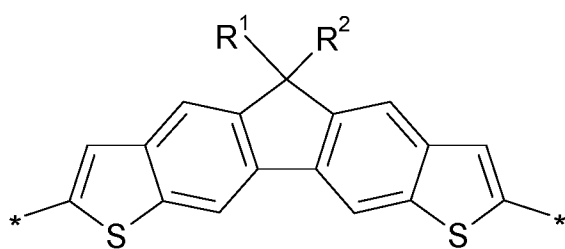
I1-30

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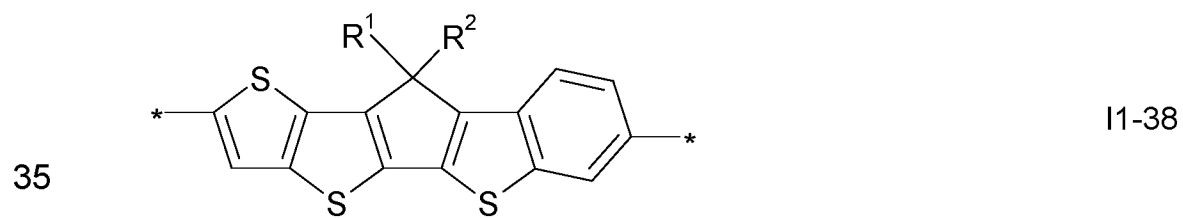
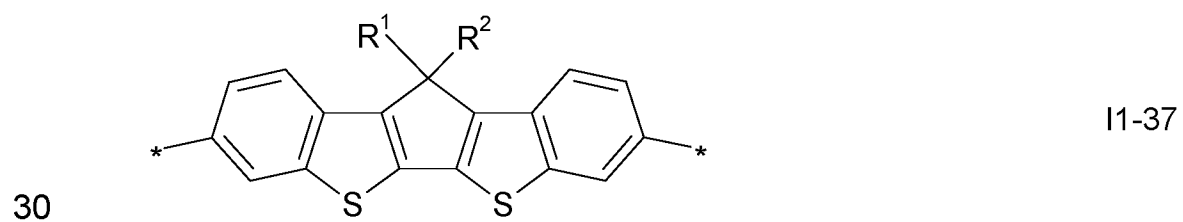
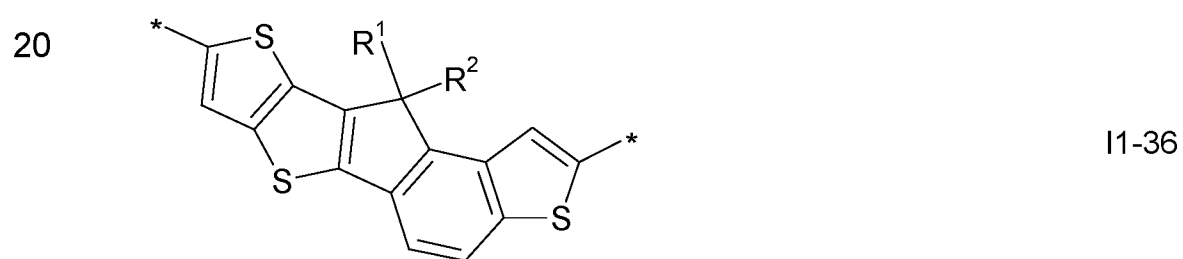
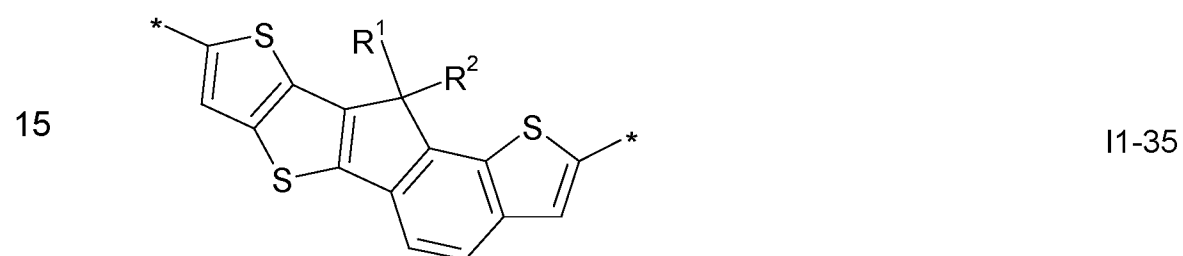
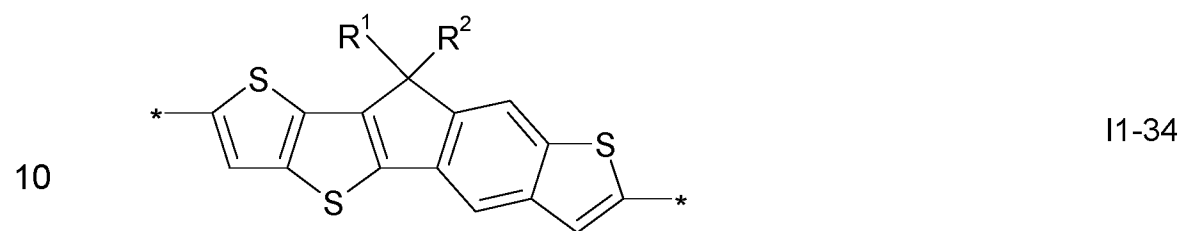
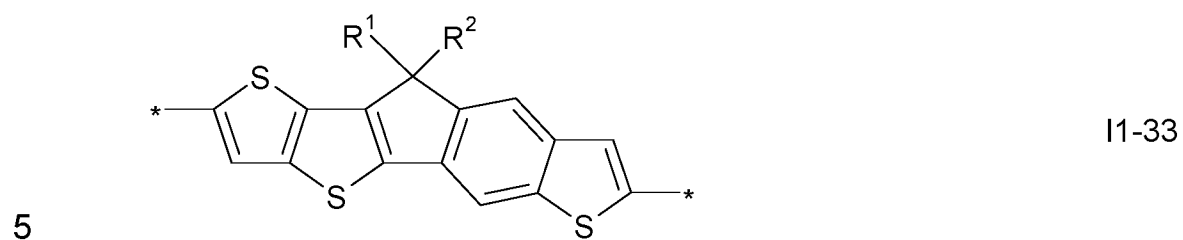
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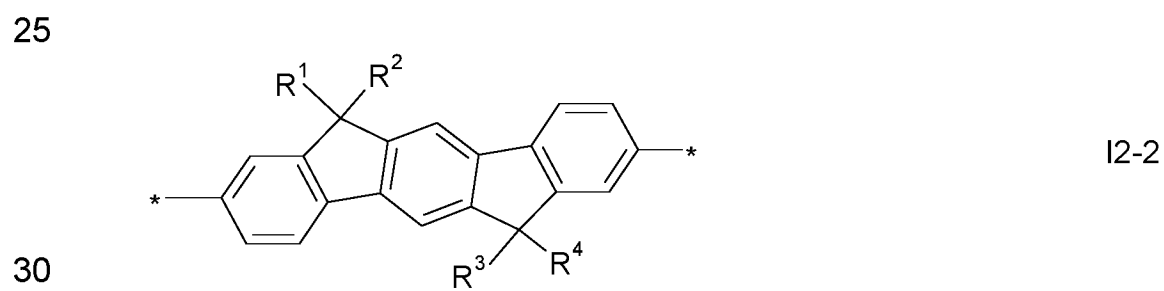
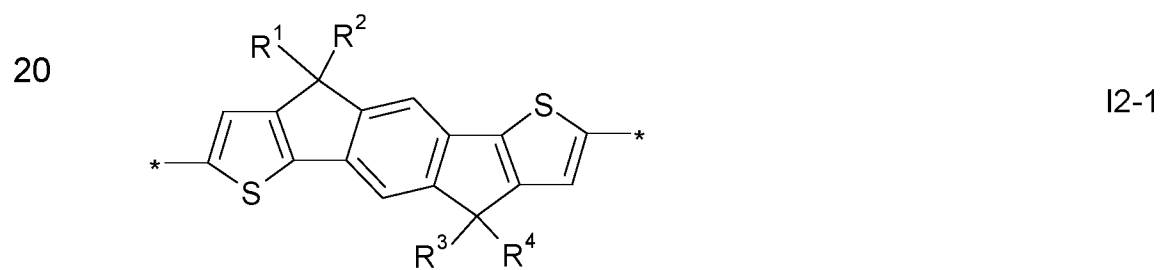
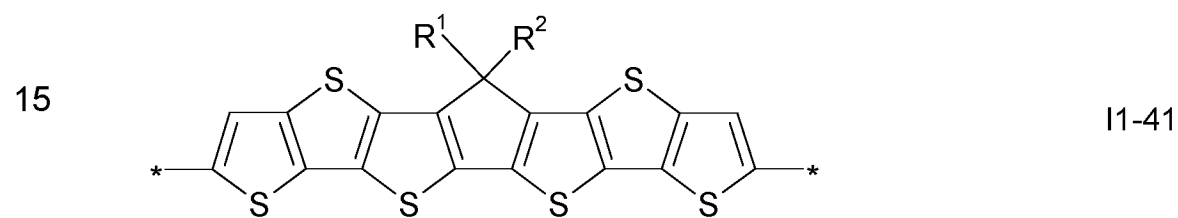
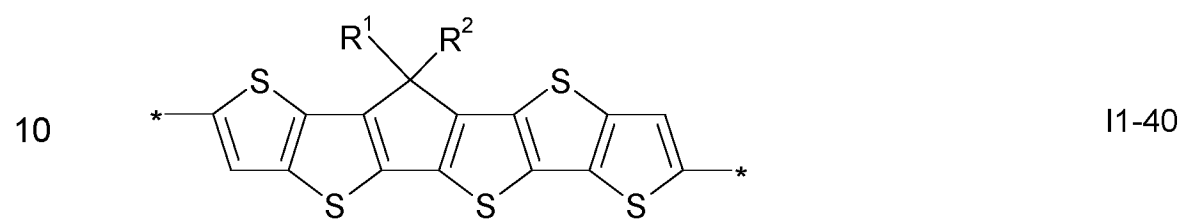
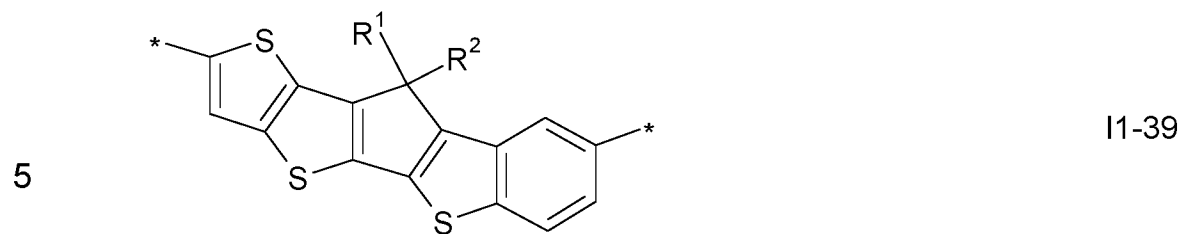
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I1-32

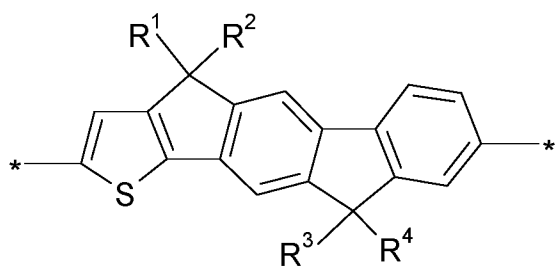
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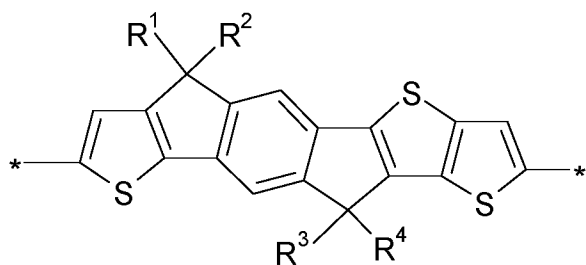
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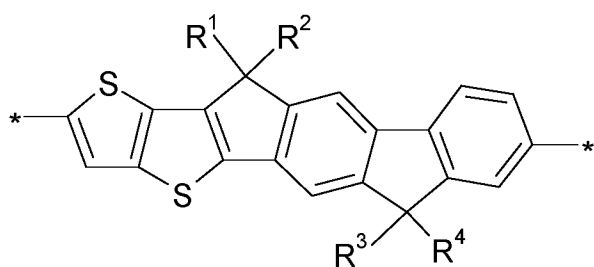
12-3

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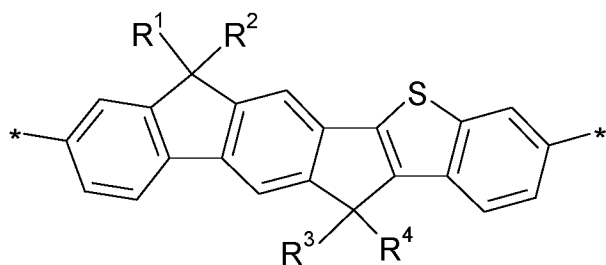
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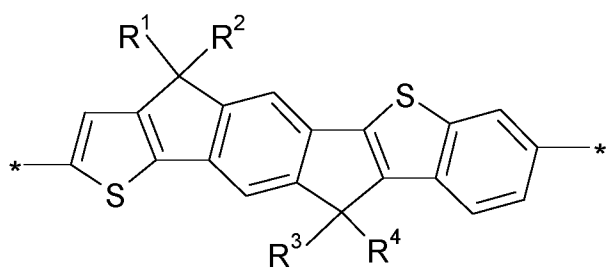
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12-6

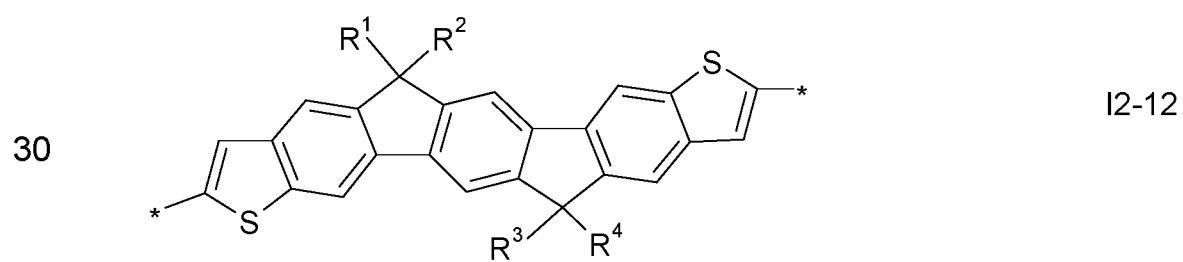
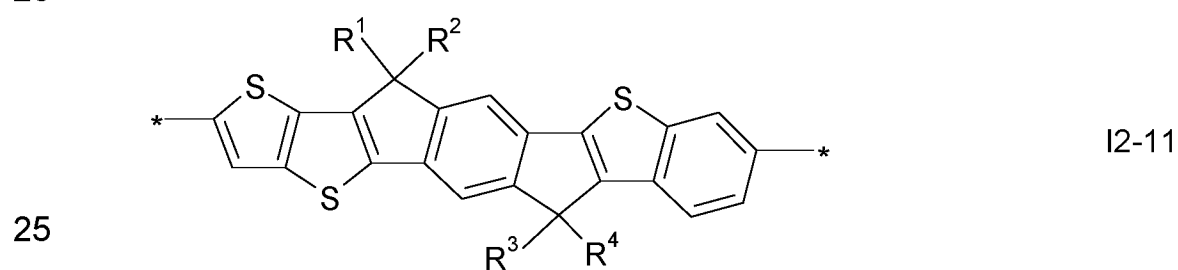
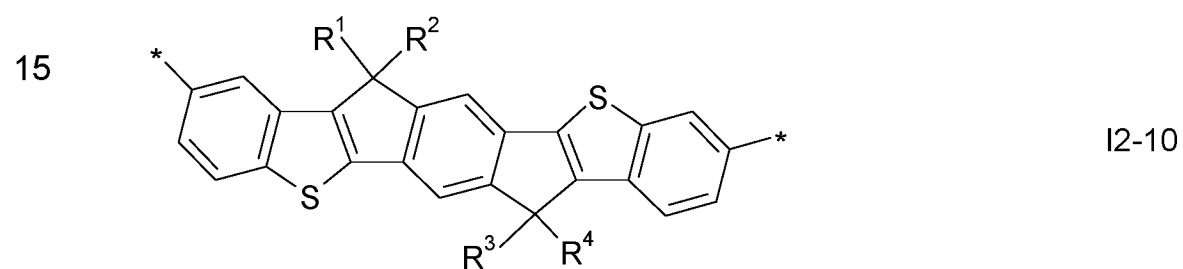
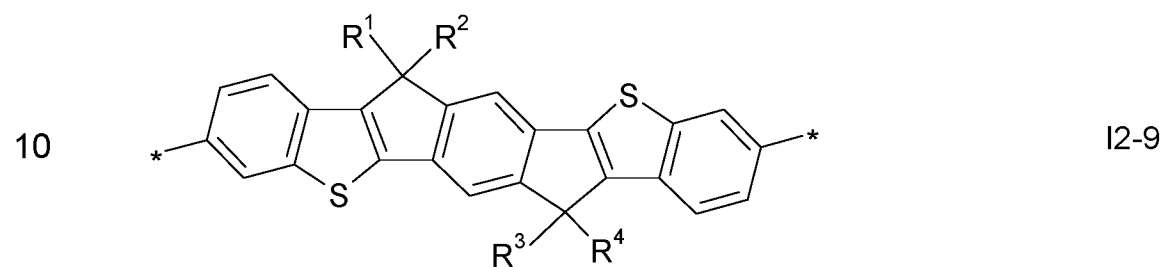
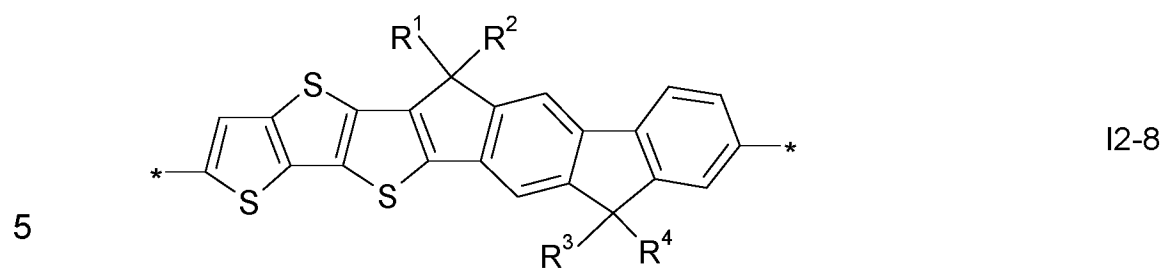
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12-7

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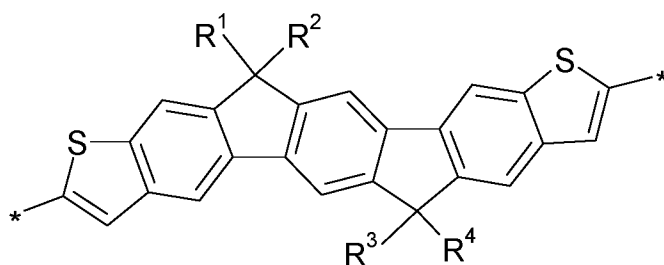
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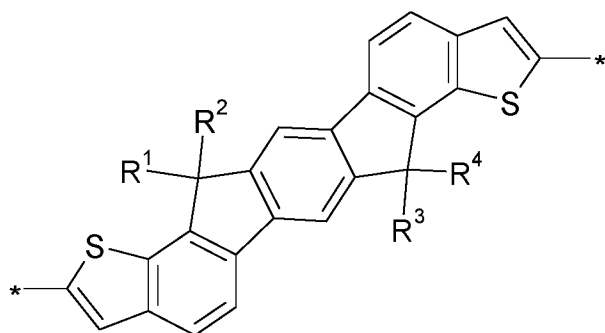
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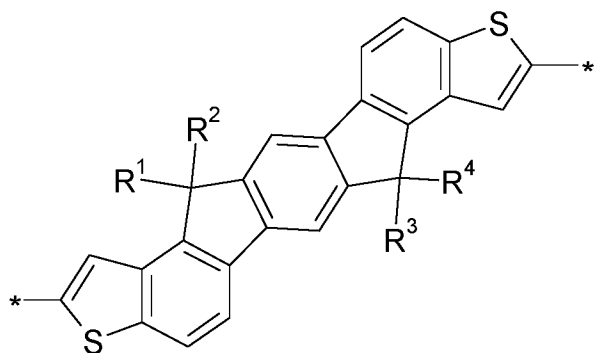
I2-13

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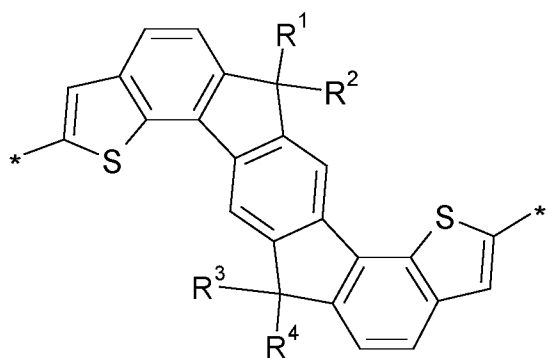
I2-14

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I2-15

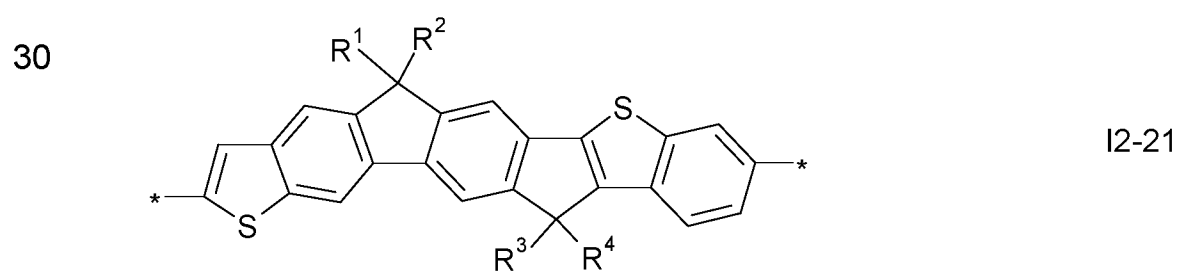
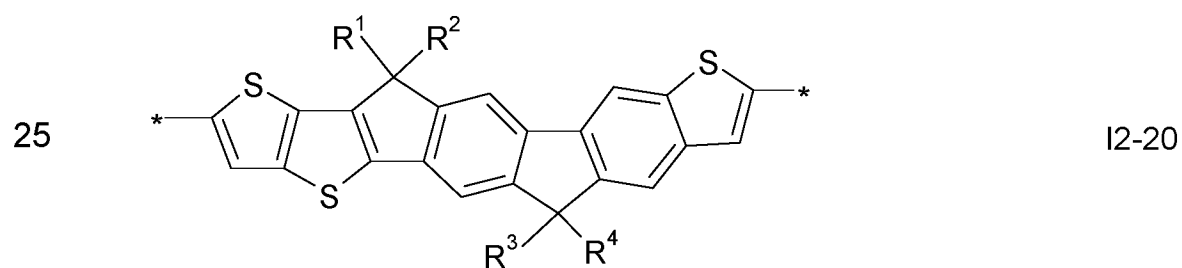
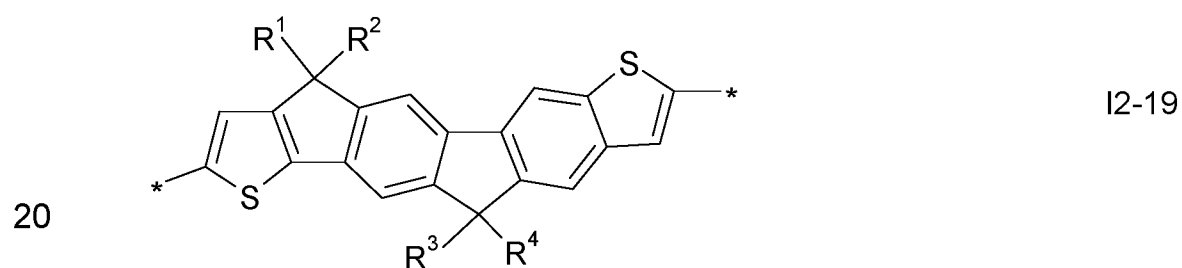
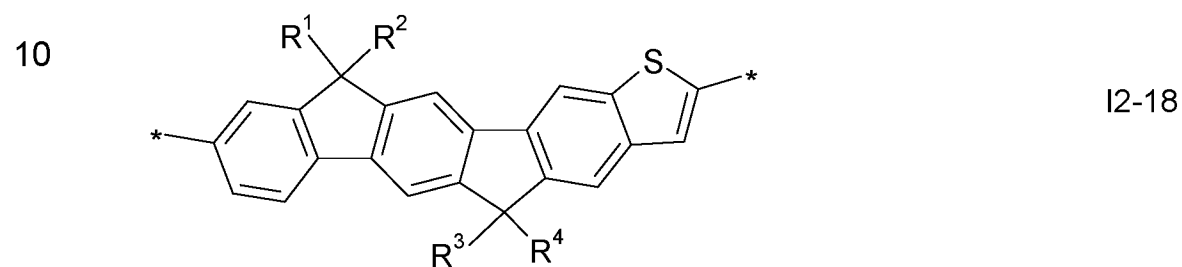
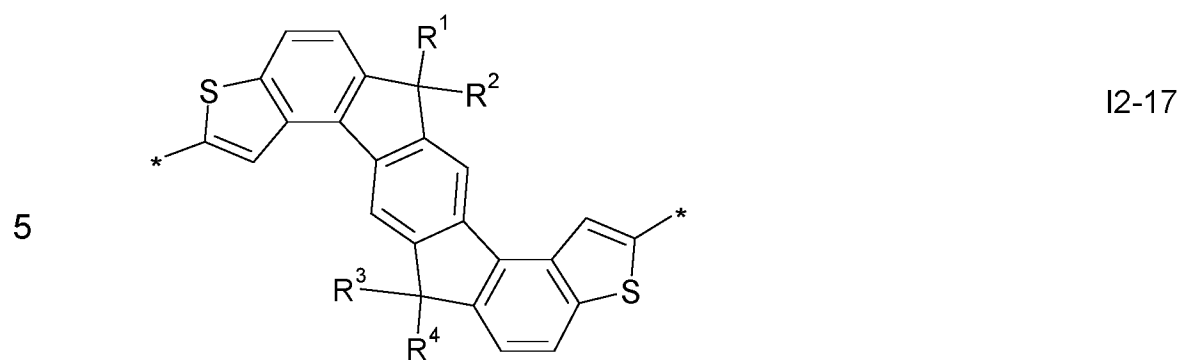
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I2-16

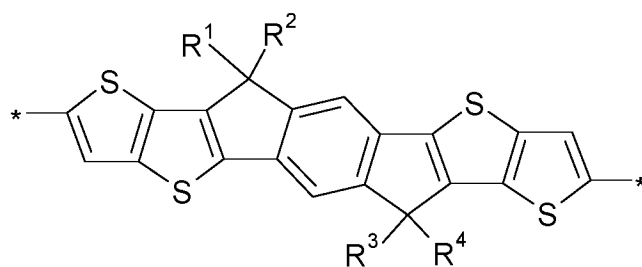
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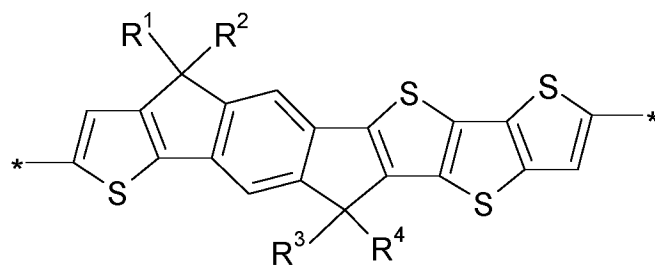


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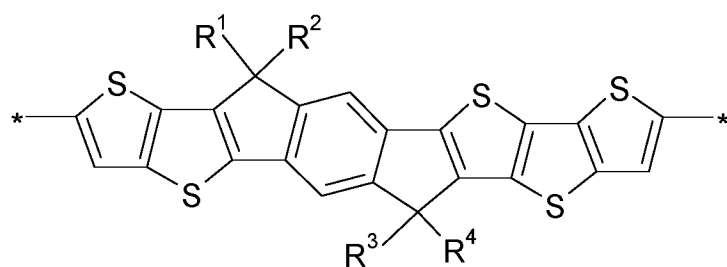
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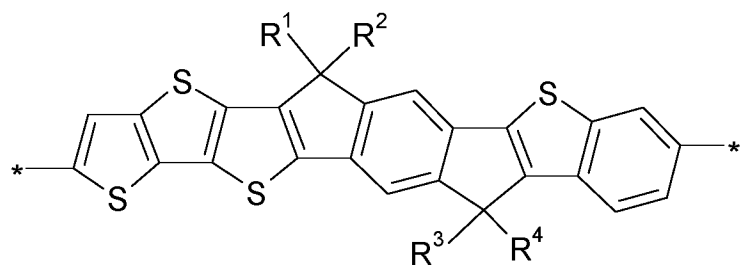
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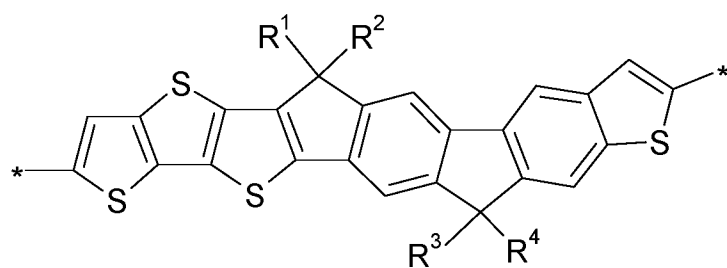
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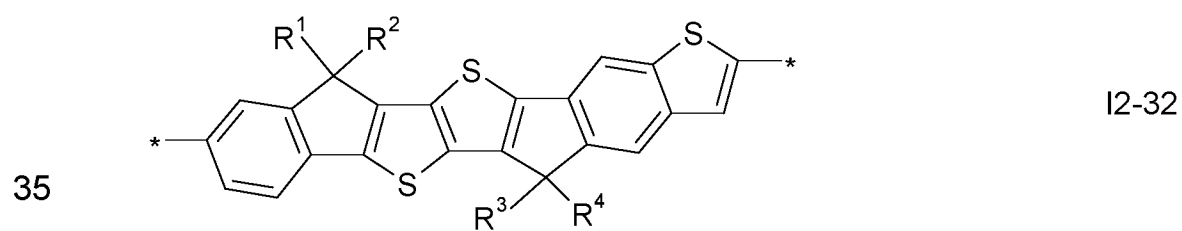
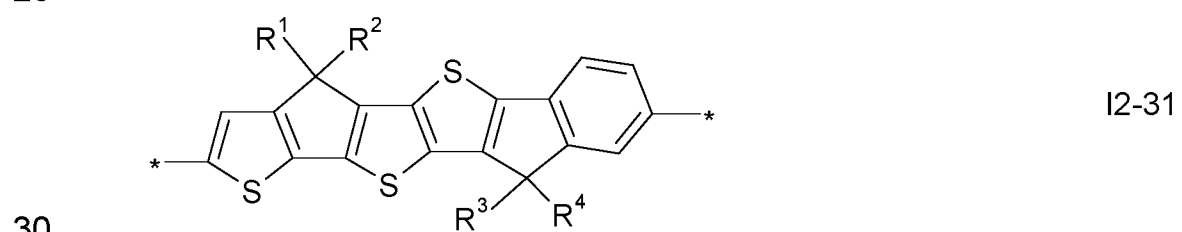
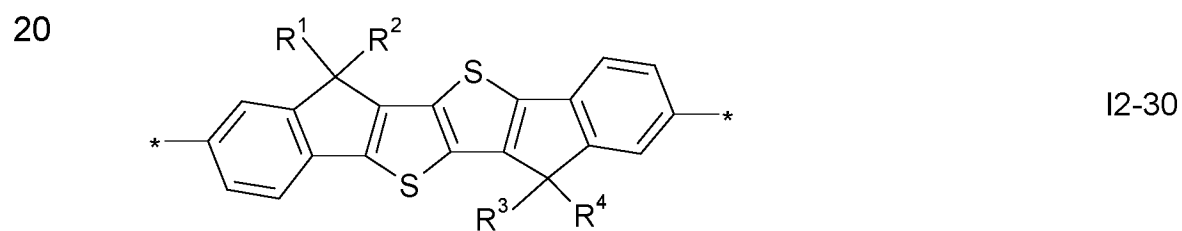
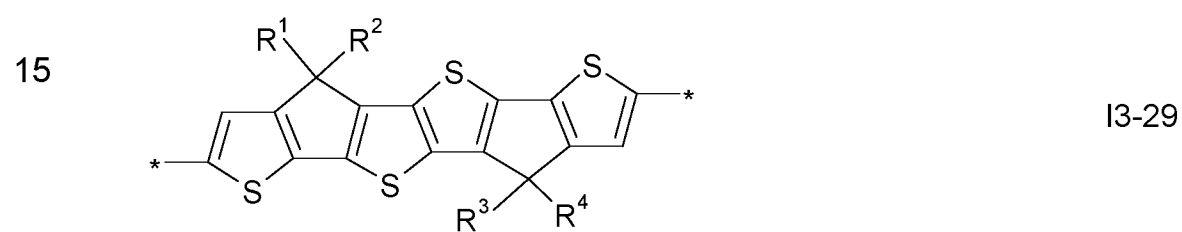
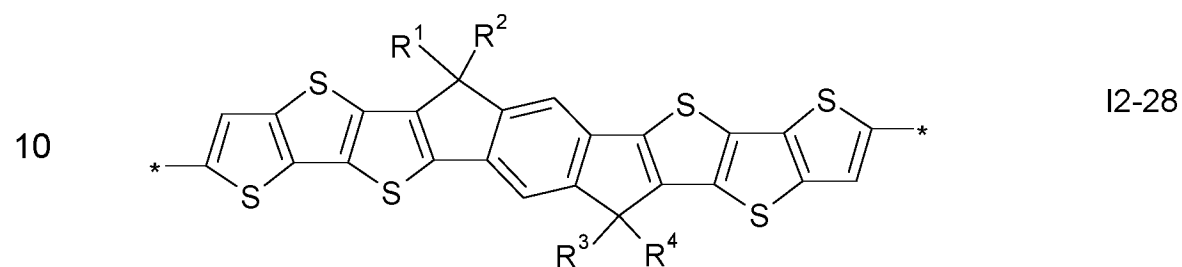
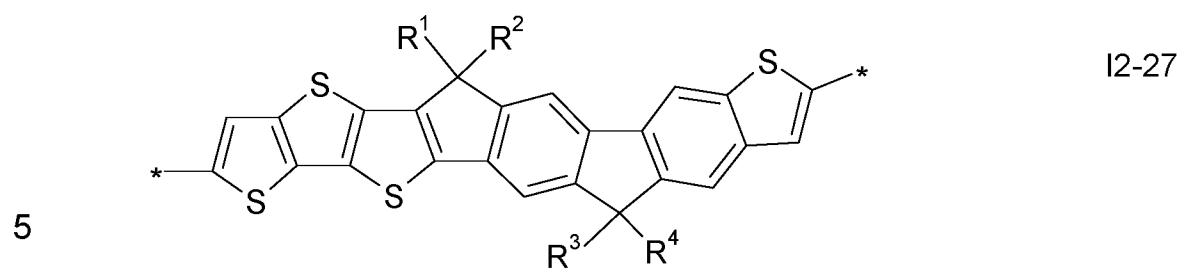


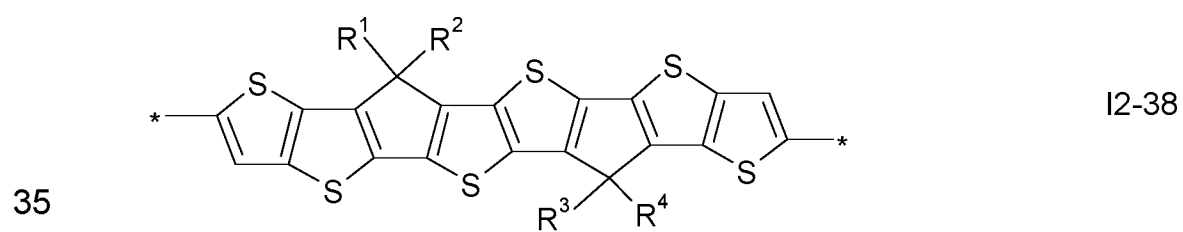
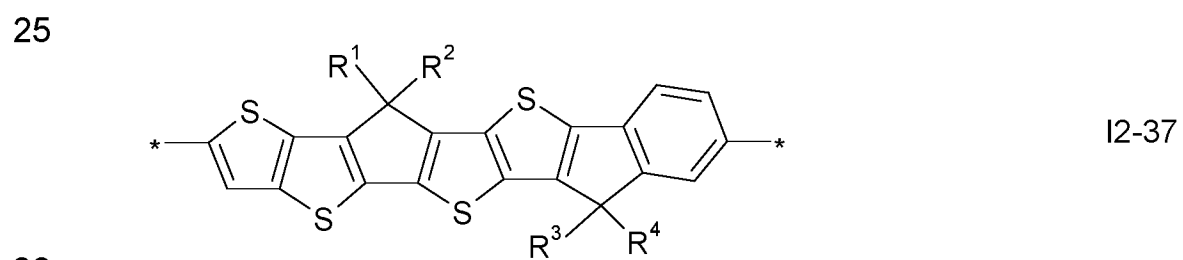
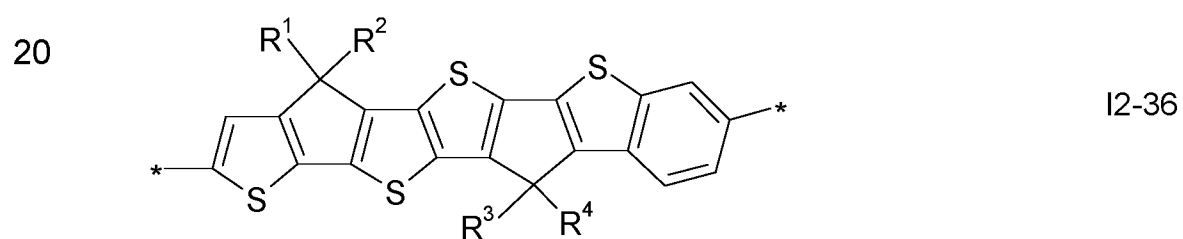
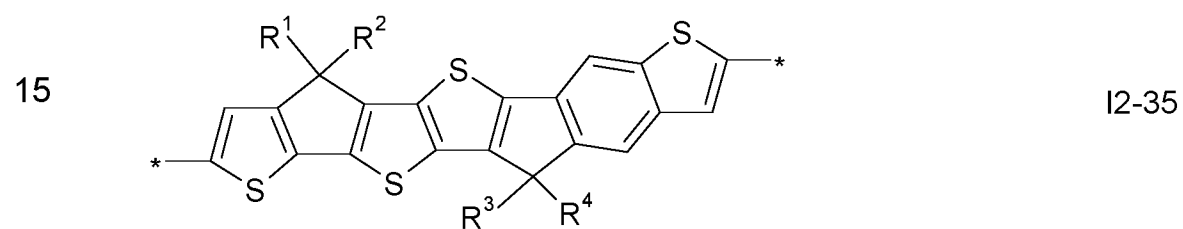
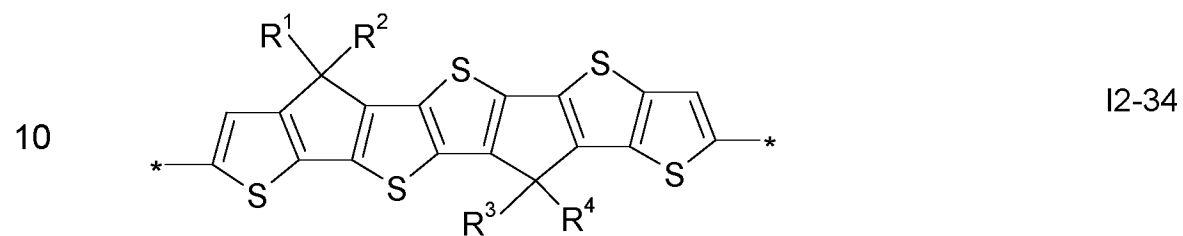
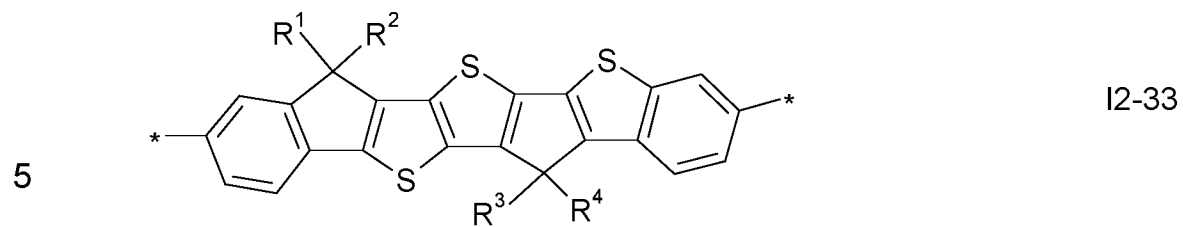
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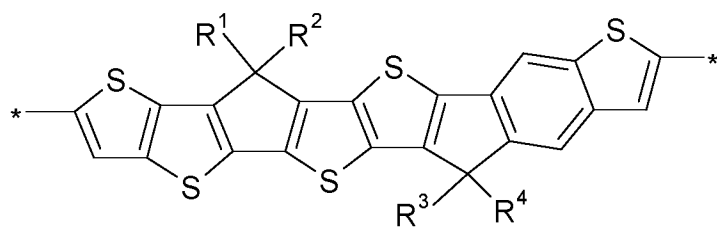
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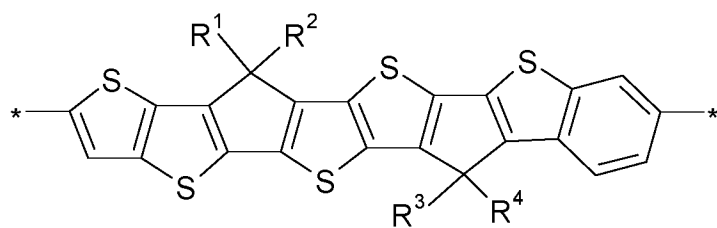
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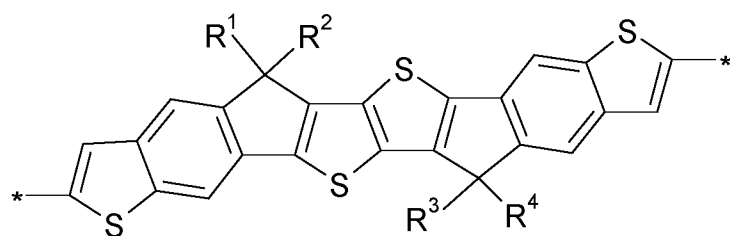
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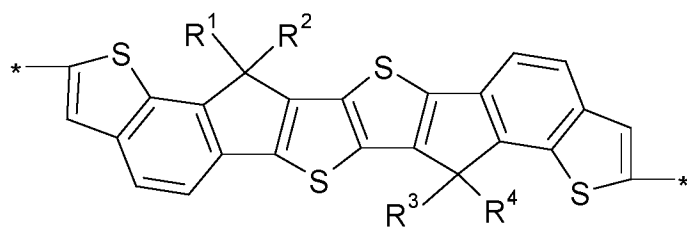
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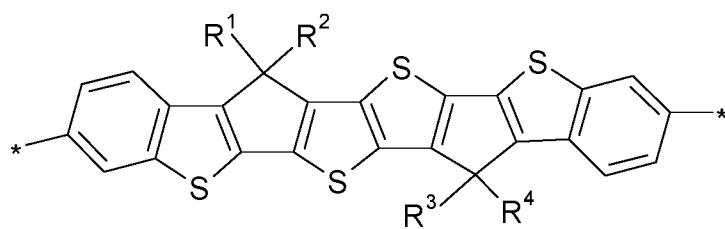
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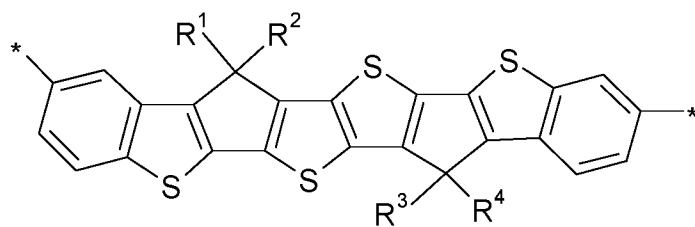
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12-43

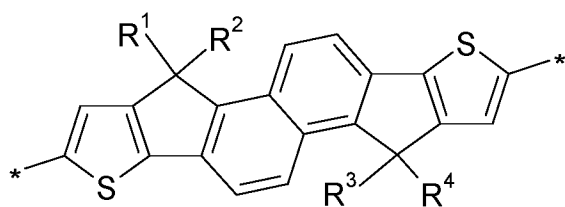
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12-44

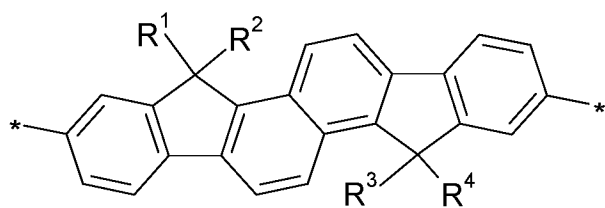
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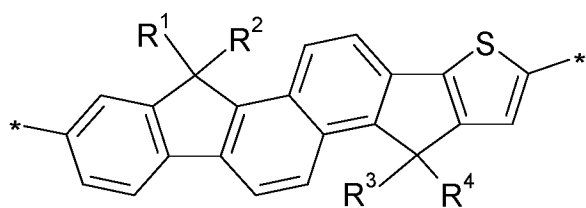
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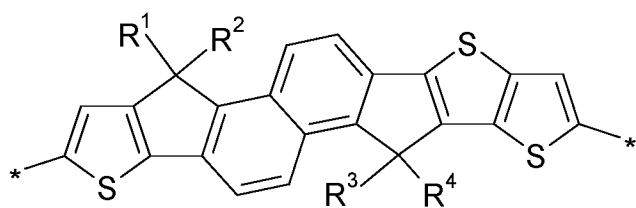
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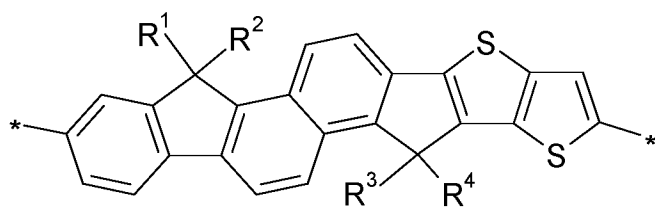
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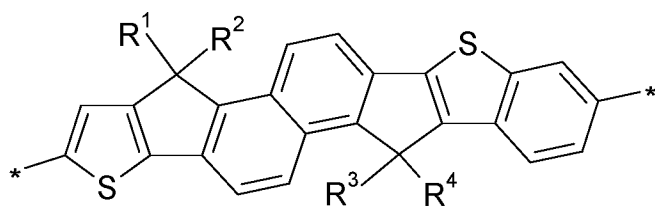
12-48

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12-49

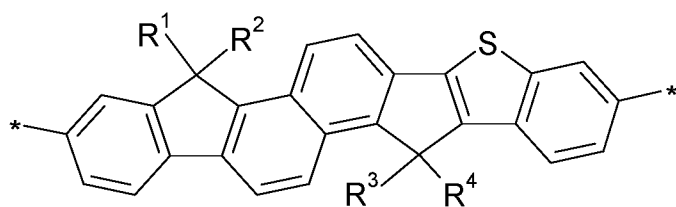
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12-50

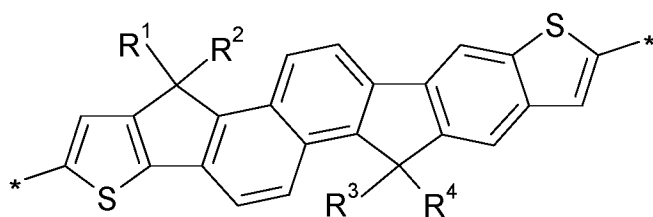
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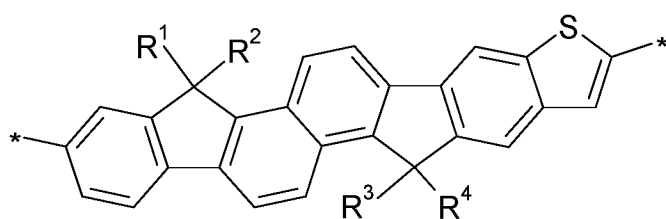
I2-51

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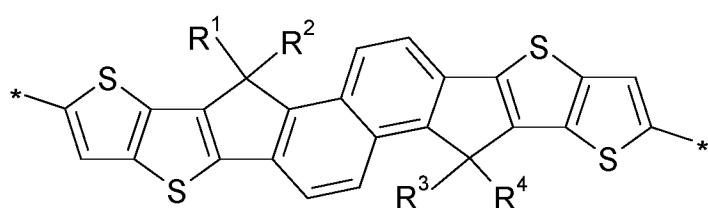
I2-52

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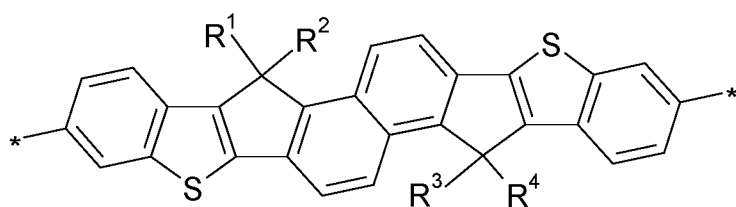
I2-53

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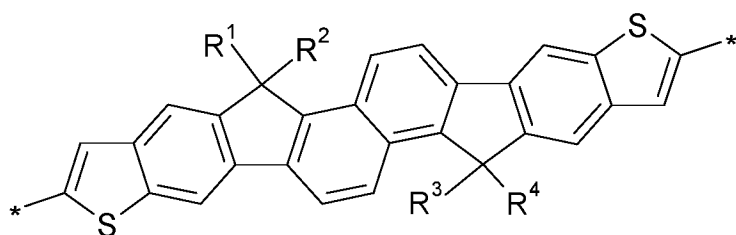
I2-54

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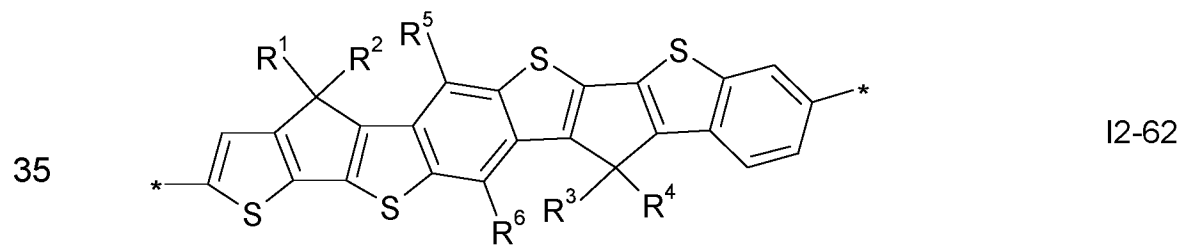
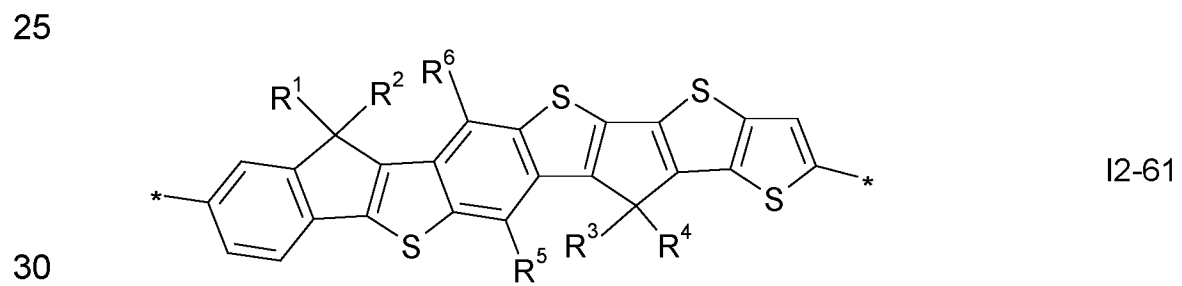
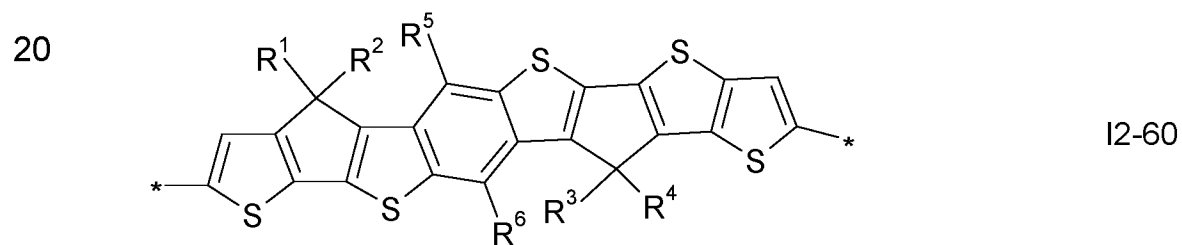
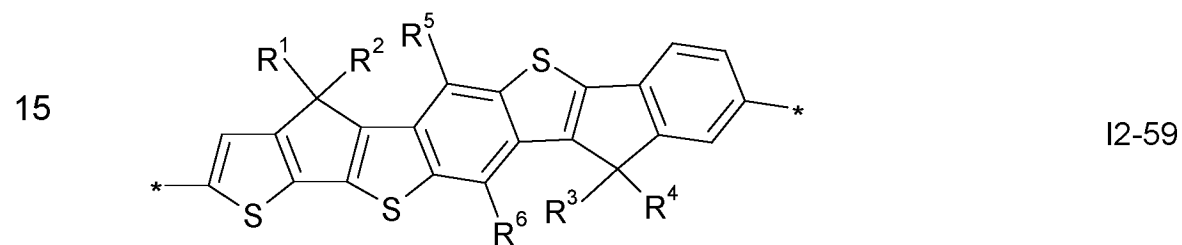
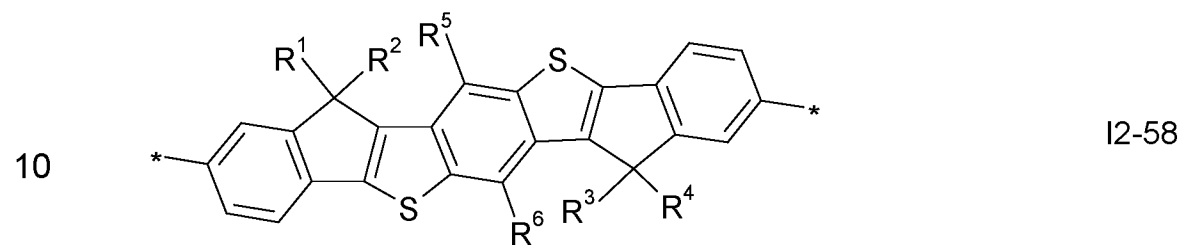
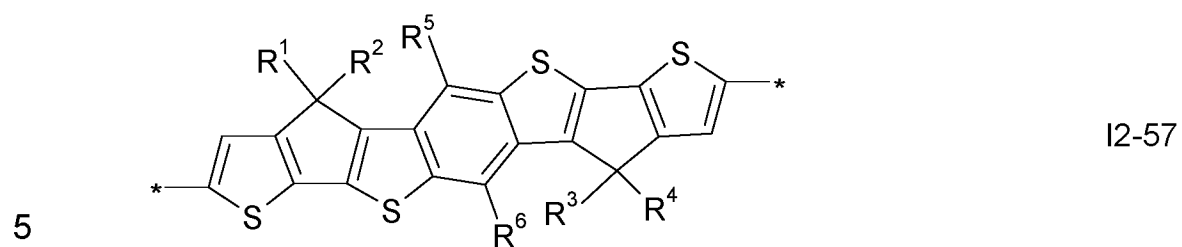
I2-55

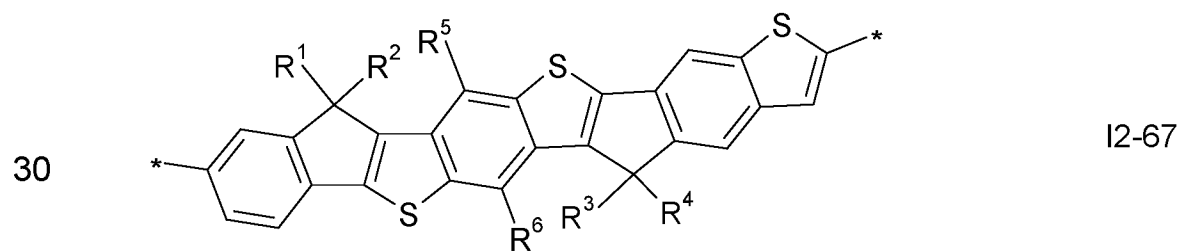
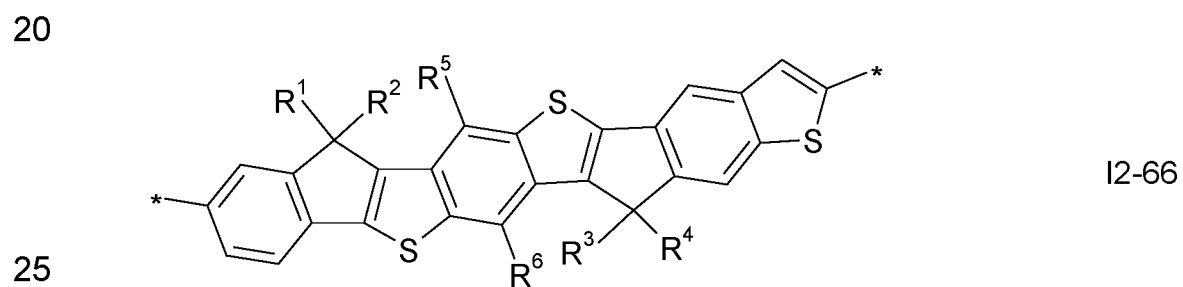
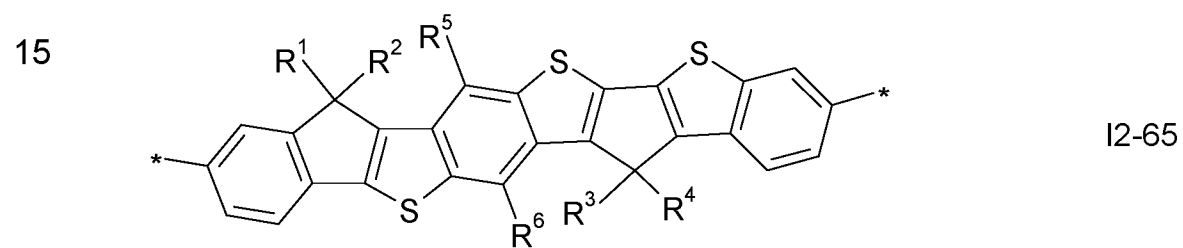
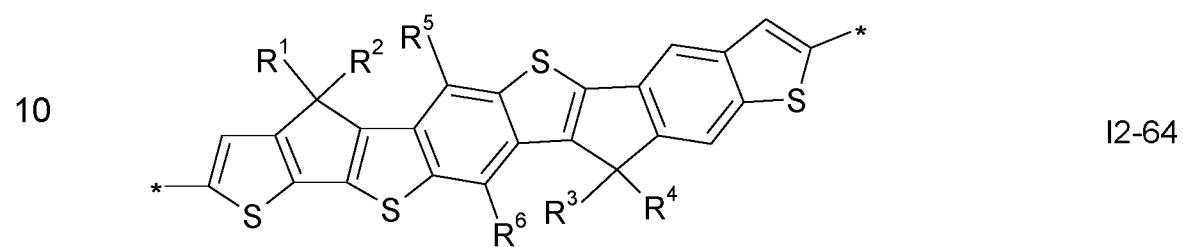
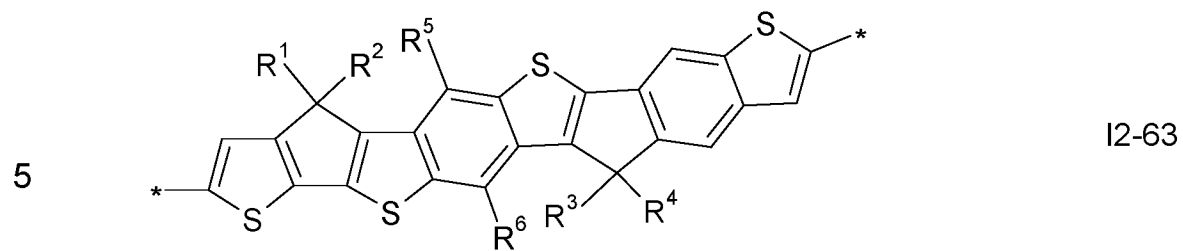
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I2-56

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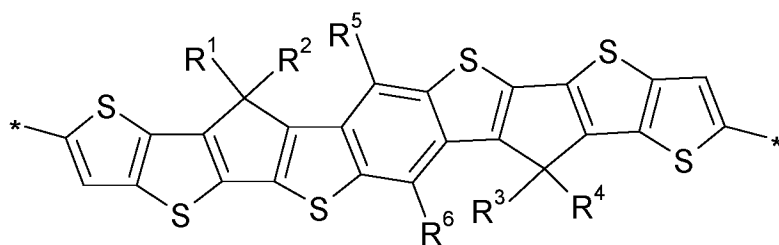




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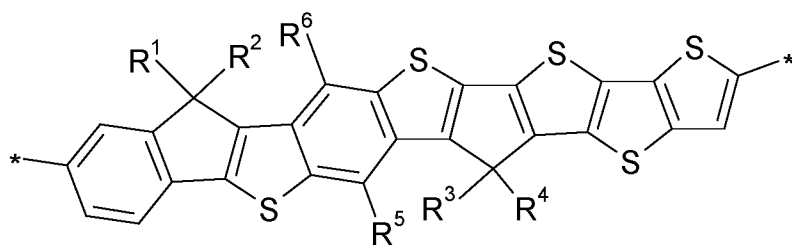
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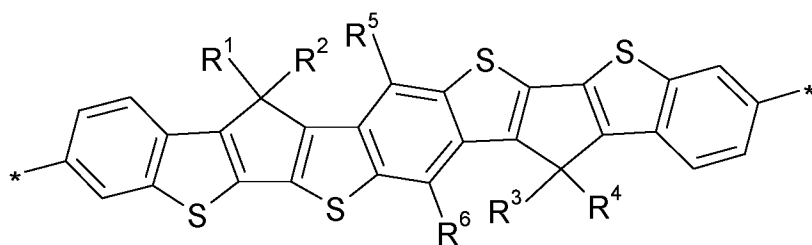
12-68

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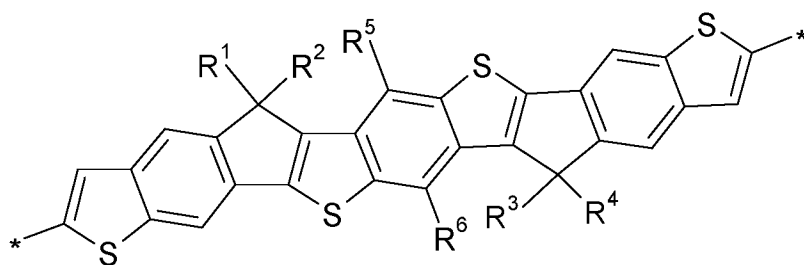
12-69

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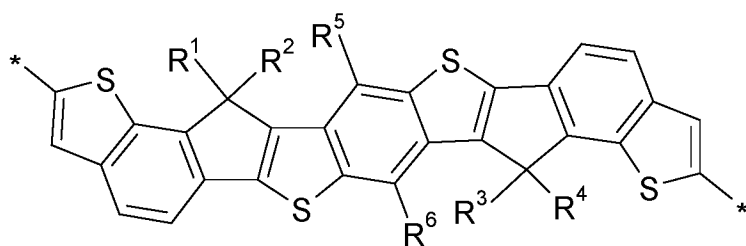
12-70

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12-71

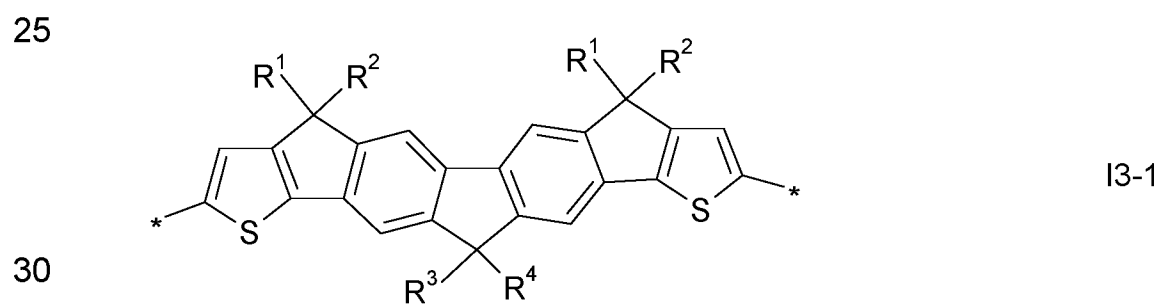
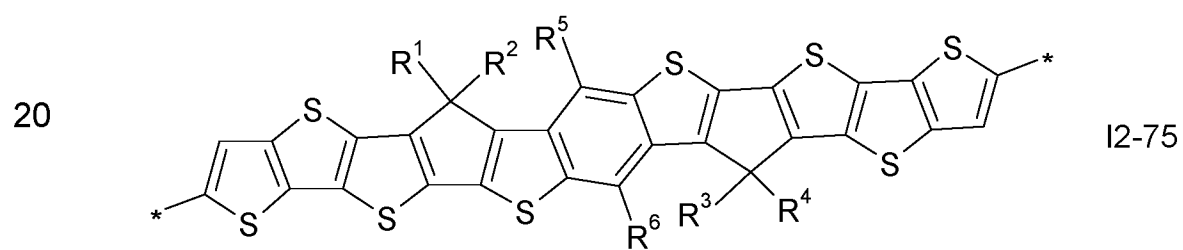
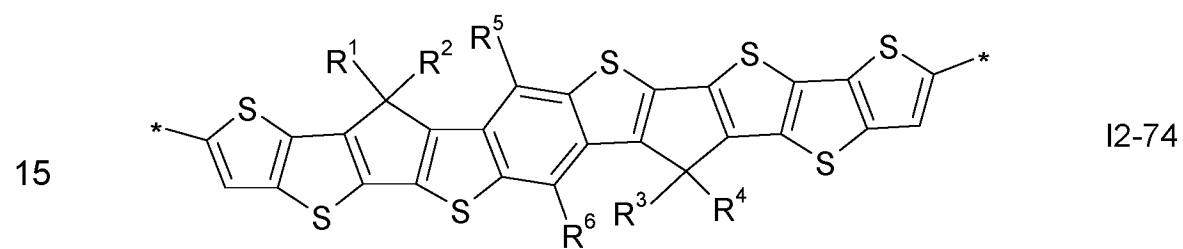
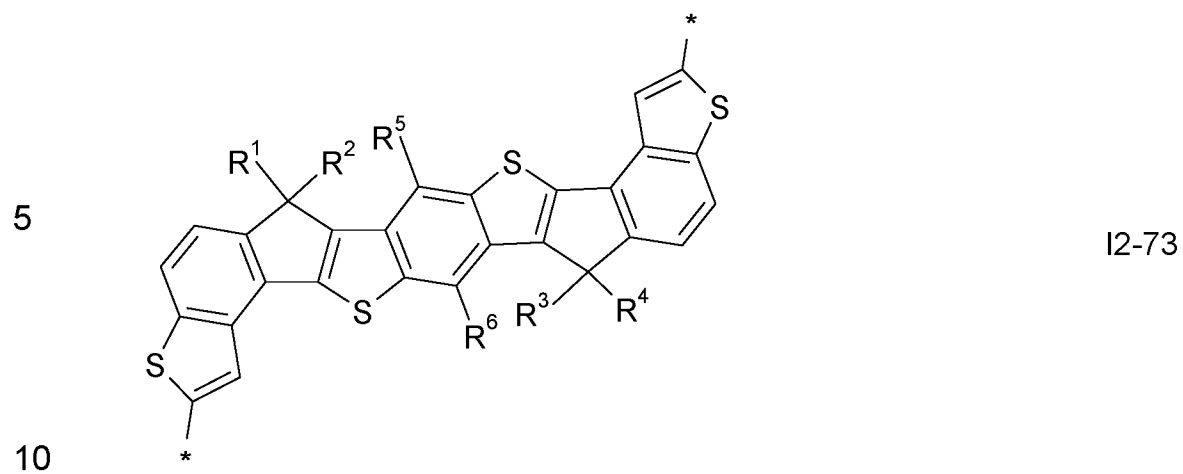
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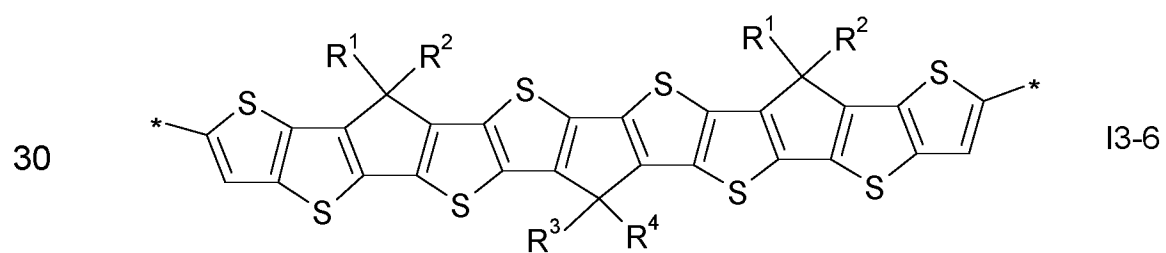
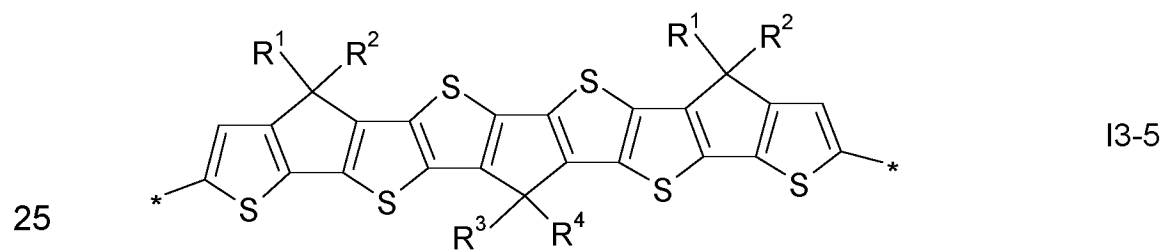
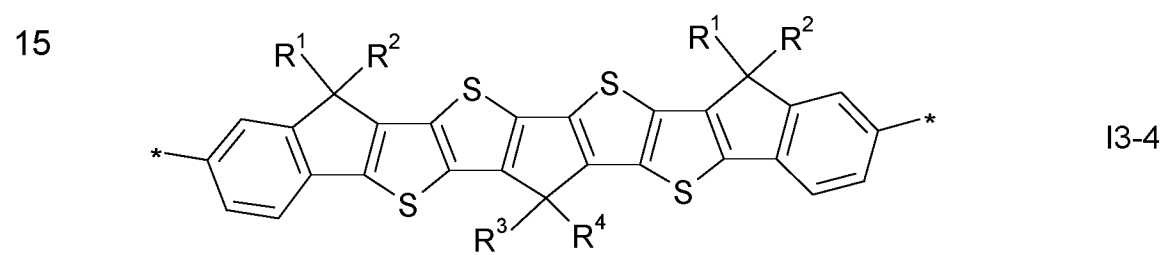
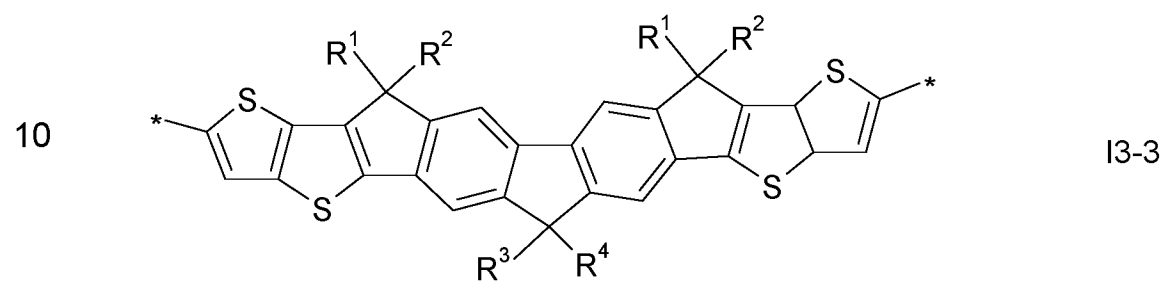
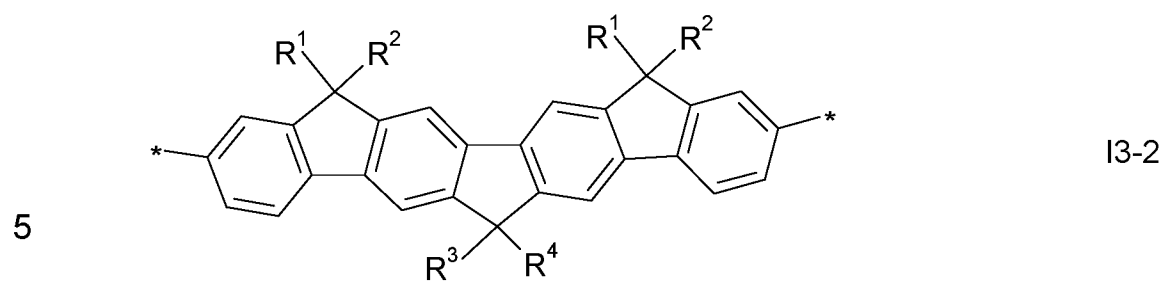
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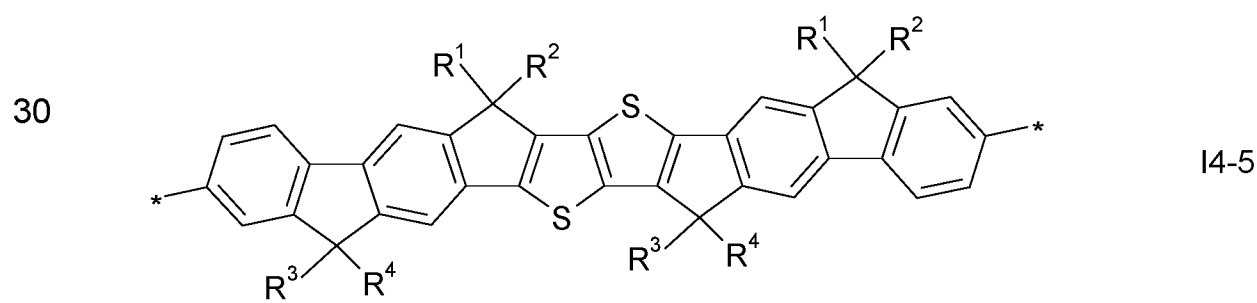
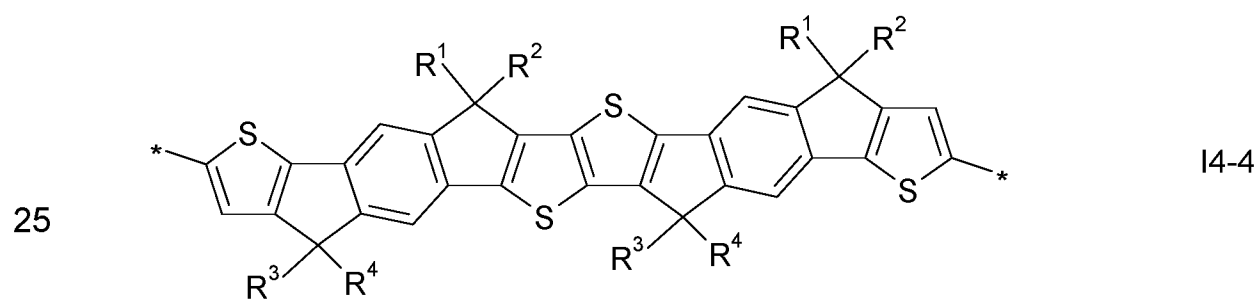
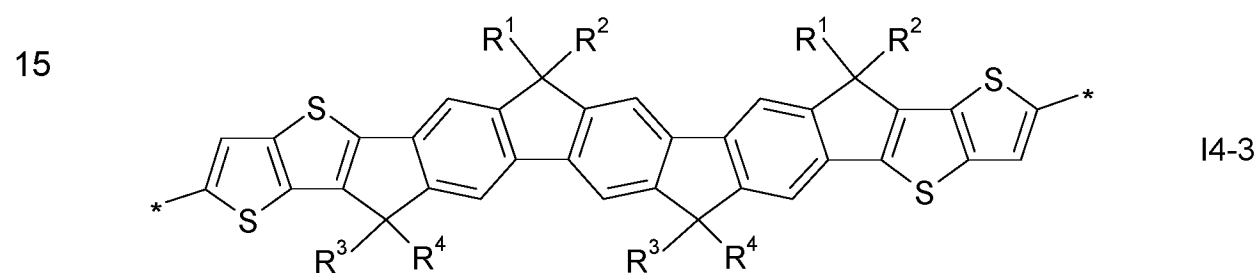
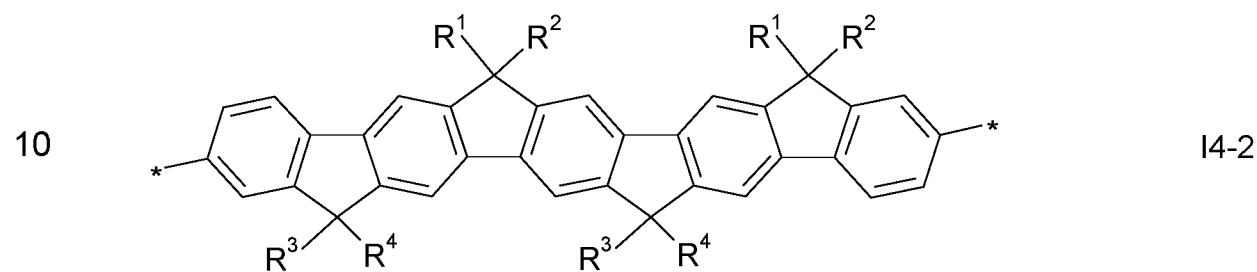
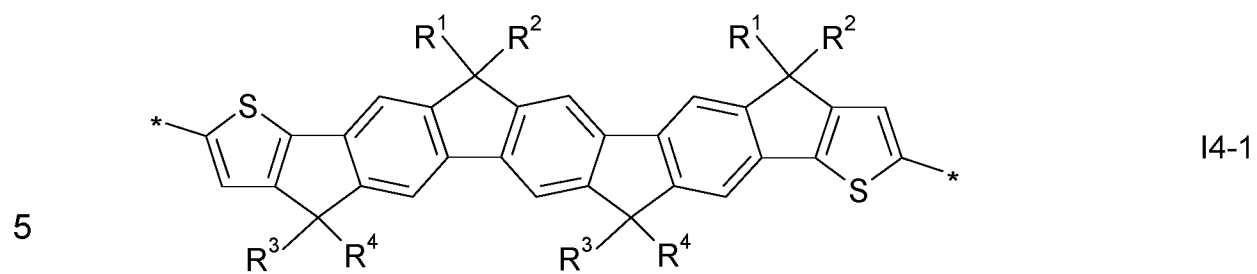


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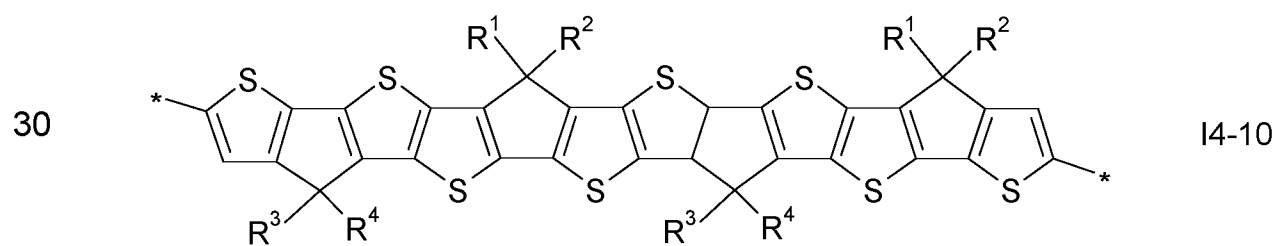
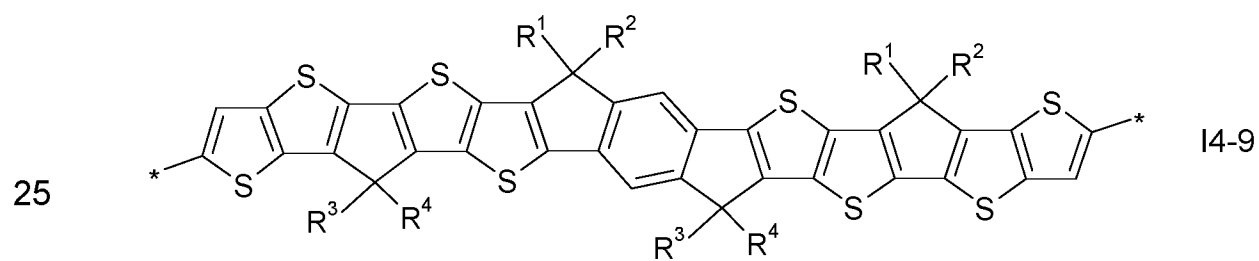
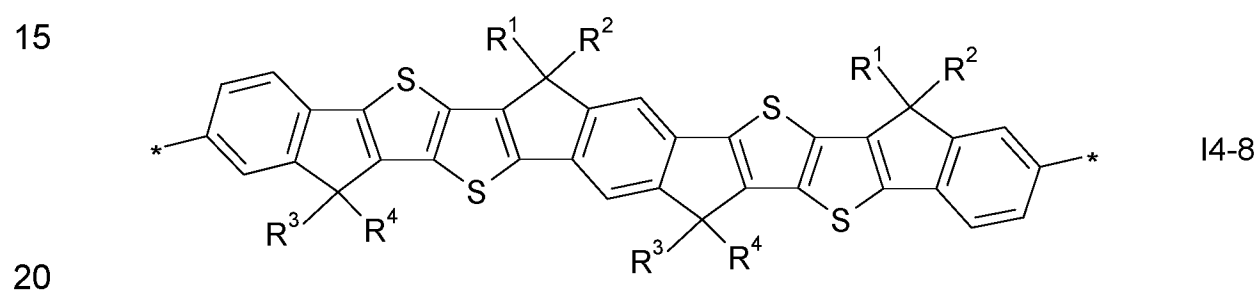
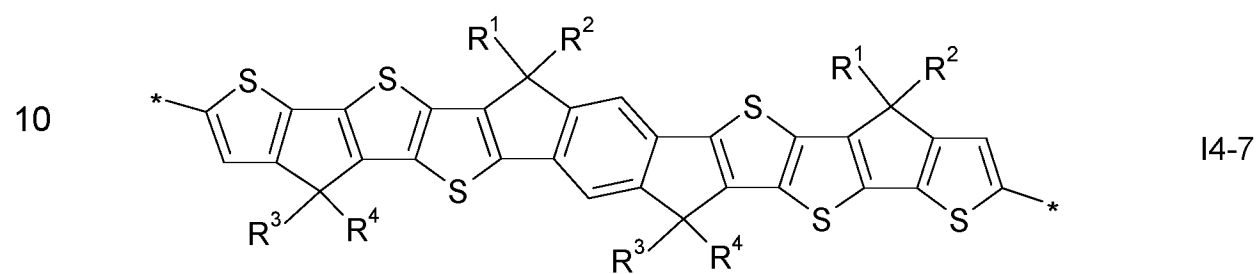
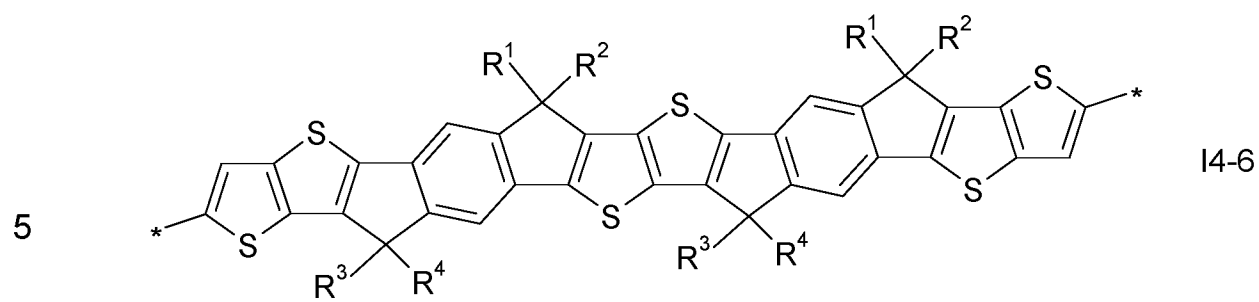


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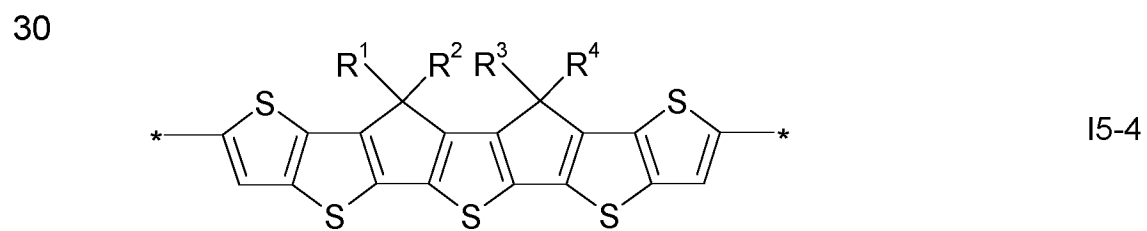
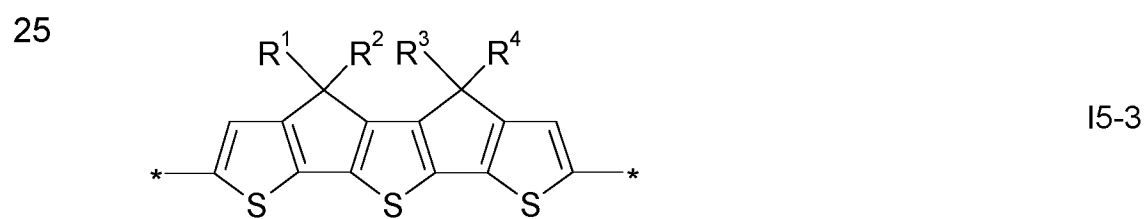
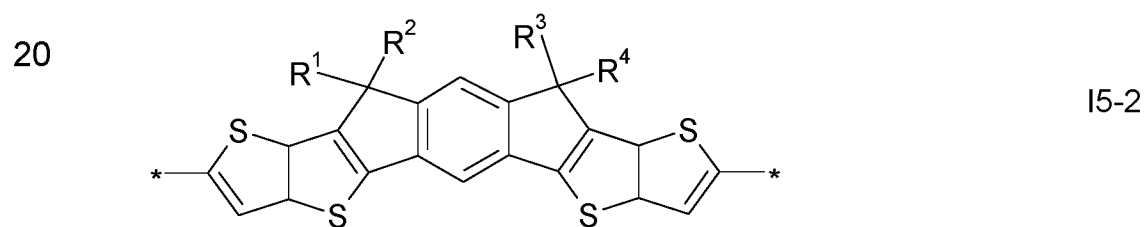
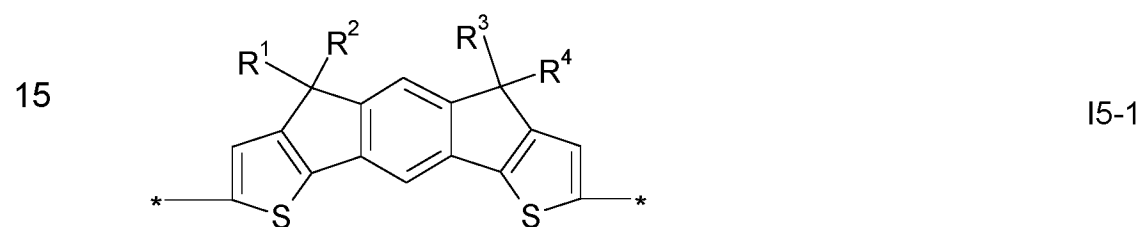
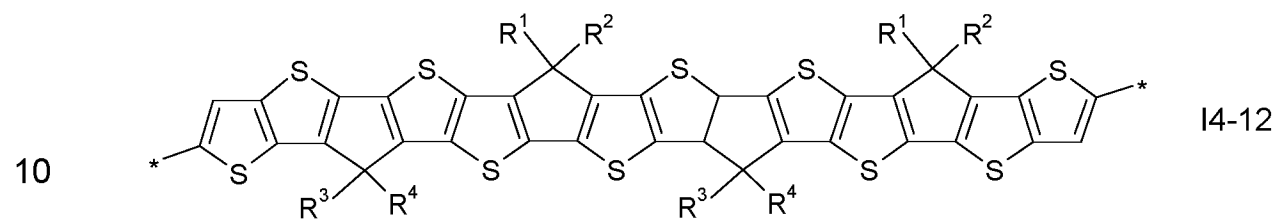
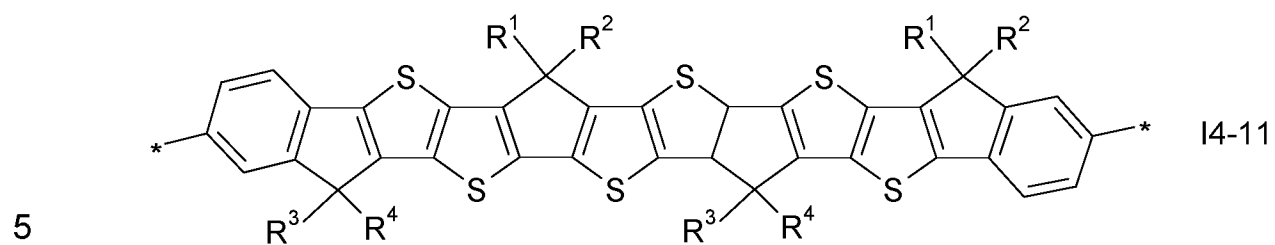


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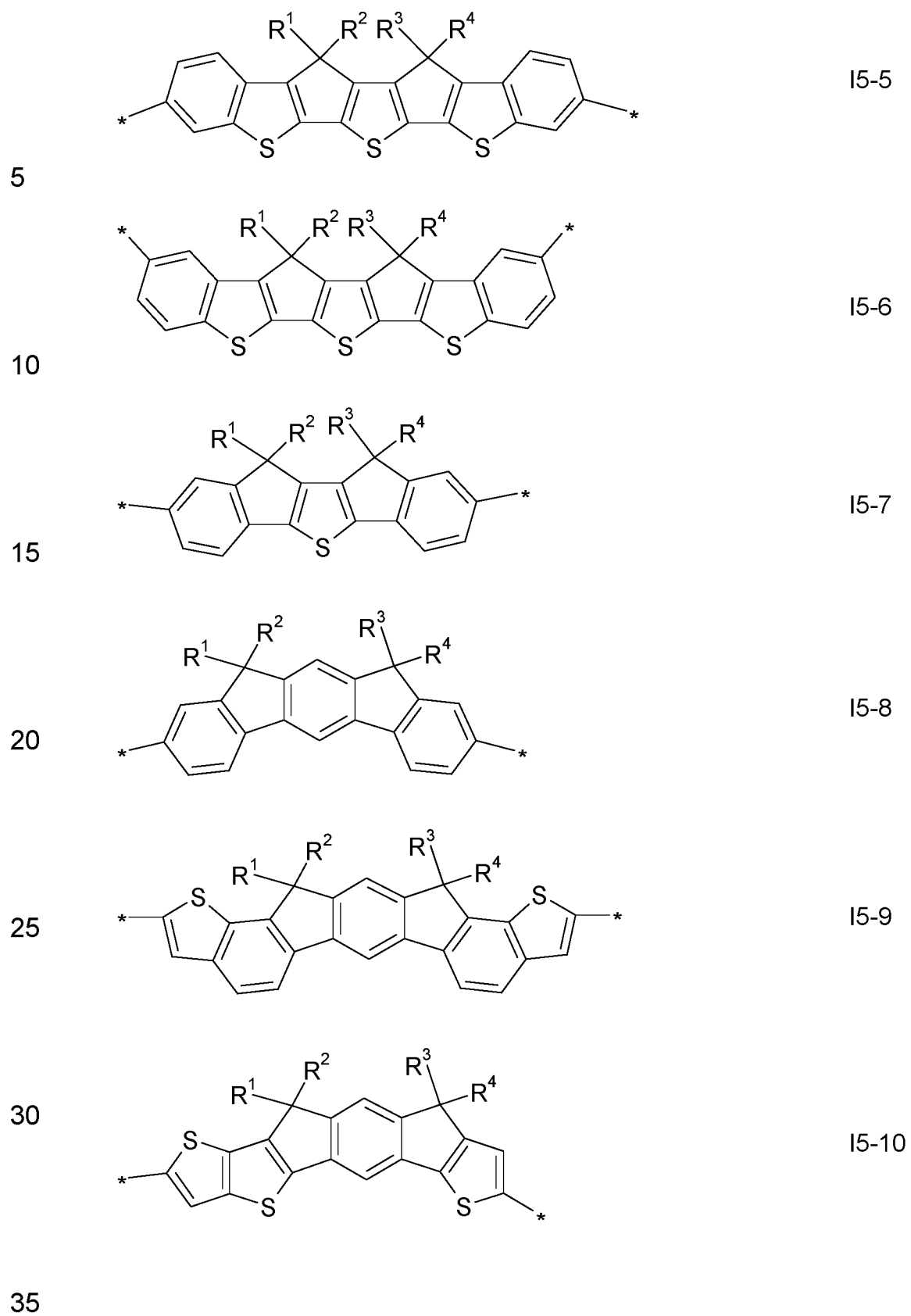


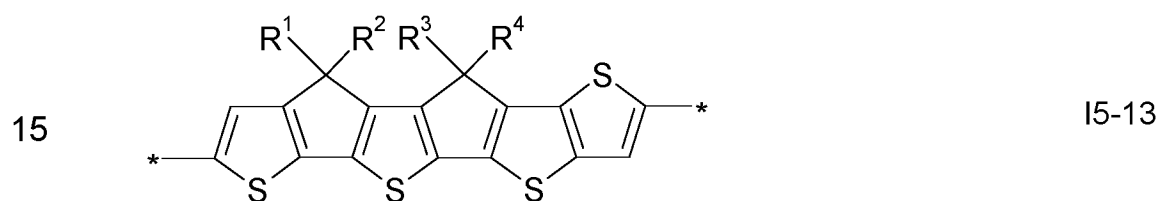
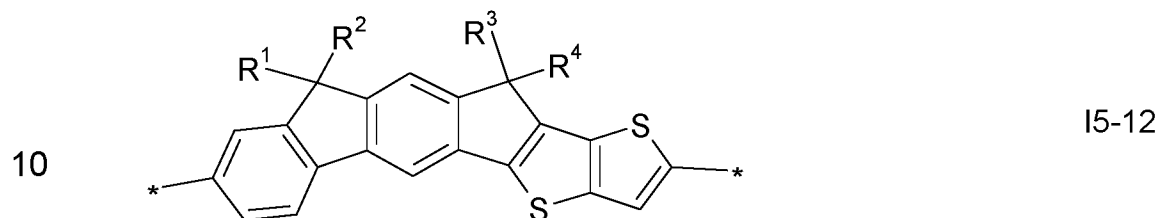
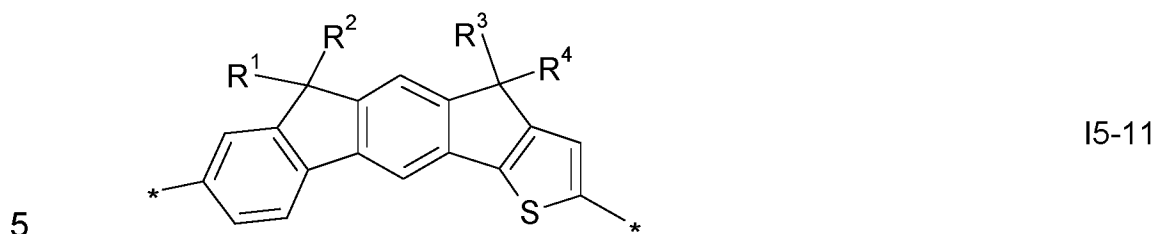
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20 wherein R^1 , R^2 , R^5 and R^6 have the meanings given above and below, R^3 and R^4 have one of the meanings given for R^1 and R^2 above and below, and the benzene and thiophene rings are optionally substituted in free positions by one or more groups R^5 , and wherein preferably in at least two groups R^1 and R^2 and/or at least two groups of R^3 and R^4 , which are attached to the same C atom, denote each $-Sp-R^C$, and very preferably all groups R^1 , R^2 , R^3 and R^4 denote $-Sp-R^C$.

25

In a preferred embodiment of the present invention, in the repeating units of formula I, I1-I7 and I1-1 to I5-13 R^1 and R^2 , when being different from $-Sp-R^C$, are selected from F, Cl, CN, or from straight-chain or branched alkyl, alkoxy, sulfanylalkyl, sulfonylalkyl, alkylcarbonyl, alkoxycarbonyl and alkylcarbonyloxy, each of which has 1 to 20 C atoms and is unsubstituted or substituted by one or more F atoms, most preferably from F, Cl or formulae SUB1-SUB6 above.

30

35 In another preferred embodiment of the present invention, in the repeating units of formula I, I1-I7 and I1-1 to I5-13 R^1 and R^2 , when being different from $-Sp-R^C$, are selected from mono- or polycyclic aryl or heteroaryl, each

of which is optionally substituted with one or more groups L as defined in formula I and has 5 to 20 ring atoms, and wherein two or more rings may be fused to each other or connected with each other by a covalent bond, very preferably phenyl that is optionally substituted, preferably in 4-position, 2,4-positions, 2,4,6-positions or 3,5-positions, or thiophene that is optionally substituted, preferably in 5-position, 4,5-positions or 3,5-positions, with alkyl, alkoxy or thioalkyl having 1 to 16 C atoms, most preferably from formulae SUB7-SUB18 above.

10 In a preferred embodiment of the present invention, in the repeating units of formula I, I1-I7 and I1-1 to I5-13 at least one substituent R^{5-9} denotes - $Sp-R^C$.

15 In another preferred embodiment of the present invention, in the repeating units of formula I, I1-I7 and I1-1 to I5-13 R^{5-9} are H.

In another preferred embodiment of the present invention, in the repeating units of formula I, I1-I7 and I1-1 to I5-13 at least one of R^{5-9} is different from H.

20 In a preferred embodiment of the present invention, in the repeating units of formula I, I1-I7 and I1-1 to I5-13 R^{5-9} , when being different from H, are each independently selected from F, Cl, CN, or from straight-chain or branched alkyl, alkoxy, sulfanylalkyl, sulfonylalkyl, alkylcarbonyl, 25 alkoxy carbonyl and alkylcarbonyloxy, each of which has 1 to 20 C atoms and is unsubstituted or substituted by one or more F atoms, most preferably from F, Cl or formulae SUB1-SUB6 above.

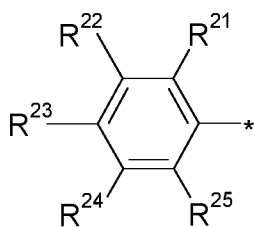
30 In another preferred embodiment of the present invention, in the repeating units of formula I, I1-I7 and I1-1 to I5-13 R^{5-9} , when being different from H, are each independently selected are selected from mono- or polycyclic aryl or heteroaryl, each of which is optionally substituted with one or more groups L as defined in formula I and has 5 to 20 ring atoms, and wherein two or more rings may be fused to each other or connected with each 35 other by a covalent bond, very preferably phenyl that is optionally substituted, preferably in 4-position, 2,4-positions, 2,4,6-positions or 3,5-

positions, or thiophene that is optionally substituted, preferably in 5-position, 4,5-positions or 3,5-positions, with alkyl, alkoxy or thioalkyl having 1 to 16 C atoms, more preferably from formulae SUB7-SUB18 above, most preferably from formulae SUB14-SUB18 above.

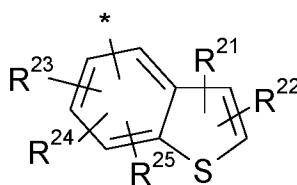
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Preferred aryl and heteroaryl groups R^{1-9} , when being different from H, are each independently selected from the following formulae

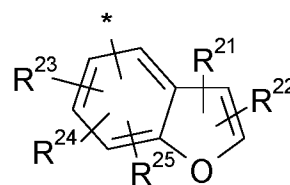
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S1

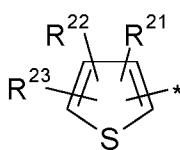


S2

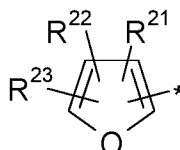


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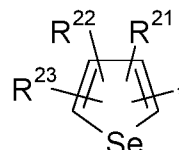
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S4

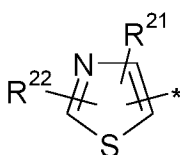


S5

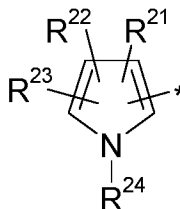


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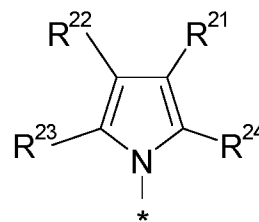
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S7

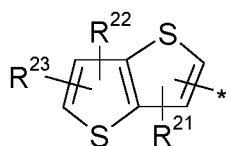


S8

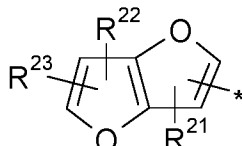


S9

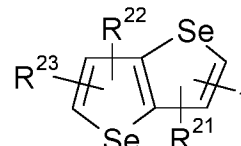
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S10



S11

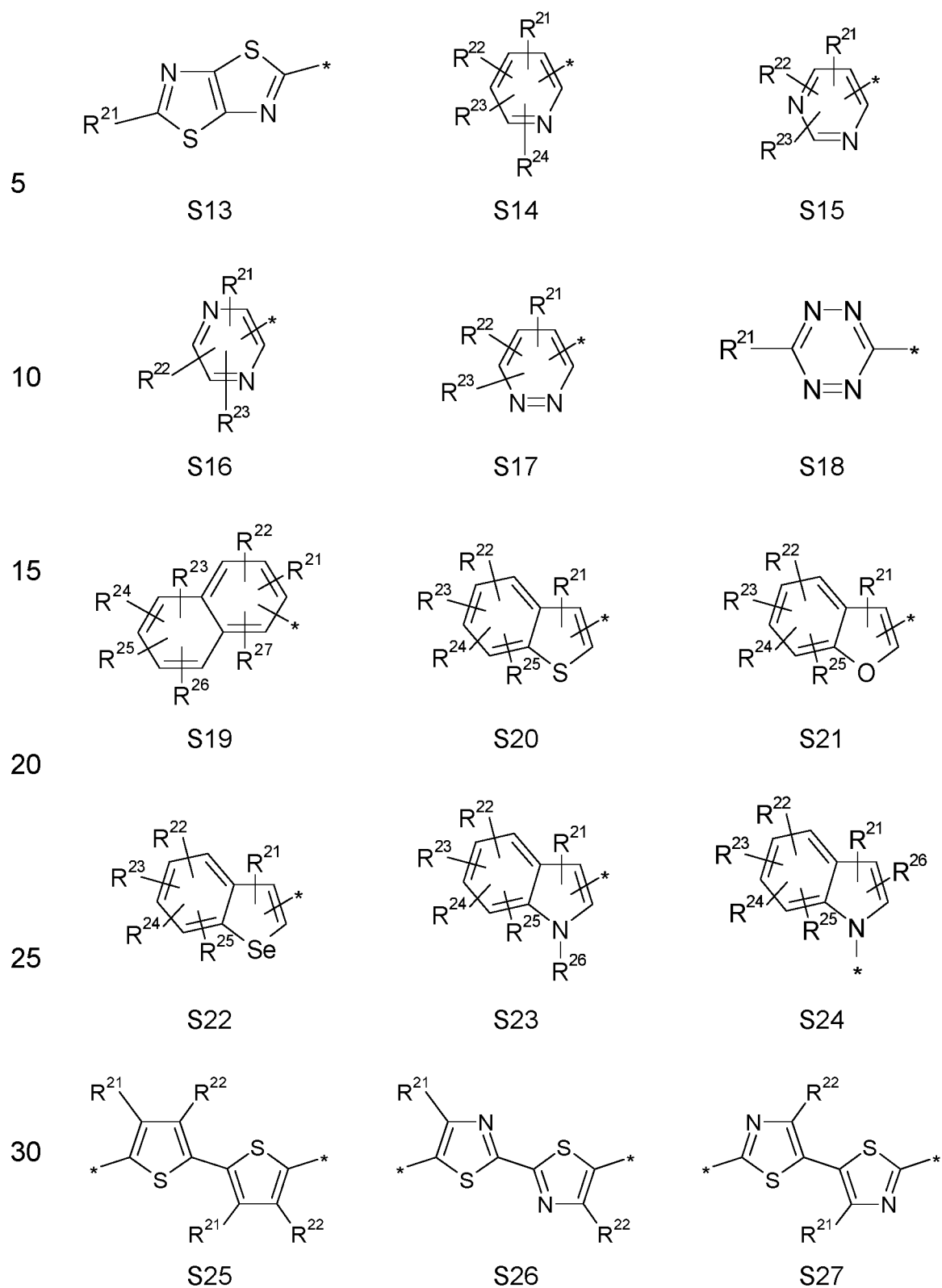


S12

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- 74 -



35 wherein R²¹⁻²⁷, independently of each other, and on each occurrence identically or differently, denote H, F, Cl, CN, or straight-chain, branched or

5 cyclic alkyl with 1 to 30, preferably 1 to 20, C atoms, in which one or more CH₂ groups are each optionally replaced by -O-, -S-, -C(=O)-, -C(=S)-, -C(=O)-O-, -O-C(=O)-, -NR⁰-, -SiR⁰R⁰⁰-, -CF₂-, -CR⁰=CR⁰⁰-, -CY¹=CY²- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, and in which one or more H atoms are each optionally replaced by F, Cl, Br, I or CN, and in which one or more CH₂ or CH₃ groups are each optionally replaced by a cationic or anionic group.

10 Very preferred aryl and heteroaryl groups R¹⁻⁹, when being different from H, are each independently selected from formulae S1, S4, S5, S7 and S10.

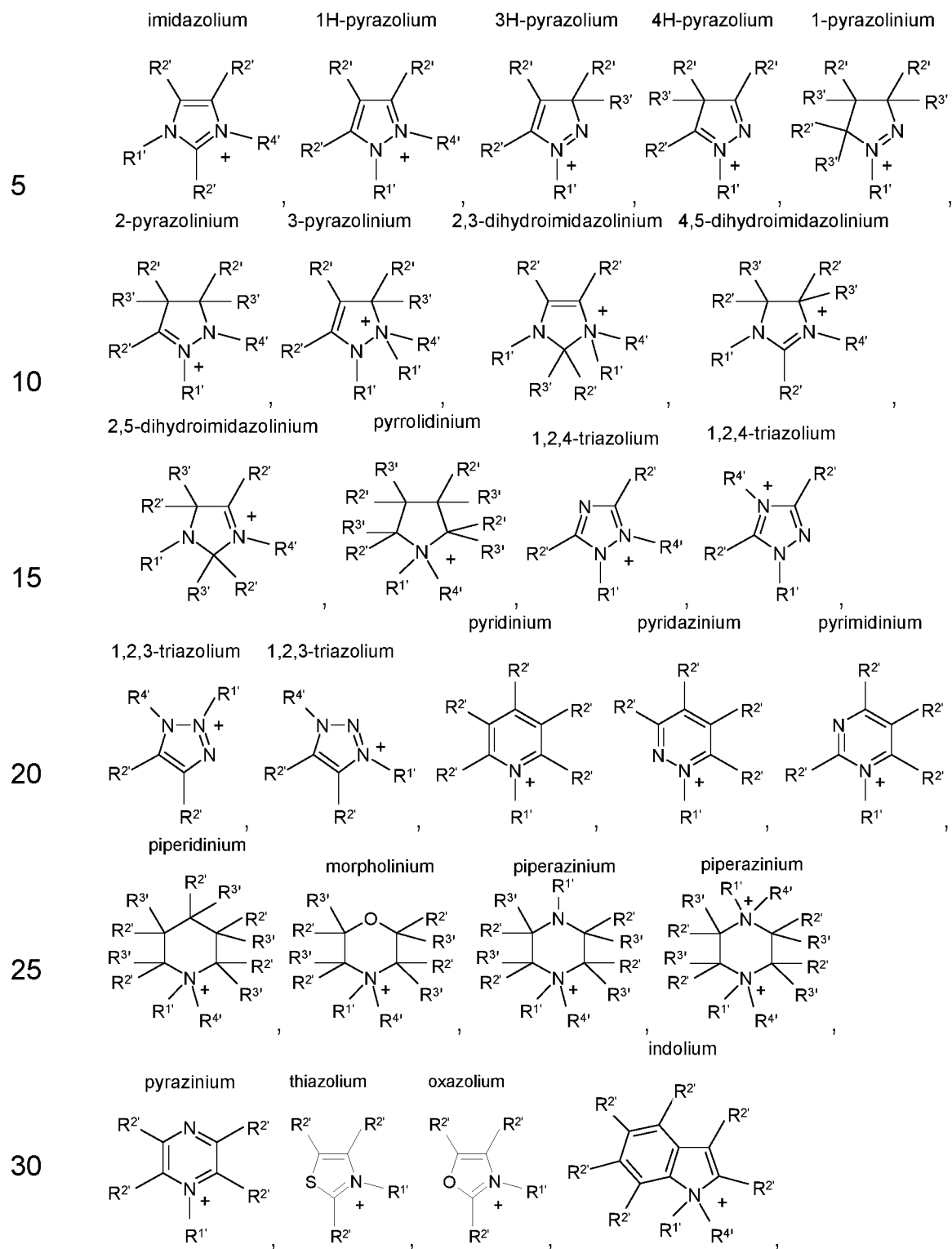
15 Most preferred aryl and heteroaryl groups R¹⁻⁹ are each independently selected from formulae SUB7-SUB16 as defined above.

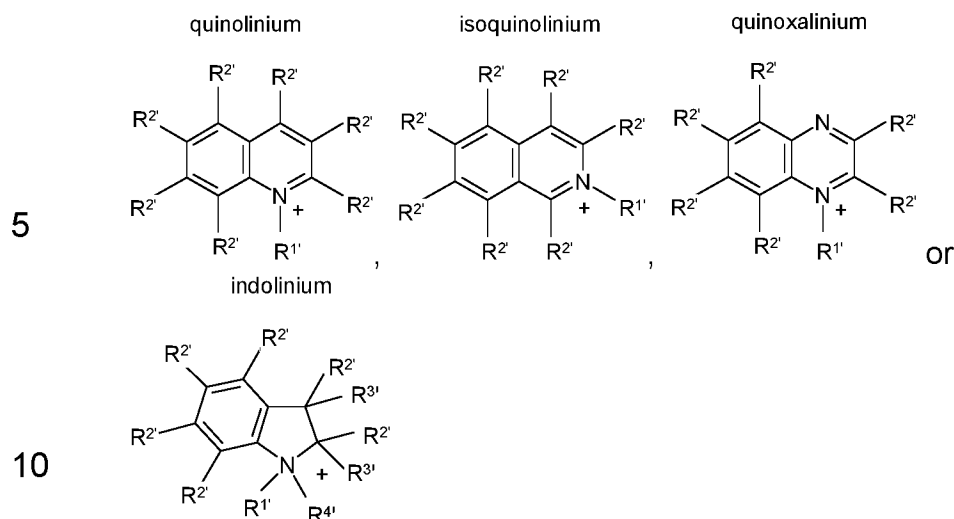
20 In another preferred embodiment one or more of R¹⁻⁹ denote a straight-chain, branched or cyclic alkyl group with 1 to 50, preferably 2 to 50, very preferably 2 to 30, more preferably 2 to 24, most preferably 2 to 16 C atoms, in which one or more CH₂ or CH₃ groups are replaced by a cationic or anionic group.

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

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

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





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

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

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

Further preferred repeating units of formula I, I1-I7 and I1-1 to I5-13 are selected from the following preferred embodiments or any combination thereof:

- at least two groups R^1 and R^2 in the same unit that are attached to the same C, Si or Ge atom denote each $-Sp-R^C$,
- all groups R^1 and R^2 in the same unit that are attached to the same C, Si or Ge atom denote each $-Sp-R^C$,

- at least one group R^1 in the same unit that is attached to an N atom denotes $-Sp-R^C$,
- all groups R^1 in the same unit that are attached to an N atom denotes $-Sp-R^C$,
- 5 - k is 0, 1, 2 or 3, preferably 0, 1 or 2, very preferably 1,
- U^1 and U^2 denote independently of each other CR^1R^2 ,
- W^1 , W^2 and W^3 are S or Se, preferably S,
- 10 - W^4 is S or NR^0 , preferably S,
- V^1 is CR^5 ,
- V^1 is N,
- Ar^1 and Ar^2 are selected from formulae A1a and A2a,
- 15 - Ar^3 is selected from formulae A3b, A3d, A3f and A3t, very preferably from formulae A3b and A3d,
- Ar^3 is selected from formulae A3b1, A3d1, A3f1 and A3t1, very preferably from formulae A3b1 and A3d1,
- 20 - in Ar^3 all substituents R^{5-8} are H,
- in Ar^3 at least one, preferably one or two of R^{5-8} are different from H,
- Ar^3 is selected from formula A3d1 wherein R^3 and R^4 denote F,
- Ar^3 is selected from formulae A3e1 and A3f1 wherein R^5 and R^6 are different from H,
- 25 - Ar^4 is selected from formulae A4a, A4b, A4c, A4d, A4f, A4g, A4h, A4i, A4k, A4l, A4m, A4n, A4o, A4p, A4q, A4u and A4v, very preferably from formula A4a, A4b, A4c, A4d, A4l, A4m, A4n, A4o, A4p, A4q, A4u and A4v,
- 30 - Ar^4 is selected from formulae A4a1, A4b1, A4c1, A4d1, A4f1, A4g1, A4h1, A4i1, A4k1, A4l1, A4m1, A4n1, A4o1, A4p1, A4q1, A4u and A4v1, very preferably from formula A4a1, A4b1, A4c1, A4d1, A4l1, A4m1, A4n1, A4o1, A4p1, A4q1, A4u1 and A4v1,
- 35 - Ar^5 is selected from formulae A5a, A5b, A5c, A5d, A5f, A5g, A5h, A5i, A5k, A5l, A5m, A5n, A5o, A5p, A5q, A5u and A5v, very preferably from

formula A5a, A5b, A5c, A5d, A5l, A5m, A5n, A5o, A5p, A5q, A5u and A5v,

- 5 - Ar⁵ is selected from formulae A5a1, A5b1, A5c1, A5d1, A5f1, A5g1, A5h1, A5i1, A5k1, A5l1, A5m1, A5n1, A5o1, A5p1, A5q1, A5u and A5v1, very preferably from formula A5a1, A5b1, A5c1, A5d1, A5l1, A5m1, A5n1, A5o1, A5p1, A5q1, A5u1 and A5v1,
- in one or both of Ar⁴ and Ar⁵ all substituents R⁵⁻⁹ are H,
- 10 - in one or both of Ar⁴ and Ar⁵ at least one, preferably one or two of R⁵⁻⁹ are different from H,
- R¹ and R² are different from H,
- R¹ and R², when being different from H and -Sp-R^C, are each independently selected from F, Cl or straight-chain or branched alkyl, alkoxy, sulfanylalkyl, sulfonylalkyl, alkylcarbonyl, alkoxy carbonyl and alkylcarbonyloxy, each having 1 to 20 C atoms and being unsubstituted or substituted by one or more F atoms, or alkyl or alkoxy having 1 to 12 C atoms that is optionally fluorinated, more preferably from formulae SUB1-SUB6 above,
- 15 - R¹ and R², when being different from H and -Sp-R^C, are each independently selected from F, Cl or straight-chain or branched alkyl, alkoxy, sulfanylalkyl, sulfonylalkyl, alkylcarbonyl, alkoxy carbonyl and alkylcarbonyloxy, each having 1 to 20 C atoms and being unsubstituted or substituted by one or more F atoms, or alkyl or alkoxy having 1 to 12 C atoms that is optionally fluorinated, more preferably from formulae SUB1-SUB6 above,
- 20 - R¹ and R², when being different from H and -Sp-R^C, are each independently selected from phenyl that is substituted, preferably in 4-position, or in 2,4-positions, or in 2,4,6-positions or in 3,5-positions, with alkyl or alkoxy having 1 to 20 C atoms, preferably 1 to 16 C atoms, very preferably 4-alkylphenyl wherein alkyl is C1-16 alkyl, most
- 25 preferably 4-methylphenyl, 4-hexylphenyl, 4-octylphenyl or 4-dodecylphenyl, or 4-alkoxyphenyl wherein alkoxy is C1-16 alkoxy, most preferably 4-hexyloxyphenyl, 4-octyloxyphenyl or 4-dodecyloxyphenyl or 2,4-dialkylphenyl wherein alkyl is C1-16 alkyl, most preferably 2,4-dihexylphenyl or 2,4-dioctylphenyl or 2,4-dialkoxyphenyl wherein alkoxy
- 30 is C1-16 alkoxy, most preferably 2,4-dihexyloxyphenyl or 2,4-dioctyloxyphenyl or 3,5-dialkylphenyl wherein alkyl is C1-16 alkyl, most preferably 3,5-dihexylphenyl or 3,5-dioctylphenyl or 3,5-dialkoxyphenyl wherein alkoxy is C1-16 alkoxy, most preferably 3,5-dihexyloxyphenyl or 3,5-dioctyloxyphenyl, or 2,4,6-trialkylphenyl wherein alkyl is C1-16
- 35 alkyl, most preferably 2,4,6-trihexylphenyl or 2,4,6-trioctylphenyl or 2,4,6-trialkoxyphenyl wherein alkoxy is C1-16 alkoxy, most preferably

- 2,4,6-trihexyloxyphenyl or 2,4,6-trioctyloxyphenyl or 4-thioalkylphenyl wherein thioalkyl is C1-16 thioalkyl, most preferably 4-thiohexylphenyl, 4-thiooctylphenyl or 4-thiododecylphenyl, or 2,4-dithioalkylphenyl wherein thioalkyl is C1-16 thioalkyl, most preferably 2,4-
- 5 dithiohexylphenyl or 2,4-dithiooctylphenyl, or 3,5-dithioalkylphenyl wherein thioalkyl is C1-16 thioalkyl, most preferably 3,5-dithiohexylphenyl or 3,5-dithiooctylphenyl, or 2,4,6-trithioalkylphenyl wherein thioalkyl is C1-16 thioalkyl, most preferably 2,4,6-
- 10 trithiohexylphenyl or 2,4,6-trithiooctylphenyl, or from thiophene that is optionally substituted, preferably in 5-position, 4,5-positions or 3,5-positions, with alkyl, alkoxy or thioalkyl having 1 to 16 C atoms, most preferably from formulae SUB7-SUB18 above,
- R^{5-9} are H,
 - 15 - at least one of R^{5-9} denotes $-Sp-R^C$,
 - at least one of R^{5-9} is different from H,
 - R^{5-9} , when being different from H and $-Sp-R^C$, are each independently selected from F, Cl, CN or straight-chain or branched alkyl, alkoxy, sulfanylalkyl, sulfonylalkyl, alkylcarbonyl, alkoxycarbonyl and
 - 20 alkylcarbonyloxy, each having up to 20 C atoms and being unsubstituted or substituted by one or more F atoms, preferably from F, or alkyl or alkoxy having up to 16 C atoms that is optionally fluorinated, more preferably from formulae SUB1-SUB6 above,
 - 25 - R^{5-9} , when being different from H and $-Sp-R^C$, are each independently selected from aryl or heteroaryl, preferably phenyl or thiophene, each of which is optionally substituted with one or more groups L as defined in formula IA and has 4 to 30 ring atoms, preferably from phenyl that is optionally substituted, preferably in 4-position, 2,4-positions, 2,4,6-
 - 30 positions or 3,5-positions, with alkyl or alkoxy having 1 to 20 C atoms, preferably 1 to 16 C atoms, more preferably from formulae SUB7-SUB18 above,
 - Ar^6 is selected from thiophene, thiazole, thieno[3,2-b]thiophene, thiazolo[5,4-d]thiazole, benzene, 2,1,3-benzothiadiazole, 1,2,3-
 - 35 benzothiadiazole, thieno[3,4-b]thiophene, benzotriazole and

thiadiazole[3,4-c]pyridine, which are optionally substituted by L or R¹ or -Sp-R^C,

- Ar⁶ is substituted by one or two groups -Sp-R^C,
- 5 - L denotes F, Cl, CN, NO₂, or alkyl or alkoxy with 1 to 16 C atoms that is optionally fluorinated.

Another embodiment of the invention relates to a polymer comprising one or more repeating units of formula I, I1-I7 or I1-1 to I5-13 and optionally
10 one or more units Ar⁶, wherein at least one of the units of formula and the units Ar⁶ is at least monosubstituted by -Sp-R^C.

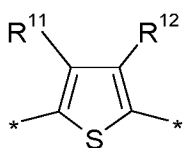
Preferred polymers are selected from the following preferred embodiments or any combination thereof:

- 15 - in at least one unit of formula I, I1-I7 or I1-1 to I5-13, preferably in all of these units, at least two groups R¹ and R² that are attached to the same C, Si or Ge atom denote each -Sp-R^C,
- in at least one unit of formula I, I1-I7 or I1-1 to I5-13, preferably in all of these units, all groups R¹ and R² in the unit that are attached to the
20 same C, Si or Ge atom denote each -Sp-R^C,
- in at least one unit of formula I, I1-I7 or I1-1 to I5-13, preferably in all of these units, at least one group R¹ in the unit that is attached to an N atom denotes -Sp-R^C,
- 25 - in at least one unit of formula I, I1-I7 or I1-1 to I5-13, preferably in all of these units, all groups R¹ in the unit that are attached to an N atom denotes -Sp-R^C,
- at least one unit Ar⁶ is at least monosubstituted, preferably mono- or disubstituted, by -Sp-R^C,
- 30 - all units Ar⁶ are at least monosubstituted, preferably mono- or disubstituted, by -Sp-R^C,
- the units Ar⁶ are not substituted by -Sp-R^C.

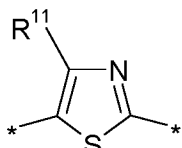
35

In a preferred embodiment the polymer comprises one or more units Ar⁶, which preferably have electron donor properties, and are selected from the group consisting of the formulae D1-D151 and their mirror images

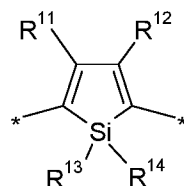
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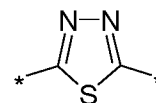
(D1)



(D2)

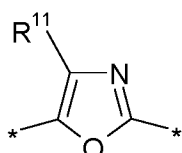


(D3)

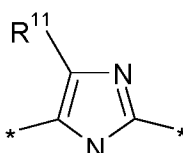


(D4)

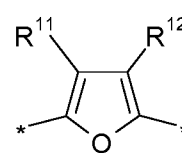
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(D5)

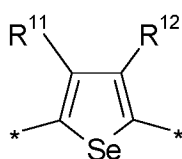


(D6)

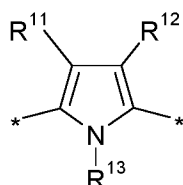


(D7)

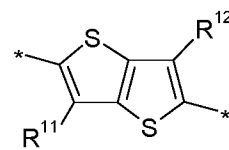
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(D8)

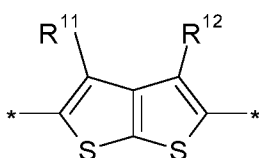


(D9)

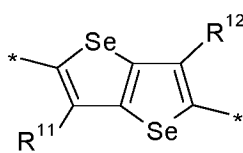


(D10)

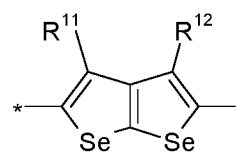
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(D11)

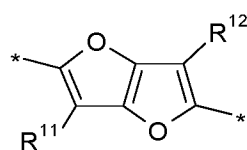


(D12)

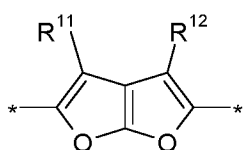


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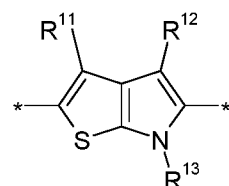
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(D14)



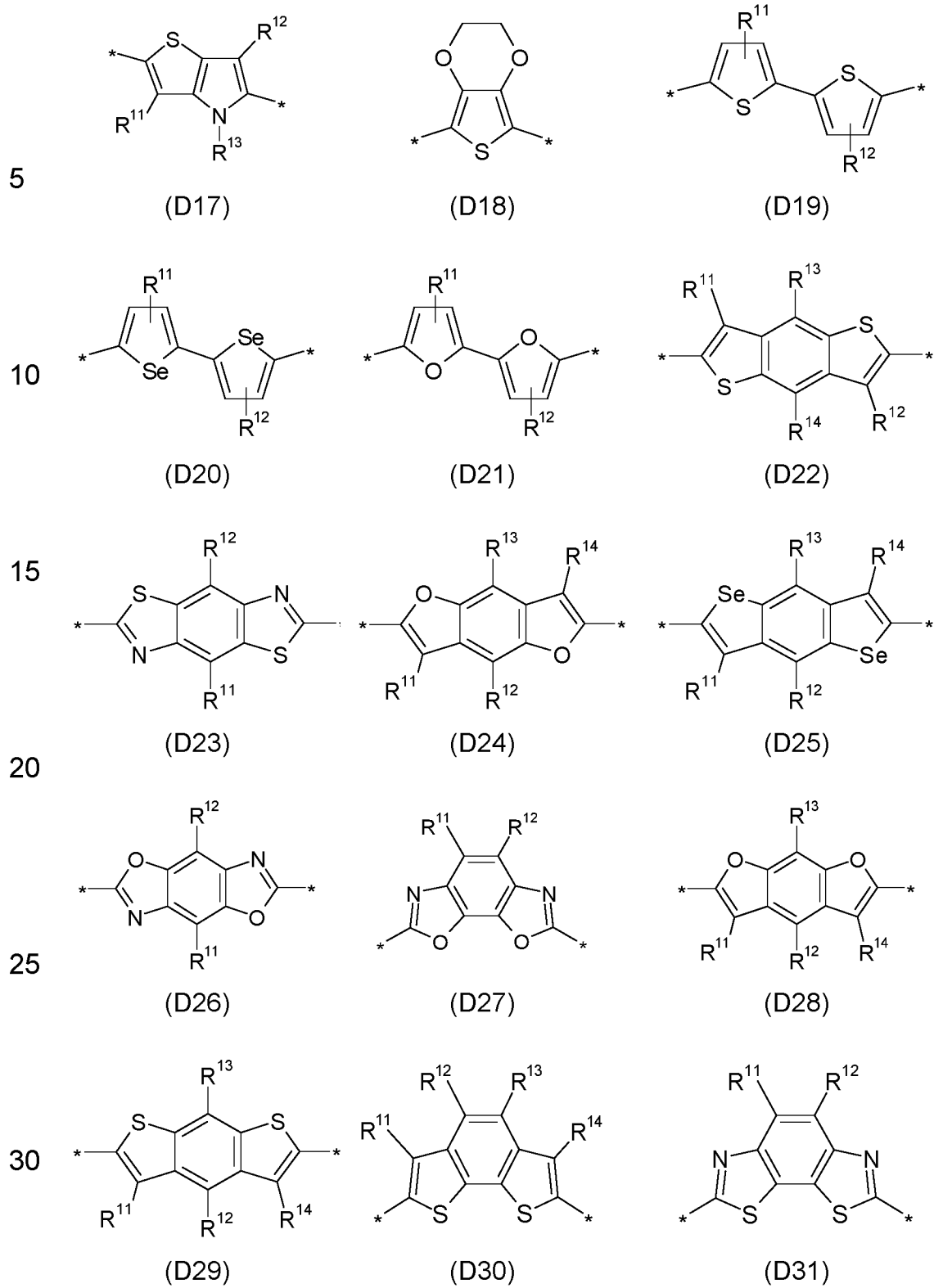
(D15)

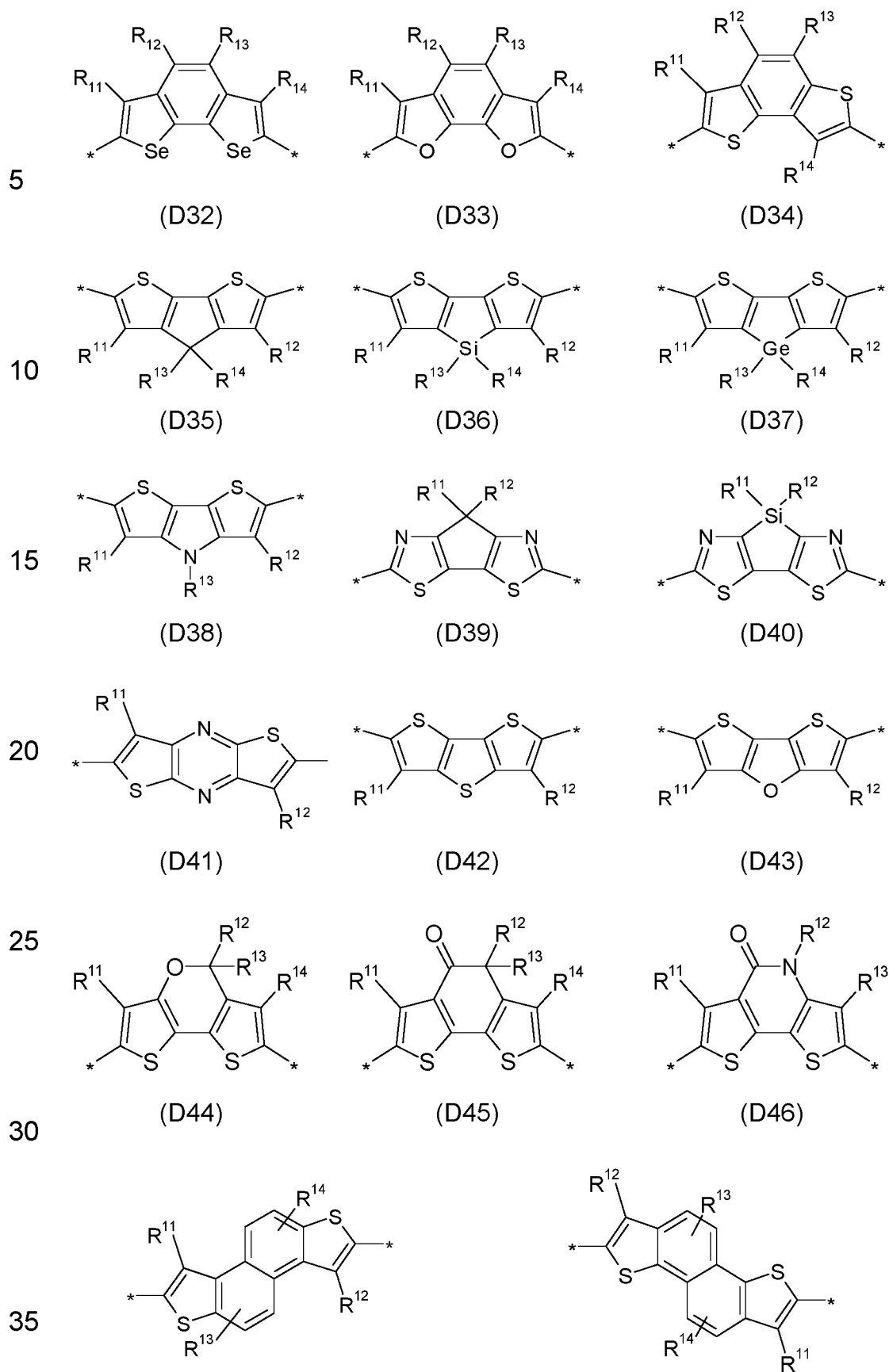


(D16)

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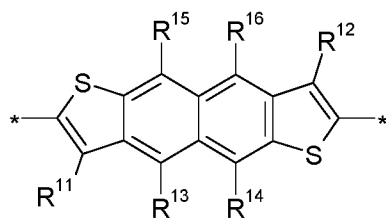
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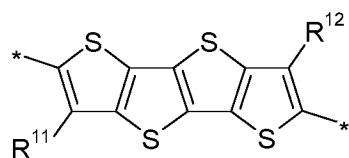
(D47)

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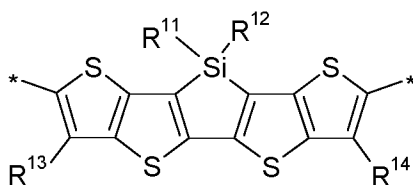
(D49)

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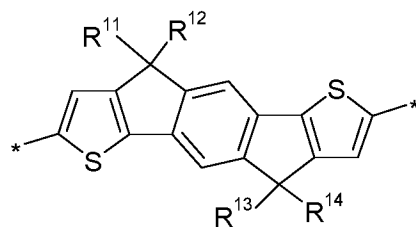
(D51)

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(D53)

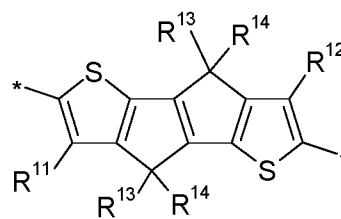
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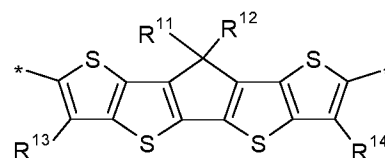
(D55)

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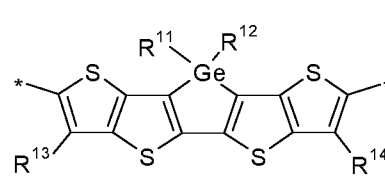
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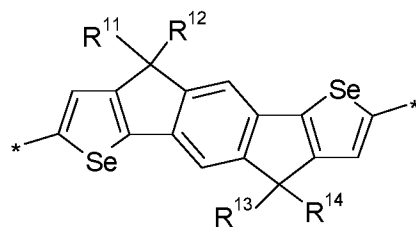
(D50)



(D52)

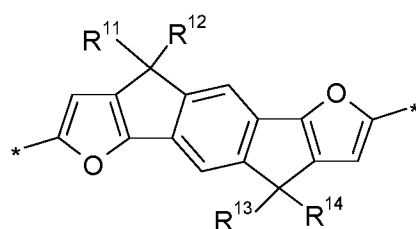


(D54)



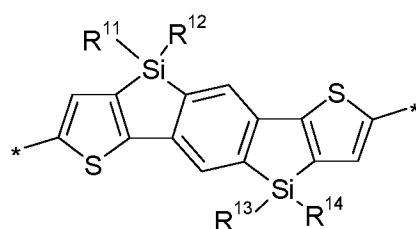
(D56)

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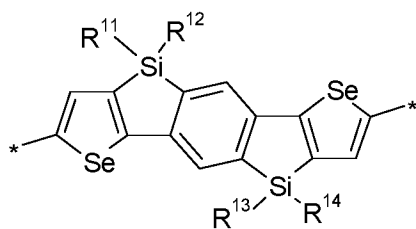
(D57)

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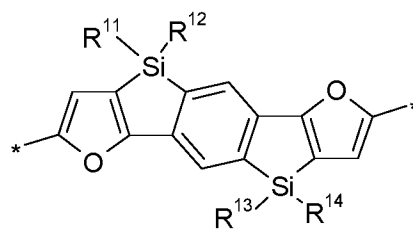


(D58)

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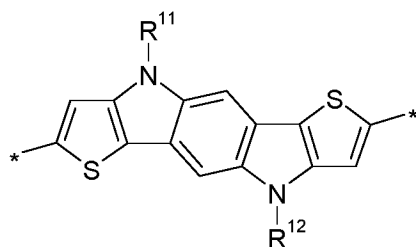


(D59)

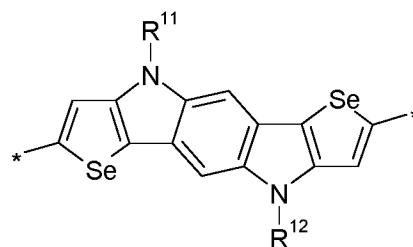


(D60)

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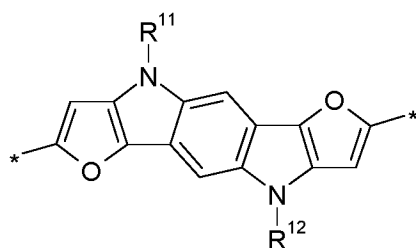


(D61)

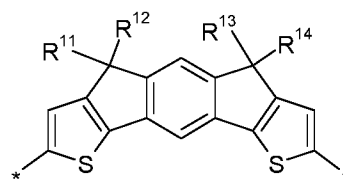


(D62)

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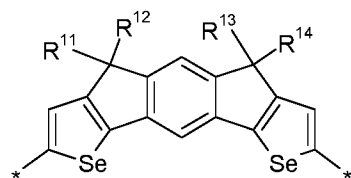


(D63)

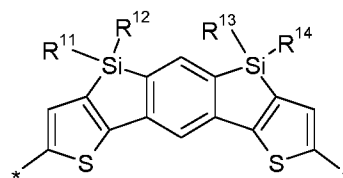


(D64)

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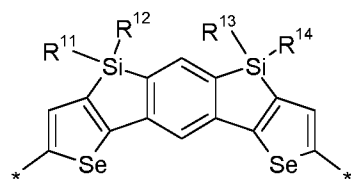


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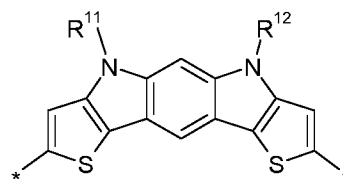


(D66)

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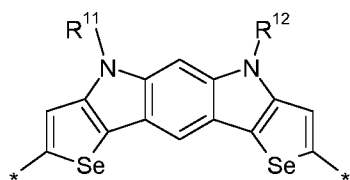
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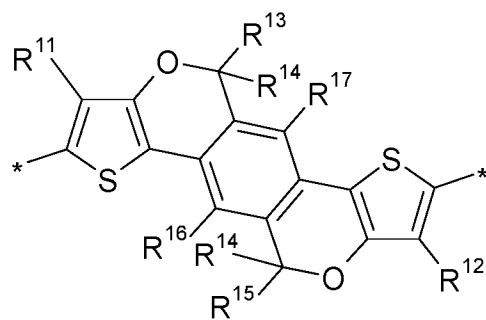
(D68)

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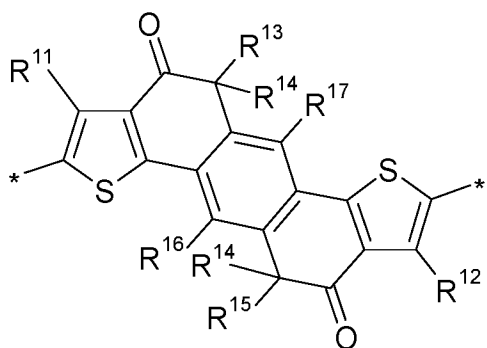


(D69)



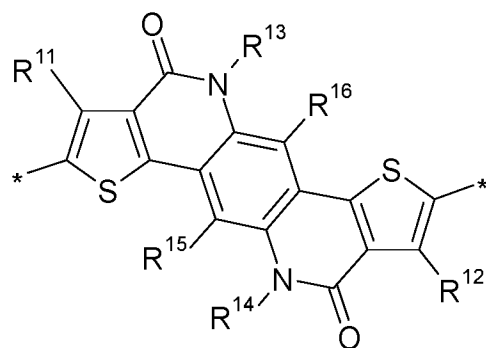
(D70)

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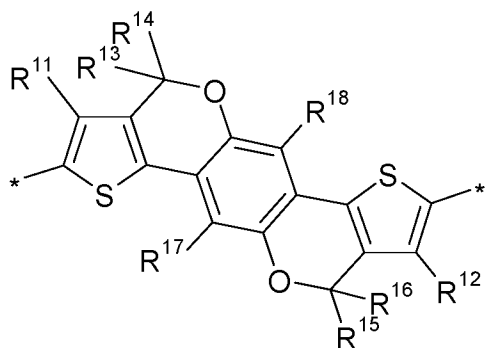
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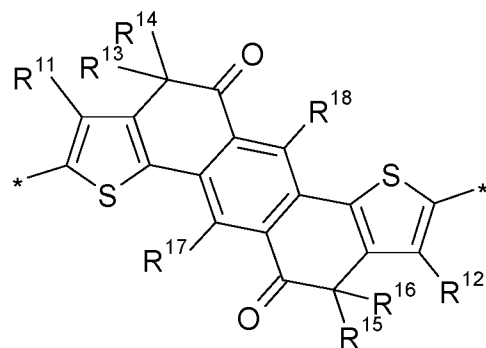
(D72)

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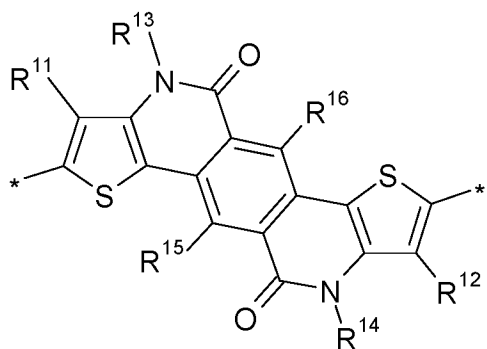
(D73)

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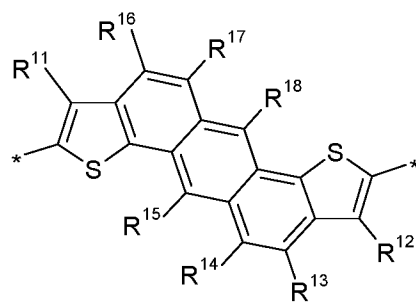
(D74)

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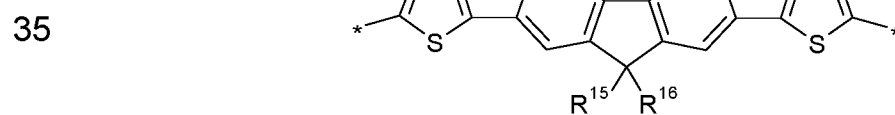
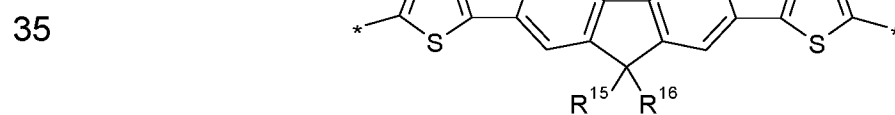
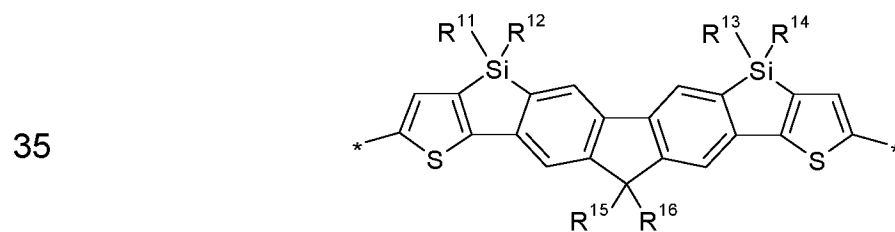
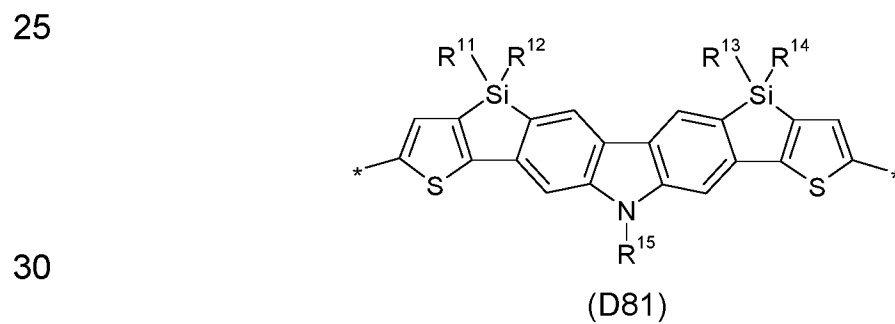
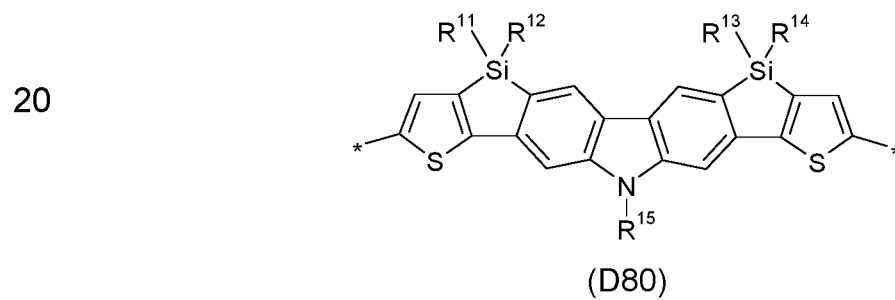
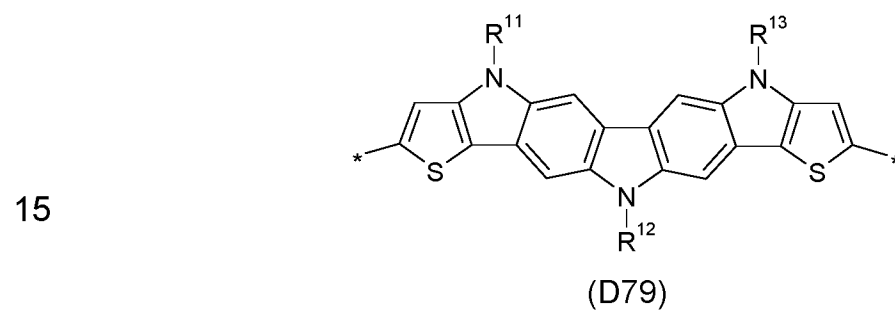
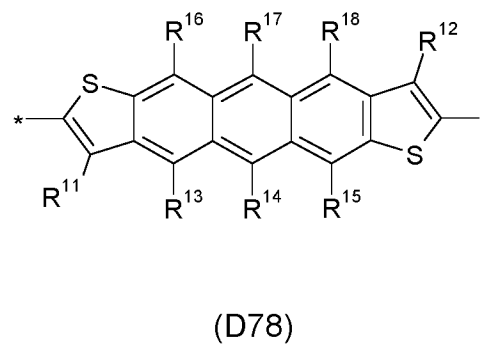
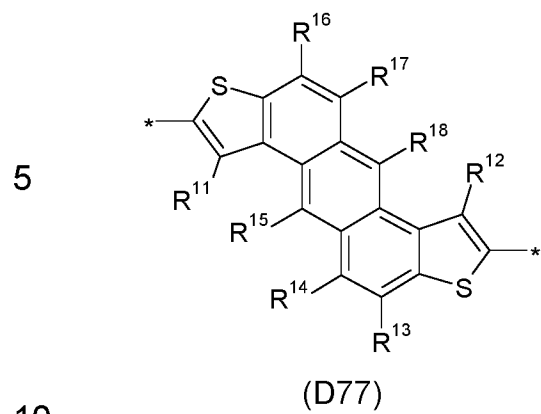


(D75)

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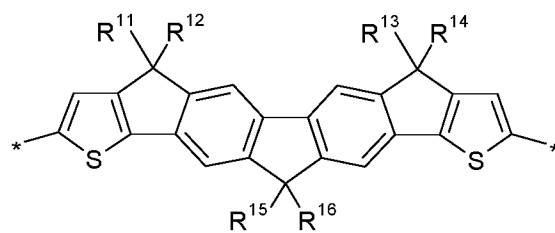


(76)



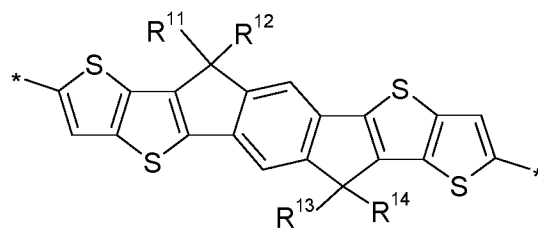
(D82)

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(D83)

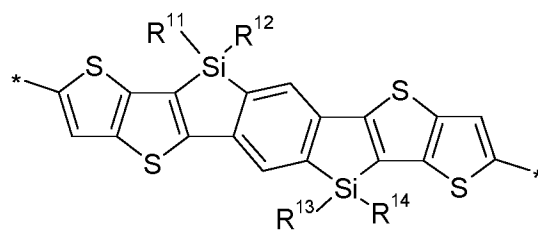
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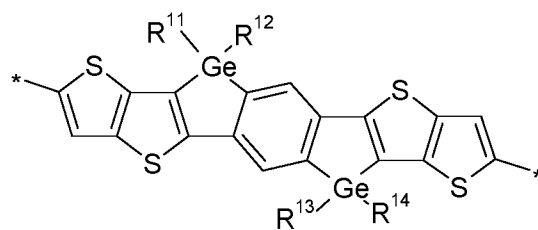
(D84)

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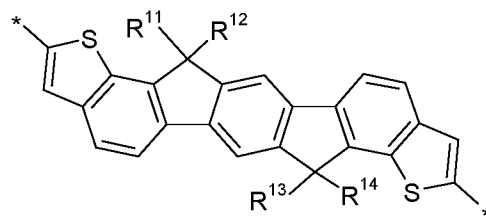
(D85)

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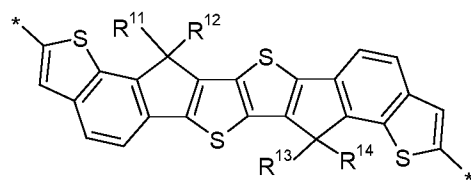
(D86)

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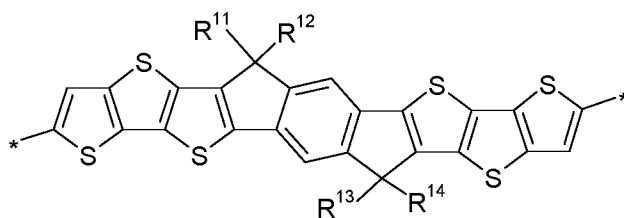


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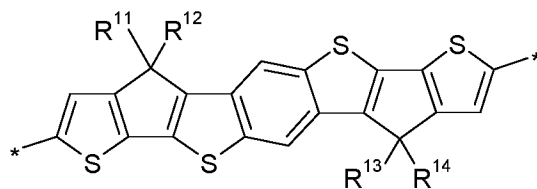
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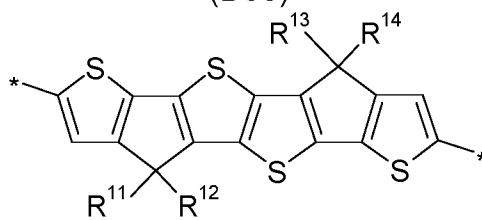
(D88)



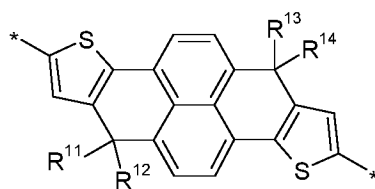
(D89)



(D90)

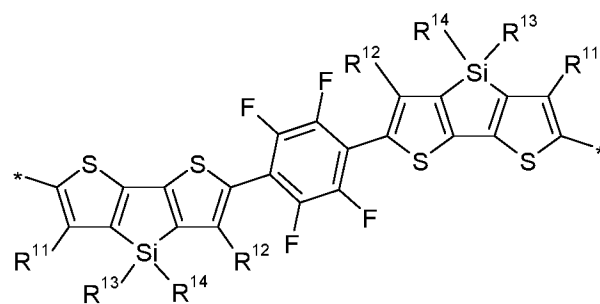


(D91)



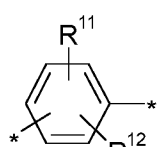
(D92)

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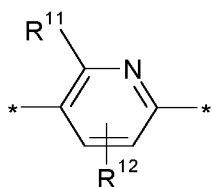


(D93)

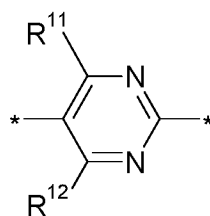
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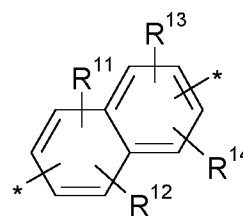
(D94)



(D95)

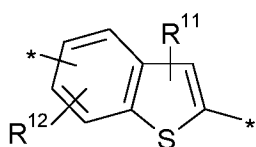


(D96)

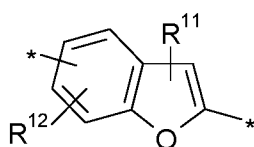


(D97)

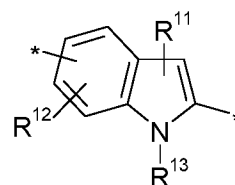
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(D98)

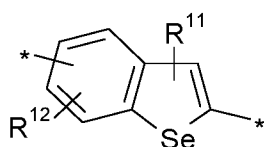


(D99)

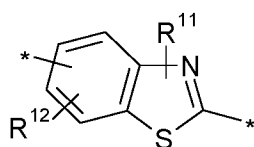


(D100)

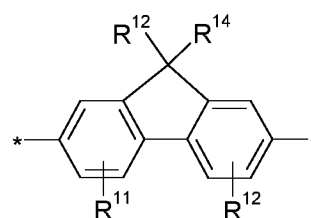
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(D101)



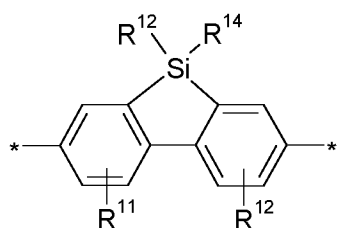
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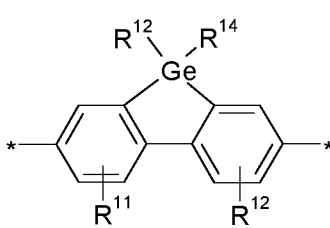
(D103)

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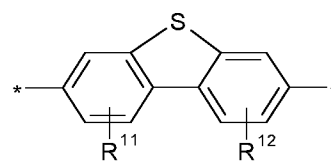
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(D104)

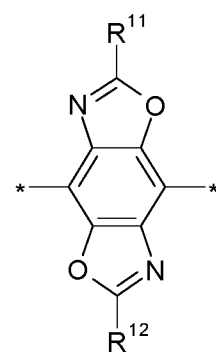
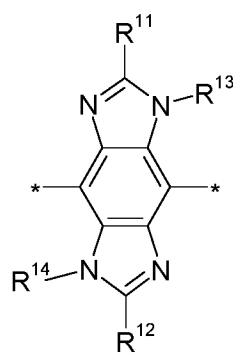
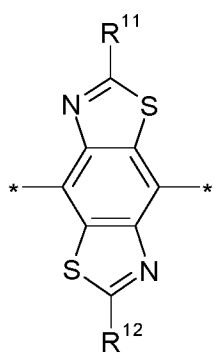
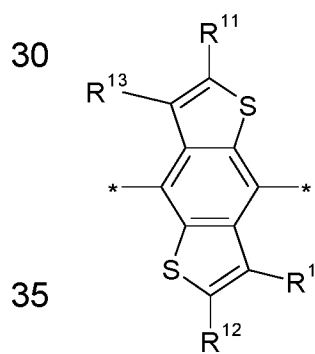
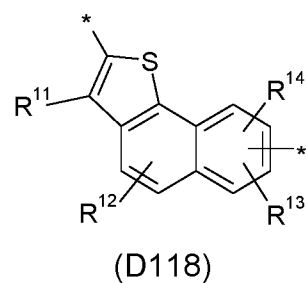
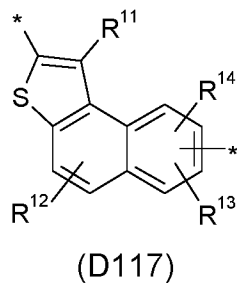
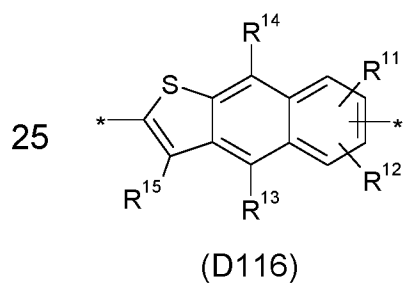
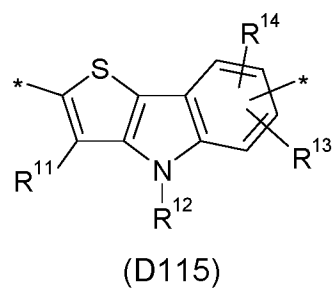
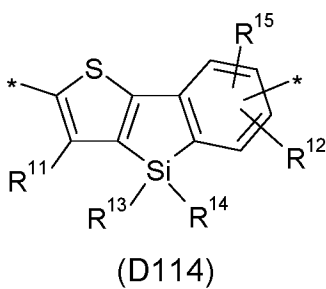
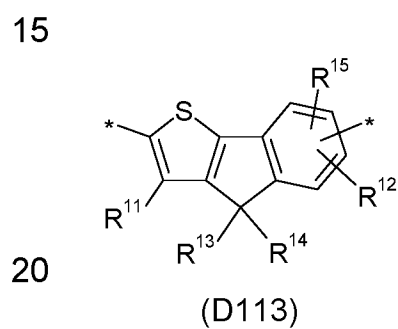
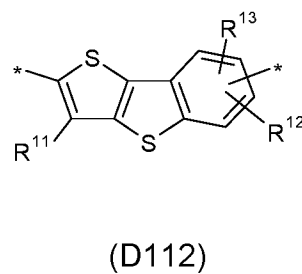
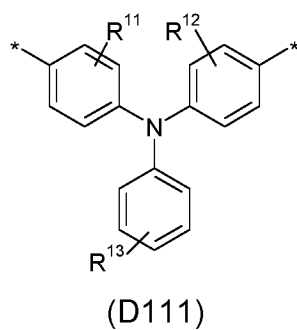
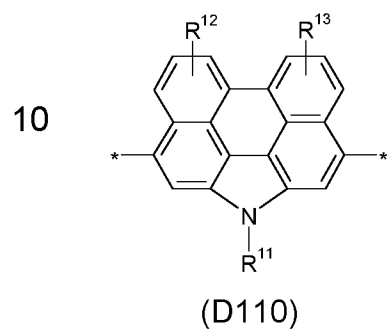
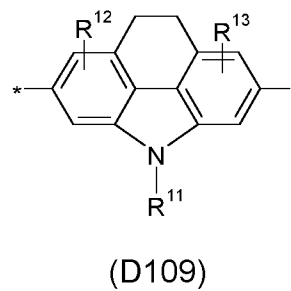
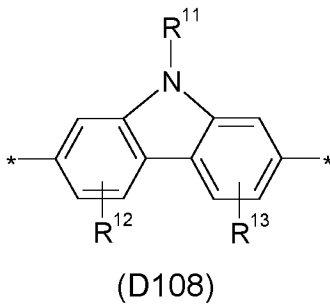
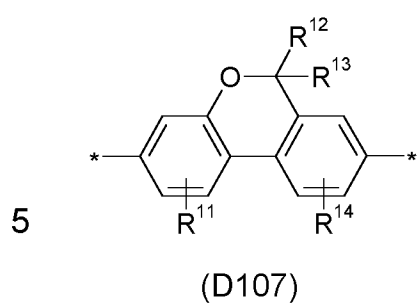


(D105)



(D106)

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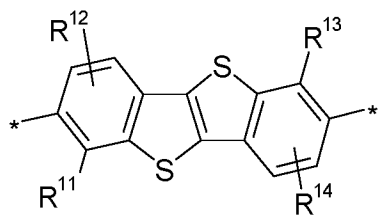
(D119)

(D120)

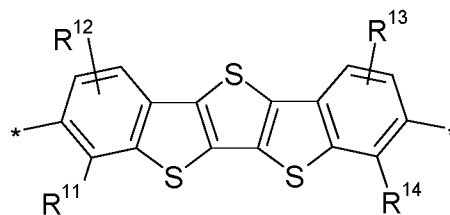
(D121)

(D122)

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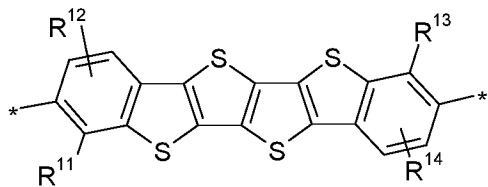


(D123)

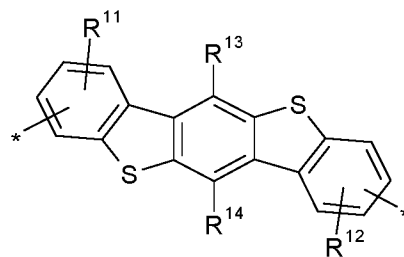


(D124)

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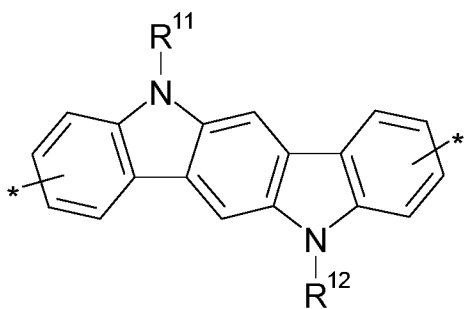
(D125)



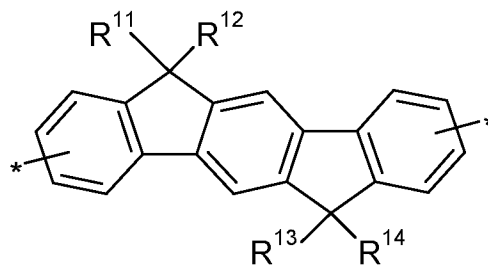
(D126)

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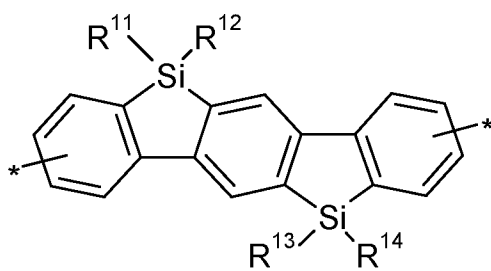
(D127)



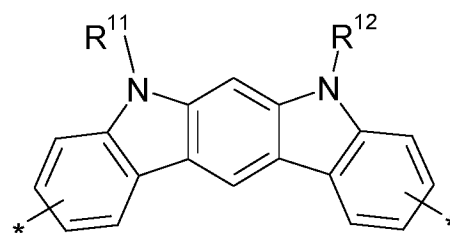
(D128)

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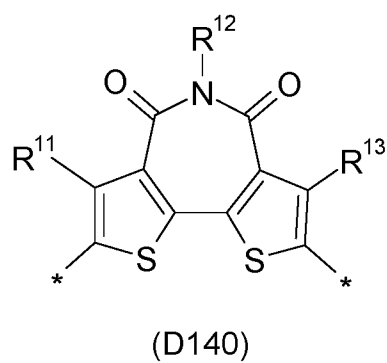
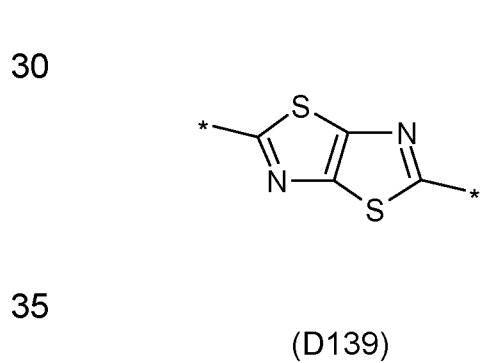
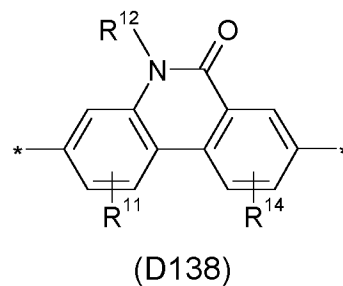
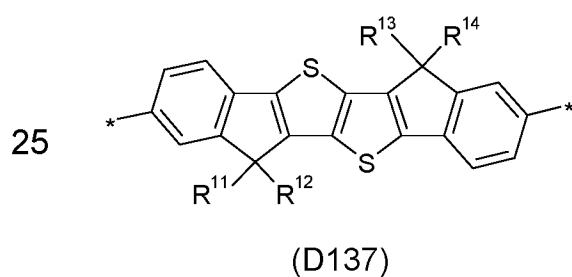
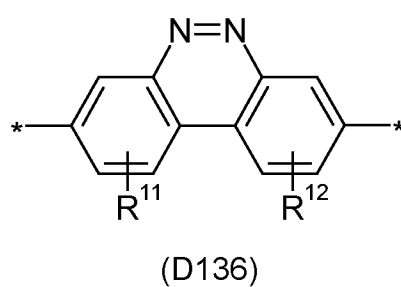
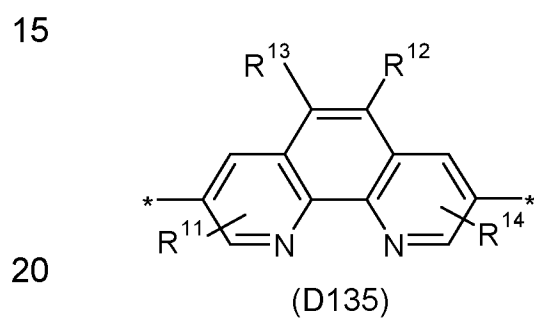
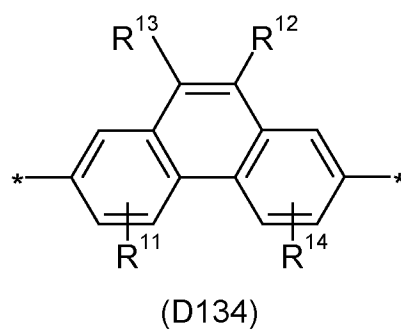
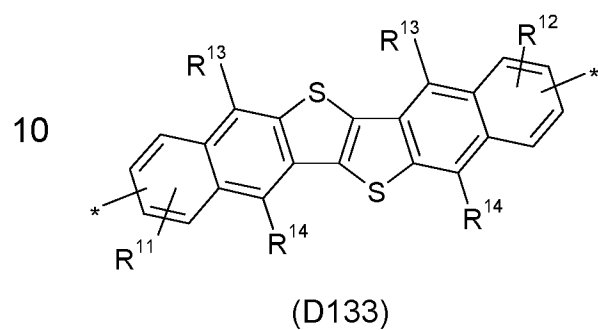
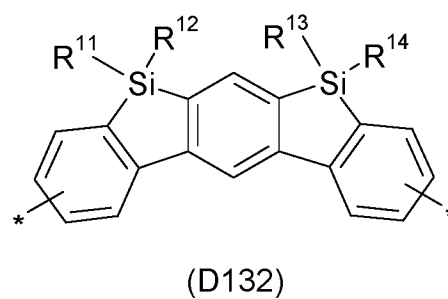
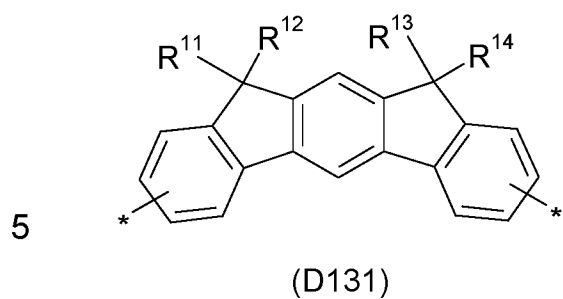


(D129)

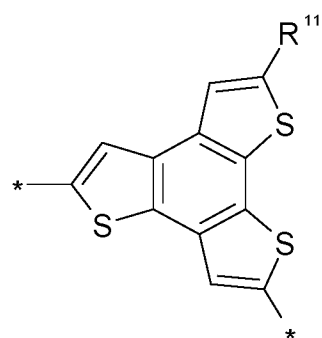
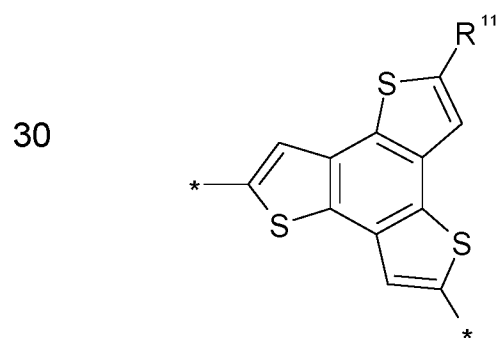
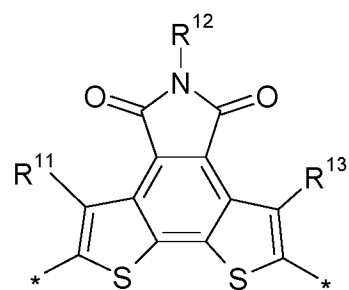
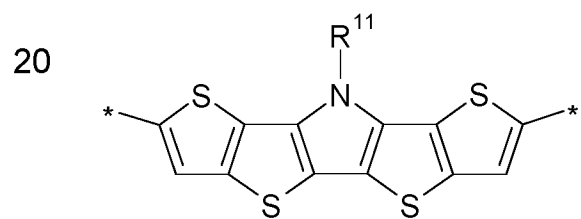
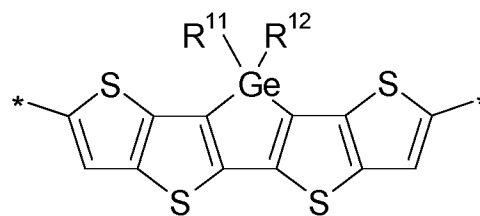
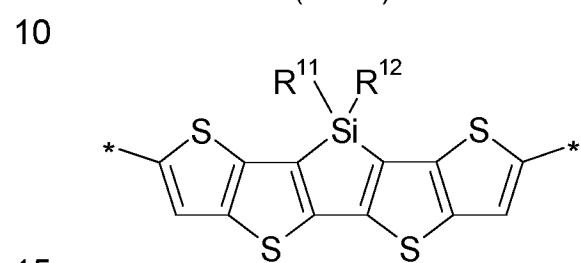
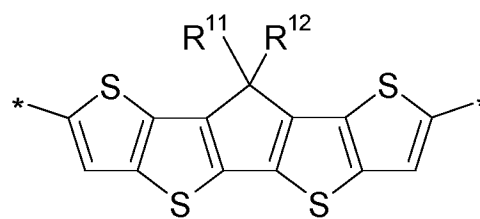
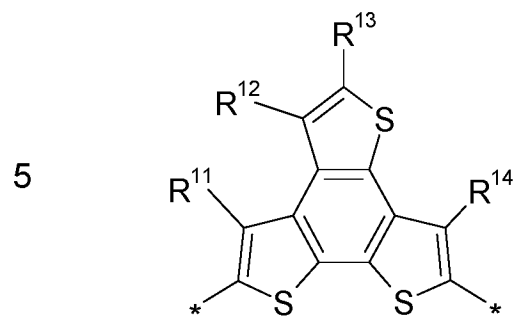


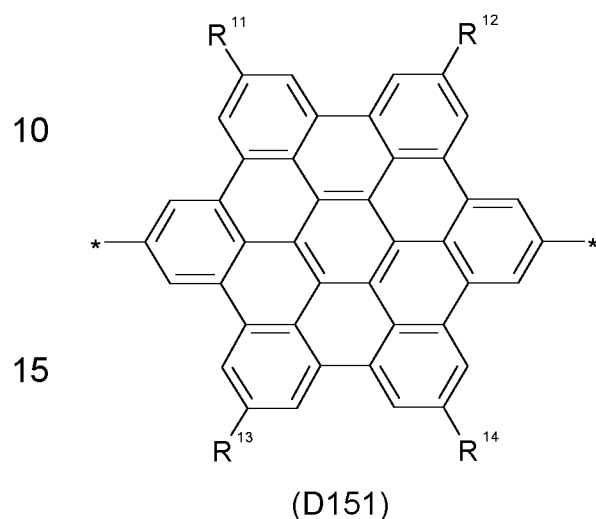
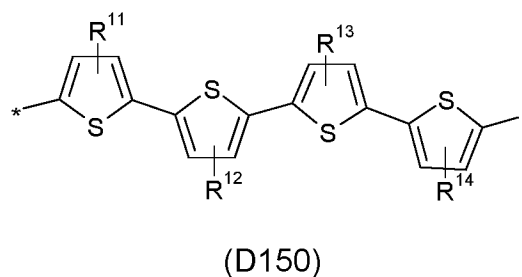
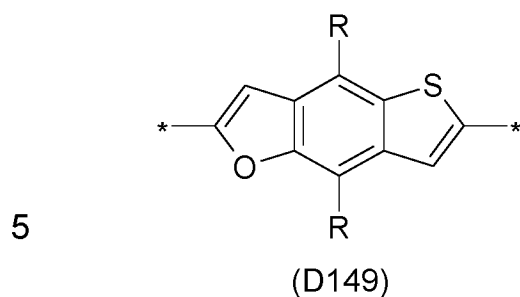
(D130)

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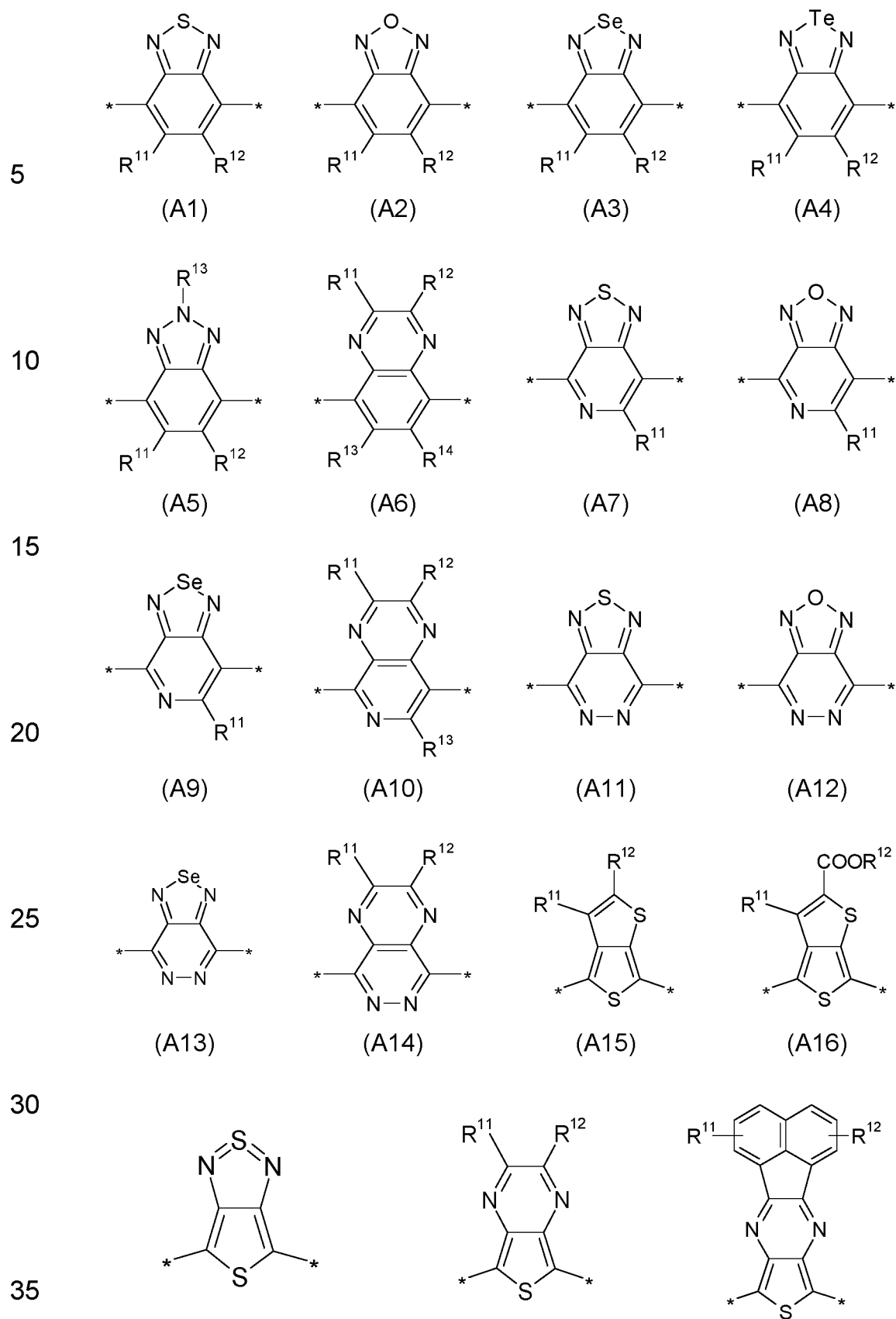


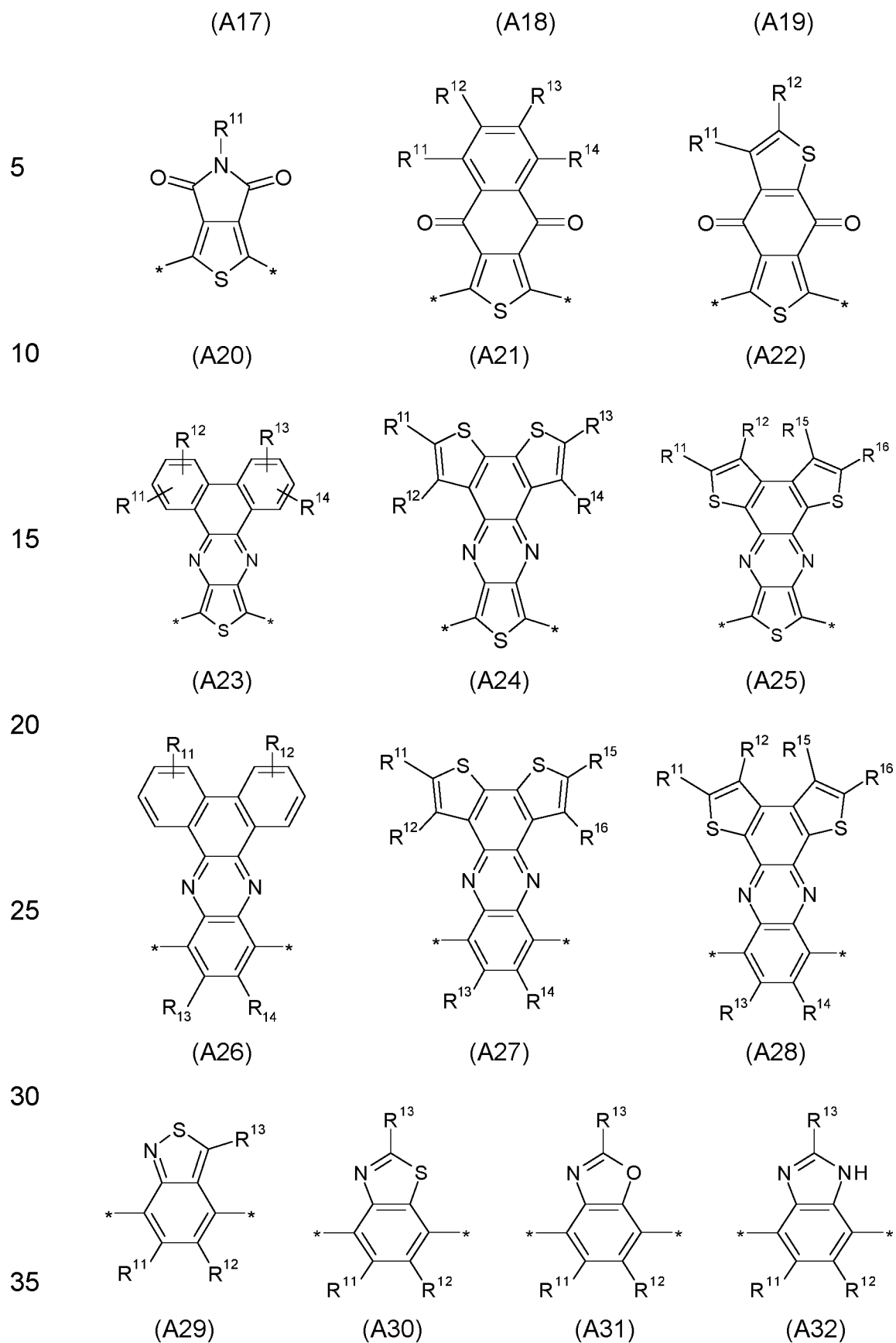
20 wherein R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} and R^{18} independently of each other have one of the meanings of R^1 as given in formula I or one of its preferred meanings as given above and below, and preferably at least one of the substituents R^{11-18} denotes $Sp-R^C$.

25 Preferred units are selected from formulae D1, D7, D10, D11, D19, D22, D29, D30, D35, D36, D37, D44, D55, D84, D87, D88, D89, D93, D94, D106, D111, D139, D140, D141, D146 or D150 wherein preferably at least one of R^{11-18} is different from H, and preferably at least one of R^{11-18} denotes $Sp-R^C$.

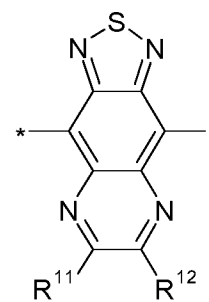
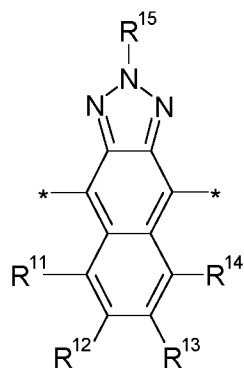
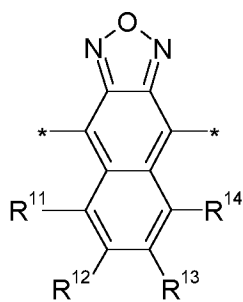
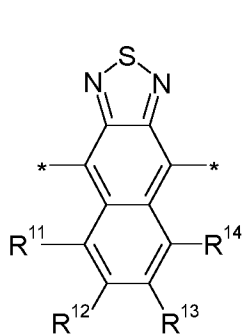
30 In another preferred embodiment the polymer comprises one or more units Ar^6 , which preferably have electron acceptor properties, and are selected from the group consisting of the formulae A1-A103 and their mirror images

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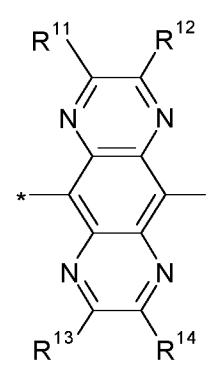
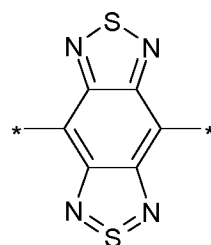
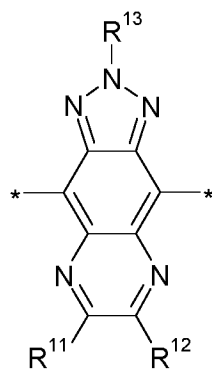
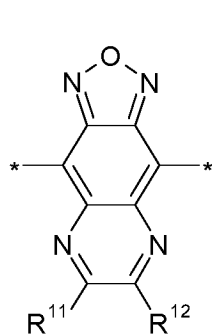




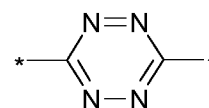
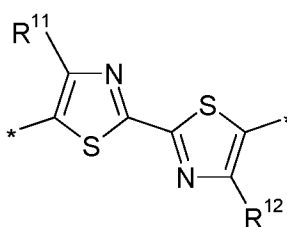
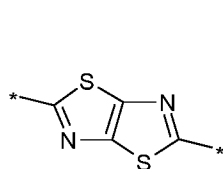
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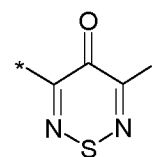
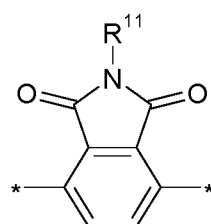
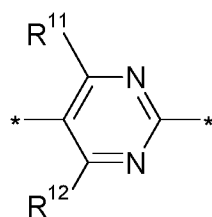
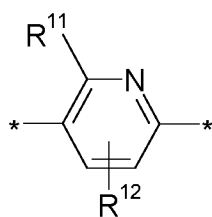
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(A41)

(A42)

(A43)

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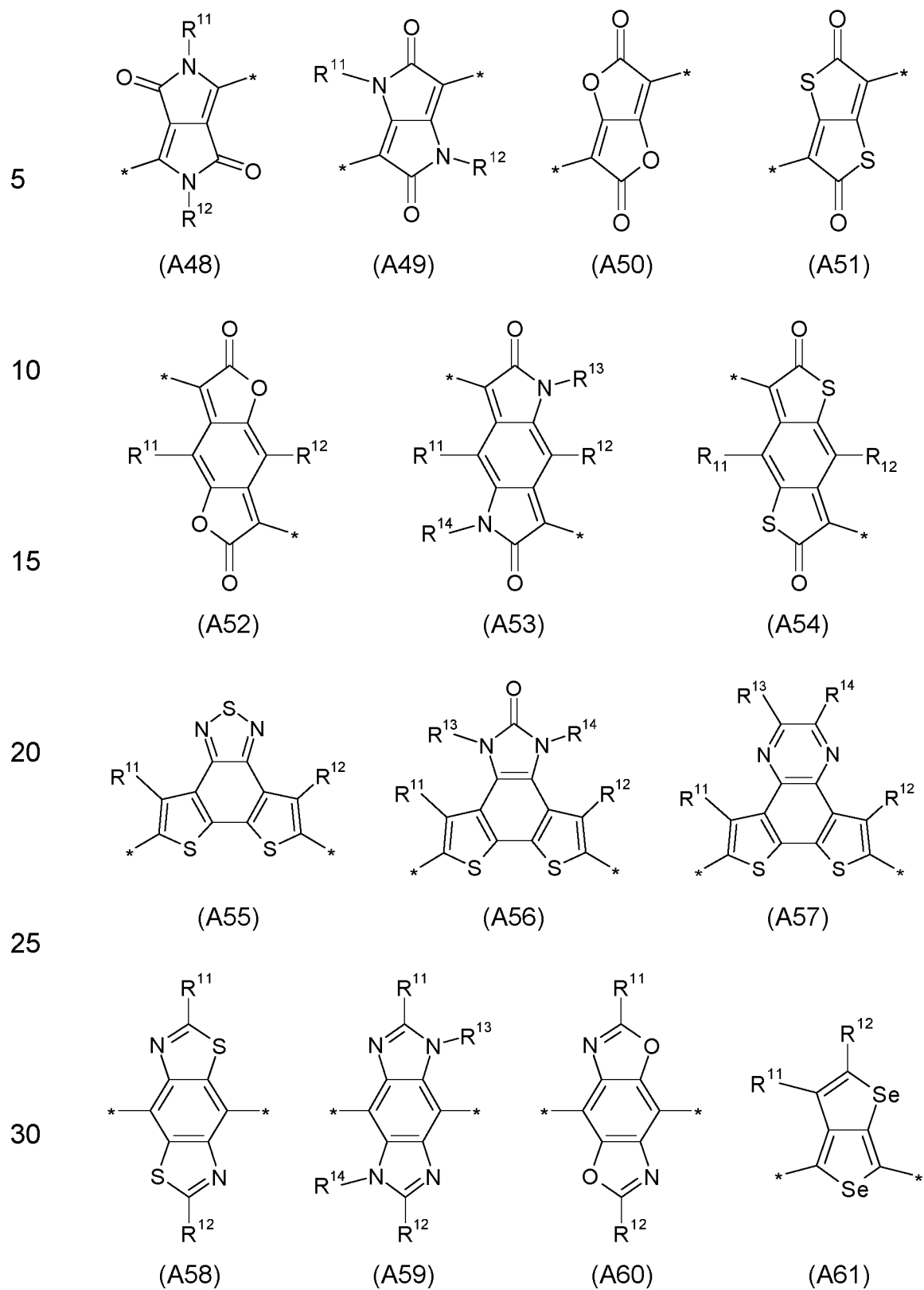
(A44)

(A45)

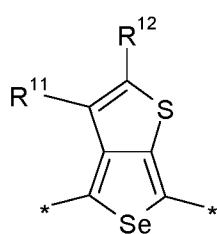
(A46)

(A47)

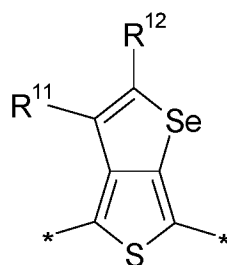
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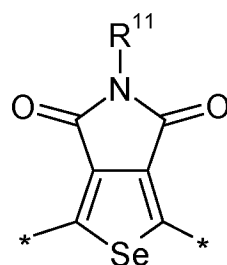
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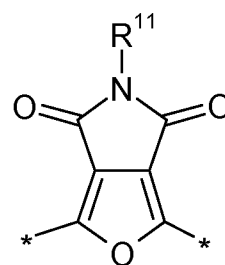
(A62)



(A63)

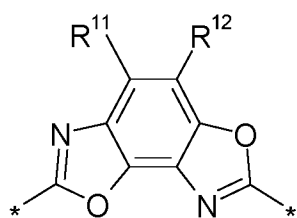


(A64)

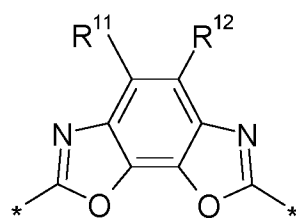


(A65)

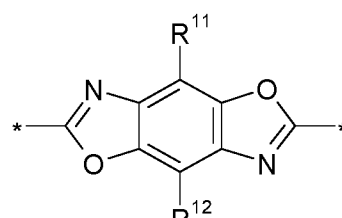
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(A66)

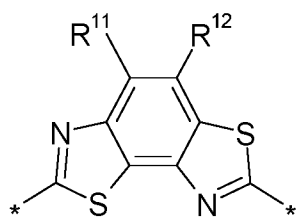


(A67)

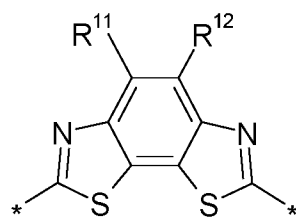


(A68)

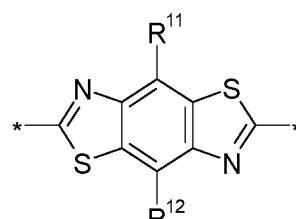
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(A69)

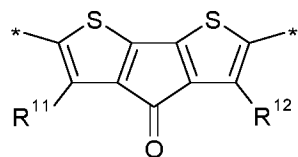


(A70)

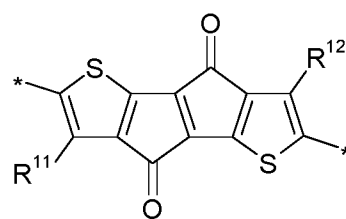


(A71)

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(A72)



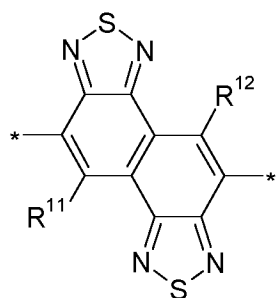
(A73)

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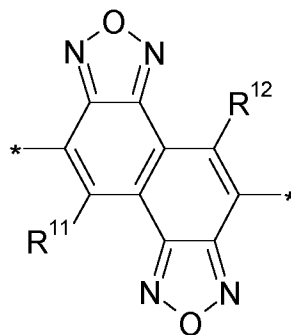
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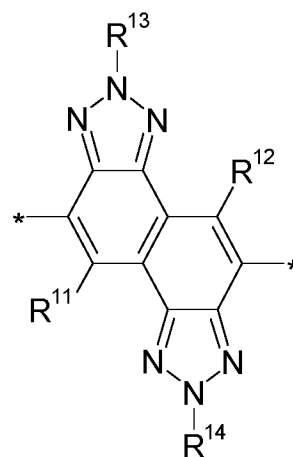
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(A74)

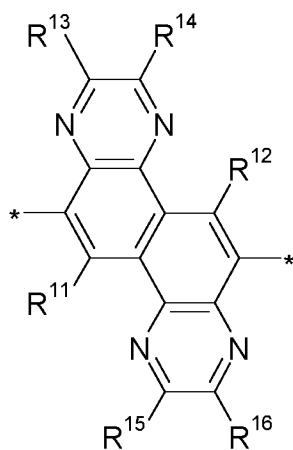


(A75)

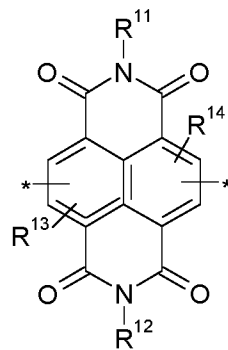


(A76)

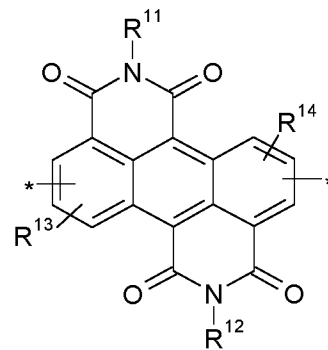
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(A77)

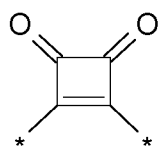


(A78)

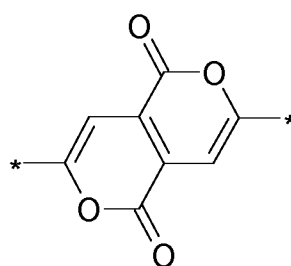


(A79)

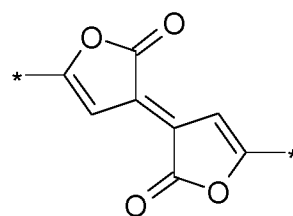
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(A80)



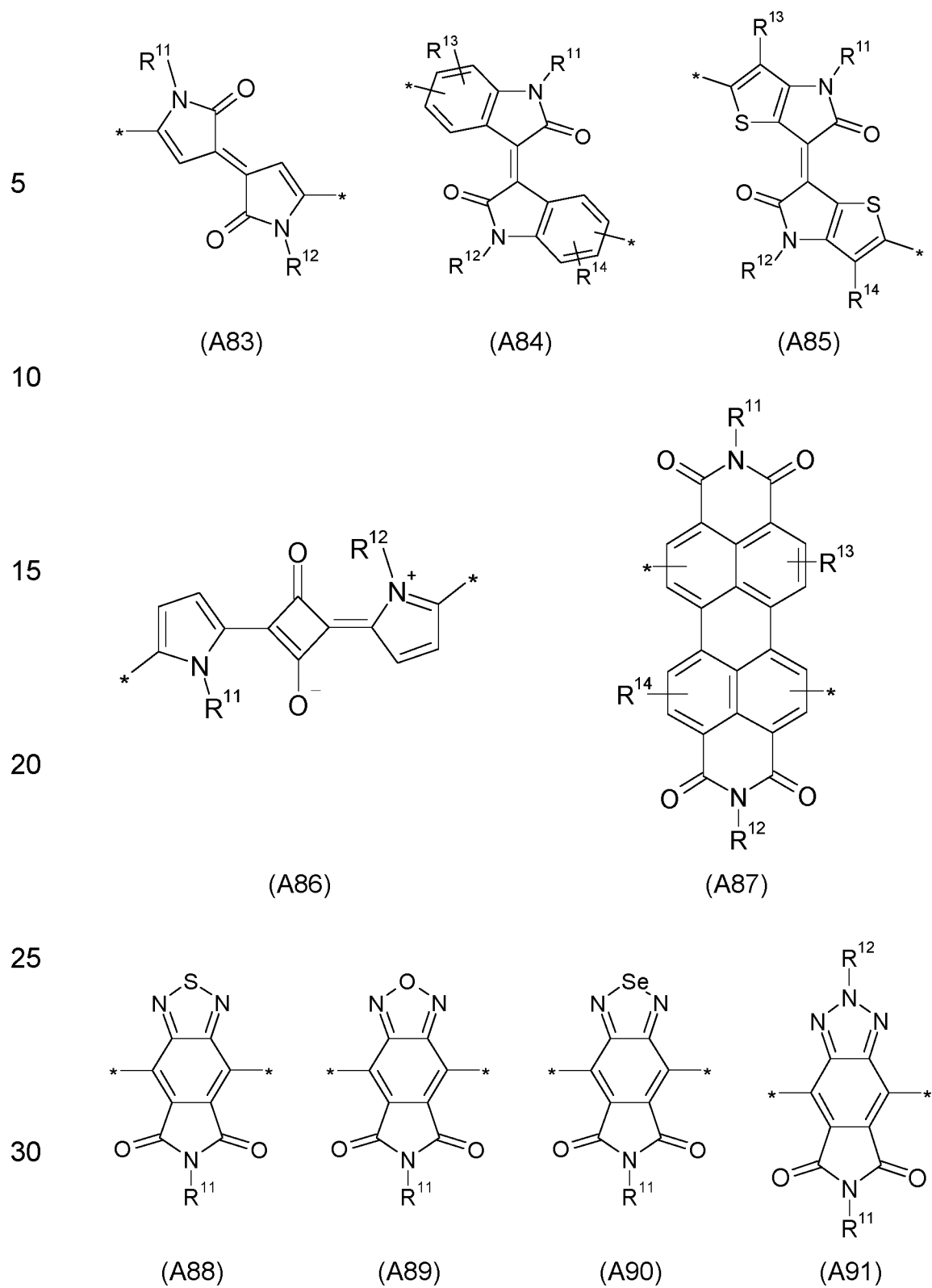
(A81)



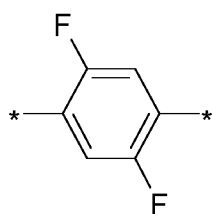
(A82)

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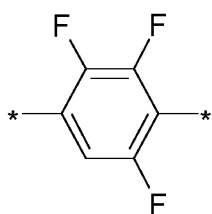
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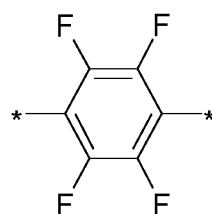
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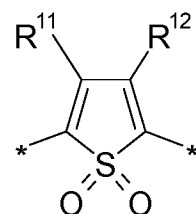
(A92)



(A93)

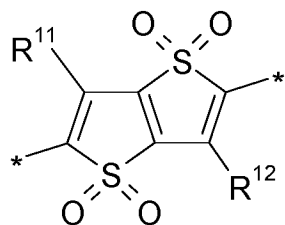


(A94)

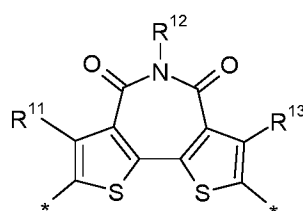


(A95)

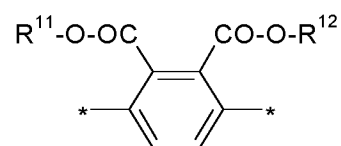
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(A96)

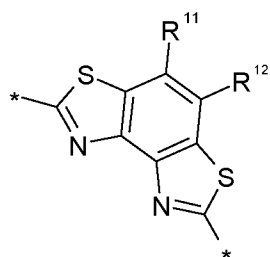


(A97)

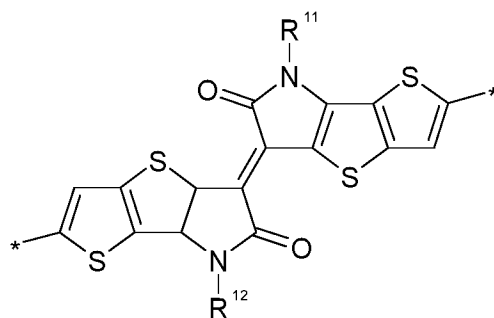


(A98)

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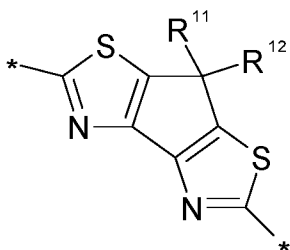
(A99)



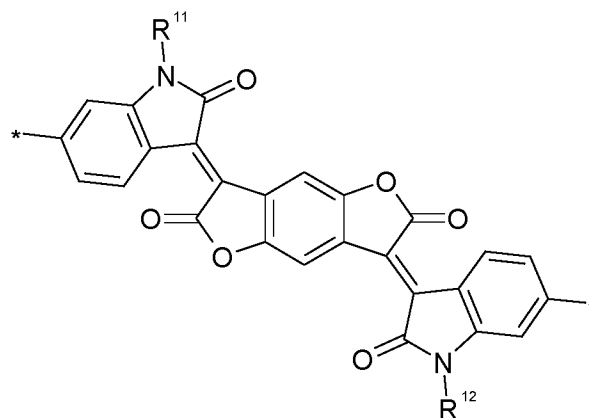
(A100)

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(A101)

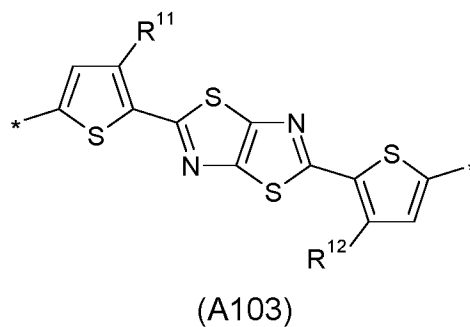


(A102)

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wherein R^{11} , R^{12} , R^{13} , R^{14} , R^{15} and R^{16} independently of each other have one of the meanings of R^1 as given in formula I or one of its preferred meanings as given above and below, and preferably at least one of the substituents R^{11-18} denotes $Sp-R^C$.

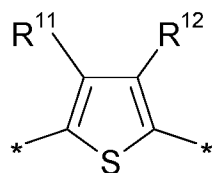
15

Preferred units are selected from formulae A1, A6, A7, A15, A16, A20, A36, A49, A74, A78, A84, A88, A92, A94, A98, A102 and A103 wherein preferably at least one of R^{11-14} is different from H, and preferably at least one of R^{11-18} denotes $Sp-R^C$.

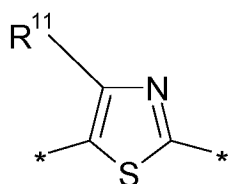
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In a further preferred embodiment, the polymer comprises one or more units Ar^6 which are selected from the group consisting of the formulae $Sp1$ - $Sp18$ and their mirror images

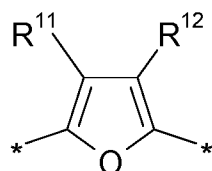
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 $Sp1$

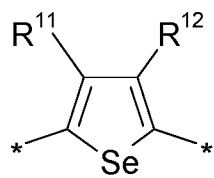
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 $Sp2$

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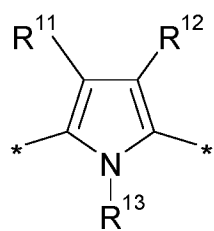
 $Sp3$

5



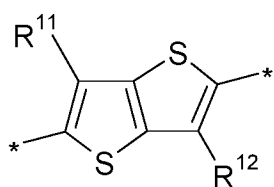
Sp4

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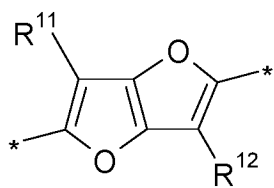
Sp5

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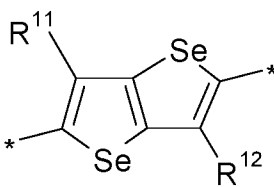
Sp6

20



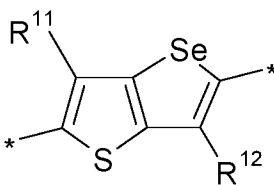
Sp7

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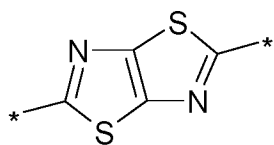
Sp8

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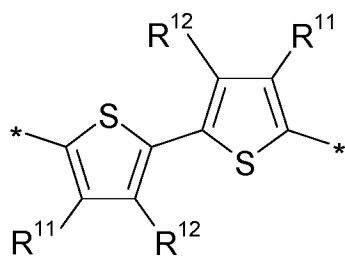
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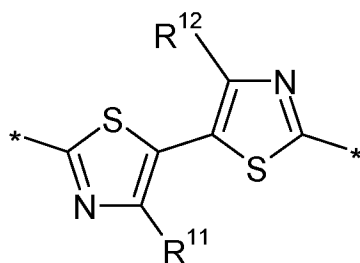
Sp10

5



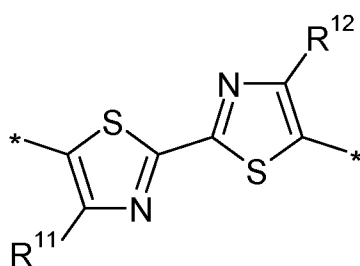
Sp11

10



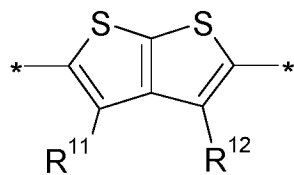
Sp12

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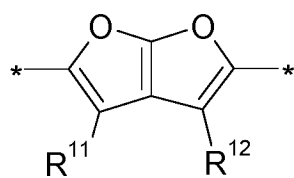
Sp13

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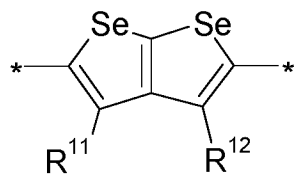
Sp14

25



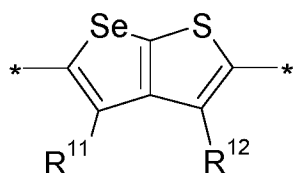
Sp15

30



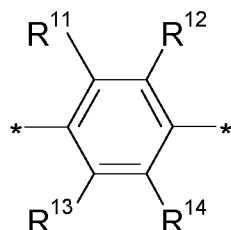
Sp16

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Sp17

5



Sp18

10

wherein R^{11} , R^{12} , R^{13} , R^{14} independently of each other have one of the meanings of R^1 as given in formula I or one of its preferred meanings as given above and below, and preferably at least one of R^{11-14} denotes $Sp-R^C$.

15

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

20 Very preferred are units selected from formulae Sp1, Sp2, Sp6, Sp10, Sp11, Sp12, Sp13 and Sp14, wherein preferably one of R^{11} and R^{12} is H or both R^{11} and R^{12} are H.

25 Further preferred are polymers comprising, preferably consisting of, one or more, preferably two or more, units of formula I, I1-I7 or or I1-1 to I5-13, and one or more units Ar^6 selected from the following groups

30 A2) the group consisting of the formulae D1-D151, very preferably from the formulae D1, D7, D10, D11, D19, D22, D29, D30, D35, D36, D37, D44, D55, D84, D87, D88, D89, D93, D94, D106, D111, D139, D140, D141, D146 and D150,

and/or

35 B2) the group consisting of the formulae A1-A103, very preferably from the formulae A1, A6, A7, A15, A16, A20, A36, A49, A74, A78, A84, A88, A92, A94, A98, A102 and A103,

and/or

C2) the group consisting of the formulae Sp1-Sp18, very preferably of the formulae Sp1, Sp2, Sp6, Sp10, Sp11, Sp12, Sp13 and Sp14.

5 In a preferred embodiment the polymer comprises one or more of the units of formula I, I1-I7 or or I1-1 to I5-13 which are at least monosubstituted by -Sp-R^C.

10 In another preferred embodiment the polymer comprises one or more of the units Ar⁶ which are at least monosubstituted by -Sp-R^C.

In another preferred embodiment, the polymer further comprises one or more units selected from -CY¹=CY²- and -C≡C-, wherein Y¹ and Y² are independently of each other H, F, Cl or CN.

15 In another preferred embodiment, the polymer comprises, very preferably consists of, one or more units selected from the following groups

- 1A) the group consisting of units of formula I, I1-I7 and or I1-1 to I5-13 which are selected from electron acceptor units,
- 20 1D) the group consisting of formula I, I1-I7 and I1-1 to I5-13 which are selected from electron donor units,
- 2A) the group consisting of units Ar⁶ which are selected from electron acceptor units, preferably selected from the group consisting of formulae A1-A103,
- 25 2D) the group consisting of units Ar⁶ which are selected from electron donor units, preferably selected from the group consisting of formulae D1-D151,
- 3) the group consisting of units Ar⁶ which are selected from spacer units, preferably selected from the group consisting of formulae Sp1-Sp18.
- 30

and wherein the polymer contains at least one unit selected from groups 1A and 1D, and the polymer contains at least one unit of group 1A, 1D, 2A, 2D or 3 which is at least monosubstituted by -Sp-R^C.

35 Preferred polymers comprise one or more units of group 1D and one or more units of group 2A.

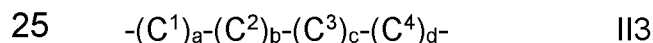
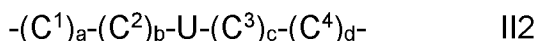
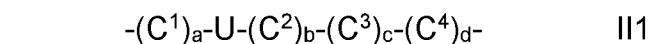
Further preferred polymers comprise one or more units of group 1A and one or more units of group 2D.

- 5 Further preferred polymers comprise one or more units of group 1D and one or more units of group 2D, and optionally one or more units selected from group 3.

- 10 Further preferred polymers comprise one or more units of group 1A and one or more units of group 2A, and optionally one or more units selected from group 3.

- 15 Further preferably the polymer comprises one or more units selected from groups 1D and 2D, one or more units selected from groups 1A and 2A, and one or more units selected from the group 3.

- 20 Further preferably the polymer comprises, preferably consists of, one or more, preferably two or more, repeating units of formula II1 and/or II2, and optionally one or more repeating units of formula II3:



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

- 30 U a unit selected from formula I, I1-I7 or I1-1 to I5-13 as defined above and below, preferably selected from groups 1A and 1D,

- 35 C^{1-4} distinct units having one of the meanings of Ar^6 as defined above and below, preferably selected from groups 2A, 2D and 3 as defined above and below,

a, b, c, d 0 or 1, wherein in formula II3 $a+b+c+d \geq 1$.

5 and wherein the polymer contains at least one unit of formula II1, II2 or II3 wherein at least one of U and C¹⁻⁴ is at least monosubstituted by -Sp-R^C.

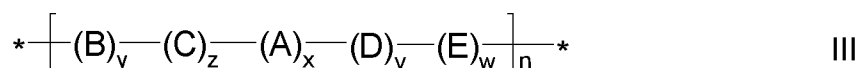
Preferably the polymer comprises one or more repeating units of formula II1 or II2 wherein $a+b+c+d \geq 1$.

10 Further preferably the polymer comprises one or more repeating units of formula II1 wherein $b=1$ and $a=c=d=0$ and one or more repeating units of formula II3 wherein $a=b=0$ and $c=d=1$.

15 Further preferably the polymer comprises two or more distinct repeating units of formula II1 wherein $b=1$ and $a=c=d=0$.

Further preferably C¹, C², C³ and C⁴ are selected from groups 2A, 2D and 3 as defined above and below.

20 Further preferably the polymer is selected of formula III:



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

A a unit of formula II1 or II2,

30 B, C, D, E a unit of formula II1, II2 or II3,

x > 0 and ≤ 1 ,

35 v, w, y, z ≥ 0 and < 1 ,

$v+w+x+y+z = 1$, and

n an integer >1, preferably ≥ 5 ,

5 and wherein at least one of A-E is at least monosubstituted by $-\text{Sp}-\text{R}^{\text{C}}$.

Further preferably the polymer comprises, very preferably consists of, one or more units selected from the group consisting of the following formulae and their mirror images

10	$-(\text{U})-$	U1
	$-(\text{U}-\text{Sp})-$	U2
15	$-(\text{Sp}-\text{U}-\text{Sp})-$	U3
	$-(\text{D}-\text{Sp})-$	U4
	$-(\text{A}-\text{Sp})-$	U5
20	$-(\text{Sp}-\text{D}-\text{Sp})-$	U6
	$-(\text{Sp}-\text{A}-\text{Sp})-$	U7
25	$-(\text{A}-\text{D})-$	U8
	$-(\text{D})-$	U9
	$-(\text{Sp}-\text{D}-\text{Sp}-\text{D})-$	U10
30	$-(\text{A})-$	U11
	$-(\text{Sp}-\text{A}-\text{Sp}-\text{A})-$	U12

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

- 113 -

U the meaning given in formula II1,

D a donor unit selected from groups 1D and 2D as defined above,

5 A an acceptor unit selected from groups 1A and 2A as defined above,

Sp a spacer unit selected from the group 3 as defined above,

10 and wherein the polymer contains at least one unit U, D, A or Sp which is at least monosubstituted by -Sp-R^C.

Preferred polymers are selected from formulae Pi-Px

15	-[(U-Sp) _n -	Pi
	-[(U-Sp) _x (Ar ⁶ -Sp) _y] _n -	Pii
	-[(U-Sp) _x (A-Sp) _y] _n -	Piii
20	-[(U-Sp) _x (D-Sp) _y] _n -	Piv
	-[(U-D) _x (U-Sp) _y] _n -	Pv
25	-[(U-A) _x (U-Sp) _y] _n -	Pvi
	-[(D) _x (Sp-U-Sp) _y] _n -	Pvii
	-[(A) _x (Sp-U-Sp) _y] _n -	Pviii
30	-[D-A] _n -	Pix
	-[(D-Sp) _x (A-Sp) _y] _n -	Pviii
35	-[A-D-A] _n -	Pix
	-[Sp-U ¹ -Sp-U ²] _n -	Px

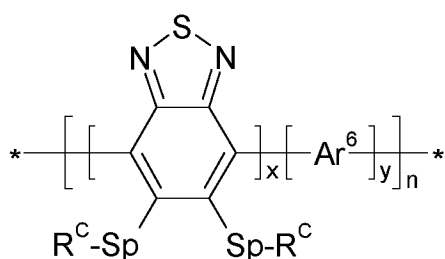
wherein A, D and Sp are as defined in formulae U2-U12, A, D and Sp can each, in case of multiple occurrence, also have different meanings, U¹ and U² have one of the meanings given for U and are different from each other, x and y denote the molar fractions of the corresponding units, x and y are each, independently of one another, a non-integer >0 and <1, with x+y=1, and n is an integer >1,

and wherein the polymer contains at least one unit U, D, A or Sp which is at least monosubstituted by -Sp-R^C.

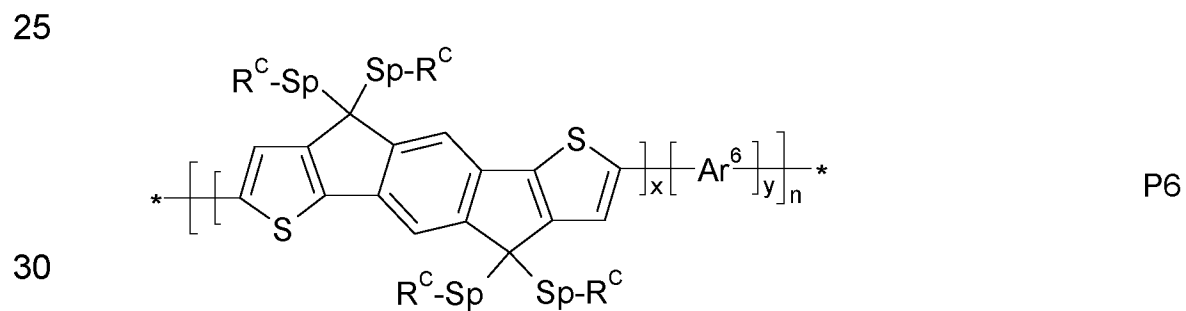
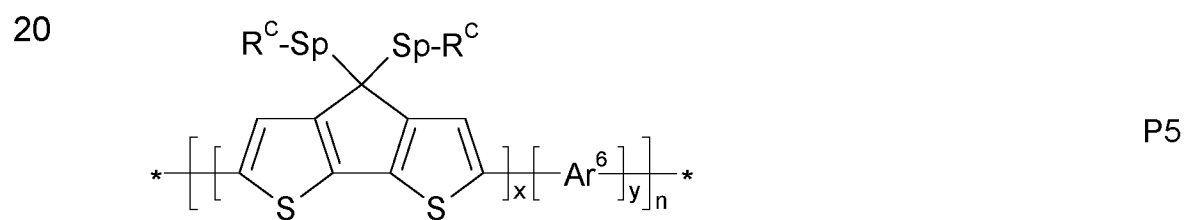
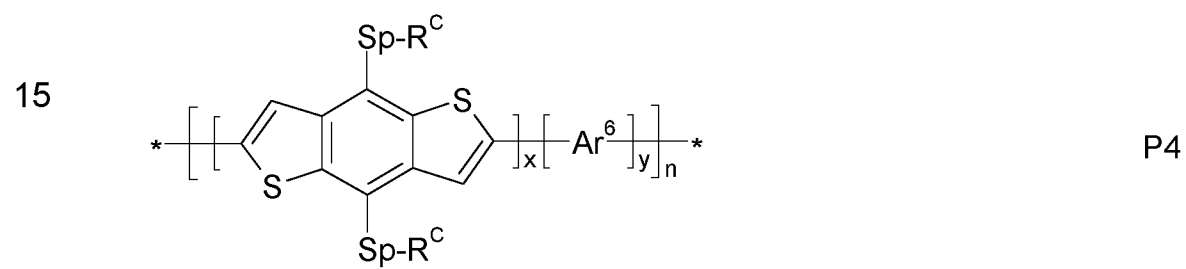
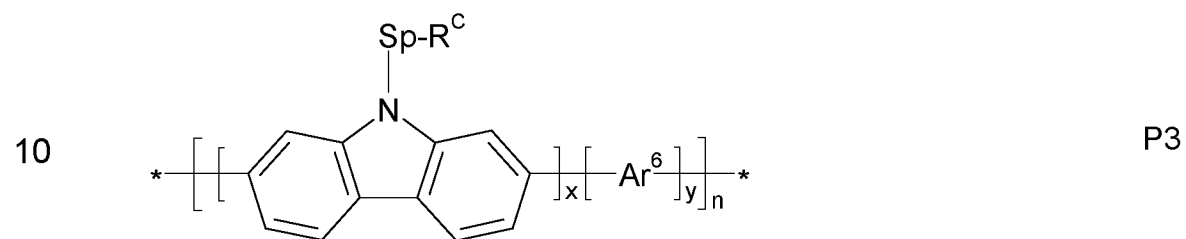
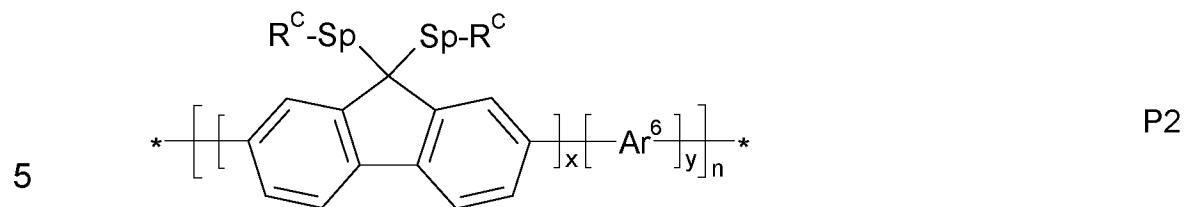
Further preferred are repeating units of formula U2-U12 and polymers of formulae Pi-Px wherein

- a) the donor units D and 2D are selected from the group consisting of the formulae D1-D151, very preferably of the formulae D1, D7, D10, D11, D19, D22, D29, D30, D35, D36, D37, D44, D55, D84, D87, D88, D89, D93, D94, D106, D111, D139, D140, D141, D146 and D150,
 - b) the acceptor units A and 2A are selected from the group consisting of the formulae A1-A103, very preferably of the formulae A1, A6, A7, A15, A16, A20, A36, A49, A74, A78, A84, A88, A92, A94, A98, A102 and A103,
- and
- c) the spacer units Sp are selected from the group consisting of the formulae Sp1-Sp18, very preferably of the formulae Sp1, Sp2, Sp6, Sp10, Sp11, Sp12, Sp13 and Sp14.

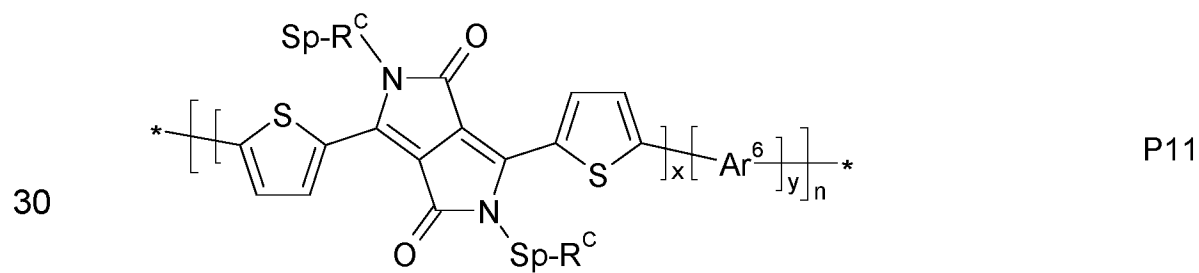
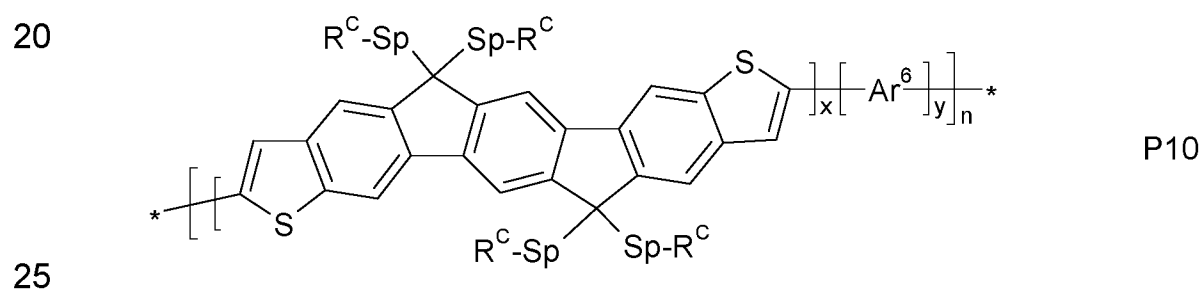
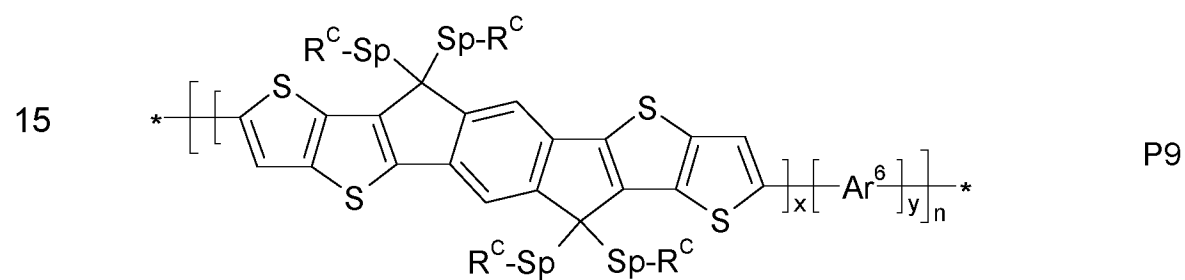
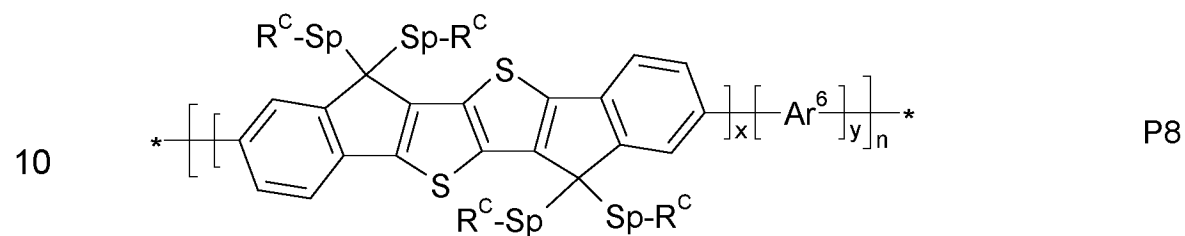
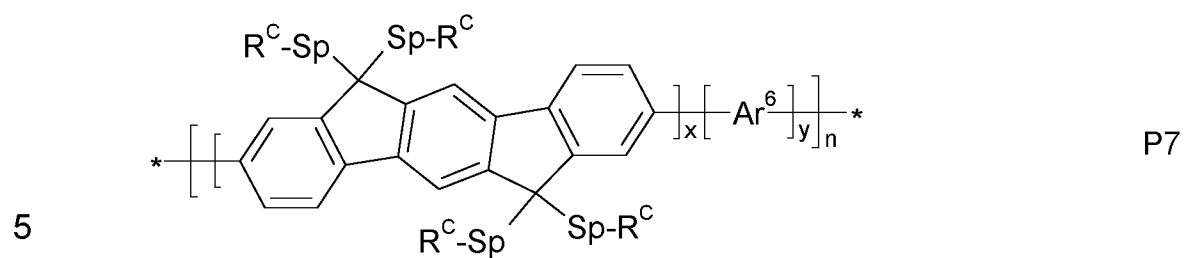
Very preferred polymers are selected from the following subformulae

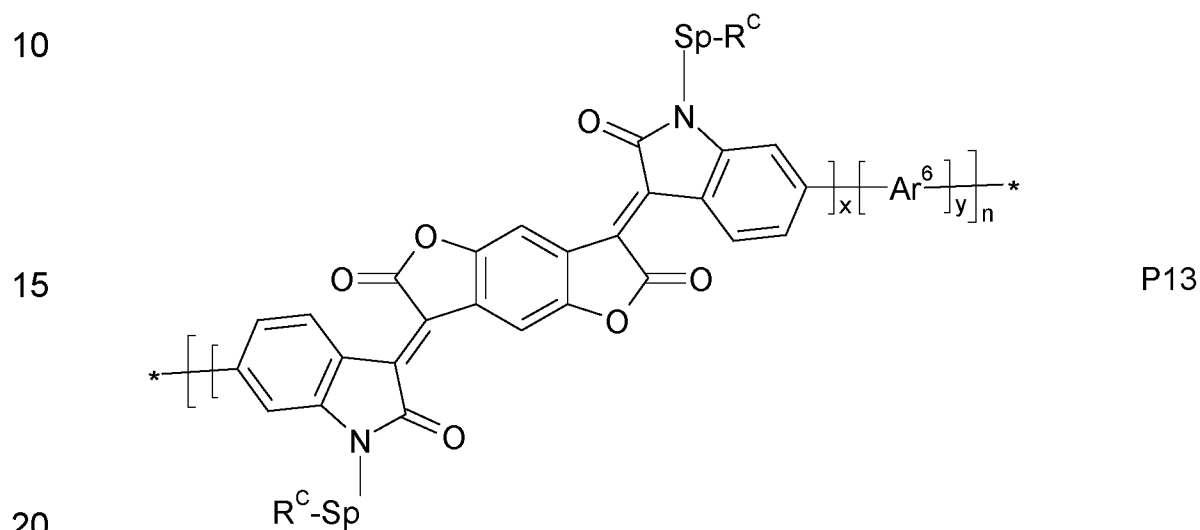
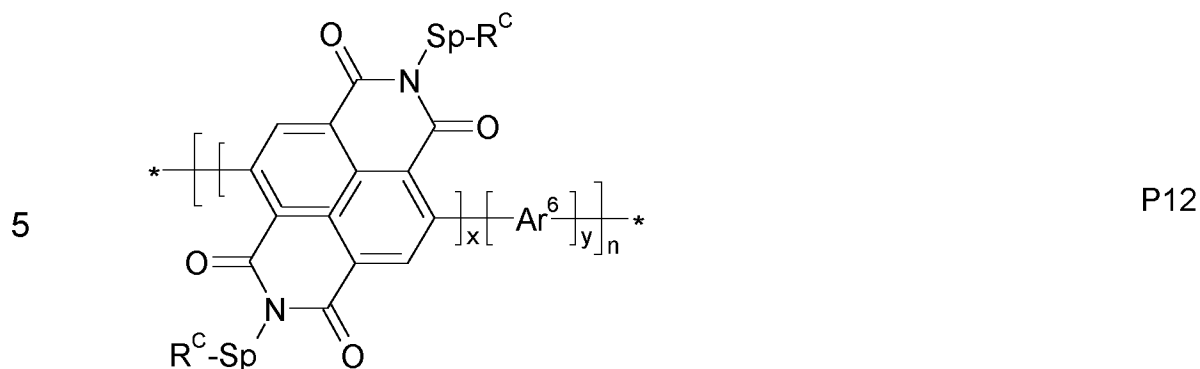


P1



35





wherein R^C , Sp, x, y and n have the meanings given above and below, R^C is preferably selected of formula M, very preferably of formula M1, and Sp- R^C is preferably selected of formula SM, very preferably of formula SM1.

Further preferably the polymer is selected of formula IV

R^{E1} -chain- R^{E2}

IV

wherein "chain" denotes a polymer chain selected from formulae III, Pi-Px, or P1-P13, and R^{E1} and R^{E2} have independently of each other one of the meanings of L as defined above, or denote, independently of each other, H, F, Br, Cl, I, $-\text{CH}_2\text{Cl}$, $-\text{CHO}$, $-\text{CR}'=\text{CR}''_2$, $-\text{SiR}'\text{R}''\text{R}'''$, $-\text{SiR}'\text{X}'\text{X}''$, $-\text{SiR}'\text{R}''\text{X}'$, $-\text{SnR}'\text{R}''\text{R}'''$, $-\text{BR}'\text{R}''$, $-\text{B}(\text{OR}')(\text{OR}'')$, $-\text{B}(\text{OH})_2$, $-\text{O}-\text{SO}_2-\text{R}'$, $-\text{C}\equiv\text{CH}$, $-\text{C}\equiv\text{C}-\text{SiR}'_3$, $-\text{ZnX}'$ or an endcap group, X' and X'' denote halogen, R' , R'' and R''' have independently of each other one of the meanings of R^0 given in formula I,

and preferably denote alkyl with 1 to 12 C atoms, and two of R', R'' and R''' may also form a cyclosilyl, cyclostannyl, cycloborane or cycloboronate group with 2 to 20 C atoms together with the respective hetero atom to which they are attached.

5

Preferred endcap groups R^{E1} and R^{E2} are H, C_{1-20} alkyl, or optionally substituted C_{6-12} aryl or C_{2-10} heteroaryl, very preferably H or phenyl.

10

In the polymers according to the present invention the indices v, w, x, y and z denote the mole fraction of the corresponding repeating units, such as units A-E in formula III, and n denotes the degree of polymerisation or total number of repeating units. These formulae include block copolymers, random or statistical copolymers and alternating copolymers, as well as homopolymers for the case when $x > 0$ and $v = w = y = z = 0$.

15

In the polymers according to the present invention wherein one of v, w, y and z is not 0 and the others of v, w, y and z are 0, x and the one of v, w, y and z which is not 0 are each preferably from 0.1 to 0.9, very preferably from 0.3 to 0.7.

20

In the polymers according to the present invention wherein two of v, w, y and z are not 0 and the others of v, w, y and z are 0, x and those of v, w, y and z which are not 0 are each preferably from 0.1 to 0.8, very preferably from 0.2 to 0.6.

25

In the polymers according to the present invention wherein three of v, w, y and z are not 0 and the others of v, w, y and z are 0, x and those of v, w, y and z which are not 0 are each preferably from 0.1 to 0.7, very preferably from 0.2 to 0.5.

30

In the polymers according to the present invention wherein all of v, w, y and z are not 0, x, v, w, y and z are each preferably from 0.1 to 0.6, very preferably from 0.2 to 0.4.

35

In the polymers according to the present invention, the total number of repeating units n is preferably from 2 to 10,000, very preferably from 5 to

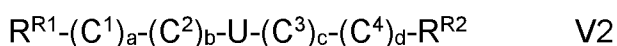
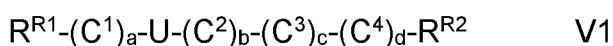
10,000. The total number of repeating units n is preferably ≥ 5 , very preferably ≥ 10 , most preferably ≥ 50 , and preferably ≤ 500 , very preferably $\leq 1,000$, most preferably $\leq 2,000$, including any combination of the aforementioned lower and upper limits of n .

5

The polymers of the present invention include homopolymers and copolymers, like statistical or random copolymers, alternating copolymers and block copolymers, as well as combinations thereof.

10

The invention further relates to monomers of formula V1 or V2



15

wherein U , C^{1-4} , a , b , c and d have the meanings of formula II1, or one of the preferred meanings as described above and below, and R^{R1} and R^{R2} are independently of each other selected from the group consisting of H, which is preferably an activated C-H bond, Cl, Br, I, O-tosylate, O-triflate, O-mesylate, O-nonaflate, $-\text{SiMe}_2\text{F}$, $-\text{SiMeF}_2$, $-\text{O-SO}_2\text{Z}^1$, $-\text{B}(\text{OZ}^2)_2$, $-\text{CZ}^3=\text{C}(\text{Z}^3)_2$, $-\text{C}\equiv\text{CH}$, $-\text{C}\equiv\text{CSi}(\text{Z}^1)_3$, $-\text{ZnX}^0$ and $-\text{Sn}(\text{Z}^4)_3$, wherein X^0 is halogen, Z^{1-4} are selected from the group consisting of alkyl and aryl, preferably C_{1-10} alkyl and C_{6-12} aryl, each being optionally substituted, and two groups Z^2 may also form a cycloboronate group having 2 to 20 C atoms together with the B- and O-atoms, and wherein at least one of R^{R1} and R^{R2} is different from H, and preferably both of R^{R1} and R^{R2} are different from H.

20

25

30

Very preferred are monomers of formula V1 and V2 wherein $a+b+c+d \geq 1$.

Further preferred are monomers of formula V1 wherein $a+b+c+d=0$.

Further preferred are monomers selected from the following subformulae

35





wherein U, C¹, C², R^{R1} and R^{R2} are as defined in formula V1.

10 Further preferred are monomers of formula V1, V2 and V1a-d wherein R^{R1} and R^{R2} are selected from Br, -B(OZ²)₂ and Sn(Z⁴)₃.

Further preferred are monomers of formulae V1, V2 and V1a-V1d wherein C¹ and/or C² are selected from groups A2, A3, A4, D2 and E2 as defined above.

15

Further preferred are monomers of formula V3



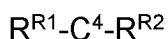
20 wherein R^{R1} and R^{R2} have the meanings given above and below, and preferably denote Br, B(OZ²)₂ or Sn(Z⁴)₃, and U* is a unit selected from formulae P1-P8 or PN1-PN6 wherein n is 1.

25 Further preferred units, monomers and polymers of formulae I, I1-I7, I1-1 to I5-13, II1, II2, II3, III, Pi-Px, P1-P13, IV, V1-V3, V1a-d and I1-1 to I5-13 are selected from the following embodiments, including any combination thereof:

- n ≥ 5,
- 30 - n is from 5 to 1,000, most preferably from 10 to 2,000,
- a=b=1 and c and d are independently of each other 0, 1 or 2, preferably 0 or 1, very preferably 0,
- a is 2, b is 1 or 2, c is 0 or 1, preferably 0, and d is 0, 1 or 2, preferably 0 or 1, very preferably 0,
- 35 - b=1 and a=c=d=0,

- $a=b=0$ and $c=d=1$.
 - one or more of R^{11-18} is different from H and is selected from alkyl, alkoxy or thiaalkyl, all of which are straight-chain or branched, have 1 to 25, preferably 1 to 18 C atoms, and are optionally fluorinated,
 - one or more of R^{11-18} is different from H and is selected from F, Cl, CN, -C(=O)- R^n , -C(=O)-OR ^{n} , -C(=O)-NHR ^{n} and -C(=O)-NR ^{n} R ^{m} , wherein R ^{m} and R ^{n} are independently of each other straight-chain or branched alkyl with 1 to 25, preferably 1 to 18 C atoms that is optionally fluorinated,
 - one or more of R^{11-18} is different from H and is selected from the group consisting of aryl, heteroaryl, aryloxy, heteroaryloxy, arylalkyl and heteroarylalkyl, each of which has 4 to 20 ring atoms and optionally contains fused rings and is unsubstituted or substituted by one or more groups L as defined in formula I,
 - R ^{E1} and R ^{E2} are selected from H, C $_{1-20}$ alkyl, or optionally substituted C $_{6-12}$ aryl or E $_{1-10}$ heteroaryl, very preferably H or phenyl,
 - R ^{R1} and R ^{R2} denote Br, B(OZ ^{2}) $_2$ or Sn(Z ^{4}) $_3$, wherein Z ^{2} and Z ^{4} are as defined in formula V1.
- The polymers according to the present invention can be synthesized according to or in analogy to methods that are known to the skilled person and are described in the literature. Other methods of preparation can be taken from the examples.
- The polymers of the present invention can be prepared from the corresponding monomers, which are preferably selected from formula V1-V3 or V1a-d, for example by copolymerising one or more monomers of formula V1-V3 or V1a-d with each other or with one or monomers of the following formulae in an aryl-aryl coupling reaction





MIV

5 wherein C^{1-4} , R^{R1} and R^{R2} have the meanings given in formula II2 and V1 or one of the preferred meanings given above and below.

10 For example, the polymers can be suitably prepared by aryl-aryl coupling reactions, such as Yamamoto coupling, C-H activation coupling, Suzuki coupling, Stille coupling, Sonogashira coupling, Heck coupling or Buchwald coupling. Suzuki coupling, Stille coupling and Yamamoto coupling are especially preferred. The monomers which are polymerised to form the repeat units of the polymers can be prepared according to methods which are known to the person skilled in the art.

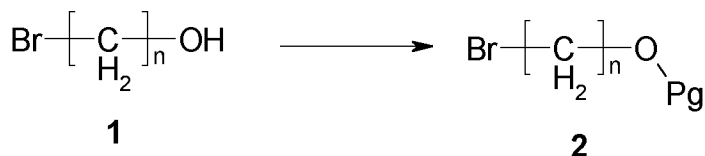
15 Preferably the polymers are prepared from monomers selected from formulae V1-V3, V1a-d and MI-MIV as described above.

20 Another aspect of the invention is a process for preparing a polymer by coupling one or more identical or different monomers selected from formulae V1, V2, V3 and V1a-d with each other and/or with one or more co-monomers, preferably selected from formulae MI-MIV, in a polymerisation reaction, preferably in an aryl-aryl coupling reaction.

25 Preferred aryl-aryl coupling methods used in the synthesis methods as described above and below are Yamamoto coupling, Kumada coupling, Negishi coupling, Suzuki coupling, Stille coupling, Sonogashira coupling, Heck coupling, C-H activation coupling, Ullmann coupling or Buchwald coupling. Especially preferred are Suzuki coupling, Negishi coupling, Stille coupling and Yamamoto coupling. Suzuki coupling is described for
30 example in WO 00/53656 A1. Negishi coupling is described for example in *J. Chem. Soc., Chem. Commun.*, **1977**, 683-684. Yamamoto coupling is described in for example in T. Yamamoto *et al.*, *Prog. Polym. Sci.*, **1993**, 17, 1153-1205, or WO 2004/022626 A1. Stille coupling is described for example in Z. Bao *et al.*, *J. Am. Chem. Soc.*, 1995, 117, 12426-12435 and
35 C-H activation is described for example in M. Leclerc *et al.*, *Angew. Chem. Int. Ed.*, 2012, 51, 2068-2071. For example, when using Yamamoto

- coupling, educts having two reactive halide groups are preferably used. When using Suzuki coupling, educts having two reactive boronic acid or boronic acid ester groups or two reactive halide groups are preferably used. When using Stille coupling, educts having two reactive stannane groups or two reactive halide groups are preferably used. When using Negishi coupling, educts having two reactive organozinc groups or two reactive halide groups are preferably used.
- Preferred catalysts, especially for Suzuki, Negishi or Stille coupling, are selected from Pd(0) complexes or Pd(II) salts. Preferred Pd(0) complexes are those bearing at least one phosphine ligand such as Pd(Ph₃P)₄. Another preferred phosphine ligand is tris(*ortho*-tolyl)phosphine, i.e. Pd(o-Tol₃P)₄. Preferred Pd(II) salts include palladium acetate, i.e. Pd(OAc)₂. Alternatively the Pd(0) complex can be prepared by mixing a Pd(0) dibenzylideneacetone complex, for example tris(dibenzylideneacetone)dipalladium(0), bis(dibenzylideneacetone)palladium(0), or Pd(II) salts e.g. palladium acetate, with a phosphine ligand, for example triphenylphosphine, tris(*ortho*-tolyl)phosphine or tri(*tert*-butyl)phosphine. Suzuki coupling is performed in the presence of a base, for example sodium carbonate, potassium carbonate, cesium carbonate, lithium hydroxide, potassium phosphate or an organic base such as tetraethylammonium carbonate or tetraethylammonium hydroxide. Yamamoto coupling employs a Ni(0) complex, for example bis(1,5-cyclooctadienyl) nickel(0).
- As alternatives to halogens as described above, leaving groups of formula -O-SO₂Z⁰ can be used wherein Z⁰ is an alkyl or aryl group, preferably C₁₋₁₀ alkyl or C₆₋₁₂ aryl. Particular examples of such leaving groups are tosylate, mesylate and triflate.
- Especially suitable and preferred synthesis methods of the repeating units of formula I and the conjugated polymers comprising them are illustrated in the synthesis schemes shown hereinafter.

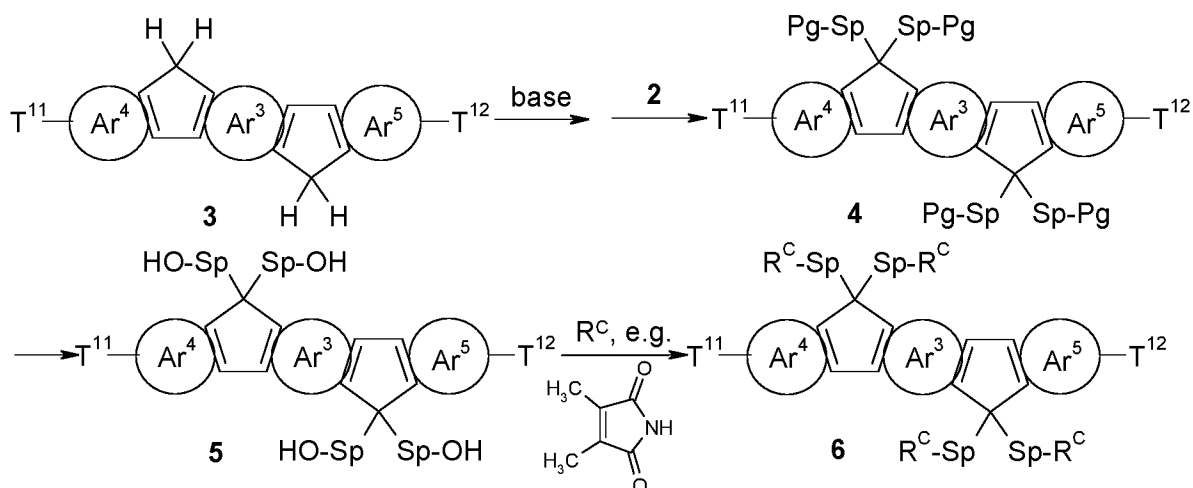
Scheme 1



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10

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wherein Pg means a protecting group, T¹¹ and T¹² are terminal groups such as H, F, Cl, Br, I, B(OR)₂, SnR₃, ZnX, MgX, and Ar³⁻⁵, Sp and R^C have the meanings as given above and below, Sp is for example (CH₂)_n with n being an integer from 1 to 20, and R^C is for example 2,3-dimethyl-N-maleimide.

20

Novel methods of preparing repeating units of formula I and monomers and polymers comprising them as described above and below are another aspect of the invention.

25

30

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

35

Thus, another aspect of the invention relates to a composition comprising one or more polymers according to the present invention and one or more small molecule compounds and/or polymers having one or more of a

charge-transport, semiconducting, electrically conducting, photoconducting, hole blocking and electron blocking property.

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

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

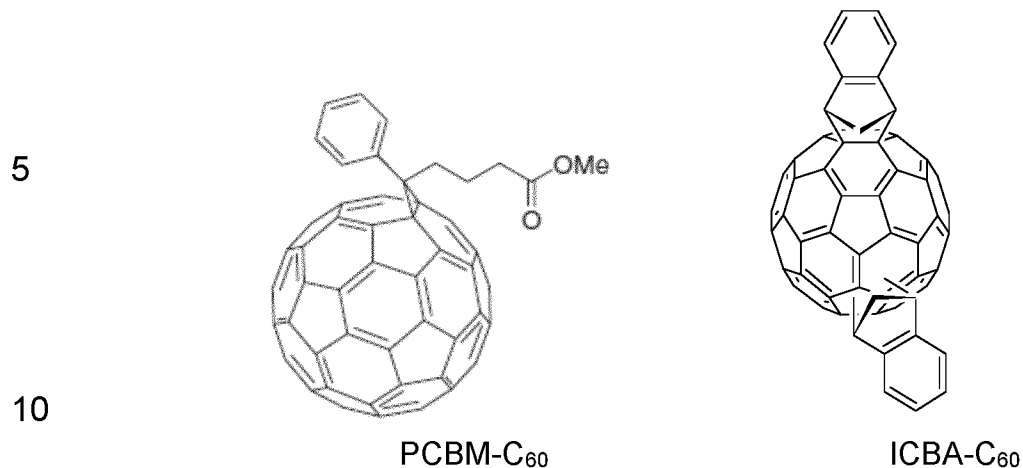
15 In a preferred embodiment the second n-type OSC compound is a non-fullerene acceptor (NFA) small molecule having an A-D-A structure as described above with an electron donating polycyclic core and two terminal electron withdrawing groups attached thereto.

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

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

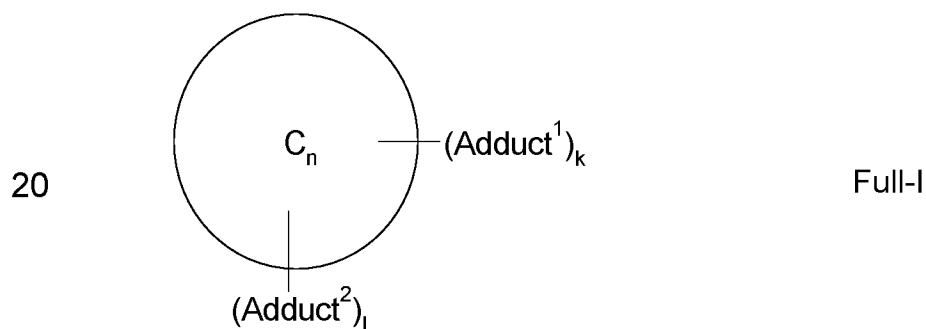
30 The fullerene is for example an indene-C₆₀-fullerene bisadduct like ICBA, or a (6,6)-phenyl-butyric acid methyl ester derivatized methano C₆₀ fullerene, also known as "PCBM-C₆₀" or "C₆₀PCBM", as disclosed for example in G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, *Science* 1995, Vol. 270, p. 1789 ff and having the structure shown below, or structural analogous
35 compounds with e.g. a C₆₁ fullerene group, a C₇₀ fullerene group, or a C₇₁ fullerene group, or an organic polymer (see for example Coakley, K. M. and

McGehee, M. D. *Chem. Mater.* 2004, 16, 4533).



15

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



wherein

25

C_n denotes a fullerene composed of n carbon atoms, optionally with one or more atoms trapped inside,

30

Adduct¹ is a primary adduct appended to the fullerene C_n with any connectivity,

Adduct² is a secondary adduct, or a combination of secondary adducts, appended to the fullerene C_n with any connectivity,

35

k is an integer ≥ 1 ,

and

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

5

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

10

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

15

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

20

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

25

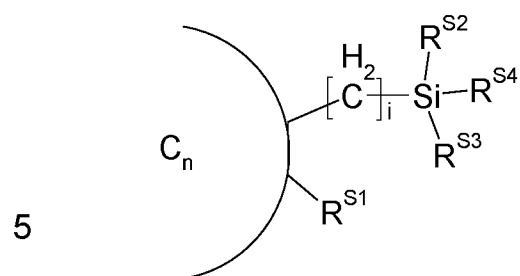
The endohedral fullerenes are preferably metallofullerenes. Suitable and preferred metallofullerenes include, without limitation, $La@C_{60}$, $La@C_{82}$, $Y@C_{82}$, $Sc_3N@C_{80}$, $Y_3N@C_{80}$, $Sc_3C_2@C_{80}$ or a mixture of two or more of the aforementioned metallofullerenes.

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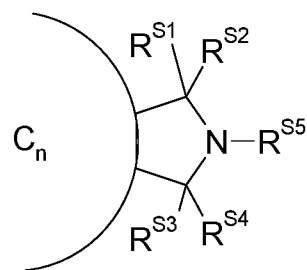
Preferably the fullerene C_n is substituted at a [6,6] and/or [5,6] bond, preferably substituted on at least one [6,6] bond.

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

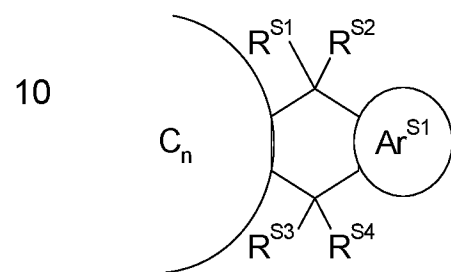
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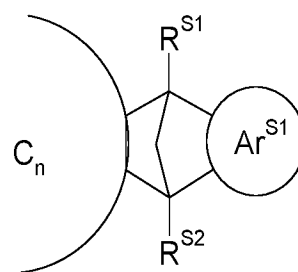
S-1



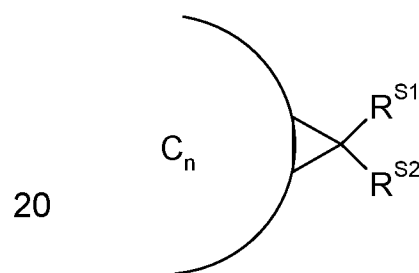
S-2



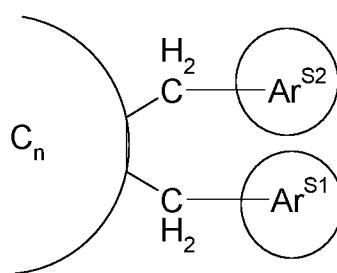
S-3



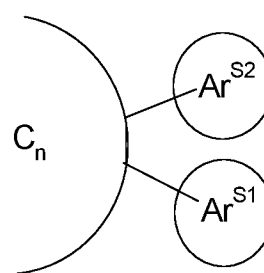
S-4



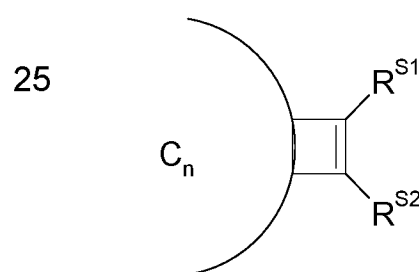
S-4



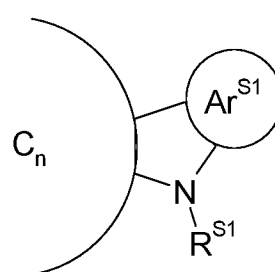
S-5



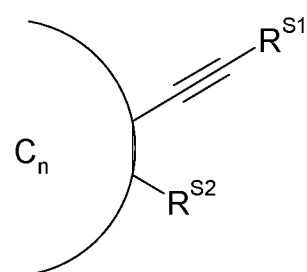
S-6



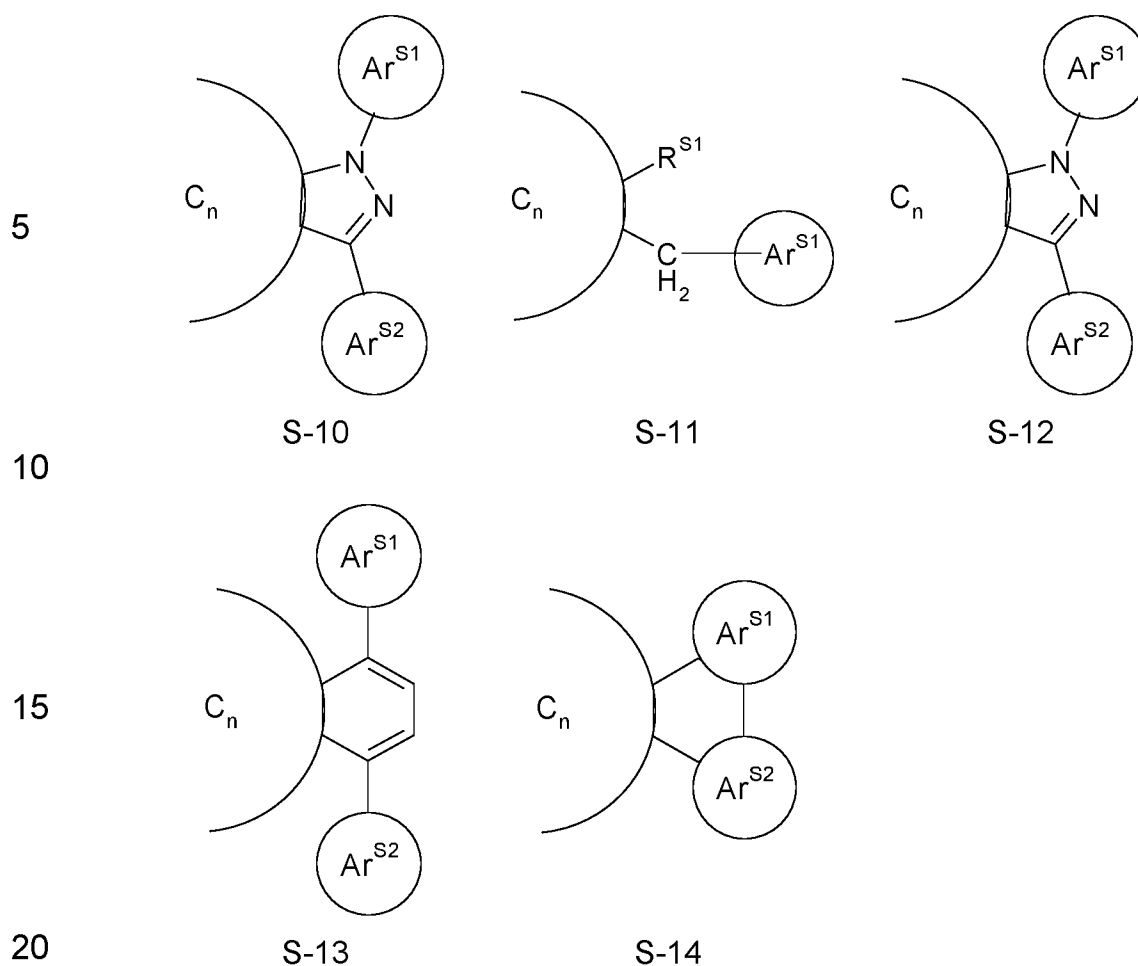
S-7



S-8



S-9



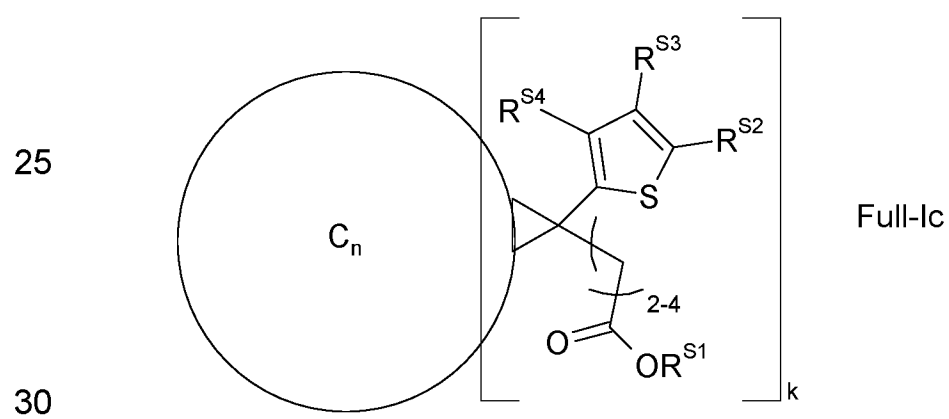
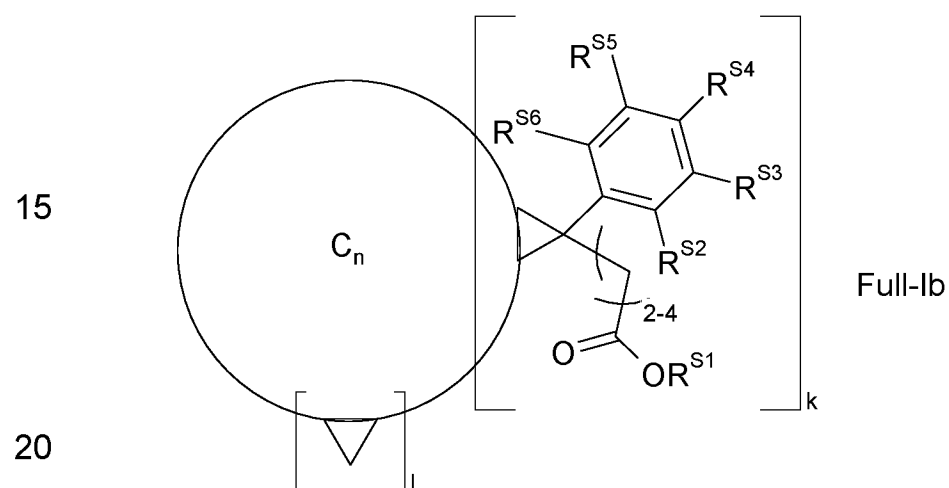
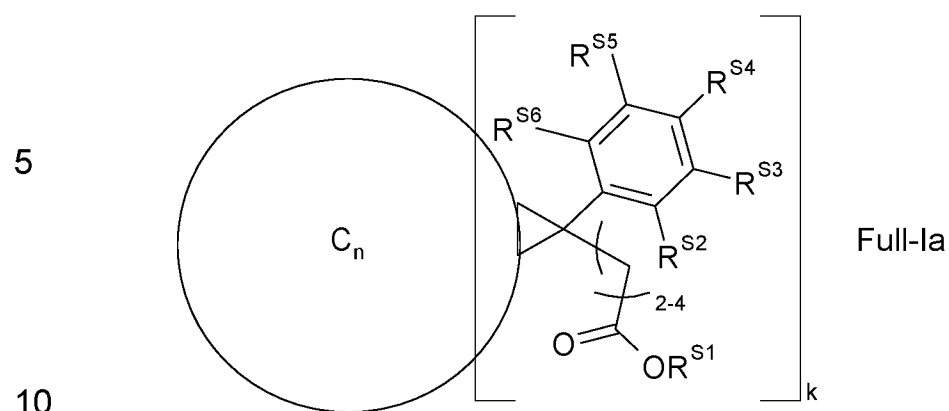
wherein

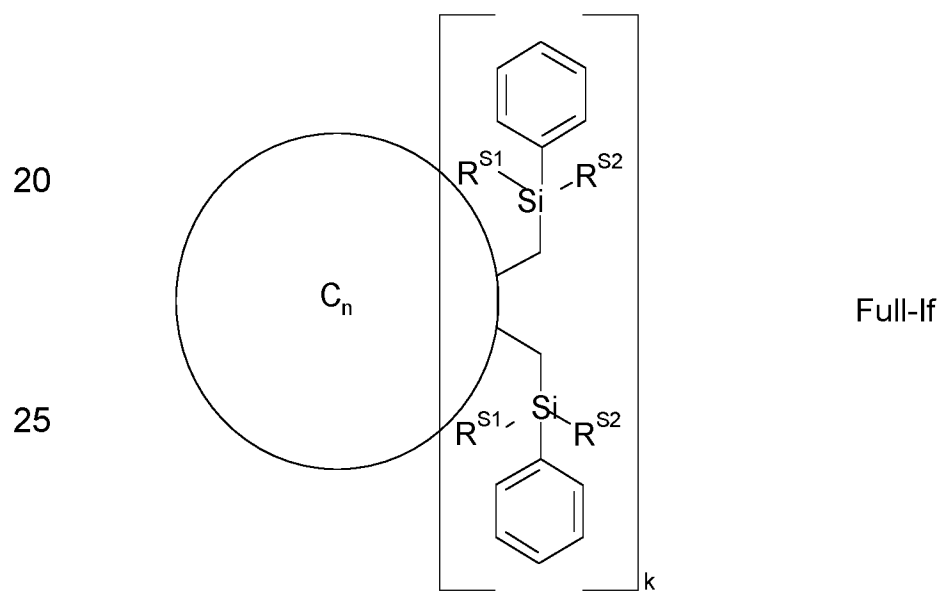
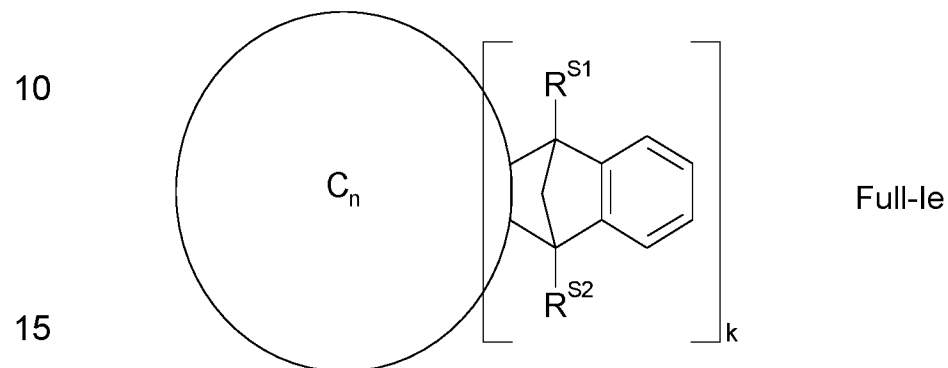
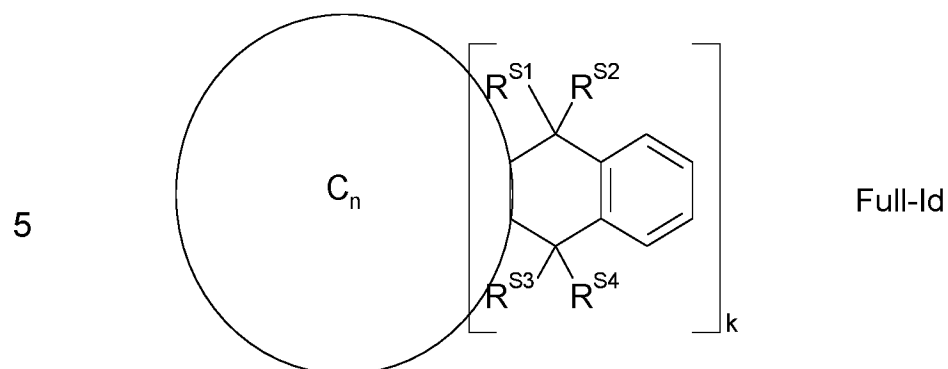
25 Ar^{S1} , Ar^{S2} denote, independently of each other, an aryl or heteroaryl group with 5 to 20, preferably 5 to 15, ring atoms, which is mono- or polycyclic, and which is optionally substituted by one or more identical or different substituents having one of the meanings of L as defined above and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

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

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

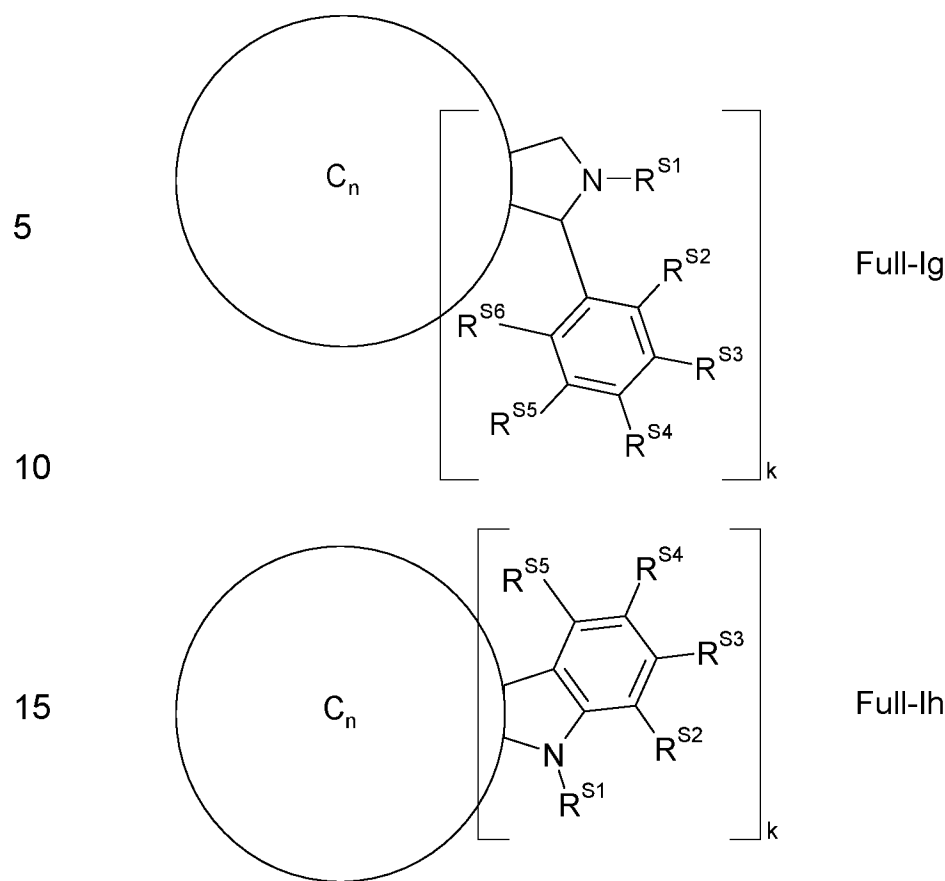
35 Preferred compounds of formula Full-I are selected from the following subformulae:





30

35



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

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

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

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

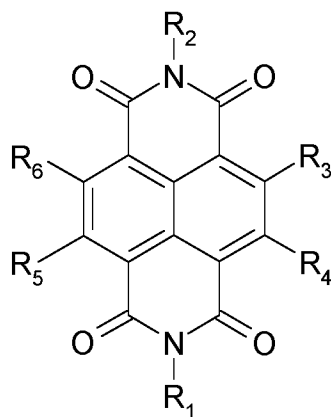
Adv. Mater. **2016**, 28, 8546–8551, *J. Am. Chem. Soc.*, **2016**, 138, 7248–7251 and *J. Mater. Chem. A*, **2016**, 4, 17604.

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

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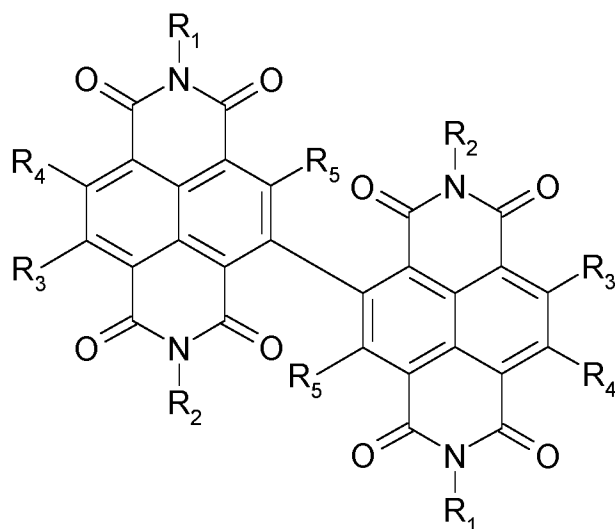
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NDI1

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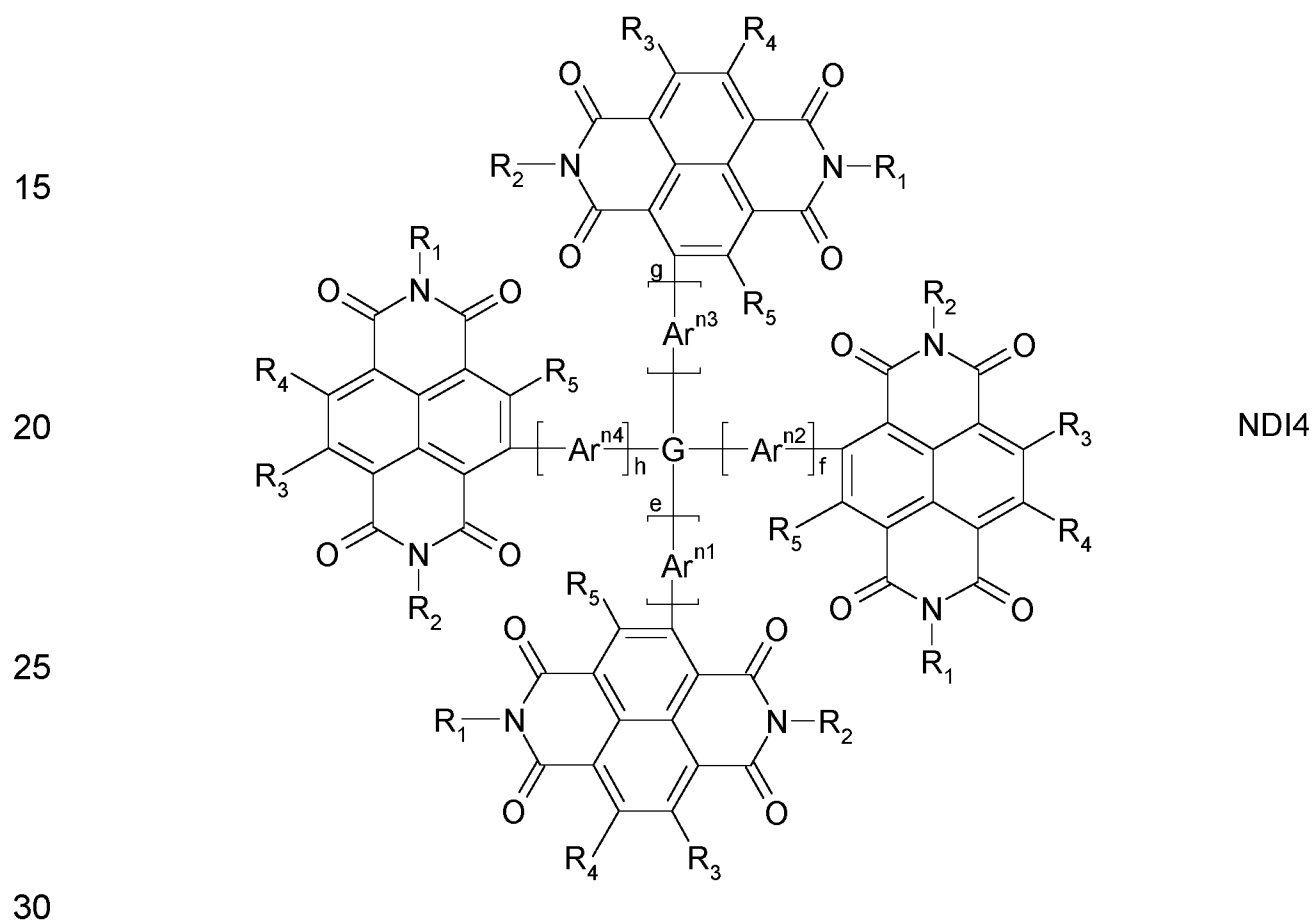
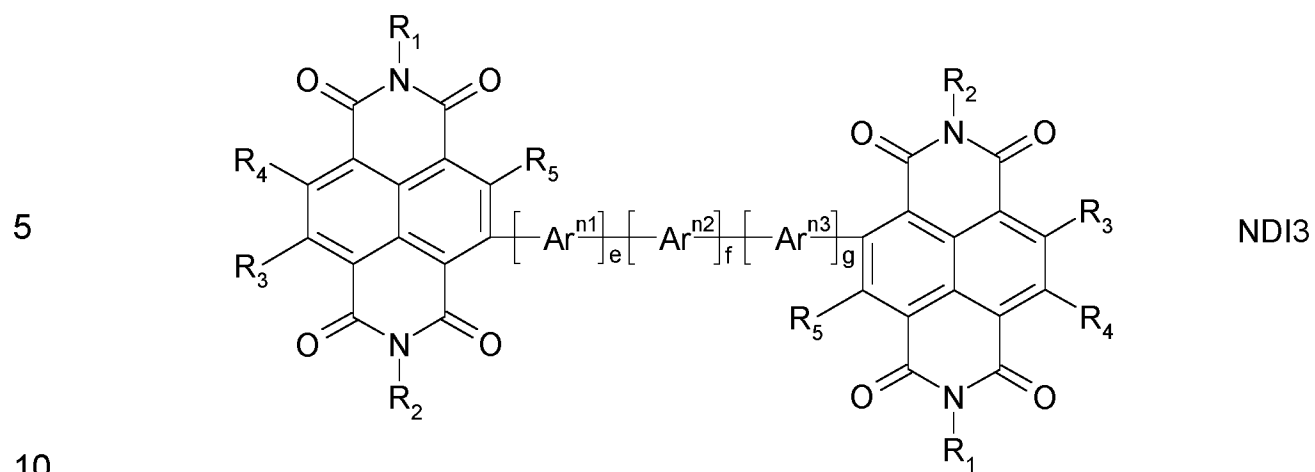
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NDI2

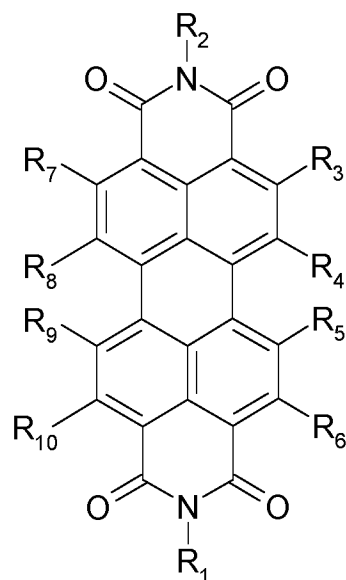
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PDI1

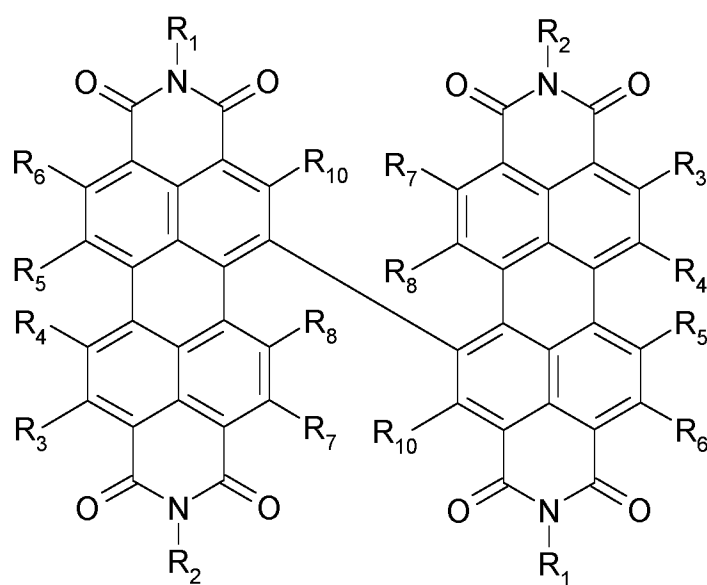
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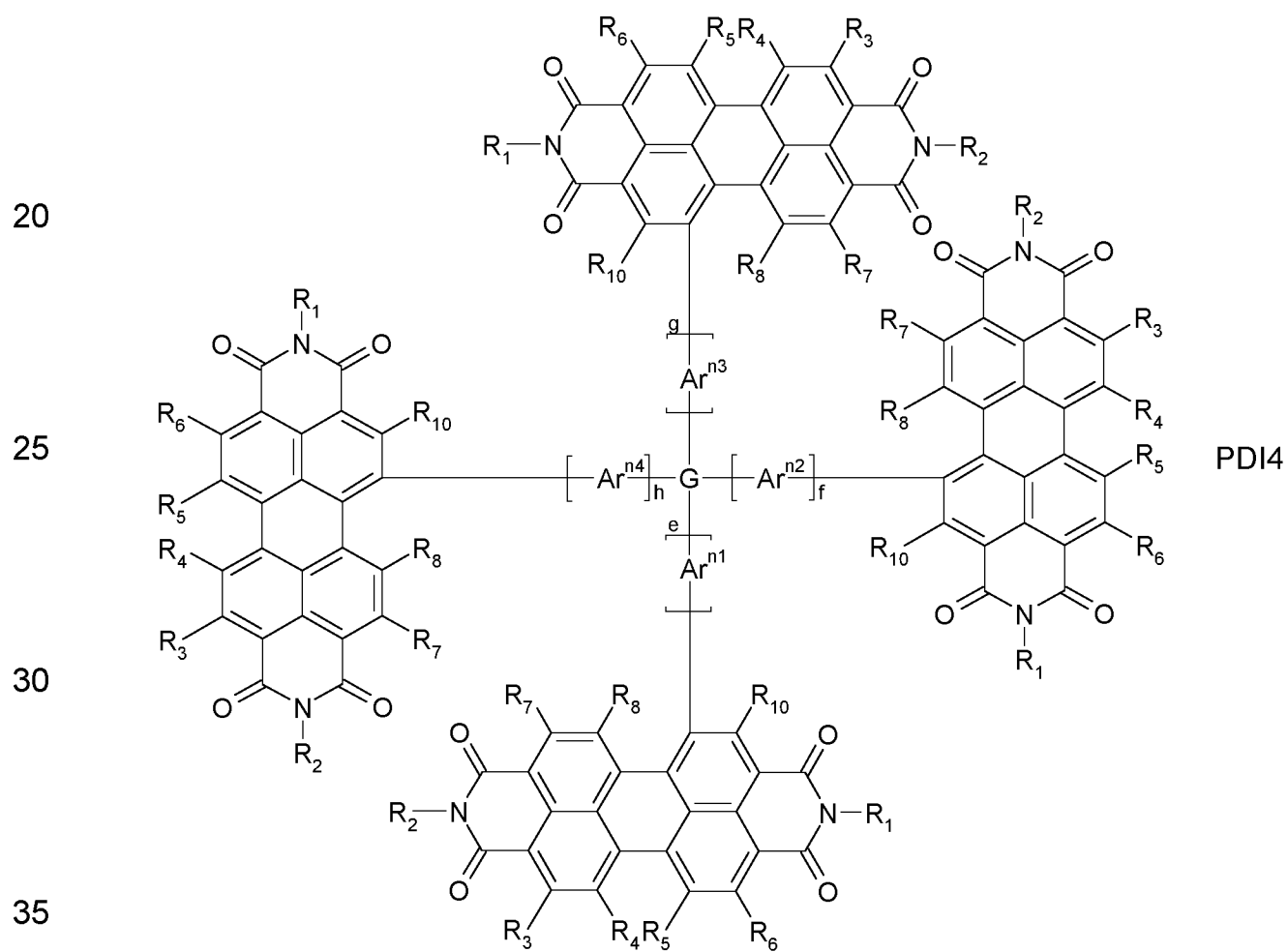
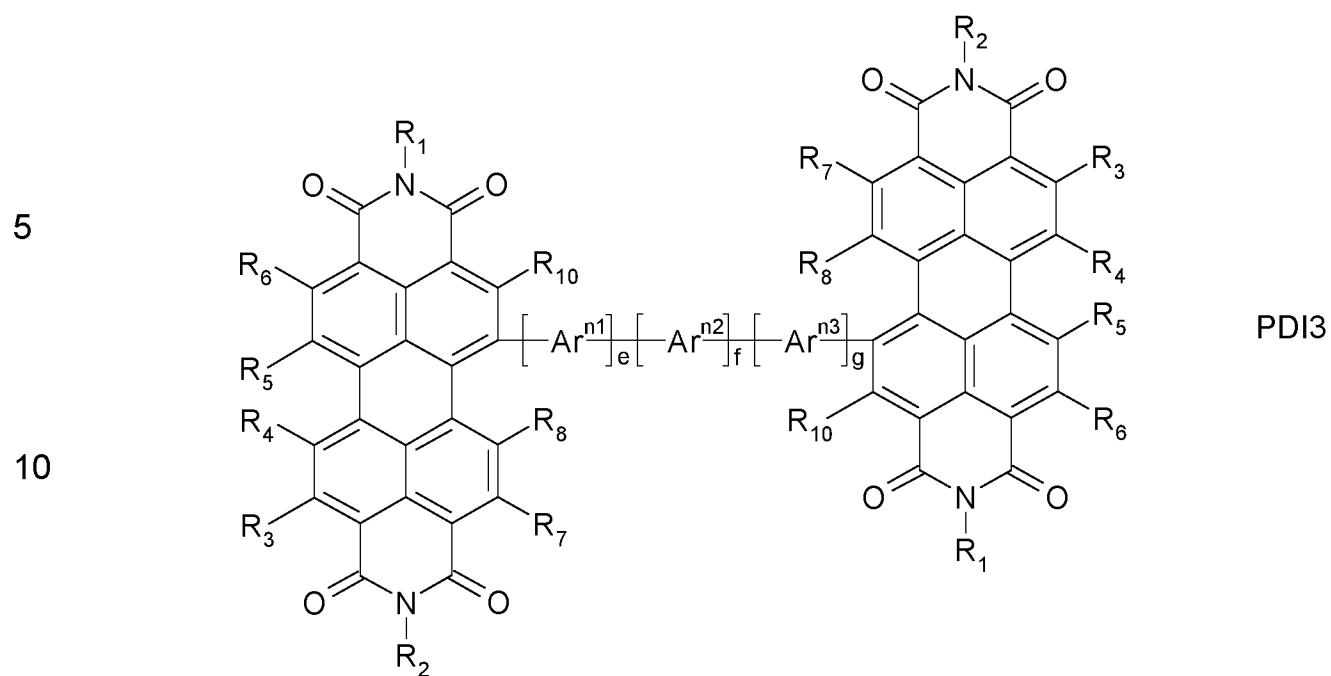
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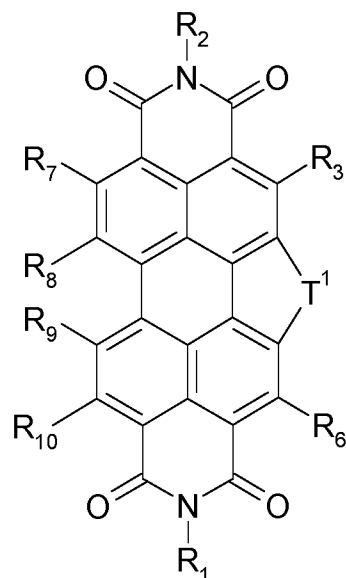


PDI2



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PDI5

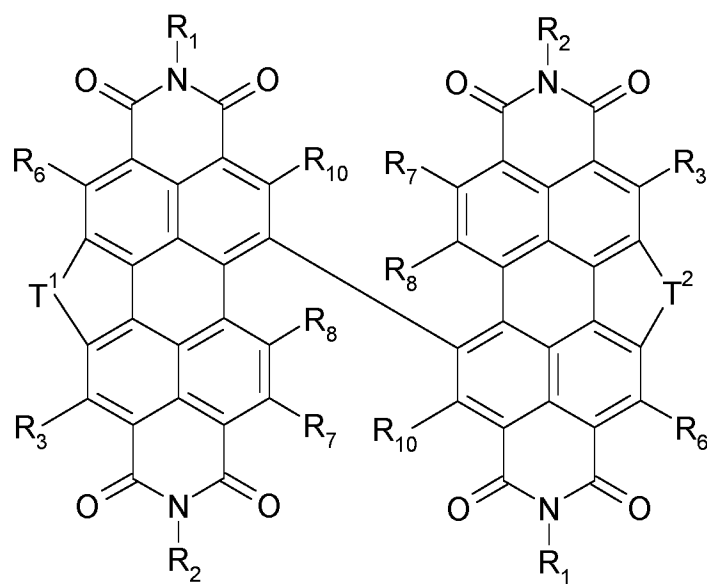
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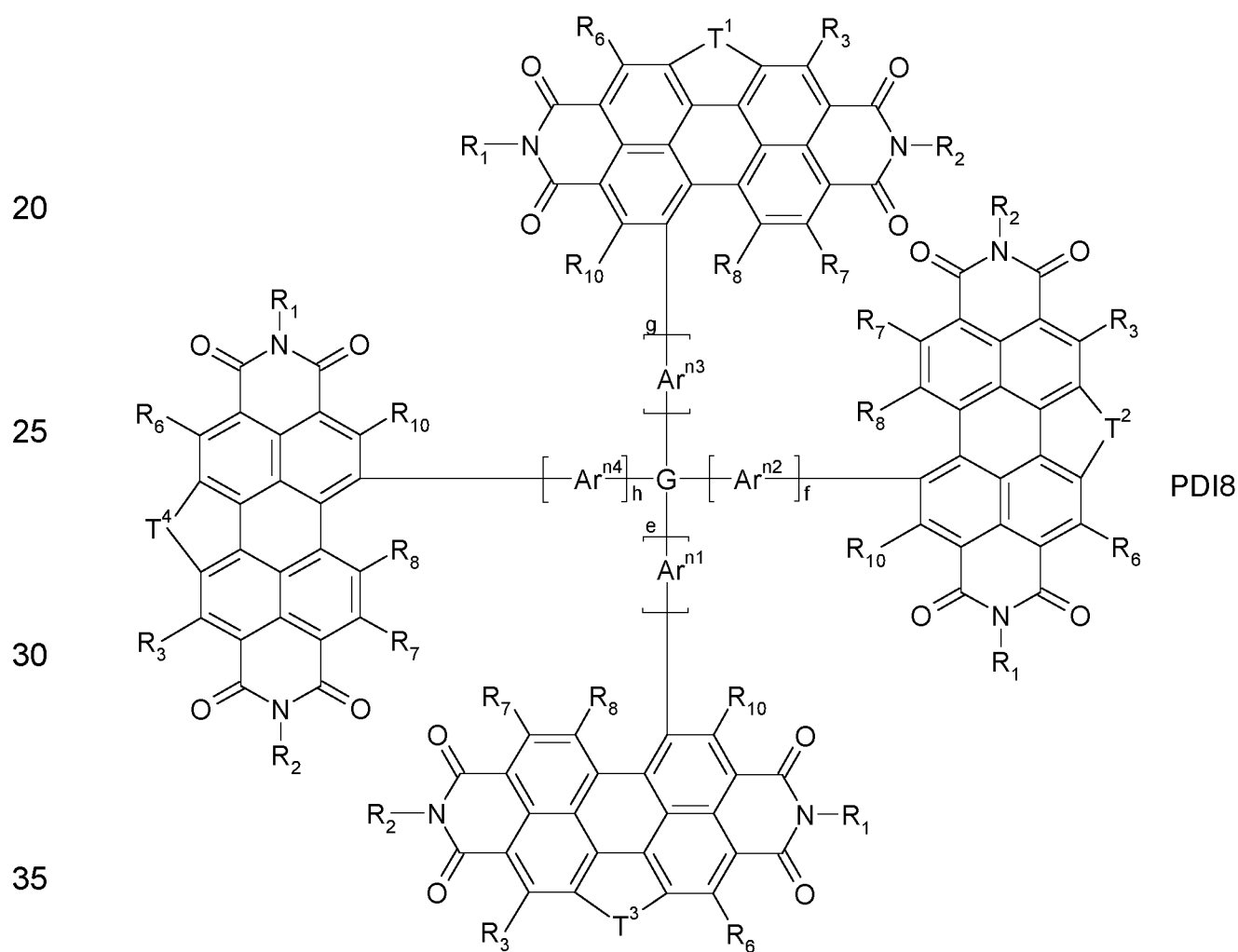
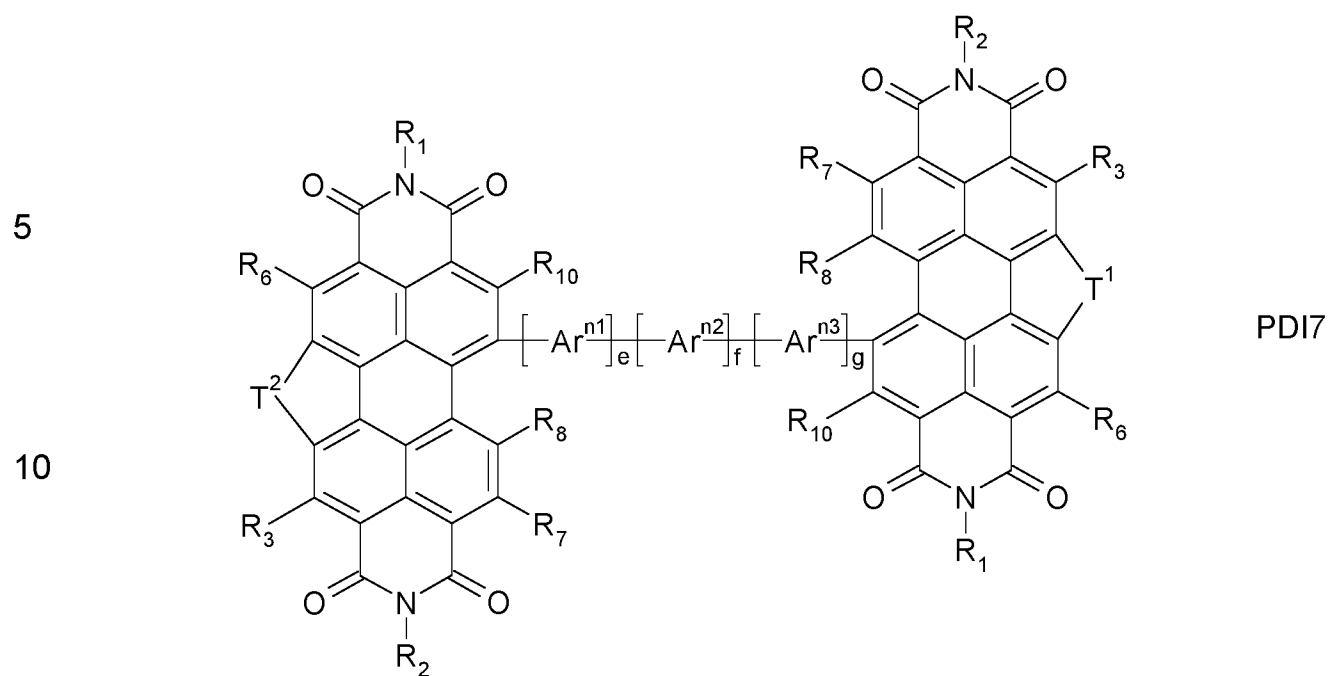
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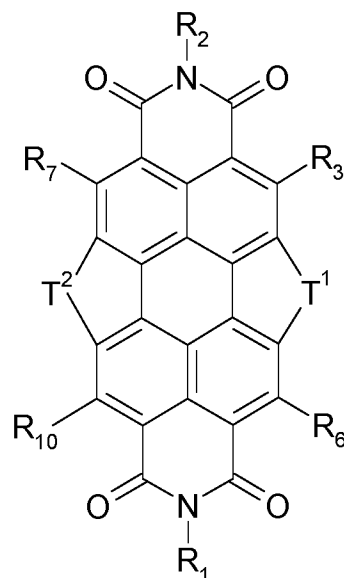


PDI6



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PDI9

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

20

R^{1-10} Z^1 , H, F, Cl, or straight-chain, branched or cyclic alkyl with 1 to 30, preferably 1 to 20, C atoms, in which one or more CH_2 groups are optionally replaced by $-O-$, $-S-$, $-C(=O)-$, $-C(=S)-$, $-C(=O)-O-$, $-O-C(=O)-$, $-NR^0-$, $-SiR^0R^{00}-$, $-CF_2-$, $-CR^0=CR^{00}-$, $-CY^1=CY^2-$ or $-C\equiv C-$ in such a manner that O and/or S atoms are not linked directly to one another, and in which one or more H atoms are optionally replaced by F, Cl, Br, I or CN, and in which one or more CH_2 or CH_3 groups are optionally replaced by a cationic or anionic group, or aryl, heteroaryl, arylalkyl, heteroarylalkyl, aryloxy or heteroaryloxy, wherein each of the aforementioned cyclic groups has 5 to 20 ring atoms, is mono- or polycyclic, does optionally contain fused rings, and is unsubstituted or substituted by one or more identical or different groups L,

25

30

35

Z^1 an electron withdrawing group, preferably having one of the preferred meanings as given above for formula T, very preferably CN,

- Y¹, Y² H, F, Cl or CN,
- 5 L F, Cl, -NO₂, -CN, -NC, -NCO, -NCS, -OCN, -SCN, R⁰, OR⁰, SR⁰, -C(=O)X⁰, -C(=O)R⁰, -C(=O)-OR⁰, -O-C(=O)-R⁰, -NH₂, -NHR⁰, -NR⁰R⁰⁰, -C(=O)NHR⁰, -C(=O)NR⁰R⁰⁰, -SO₃R⁰, -SO₂R⁰, -OH, -NO₂, -CF₃, -SF₅, or optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 30, preferably 1 to 20 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, preferably F, -CN, R⁰, -OR⁰, -SR⁰, -C(=O)-R⁰, -C(=O)-OR⁰, -O-C(=O)-R⁰, -O-C(=O)-OR⁰, -C(=O)-NHR⁰, or -C(=O)-NR⁰R⁰⁰,
- 10 T¹⁻⁴ -O-, -S-, -C(=O)-, -C(=S)-, -CR⁰R⁰⁰-, -SiR⁰R⁰⁰-, -NR⁰-, -CR⁰=CR⁰⁰- or -C≡C-,
- 15 G C, Si, Ge, C=C or a four-valent aryl or heteroaryl group that has from 5 to 20 ring atoms, is mono- or polycyclic, optionally contains fused rings, and is unsubstituted or substituted by one or more identical or different groups R¹ or L,
- 20 Arⁿ¹⁻ⁿ⁴ independently of each other, and on each occurrence identically or differently arylene or heteroarylene that has from 5 to 20 ring atoms, is mono- or polycyclic, optionally contains fused rings, and is unsubstituted or substituted by one or more identical or different groups R¹ or L, or CY¹=CY² or -C≡C-,
- 25 e, f, g, h 0 or an integer from 1 to 10.
- 30 In another preferred embodiment the second n-type OSC compound is a conjugated OSC polymer. Preferred n-type OSC polymers are described, for example, in Acc. Chem. Res., 2016, 49 (11), pp 2424–2434 and WO 2013/142841 A1.
- 35 Preferred n-type conjugated OSC polymers for use as second n-type OSC compound in this preferred embodiment comprise one or more units

derived from perylene or naphthalene are poly[[N,N'-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)], poly[[N,N'-bis(2-hexyldecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-thiophene].

5

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

10

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

15

Preferred solvents are aliphatic hydrocarbons, chlorinated hydrocarbons, aromatic hydrocarbons, ketones, ethers and mixtures thereof. Further suitable and preferred solvents used include 1,2,4-trimethylbenzene, 1,2,3,4-tetra-methyl benzene, pentylbenzene, mesitylene, cumene, cymene, cyclohexylbenzene, diethylbenzene, tetralin, indane, 1,5-

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dimethyltetraline, decalin, 1-methylnaphthalene, 2,6-lutidine, 2-chlorobenzotrifluoride, N,N-dimethylformamide, 2-chloro-6-fluorotoluene, 2-fluoroanisole, anisole, 2,3-dimethylpyrazine, 4-fluoroanisole, 3-fluoroanisole, 3-trifluoro-methylanisole, 2-methylanisole, phenetol, 4-methylanisole, 3-methylanisole, 4-fluoro-3-methylanisole, 2-fluorobenzonitrile, 4-fluoroveratrol, 2,6-dimethylanisole, 3-fluorobenzonitrile, 2,5-dimethylanisole, 2,4-dimethylanisole, benzonitrile, 3,5-dimethylanisole, N,N-dimethylaniline, ethyl benzoate, 1-fluoro-3,5-dimethoxybenzene, N-methylpyrrolidinone, 3-fluorobenzo-trifluoride, benzotrifluoride, dioxane, trifluoromethoxy-benzene, 4-fluorobenzotrifluoride, 3-fluoropyridine, toluene, 2-fluoro-toluene, 2-fluorobenzotrifluoride, 3-fluorotoluene, 4-isopropylbiphenyl, phenyl ether, pyridine, 4-fluorotoluene, 2,5-difluorotoluene, 1-chloro-2,4-difluorobenzene, 2-fluoropyridine, 3-chlorofluoro-benzene, 1-chloro-2,5-difluorobenzene, 4-chlorofluorobenzene, chloro-benzene, o-dichlorobenzene, 2-chlorofluorobenzene, p-xylene, m-xylene, o-xylene, a mixture of o-, m-, and p-xylene, 2-fluoro-m-xylene, 3-fluoro-o-xylene, tetrahydrofuran,

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- morpholine, 1,4-dioxane, 2-methylthiophene, 3-methylthiophene, chloroform, 1,2-dichloroethane, dichloromethane, carbon tetrachloride, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, acetone, methylethylketone, propiophenone, acetophenone, cyclohexanone, ethyl acetate, n-butyl acetate, ethyl benzoate, ethyl benzoate, dimethylacetamide, dimethylsulfoxide, or mixtures of the aforementioned. Solvents with relatively low polarity are generally preferred.
- Examples of especially preferred solvents include, without limitation, dichloromethane, trichloromethane, chlorobenzene, o-dichlorobenzene, tetrahydrofuran, anisole, 2,4-dimethylanisole, 1-methylnaphthalene, morpholine, toluene, o-xylene, m-xylene, p-xylene, 1,4-dioxane, acetone, methylethylketone, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, ethyl acetate, n-butyl acetate, N,N-dimethylformamide, dimethylacetamide, dimethylsulfoxide, 1,5-dimethyltetraline, propiophenone, acetophenone, tetralin, 2-methylthiophene, 3-methylthiophene, decaline, indane, methyl benzoate, ethyl benzoate, mesitylene, or mixtures thereof.
- The concentration of the compounds or polymers in the solution is preferably 0.1 to 10% by weight, more preferably 0.5 to 5% by weight. Optionally, the solution also comprises one or more binders to adjust the rheological properties, as described for example in WO 2005/055248 A1.
- After the appropriate mixing and ageing, solutions are evaluated as one of the following categories: complete solution, borderline solution or insoluble. The contour line is drawn to outline the solubility parameter-hydrogen bonding limits dividing solubility and insolubility. 'Complete' solvents falling within the solubility area can be chosen from literature values such as published in "Crowley, J.D., Teague, G.S. Jr and Lowe, J.W. Jr., *Journal of Paint Technology*, **1966**, 38 (496), 296 ". Solvent blends may also be used and can be identified as described in "Solvents, W. H. Ellis, Federation of Societies for Coatings Technology, p9-10, 1986".
- Such a procedure may lead to a blend of 'non' solvents that will dissolve both the polymers of the present invention, although it is desirable to have

at least one true solvent in a blend.

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

10 In a composition according to the present invention comprising a first polymer, which is polymer according to the present invention, and a second conjugated polymer, the ratio 1st polymer: 2nd polymer is preferably from 5:1 to 1:5 by weight, more preferably from 3:1 to 1:3 by weight, most
15 preferably 2:1 to 1:2 by weight.

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

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

Preferably, the polymeric binder comprises a weight average molecular weight in the range of 1,000 to 5,000,000 g/mol, especially 1,500 to
30 1,000,000 g/mol and more preferable 2,000 to 500,000 g/mol. Surprising effects can be achieved with polymers having a weight average molecular weight of at least 10,000 g/mol, more preferably at least 100,000 g/mol.

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

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

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

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

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

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

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

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

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

- 5 Suitable polymers as binders include poly(1,3-butadiene), polyphenylene, polystyrene, poly(α -methylstyrene), poly(α -vinyl naphthalene), poly(vinyltoluene), polyethylene, cis-polybutadiene, polypropylene, polyisoprene, poly(4-methyl-1-pentene), poly(4-methylstyrene), poly(chlorotrifluoroethylene), poly(2-methyl-1,3-butadiene), poly(p-xylylene), poly(α - α '- α '- α ' tetrafluoro-p-xylylene), poly[1,1-(2-methyl
- 10 propane)bis(4-phenyl)carbonate], poly(cyclohexyl methacrylate), poly(chlorostyrene), poly(2,6-dimethyl-1,4-phenylene ether), polyisobutylene, poly(vinyl cyclohexane), poly(vinylcinnamate), poly(4-vinylbiphenyl), 1,4-polyisoprene, polynorbornene, poly(styrene-block-butadiene); 31% wt styrene, poly(styrene-block-butadiene-block-styrene);
- 15 30% wt styrene, poly(styrene-co-maleic anhydride) (and ethylene/butylene) 1 - 1.7% maleic anhydride, poly(styrene-block-ethylene/butylene-block-styrene) triblock polymer 13% styrene, poly(styrene-block-ethylene-propylene-block-styrene) triblock polymer
- 20 37% wt styrene, poly(styrene-block-ethylene/butylene-block-styrene) triblock polymer 29% wt styrene, poly(1-vinylnaphthalene), poly(1-vinylpyrrolidone-co-styrene) 64% styrene, poly(1-vinylpyrrolidone-co-vinyl acetate) 1.3:1, poly(2-chlorostyrene), poly(2-vinylnaphthalene), poly(2-vinylpyridine-co-styrene) 1:1, poly(4,5-Difluoro-2,2-bis(CF₃)-1,3-dioxole-co-tetrafluoroethylene) Teflon, poly(4-chlorostyrene), poly(4-methyl-1-pentene), poly(4-methylstyrene), poly(4-vinylpyridine-co-styrene) 1:1,
- 25 poly(alpha-methylstyrene), poly(butadiene-graft-poly(methyl acrylate-co-acrylonitrile)) 1:1:1, poly(butyl methacrylate-co-isobutyl methacrylate) 1:1, poly(butyl methacrylate-co-methyl methacrylate) 1:1,
- 30 poly(cyclohexylmethacrylate), poly(ethylene-co-1-butene-co-1-hexene) 1:1:1, poly(ethylene-co-ethylacrylate-co-maleic anhydride); 2% anhydride, 32% ethyl acrylate, poly(ethylene-co-glycidyl methacrylate) 8% glycidyl methacrylate, poly(ethylene-co-methyl acrylate-co-glycidyl methacrylate) 8% glycidyl methacrylate 25% methyl acrylate,
- 35 poly(ethylene-co-octene) 1:1, poly(ethylene-co-propylene-co-5-methylene-2-norbornene) 50% ethylene, poly(ethylene-co-tetrafluoroethylene) 1:1,

poly(isobutyl methacrylate), poly(isobutylene), poly(methyl methacrylate)-
 co-(fluorescein O-methacrylate) 80% methyl methacrylate, poly(methyl
 methacrylate-co-butyl methacrylate) 85% methyl methacrylate, poly(methyl
 methacrylate-co-ethyl acrylate) 5% ethyl acrylate, poly(propylene-co-
 5 butene) 12% 1-butene, poly(styrene-co-allyl alcohol) 40% allyl alcohol,
 poly(styrene-co-maleic anhydride) 7% maleic anhydride, poly(styrene-co-
 maleic anhydride) cumene terminated (1.3:1), poly(styrene-co-methyl
 methacrylate) 40% styrene, poly(vinyltoluene-co-alpha-methylstyrene)
 1:1, poly-2-vinylpyridine, poly-4-vinylpyridine, poly-alpha-pinene,
 10 polymethylmethacrylate, polybenzylmethacrylate, polyethylmethacrylate,
 polyethylene, polyethylene terephthalate, polyethylene-co-ethylacrylate
 18% ethyl acrylate, polyethylene-co-vinylacetate 12% vinyl acetate,
 polyethylene-graft-maleic anhydride 0.5% maleic anhydride,
 polypropylene, polypropylene-graft-maleic anhydride 8-10% maleic
 15 anhydride, polystyrene poly(styrene-block- ethylene/butylene-block -
 styrene) graft maleic anhydride 2% maleic anhydride 1:1:1 others,
 poly(styrene-block-butadiene) branched 1:1, poly(styrene-block-butadiene-
 block-styrene), 30% styrene, poly(styrene-block-isoprene) 10% wt styrene,
 poly(styrene-block-isoprene-block-styrene) 17% wt styrene, poly(styrene-
 20 co-4-chloromethylstyrene-co-4-methoxymethylstyrene 2:1:1, polystyrene-
 co-acrylonitrile 25% acrylonitrile, polystyrene-co-alpha-methylstyrene 1:1,
 polystyrene-co-butadiene 4% butadiene, polystyrene-co-butadiene
 45% styrene, polystyrene-co-chloromethylstyrene 1:1, polyvinylchloride,
 polyvinylcinnamate, polyvinylcyclohexane, polyvinylidenefluoride,
 25 polyvinylidenefluoride-co-hexafluoropropylene assume 1:1, poly(styrene-
 block-ethylene/propylene-block-styrene) 30% styrene, poly(styrene- block-
 ethylene/propylene-block-styrene) 18% styrene, poly(styrene- block-
 ethylene/propylene-block-styrene) 13% styrene, poly(styrene- block
 ethylene block-ethylene/propylene-block styrene) 32% styrene,
 30 poly(styrene- block ethylene block-ethylene/propylene-block styrene) 30%
 styrene, poly(styrene- block-ethylene/butylene-block-styrene) 31%
 styrene, poly(styrene- block-ethylene/butylene-block-styrene) 34%
 styrene, poly(styrene- block-ethylene/butylene-block-styrene) 30%
 styrene, poly(styrene- block-ethylene/butylene-block-styrene) 60%,
 35 styrene, branched or non-branched polystyrene-block-
 polybutadiene, polystyrene-block(polyethylene-ran-butylene)-block-

polystyrene, polystyrene-block-polybutadiene-block-polystyrene, polystyrene-(ethylene-propylene)-diblock-copolymers (e.g. KRATON®-G1701E, Shell), poly(propylene-co-ethylene) and poly(styrene-co-methylmethacrylate).

5

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

10

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

15

The organic binder may itself be a semiconductor, in which case it will be referred to herein as a semiconducting binder. The semiconducting binder is still preferably a binder of low permittivity as herein defined.

20

Semiconducting binders for use in the present invention preferably have a number average molecular weight (M_n) of at least 1500-2000, more preferably at least 3000, even more preferably at least 4000 and most preferably at least 5000. The semiconducting binder preferably has a charge carrier mobility of at least $10^{-5}\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, more preferably at least $10^{-4}\text{cm}^2\text{V}^{-1}\text{s}^{-1}$.

25

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

30

Another preferred embodiment of the invention relates to a polymer, or a composition comprising it, as described above and below, wherein the groups R^C are crosslinked, preferably by photocrosslinking or thermal crosslinking.

35

Another preferred embodiment of the invention relates to a pattern or patterned film comprising a polymer, or a composition comprising it, as

described above and below, wherein the groups R^C are crosslinked. The pattern or patterned a film is for example comprising, or consisting of, regions comprising the crosslinked polymer and regions without the polymer as described above and below.

5

Crosslinking of the groups R^C can be achieved by conventional means and methods that are known to the skilled person and are described in the literature, for example by a photo- or thermal crosslinking reaction. In order to facilitate or enhance the crosslinking reaction, the composition

10 comprising the polymer may further comprise an initiator, a catalyst or a sensitizer.

Patterns and patterned films can be made by means and methods that are known to the skilled person and are described in the literature, or in the

15 examples below, for example by exposing the polymer through a photomask or shadow mask to light or other actinic radiation, e.g. UV light, causing a photocrosslinking reaction of the groups R^C in the exposed regions, and subsequently rinsing the non-crosslinked polymer in the non-exposed regions.

20

The polymers and compositions according to the present invention are useful as charge transport, semiconducting, electrically conducting, photoconducting or light emitting materials in optical, electronic, optoelectronic, electroluminescent or photoluminescent components or

25 devices. In these devices, the polymers and compositions of the present invention are typically applied as thin layers or films.

Thus, the present invention also provides the use of the polymer or composition or layer in an electronic device. The polymer or composition

30 may be used as a high mobility semiconducting material in various devices and apparatus. The polymer or composition may be used, for example, in the form of a semiconducting layer or film. Accordingly, in another aspect, the present invention provides a semiconducting layer for use in an electronic device, the layer comprising a polymer or composition according

35 to the invention. The layer or film may be less than about 30 microns. For various electronic device applications, the thickness may be less than

about 1 micron thick. The layer may be deposited, for example on a part of an electronic device, by any of the aforementioned solution coating or printing techniques.

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

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

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

30 Ink jet printing is particularly preferred when high resolution layers and devices needs to be prepared. Selected formulations of the present invention may be applied to prefabricated device substrates by ink jet printing or microdispensing. Preferably industrial piezoelectric print heads
35 such as but not limited to those supplied by Aprion, Hitachi-Koki, InkJet Technology, On Target Technology, Picojet, Spectra, Trident, Xaar may be

used to apply the organic semiconductor layer to a substrate. Additionally semi-industrial heads such as those manufactured by Brother, Epson, Konica, Seiko Instruments Toshiba TEC or single nozzle microdispensers such as those produced by Microdrop and Microfab may be used.

5

In order to be applied by ink jet printing or microdispensing, the compounds or polymers should be first dissolved in a suitable solvent.

10

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

15

Apart from the requirements stated above the solvents should not have any detrimental effect on the chosen print head. Additionally, the solvents should preferably have boiling points $>100^{\circ}\text{C}$, 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.

20

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

25

A preferred solvent for depositing a polymer 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 reduces or prevents clogging of the jets and separation of

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the components during spraying. The solvent(s) may include those selected from the following list of examples: dodecylbenzene, 1-methyl-4-tert-butylbenzene, terpineol, limonene, isodurene, terpinolene, cymene, and diethylbenzene. The solvent may be a solvent mixture, that is a
5 combination of two or more solvents, each solvent preferably having a boiling point $>100^{\circ}\text{C}$, more preferably $>140^{\circ}\text{C}$. Such solvent(s) also enhance film formation in the layer deposited and reduce defects in the layer.

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

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

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

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

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

side of the photoactive layer.

Further preferably the OPV or OPD device comprises, between the photoactive layer and the first or second electrode, one or more additional
 5 buffer layers acting as hole transporting layer and/or electron blocking layer, which comprise a material such as metal oxide, like for example, ZTO, MoO_x, NiO_x, a conjugated polymer electrolyte, like for example PEDOT:PSS, a conjugated polymer, like for example polytriarylamine (PTAA), an insulating polymer, like for example nafion, polyethyleneimine
 10 or polystyrenesulphonate, an organic compound, like for example N,N'-diphenyl-N,N'-bis(1-naphthyl)(1,1'-biphenyl)-4,4'-diamine (NPB), N,N'-diphenyl-N,N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), or alternatively as hole blocking layer and/or electron transporting layer, which comprise a material such as metal oxide, like for example, ZnO_x,
 15 TiO_x, a salt, like for example LiF, NaF, CsF, a conjugated polymer electrolyte, like for example poly[3-(6-trimethylammoniumhexyl)thiophene], poly(9,9-bis(2-ethylhexyl)-fluorene)-*b*-poly[3-(6-trimethylammoniumhexyl)thiophene], or poly [(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] or an
 20 organic compound, like for example tris(8-quinolinolato)-aluminum(III) (Alq₃), 4,7-diphenyl-1,10-phenanthroline.

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

25

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

- optionally a substrate,
- a high work function electrode, preferably comprising a metal oxide, like
 30 for example ITO, serving as anode,
- an optional conducting polymer layer or hole transport layer, preferably comprising an organic polymer or polymer blend, for example of PEDOT:PSS (poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate), or TBD (N,N'-dyphenyl-N-N'-bis(3-methylphenyl)-
 35 1,1'biphenyl-4,4'-diamine) or NBD (N,N'-dyphenyl-N-N'-bis(1-naphthylphenyl)-1,1'biphenyl-4,4'-diamine),

- a layer, also referred to as "photoactive layer", comprising a p-type and an n-type organic semiconductor, which can exist for example as a p-type/n-type bilayer or as distinct p-type and n-type layers, or as blend or p-type and n-type semiconductor, forming a BHJ,
 - 5 - optionally a layer having electron transport properties, for example comprising LiF or PFN,
 - a low work function electrode, preferably comprising a metal like for example aluminum, serving as cathode,
 - 10 wherein at least one of the electrodes, preferably the anode, is transparent to visible light, and
 - wherein the n-type semiconductor is a polymer according to the present invention.
- 15 A second preferred OPV device according to the invention is an inverted OPV device and comprises the following layers (in the sequence from bottom to top):
- optionally a substrate,
 - a high work function metal or metal oxide electrode, comprising for
 - 20 example ITO, serving as cathode,
 - a layer having hole blocking properties, preferably comprising an organic polymer, polymer blend, metal or metal oxide like TiO_x , ZnO_x , Ca, Mg, poly(ethyleneimine), poly(ethyleneimine) ethoxylated or poly [(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)],
 - 25 - a photoactive layer comprising a p-type and an n-type organic semiconductor, situated between the electrodes, which can exist for example as a p-type/n-type bilayer or as distinct p-type and n-type layers, or as blend or p-type and n-type semiconductor, forming a BHJ,
 - 30 - an optional conducting polymer layer or hole transport layer, preferably comprising an organic polymer or polymer blend, metal or metal oxide, for example PEDOT:PSS, nafion, a substituted triaryl amine derivative like for example TBD or NBD, or WO_x , MoO_x , NiO_x , Pd or Au,
 - an electrode comprising a high work function metal like for example
 - 35 silver, serving as anode,
 - wherein at least one of the electrodes, preferably the cathode, is

transparent to visible light, and

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

5 In the OPV devices of the present invention the p-type and n-type semiconductor materials are preferably selected from the materials, like the polymer/polymer/fullerene systems, as described above.

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

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

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

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

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

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

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

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

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

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

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

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

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

The light absorber which is at least in part inorganic is without limitation composed of a material having perovskite crystalline structure, a material having 2D crystalline perovskite structure (e.g. CrystEngComm, 2010,12, 2646-2662), Sb_2S_3 (stibnite), $\text{Sb}_2(\text{S}_x\text{Se}_{(x-1)})_3$, $\text{PbS}_x\text{Se}_{(x-1)}$, $\text{CdS}_x\text{Se}_{(x-1)}$, ZnTe , CdTe , $\text{ZnS}_x\text{Se}_{(x-1)}$, InP , FeS , FeS_2 , Fe_2S_3 , Fe_2SiS_4 , Fe_2GeS_4 , Cu_2S , CuInGa , $\text{CuIn}(\text{Se}_x\text{S}_{(1-x)})_2$, $\text{Cu}_3\text{Sb}_x\text{Bi}_{(x-1)}$, $(\text{S}_y\text{Se}_{(y-1)})_3$, Cu_2SnS_3 , $\text{SnS}_x\text{Se}_{(x-1)}$, Ag_2S , AgBiS_2 , BiSI , BiSeI , $\text{Bi}_2(\text{S}_x\text{Se}_{(x-1)})_3$, $\text{BiS}_{(1-x)}\text{Se}_x\text{I}$, WSe_2 , AlSb , metal halides (e.g. BiI_3 , Cs_2SnI_6), chalcopyrite (e.g. $\text{CuIn}_x\text{Ga}_{(1-x)}(\text{S}_y\text{Se}_{(1-y)})_2$), kesterite (e.g. $\text{Cu}_2\text{ZnSnS}_4$, $\text{Cu}_2\text{ZnSn}(\text{Se}_x\text{S}_{(1-x)})_4$, $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{S}_4$) and metal oxide (e.g. CuO , Cu_2O) or a mixture thereof.

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

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

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

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

A is a monovalent organic cation, a metal cation or a mixture of two or more of these cations
 B is a divalent cation and
 X is F, Cl, Br, I, BF_4 or a combination thereof.

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

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

Suitable and preferred perovskite materials are CsSnI_3 , $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$, $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$, $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}(\text{BF}_4)_x)_3$,
5 $\text{CH}_3\text{NH}_3\text{Sn}(\text{I}_{1-x}\text{Cl}_x)_3$, $\text{CH}_3\text{NH}_3\text{SnI}_3$ or $\text{CH}_3\text{NH}_3\text{Sn}(\text{I}_{1-x}\text{Br}_x)_3$ wherein x is each independently defined as follows: ($0 < x \leq 1$).

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

Suitable and preferred perovskites are also disclosed in WO 2013/171517,
15 claims 52 to 71 and claims 72 to 79, which is entirely incorporated herein by reference. The materials are defined as mixed-anion perovskites comprising two or more different anions selected from halide anions and chalcogenide anions. Preferred perovskites are disclosed on page 18, lines 5 to 17. As described, the perovskite is usually selected from
20 $\text{CH}_3\text{NH}_3\text{PbBrI}_2$, $\text{CH}_3\text{NH}_3\text{PbBrCl}_2$, $\text{CH}_3\text{NH}_3\text{PbIBr}_2$, $\text{CH}_3\text{NH}_3\text{PbICl}_2$, $\text{CH}_3\text{NH}_3\text{SnF}_2\text{Br}$, $\text{CH}_3\text{NH}_3\text{SnF}_2\text{I}$ and $(\text{H}_2\text{N}=\text{CH}-\text{NH}_2)\text{PbI}_{3z}\text{Br}_{3(1-z)}$, wherein z is greater than 0 and less than 1.

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

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

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

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

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

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

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

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

- 20 - optionally a substrate which, in any combination, can be flexible or rigid and transparent, semi-transparent or non-transparent and electrically conductive or non-conductive;
- a high work function electrode, preferably comprising a doped metal oxide, for example fluorine-doped tin oxide (FTO), tin-doped indium oxide (ITO), or aluminum-doped zinc oxide;
- 25 - an electron-selective layer which comprises one or more electron-transporting materials, at least one of which is a polymer according to the present invention, and which, in some cases, can also be a dense layer and/or be composed of nanoparticles, and which preferably comprises a metal oxide such as TiO_2 , ZnO_2 , SnO_2 , Y_2O_5 , Ga_2O_3 ,
30 SrTiO_3 , BaTiO_3 or combinations thereof;
- optionally a porous scaffold which can be conducting, semi-conducting or insulating, and which preferably comprises a metal oxide such as TiO_2 , ZnO_2 , SnO_2 , Y_2O_5 , Ga_2O_3 , SrTiO_3 , BaTiO_3 , Al_2O_3 , ZrO_2 , SiO_2 or combinations thereof, and which is preferably composed of
35 nanoparticles, nanorods, nanoflakes, nanotubes or nanocolumns;

- a layer comprising a light absorber which is at least in part inorganic, particularly preferably a metal halide perovskite as described above which, in some cases, can also be a dense or porous layer and which optionally partly or fully infiltrates into the underlying layer;
- 5 - optionally a hole selective layer, which comprises one or more hole-transporting materials, and which, in some cases, can also comprise additives such as lithium salts, for example LiY, where Y is a monovalent organic anion, preferably bis(trifluoromethylsulfonyl)imide, tertiary amines such as 4-tert-butylpyridine, or any other covalent or
- 10 ionic compounds, for example tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl)imide)), which can enhance the properties of the hole selective layer, for example the electrical conductivity, and/or facilitate its processing;
- and a back electrode which can be metallic, for example made of Au, Ag,
- 15 Al, Cu, Ca, Ni or combinations thereof, or non-metallic and transparent, semi-transparent or non-transparent.

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

20 top):

- optionally a substrate which, in any combination, can be flexible or rigid and transparent, semi-transparent or non-transparent and electrically conductive or non-conductive;
- a high work function electrode, preferably comprising a doped metal
- 25 oxide, for example fluorine-doped tin oxide (FTO), tin-doped indium oxide (ITO), or aluminum-doped zinc oxide;
- optionally a hole injection layer which, for example, changes the work function of the underlying electrode, and/or modifies the surface of the underlying layer and/or helps to planarize the rough surface of the
- 30 underlying layer and which, in some cases, can also be a monolayer;
- optionally a hole selective layer, which comprises one or more hole-transporting materials and which, in some cases, can also comprise additives such as lithium salts, for example LiY, where Y is a monovalent organic anion, preferably bis(trifluoromethylsulfonyl)imide, tertiary amines such as 4-tert-butylpyridine, or any other covalent or
- 35 ionic compounds, for example tris(2-(1H-pyrazol-1-yl)-4-tert-

butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl)imide)), which can enhance the properties of the hole selective layer, for example the electrical conductivity, and/or facilitate its processing;

- 5 - a layer comprising a light absorber which is at least in part inorganic, particularly preferably a metal halide perovskite as described or preferably described above;
- an electron-selective layer, which comprises one or more electron-transporting materials, at least one of which is a polymer according to the present invention and which, in some cases, can also be a dense
10 layer and/or be composed of nanoparticles, and which, for example, can comprise a metal oxide such as TiO₂, ZnO₂, SnO₂, Y₂O₅, Ga₂O₃, SrTiO₃, BaTiO₃ or combinations thereof, and/or which can comprise a substituted fullerene, for example [6,6]-phenyl C61-butyric acid methyl ester, and/or which can comprise a molecular, oligomeric or polymeric
15 electron-transport material, for example 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline, or a mixture thereof;

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

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

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

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

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

- (i) first mixing a polymer according to the present invention, optionally a binder or a precursor of a binder as described before, optionally a further electron transport material, optionally one or more further additives as described above and below and a solvent or solvent mixture as described above and below and
- (ii) applying such mixture to a substrate; and optionally evaporating the solvent(s) to form an electron selective layer according to the present invention.

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

Alternatively, the binder may be formed *in situ* by mixing or dissolving a polymer according to the present invention in a precursor of a binder, for example a liquid monomer, oligomer or crosslinkable polymer, optionally in the presence of a solvent, and depositing the mixture or solution, for example by dipping, spraying, painting or printing it, on a substrate to form

a liquid layer and then curing the liquid monomer, oligomer or crosslinkable polymer, for example by exposure to radiation, heat or electron beams, to produce a solid layer. If a preformed binder is used it may be dissolved together with the polymer in a suitable solvent as described before, and the solution deposited for example by dipping, spraying, painting or printing it on a substrate to form a liquid layer and then removing the solvent to leave a solid layer. It will be appreciated that solvents are chosen which are able to dissolve all ingredients of the formulation, and which upon evaporation from the solution blend give a coherent defect free layer.

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

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

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

or more additives into a material or a formulation as described before, or by ion-implantation of one or more additives into a material or a formulation as described before.

- 5 Additives used for this purpose can be organic, inorganic, metallic or hybrid materials. Additives can be molecular compounds, for example organic molecules, salts, ionic liquids, coordination complexes or organometallic compounds, polymers or mixtures thereof. Additives can also be particles, for example hybrid or inorganic particles, preferably
 10 nanoparticles, or carbon based materials such as fullerenes, carbon nanotubes or graphene flakes.

- Examples for additives that can enhance the electrical conductivity are for example halogens (e.g. I₂, Cl₂, Br₂, ICl, ICl₃, IBr and IF), Lewis acids (e.g.
 15 PF₅, AsF₅, SbF₅, BF₃, BCl₃, SbCl₅, BBr₃ and SO₃), protonic acids, organic acids, or amino acids (e.g. HF, HCl, HNO₃, H₂SO₄, HClO₄, FSO₃H and ClSO₃H), transition metal compounds (e.g. FeCl₃, FeOCl, Fe(ClO₄)₃, Fe(4-CH₃C₆H₄SO₃)₃, TiCl₄, ZrCl₄, HfCl₄, NbF₅, NbCl₅, TaCl₅, MoF₅, MoCl₅, WF₅, WCl₆, UF₆ and LnCl₃ (wherein Ln is a lanthanoid)), anions (e.g. Cl⁻, Br⁻, I⁻, I₃⁻, HSO₄⁻, SO₄²⁻, NO₃⁻, ClO₄⁻, BF₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻, FeCl₄⁻, Fe(CN)₆³⁻,
 20 and anions of various sulfonic acids, such as aryl-SO₃⁻), cations (e.g. H⁺, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Co³⁺ and Fe³⁺), O₂, redox active salts (e.g. XeOF₄, (NO₂⁺) (SbF₆⁻), (NO₂⁺) (SbCl₆⁻), (NO₂⁺) (BF₄⁻), NOBF₄, NOPF₆, AgClO₄, H₂IrCl₆ and La(NO₃)₃ · 6H₂O), strongly electron-accepting organic
 25 molecules (e.g. 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄-TCNQ)), transition metal oxides (e.g. WO₃, Re₂O₇ and MoO₃), metal-organic complexes of cobalt, iron, bismuth and molybdenum, (p-BrC₆H₄)₃NSbCl₆, bismuth(III) tris(trifluoroacetate), FSO₂OOSO₂F, acetylcholine, R₄N⁺, (R is an alkyl group), R₄P⁺ (R is a straight-chain or
 30 branched alkyl group 1 to 20), R₆As⁺ (R is an alkyl group), R₃S⁺ (R is an alkyl group) and ionic liquids (e.g. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide). Suitable cobalt complexes beside of tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl)imide)) are cobalt complex salts as
 35 described in WO 2012/114315, WO 2012/114316, WO 2014/082706, WO 2014/082704, EP 2883881 or JP 2013-131477.

Suitable lithium salts are beside of lithium bis(trifluoromethylsulfonyl)imide, lithium tris(pentafluoroethyl)trifluorophosphate, lithium dicyanamide, lithium methylsulfate, lithium trifluormethanesulfonate, lithium tetracyanoborate, lithium dicyanamide, lithium tricyanomethide, lithium thiocyanate, lithium chloride, lithium bromide, lithium iodide, lithium hexafluorophosphate, lithium tetrafluoroborate, lithium perchlorate, lithium hexafluoroantimonate, lithium hexafluoroarsenate or a combination of two or more. A preferred lithium salt is lithium bis(trifluoromethylsulfonyl)imide.

10

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

15

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

20

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

25

Suitable device structures for PSCs comprising a polymer according to the present invention, a semiconductor and a perovskite are described in WO 2014/020499, claims 1 and 3 to 14, which is entirely incorporated herein by reference. The surface-increasing scaffold structure described therein comprises nanoparticles which are applied and/or fixed on a support layer, e.g. porous TiO₂.

30

35

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

conducting) and p-type (hole-conducting) layers. Preferably, the thin film is a compact thin film.

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

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

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

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

20 There are two different types of tandem solar cells known in the art. The so called 2-terminal or monolithic tandem solar cells have only two connections. The two subcells (or synonymously semi cells) are connected in series. Therefore, the current generated in both subcells is identical (current matching). The gain in power conversion efficiency is due to an increase in voltage as the voltages of the two subcells add up.

25 The other type of tandem solar cells is the so called 4-terminal or stacked tandem solar cell. In this case, both subcells are operated independently. Therefore, both subcells can be operated at different voltages and can
30 also generate different currents. The power conversion efficiency of the tandem solar cell is the sum of the power conversion efficiencies of the two subcells.

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

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

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

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

25 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.

30 An OFET device according to the present invention preferably comprises:

- 35 - a source electrode,
- a drain electrode,
- a gate electrode,
- a semiconducting layer,

- one or more gate insulator layers,
- optionally a substrate.

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

The OFET device can be a top gate device or a bottom gate device. Suitable structures and manufacturing methods of an OFET device are known to the skilled in the art and are described in the literature, for
10 example in US 2007/0102696 A1.

The gate insulator layer preferably comprises a fluoropolymer, like e.g. the commercially available Cytop 809M® or Cytop 107M® (from Asahi Glass). Preferably the gate insulator layer is deposited, e.g. by spin-coating,
15 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
20 fluorosolvents are known in prior art, like for example the perfluoropolymers Teflon AF® 1600 or 2400 (from DuPont) or Fluoropel® (from Cytonix) or the perfluorosolvent FC 43® (Acros, No. 12377). Especially preferred are organic dielectric materials having a low permittivity (or dielectric constant) from 1.0 to 5.0, very preferably from 1.8
25 to 4.0 ("low *k* materials"), as disclosed for example in US 2007/0102696 A1 or US 7,095,044.

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

35 Alternatively, the polymers and compositions (hereinafter referred to as "materials") according to the present invention can be used in OLEDs, e.g.

as the active display material in a flat panel display applications, or as backlight of a flat panel display like e.g. a liquid crystal display. Common OLEDs are realized using multilayer structures. An emission layer is generally sandwiched between one or more electron-transport and/or hole-transport layers. By applying an electric voltage electrons and holes as charge carriers move towards the emission layer where their recombination leads to the excitation and hence luminescence of the lumophor units contained in the emission layer. The materials according to the present invention may be employed in one or more of the charge transport layers and/or in the emission layer, corresponding to their electrical and/or optical properties. Furthermore their use within the emission layer is especially advantageous, if the materials according to the present invention show electroluminescent properties themselves or comprise electroluminescent groups or compounds. The selection, characterization as well as the processing of suitable monomeric, oligomeric and polymeric compounds or materials for the use in OLEDs is generally known by a person skilled in the art, see, e.g., Müller *et al*, *Synth. Metals*, **2000**, 111-112, 31-34, Alcala, *J. Appl. Phys.*, **2000**, 88, 7124-7128 and the literature cited therein.

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

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

The doping process typically implies treatment of the semiconductor material with an oxidating or reducing agent in a redox reaction to form delocalized ionic centers in the material, with the corresponding counterions derived from the applied dopants. Suitable doping methods

comprise for example exposure to a doping vapor in the atmospheric pressure or at a reduced pressure, electrochemical doping in a solution containing a dopant, bringing a dopant into contact with the semiconductor material to be thermally diffused, and ion-implantation of the dopant into the semiconductor material.

When electrons are used as carriers, suitable dopants are for example halogens (e.g., I₂, Cl₂, Br₂, ICl, ICl₃, IBr and IF), Lewis acids (e.g., PF₅, AsF₅, SbF₅, BF₃, BCl₃, SbCl₅, BBr₃ and SO₃), protonic acids, organic acids, or amino acids (e.g., HF, HCl, HNO₃, H₂SO₄, HClO₄, FSO₃H and ClSO₃H), transition metal compounds (e.g., FeCl₃, FeOCl, Fe(ClO₄)₃, Fe(4-CH₃C₆H₄SO₃)₃, TiCl₄, ZrCl₄, HfCl₄, NbF₅, NbCl₅, TaCl₅, MoF₅, MoCl₅, WF₅, WCl₆, UF₆ and LnCl₃ (wherein Ln is a lanthanoid), anions (e.g., Cl⁻, Br⁻, I⁻, I₃⁻, HSO₄⁻, SO₄²⁻, NO₃⁻, ClO₄⁻, BF₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻, FeCl₄⁻, Fe(CN)₆³⁻, and anions of various sulfonic acids, such as aryl-SO₃⁻). When holes are used as carriers, examples of dopants are cations (e.g., H⁺, Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺), alkali metals (e.g., Li, Na, K, Rb, and Cs), alkaline-earth metals (e.g., Ca, Sr, and Ba), O₂, XeOF₄, (NO₂⁺) (SbF₆⁻), (NO₂⁺) (SbCl₆⁻), (NO₂⁺) (BF₄⁻), AgClO₄, H₂IrCl₆, La(NO₃)₃ · 6H₂O, FSO₂OOSO₂F, Eu, acetylcholine, R₄N⁺, (R is an alkyl group), R₄P⁺ (R is an alkyl group), R₆As⁺ (R is an alkyl group), and R₃S⁺ (R is an alkyl group).

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

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

According to another use, the materials according to the present invention can be used alone or together with other materials in or as alignment layers in LCD or OLED devices, as described for example in US

2003/0021913. The use of charge transport compounds according to the present invention can increase the electrical conductivity of the alignment layer. When used in an LCD, this increased electrical conductivity can reduce adverse residual dc effects in the switchable LCD cell and
5 suppress image sticking or, for example in ferroelectric LCDs, reduce the residual charge produced by the switching of the spontaneous polarization charge of the ferroelectric LCs. When used in an OLED device comprising a light emitting material provided onto the alignment layer, this increased electrical conductivity can enhance the electroluminescence of the light
10 emitting material.

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

According to another use, the materials according to the present invention are suitable for use in liquid crystal (LC) windows, also known as smart
20 windows.

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

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

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

5 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.

10 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
15 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
20 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).

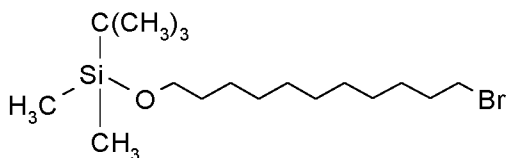
25 Above and below, unless stated otherwise percentages are percent by weight and temperatures are given in degrees Celsius.

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

Monomer Examples

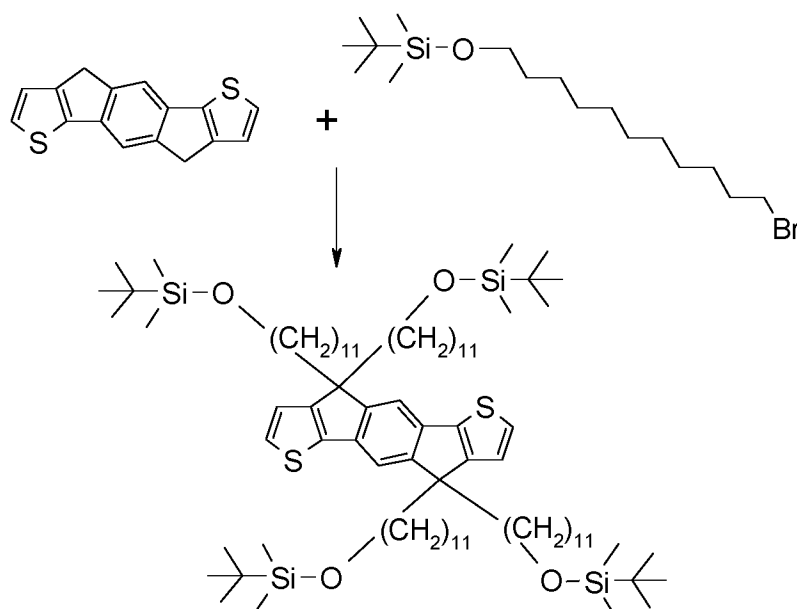
Monomer 1

35 (11-Bromoundecyloxy)-tert-butyldimethylsilane



5 To a solution of *tert*-butyldimethylsilyl chloride (16.58 g, 110.0 mmol) and 1H-imidazole (14.98 g, 220.0 mmol) in anhydrous dichloromethane (200 cm³) was added a solution of 11-bromoundecan-1-ol (25.12 g, 100.0 mmol) in dichloromethane (50 cm³) under stirring within 20 minutes. The mixture was stirred at 23 °C for 1 hour and then the volatiles removed *in vacuo*. Petroleum ether (40-60 °C, 200 cm³) was added to the residue, the suspension filtered through Celite and the volatiles removed *in vacuo*. The crude was then passed through a silica plug (petroleum ether 40-60 °C) to give the titled compound (34.02 g, 93%) as a colourless liquid. EI (m/z): 363. ¹H NMR (400 MHz, CDCl₃) 3.59 (t, *J* = 6.6 Hz, 2H), 3.40 (t, *J* = 6.9 Hz, 2H), 1.90 – 1.79 (m, 2H), 1.50 (m, 2H), 1.45 – 1.37 (m, 2H), 1.28 (m, 12H), 0.89 (s, 9H), 0.04 (s, 6H).

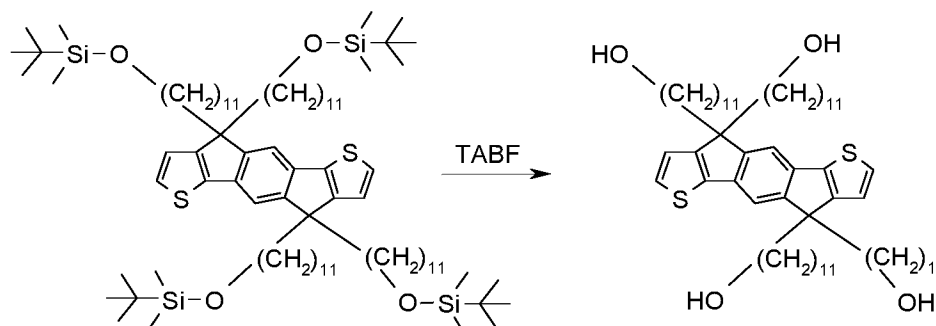
4,4,9,9-Tetrakis(11-*tert*-butyldimethylsiloxyundecyl)-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene



35 A mixture of 4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene (2.000 g, 7.508 mmol), anhydrous *N,N*-dimethylformamide (60 cm³), (11-

bromoundecyloxy)-*tert*-butyldimethylsilane (13.72 g, 37.54 mmol) and sodium iodide (100 mg, 0.667 mmol) was degassed by bubbling nitrogen for 30 minutes, followed by the addition of sodium hydride (1.50 g, 37.5 mmol, 60% dispersion in mineral oil). The mixture was stirred at 20 °C for 0.5 hours and at 100 °C for 16 hours. The mixture was cooled to 20 °C then the volatiles removed *in vacuo*. Petroleum ether (40-60 °C, 100 cm³) was added and the mixture filtered through Celite. The volatiles removed *in vacuo* and the residue purified by chromatography on silica (30% dichloromethane in petroleum ether 40-60 °C) to give the titled compound (5.21 g, 49%) as a thick yellow oil. ¹H NMR (400 MHz, CDCl₃) 7.27 (s, 1H), 7.25 (d, *J* = 4.8 Hz, 1H), 6.96 (d, *J* = 4.8 Hz, 1H), 3.58 (dt, *J* = 9.6, 6.7 Hz, 4H), 1.97 (ddd, *J* = 13.1, 11.0, 5.4 Hz, 2H), 1.83 (ddd, *J* = 13.2, 10.9, 5.5 Hz, 2H), 1.54 – 1.43 (m, 4H), 1.35 – 1.04 (m, 28H), 0.89 (s, 18H), 0.79 (m, 4H), 0.04 (s, 12H).

4,4,9,9-Tetrakis(11-hydroxyundecyl)-4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene



4,4,9,9-Tetrakis(11-*tert*-butyldimethylsiloxyundecyl)-4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene (5.20 g, 3.70 mmol) was dissolved in tetrahydrofuran (50 cm³) followed by the addition of tetrabutylammonium fluoride (19 cm³, 19 mmol, 1.0 M in tetrahydrofuran). The solution was stirred at 20 °C for 2 hours. The volatiles were removed *in vacuo*, diethyl ether (50 cm³) added and the solution washed with water (3 x 50 cm³). The ether phase was dried over anhydrous magnesium sulfate, filtered and the volatiles removed *in vacuo*. The residue was purified by chromatography on silica (30-40% acetone in dichloromethane) to give the titled compound (2.96 g, 84%) as a thick yellow oil. ¹H NMR (400 MHz,

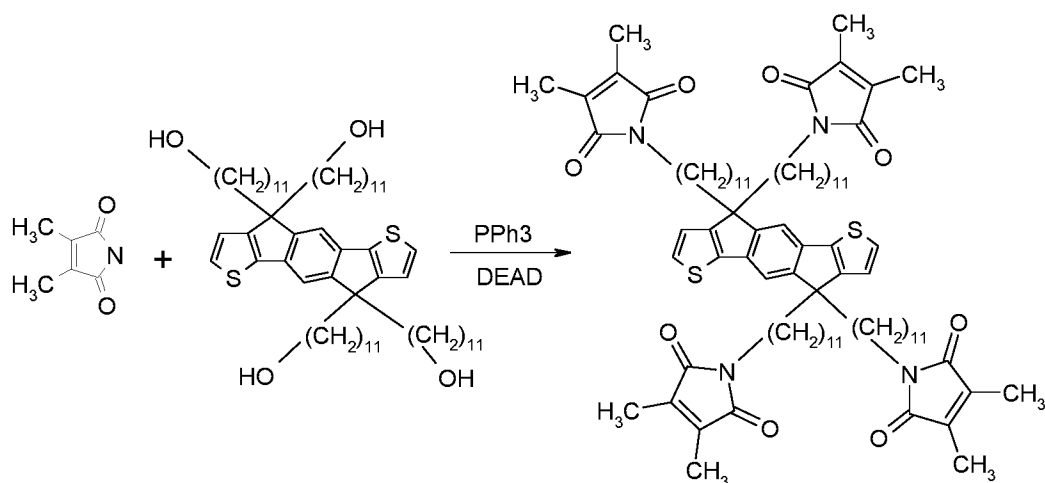
CDCl₃) 7.26 (s, 1H), 7.25 (d, J = 4.8 Hz, 1H), 6.95 (d, J = 4.8 Hz, 1H), 3.60 (t, J = 6.7 Hz, 4H), 1.96 (ddd, J = 13.1, 11.1, 5.3 Hz, 2H), 1.84 (ddd, J = 13.3, 11.0, 5.3 Hz, 2H), 1.51 (dt, J = 8.1, 6.6 Hz, 4H), 1.34 – 1.00 (m, 28H), 0.89 – 0.72 (m, 4H).

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4,4,9,9-Tetrakis[11-(2,3-dimethyl-N-maleimido)undecyl]-4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene

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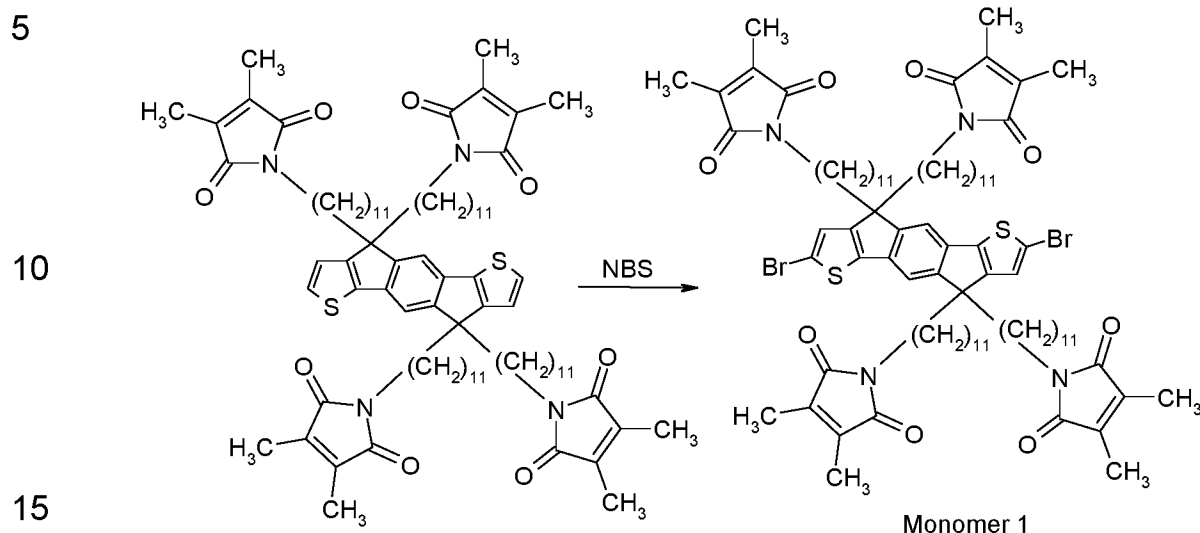
To a mixture of triphenylphosphine (4.097 g, 15.619 mmol), 4,4,9,9-tetrakis(11-hydroxyundecyl)-4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene (2.960 g, 3.124 mmol), anhydrous tetrahydrofuran (100 cm³) and 3,4-dimethylmaleimide (1.954 g, 15.619 mmol) at -78 °C was added diethyl azodicarboxylate (2.46 cm³, 15.6 mmol) dropwise. The cooling bath was removed and the reaction mixture stirred for 30 minutes. The solution re-cooled to -78 °C and stirred for 10 minutes before removing the cooling and stirring the reaction mixture at 23 °C for 18 hours. The volatiles were removed *in vacuo*. The residue was purified by chromatography on silica (dichloromethane) to give the titled compound

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(2.64 g, 61%) as a thick yellow oil which solidified upon standing. ¹H NMR (400 MHz, CDCl₃) 7.20 (s, 1H), 7.18 (d, J = 4.9 Hz, 1H), 6.89 (d, J = 4.8 Hz, 1H), 3.41 – 3.32 (m, 4H), 1.87 (m+s, 14H), 1.76 (ddd, J = 13.3, 11.0, 5.5 Hz, 2H), 1.44 (t, J = 7.2 Hz, 4H), 1.22 – 0.92 (m, 28H), 0.84 – 0.69 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) 172.29, 172.26, 155.02, 153.19, 141.55, 136.90, 135.46, 126.08, 121.70, 113.08, 53.57, 53.40, 39.01, 37.91, 29.96, 29.50, 29.45, 29.42, 29.39, 29.27, 29.13, 28.66, 26.73, 24.13, 8.63.

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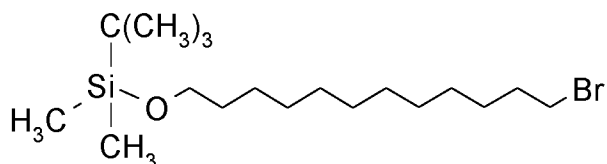
2,7-Dibromo-4,4,9,9-tetrakis[11-(2,3-dimethyl-N-maleimido)undecyl]-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (Monomer 1)



To a solution of 4,4,9,9-tetrakis[11-(2,3-dimethyl-N-maleimido)undecyl]-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (2.500 g, 1.817 mmol) in dichloromethane (40 cm³) was added acetic acid (10 cm³). The solution was cooled to 0 °C followed by the addition of *N*-bromosuccinimide (698 mg, 3.882 mmol). The mixture was stirred at 20 °C for 1 hour and the volatiles removed *in vacuo*. The residue was purified by chromatography on silica (dichloromethane) to give Monomer 1 (2.54 g, 91%) as a thick yellow oil which solidified into a yellow solid after vacuum drying and standing. ¹H NMR (400 MHz, dichloromethane-d₂) 7.16 (d, *J* = 1.7 Hz, 1H), 6.93 (d, *J* = 1.7 Hz, 1H), 3.32 (t, *J* = 7.2 Hz, 4H), 1.86 (m, 2H), 1.83 (s, 12H), 1.76 (dt, *J* = 13.1, 6.7 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 4H), 1.22 – 0.93 (m, 28H), 0.83 – 0.56 (m, 4H). ¹³C NMR (101 MHz, CD₂Cl₂) 172.19, 154.23, 152.18, 141.85, 136.86, 135.49, 124.99, 113.10, 112.21, 54.78, 38.87, 37.79, 29.88, 29.51, 29.50, 29.48, 29.45, 29.27, 29.18, 28.66, 26.76, 24.09, 8.33.

Monomer 2

(12-Bromododecyloxy)-*tert*-butyldimethylsilane



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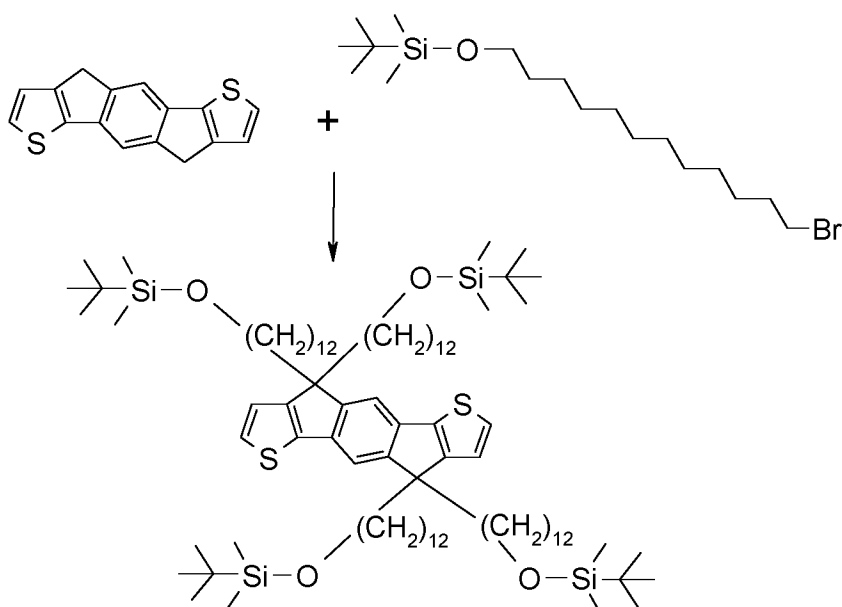
To a solution of *tert*-butyldimethylsilyl chloride (3.125 g, 20.74 mmol) and 1H-imidazole (2.823 g, 41.47 mmol) in anhydrous dichloromethane (50 cm³) was added a solution of 12-bromododecan-1-ol (5.000 g, 18.85 mmol) in anhydrous dichloromethane (10 cm³) over 5 minutes. The mixture was stirred at 20 °C for 2 hours and then the volatiles removed *in vacuo*. Petroleum ether (40-60 °C, 50 cm³) was added, the suspension filtered through Celite and the volatiles removed *in vacuo*. The crude was passed through a silica plugg (*n*-pentane) to give the titled compound (6.79 g, 95%) as a colourless liquid. EI (m/z): 379. ¹H NMR (400 MHz, CDCl₃) 3.59 (t, *J* = 6.6 Hz, 2H), 3.40 (t, *J* = 6.9 Hz, 2H), 1.85 (p, *J* = 7.0 Hz, 2H), 1.50 (t, *J* = 6.6 Hz, 2H), 1.45 – 1.37 (m, 2H), 1.34 – 1.22 (m, 14H), 0.89 (s, 9H), 0.04 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) -5.25, 18.37, 25.80, 25.99, 28.18, 28.77, 29.43, 29.51, 29.54, 29.60, 32.85, 32.89, 33.98, 63.31.

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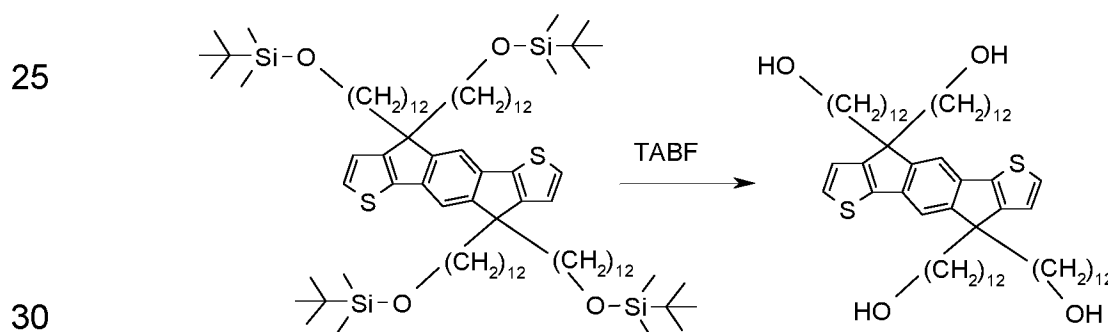
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4,4,9,9-Tetrakis(12-*tert*-butyldimethylsiloxydodecyl)-4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene



A mixture of 4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene (800 mg, 3.00 mmol), anhydrous *N,N*-dimethylformamide (30 cm³), (12-bromododecyloxy)-*tert*-butyldimethylsilane (5.698 g, 15.02 mmol) and sodium iodide (100 mg, 0.667 mmol) was degassed by bubbling nitrogen for 30 minutes, followed by the addition of sodium hydride (601 mg, 15.0 mmol, 60% dispersion in mineral oil). The mixture was stirred at 50 °C for 1 hour and at 100 °C for 16 hours. The mixture was cooled to 23 °C then the volatiles removed *in vacuo*. Petroleum ether (80-100 °C, 50 cm³) was added and the mixture was filtered through Celite. The filtrate was purified by chromatography on silica (20% dichloromethane in petroleum ether 40-60 °C) to give the titled product (2.62 g, 60%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) 7.30 (s, 1H), 7.26 (d, *J* = 4.8 Hz, 1H), 6.96 (d, *J* = 4.8 Hz, 1H), 3.55 (t, *J* = 6.6 Hz, 4H), 1.97 (ddd, *J* = 13.1, 10.9, 5.6 Hz, 2H), 1.85 (ddd, *J* = 13.2, 10.7, 5.6 Hz, 2H), 1.48 – 1.39 (m, 4H), 1.33 – 1.01 (m, 32H), 0.86 (s, 18H), 0.83 – 0.73 (m, 4H), 0.01 (s, 12H). ¹³C NMR (101 MHz, CD₂Cl₂) 155.81, 153.85, 142.15, 136.22, 126.80, 122.32, 113.72, 63.78, 39.71, 33.51, 30.58, 30.25, 30.19, 30.16, 30.04, 29.96, 26.46, 26.42, 26.33, 24.79, 18.80, -4.99.

4,4,9,9-Tetrakis(12-hydroxydodecyl)-4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene



To a solution of 4,4,9,9-tetrakis(12-*tert*-butyldimethylsiloxydodecyl)-4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene (2.810 g, 1.924 mmol) in anhydrous tetrahydrofuran (40 cm³) was added tetrabutylammonium fluoride (10 cm³, 10 mmol, 1.0 M in tetrahydrofuran). The solution was stirred at 20 °C for 2 hours. The volatiles were removed *in vacuo*, dithey

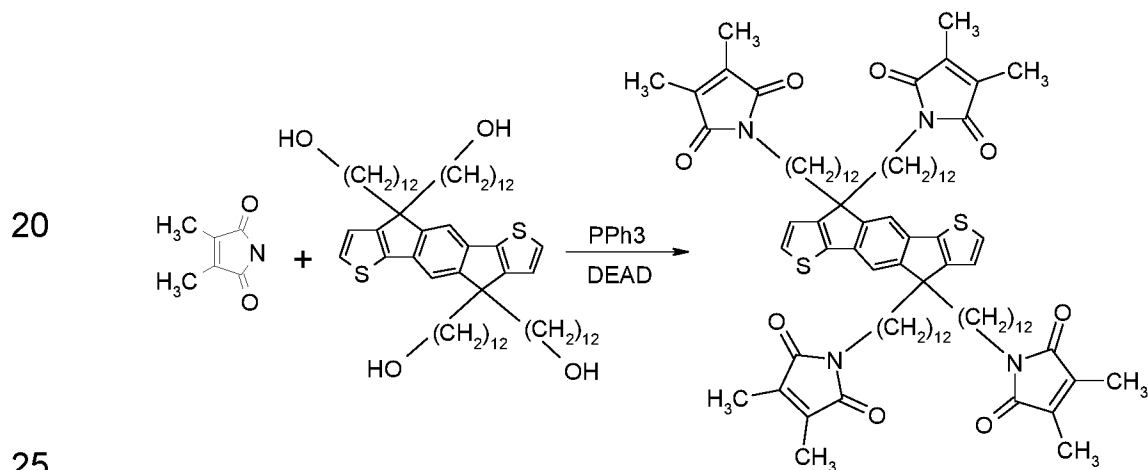
ether (50 cm³) added and the solution washed with water (3 x 50 cm³). The ether phase was dried over anhydrous magnesium sulfate, filtered and the volatiles removed *in vacuo*. The residue was purified by chromatography on silica (30-40% acetone in dichloromethane) to give the

5 titled compound (1.87 g, 97%) as a thick yellow oil. ¹H NMR (400 MHz, CDCl₃) 7.27 (s, 1H), 7.25 (d, *J* = 4.8 Hz, 1H), 6.95 (d, *J* = 4.8 Hz, 1H), 3.61 (t, *J* = 6.6 Hz, 4H), 2.17 (s, 2H), 1.97 (ddd, *J* = 13.2, 11.1, 5.4 Hz, 2H), 1.84 (ddd, *J* = 13.2, 10.9, 5.4 Hz, 2H), 1.36 – 1.01 (m, 32H), 0.81 (dq, *J* = 10.4, 5.0 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) 155.05, 153.19, 141.60,

10 135.53, 126.08, 121.69, 113.09, 63.04, 53.63, 39.11, 32.78, 30.92, 29.99, 29.58, 29.56, 29.54, 29.52, 29.39, 29.33, 25.72, 24.14.

4,4,9,9-Tetrakis[12-(2,3-dimethyl-N-maleimido)dodecyl]-4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene

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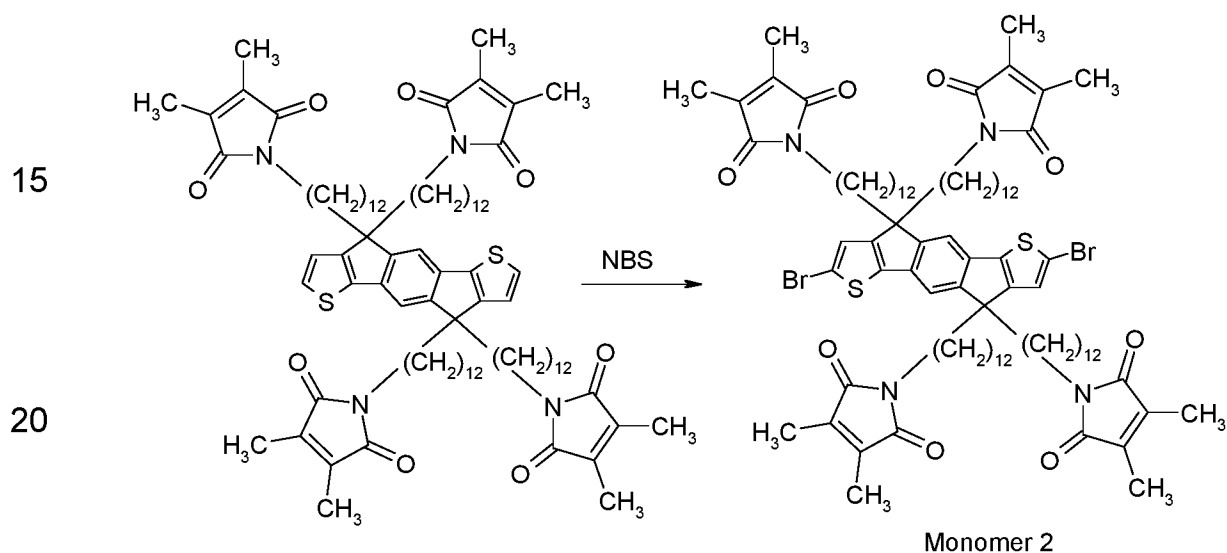
A solution of triphenylphosphine (670 mg, 2.55 mmol), 4,4,9,9-tetrakis(12-hydroxydodecyl)-4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene (534 mg, 0.532 mmol) in anhydrous tetrahydrofuran (25 cm³) was cooled to -78 °C. Diethyl azodicarboxylate (0.40 cm³, 2.5 mmol) was added dropwise and the mixture was stirred with cooling for 10 minutes. 3,4-Dimethylmaleimide (320 mg, 2.55 mmol) was added in one portion and the flask was removed from the cooling bath and the gel was shaken manually at 20 °C until it was stirrable. The gel was gradually dissolved over ca 30 minutes to yield

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35 a solution. The solution was stirred at 20 °C for 18 hours. The volatiles were removed *in vacuo* and the crude chromatographed on silica

(dichloromethane) to give the titled product (0.43 g, 57%) as a very thick yellow oil. ¹H NMR (400 MHz, DCM-*d*₂) 7.29 (s, 1H), 7.25 (d, *J* = 4.7, 1H), 6.95 (d, *J* = 4.9, 1H), 3.38 (t, *J* = 7.2 Hz, 4H), 2.02 – 1.91 (m, 2H), 1.88 (s, 12H), 1.82 (m, 2H), 1.47 (p, *J* = 7.3 Hz, 4H), 1.30 – 0.94 (m, 32H), 0.77 (dp, *J* = 13.8, 7.3 Hz, 4H). ¹³C NMR (101 MHz, CD₂Cl₂) 172.75, 155.78, 153.82, 142.09, 137.43, 136.16, 126.79, 122.31, 113.70, 39.64, 38.37, 30.53, 30.11, 30.07, 29.90, 29.74, 29.23, 27.35, 24.75, 8.90, 8.87.

2,7-Dibromo-4,4,9,9-tetrakis[12-(2,3-dimethyl-N-maleimido)dodecyl]-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (Monomer 2)



To a solution of 4,4,9,9-tetrakis[12-(2,3-dimethyl-N-maleimido)dodecyl]-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (750 mg, 0.524 mmol) in anhydrous dichloromethane (20 cm³) was added acetic acid (5 cm³). The solution was cooled to 0 °C followed by the addition of *N*-bromosuccinimide (193 mg, 1.08 mmol) in one portion. The mixture was stirred at 20 °C for 1 hour before the volatiles were removed *in vacuo*. The residue was purified by chromatography on silica (dichloromethane) to give Monomer 2 (737 mg, 89%) as a thick yellow oil which solidified upon standing. ¹H NMR (400 MHz, CD₂Cl₂) 7.23 (s, 1H), 7.00 (s, 1H), 3.40 (t, *J* = 7.2 Hz, 4H), 2.01 – 1.92 (m, 2H), 1.90 (s, 12H), 1.87 – 1.76 (m, 2H), 1.49 (t, *J* = 7.1 Hz, 4H), 1.29 – 0.99 (m, 32H), 0.89 – 0.64 (m, 4H). ¹³C NMR (101 MHz, CD₂Cl₂) 172.76, 154.79, 152.74, 142.42, 137.42, 136.06,

125.54, 113.66, 112.79, 55.35, 39.45, 38.36, 30.43, 30.12, 30.10, 30.08, 29.85, 29.75, 29.24, 27.35, 24.64, 8.90.

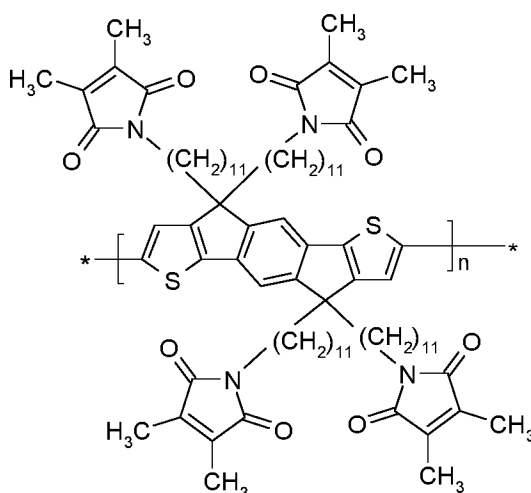
Polymer Examples

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Polymer 1

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Polymer 1

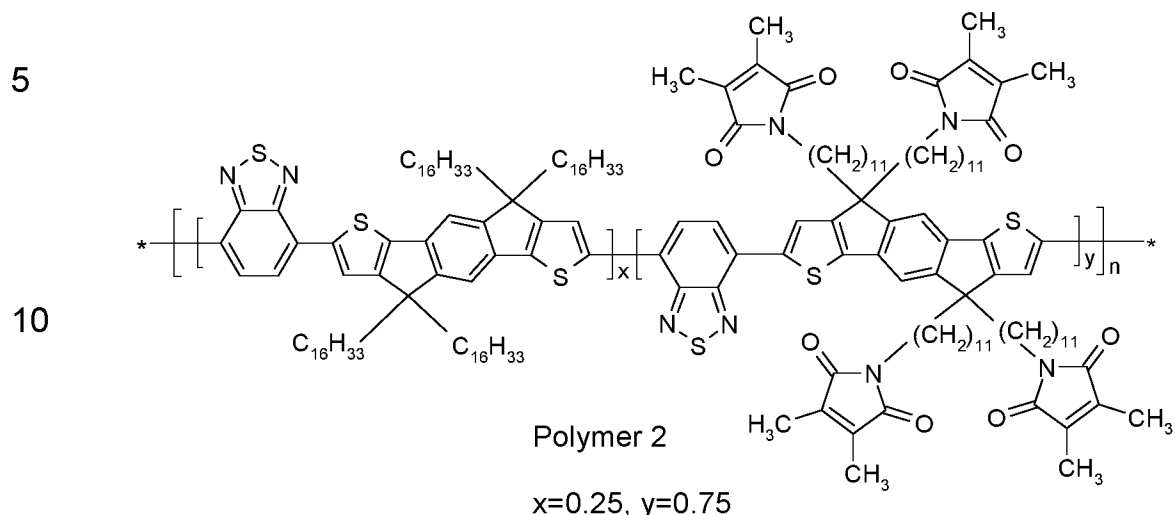
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To a degassed mixture of Monomer 1 (443.3 mg, 0.289 mmol), 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole (112.2 mg, 0.289 mmol), anhydrous tetrahydrofuran (4.0 cm³), aqueous sodium carbonate solution (0.58 cm³, 1.2 mmol, 2.0 M) and Aliquat 336 (10 mg) was added tris(dibenzylideneacetone) dipalladium(0) (5.3 mg, 0.006 mmol) and tri(o-tolyl)phosphine (7.0 mg, 0.023 mmol) the mixture further degassed over 5 minutes. The mixture was heated at reflux for 15 minutes. Anhydrous toluene (4.0 cm³) was added and the mixture was stirred at reflux for 4 hours. Toluene (5 cm³) was added and the solution cooled briefly then precipitated into methanol (150 cm³). The solid was collected by filtration, washed with water and acetone. The solid was subjected to Soxhlet extraction (acetone, petroleum ether (80-100 °C) and chloroform). The chloroform fraction was concentrated *in vacuo* and then precipitated into methanol. The solid was collected by filtration to give Polymer 1 (380 mg, 87%) as a brown/blue solid. GPC (chlorobenzene, 50 °C) $M_n = 65,000$ g/mol, $M_w = 185,000$ g/mol.

Polymer 2

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To a degassed mixture of Monomer 1 (461.9 mg, 0.301 mmol), 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole (155.8 mg, 0.402 mmol), anhydrous tetrahydrofuran (5.0 cm³), aqueous sodium carbonate solution (0.80 cm³, 1.6 mmol, 2.0 M) and Aliquat 336 (10 mg) was added tris(dibenzylideneacetone)di-palladium(0) (7.4 mg, 0.008 mmol) and tri(o-tolyl)phosphine (9.8 mg, 0.032 mmol) and the mixture degassed for an additional 10 minutes. The mixture was heated at reflux for 15 minutes. Anhydrous toluene (5.0 cm³) was added and the mixture heated at reflux for 1.5 hours. Toluene (5 cm³) was added, the solution cooled briefly then precipitated into methanol (150 cm³). The solid was collected by suction filtration, washed with water and acetone. The solid subjected to Soxhlet extraction (acetone, petroleum ether (80-100 °C) and chloroform). The chloroform solution was concentrated *in vacuo* before precipitation in methanol. The solid collected by filtration to give Polymer 2 (520 mg, 92%) as a brown/blue solid. GPC (chlorobenzene, 50 °C) $M_n = 120,000$ g/mol, $M_w = 470,000$ g/mol.

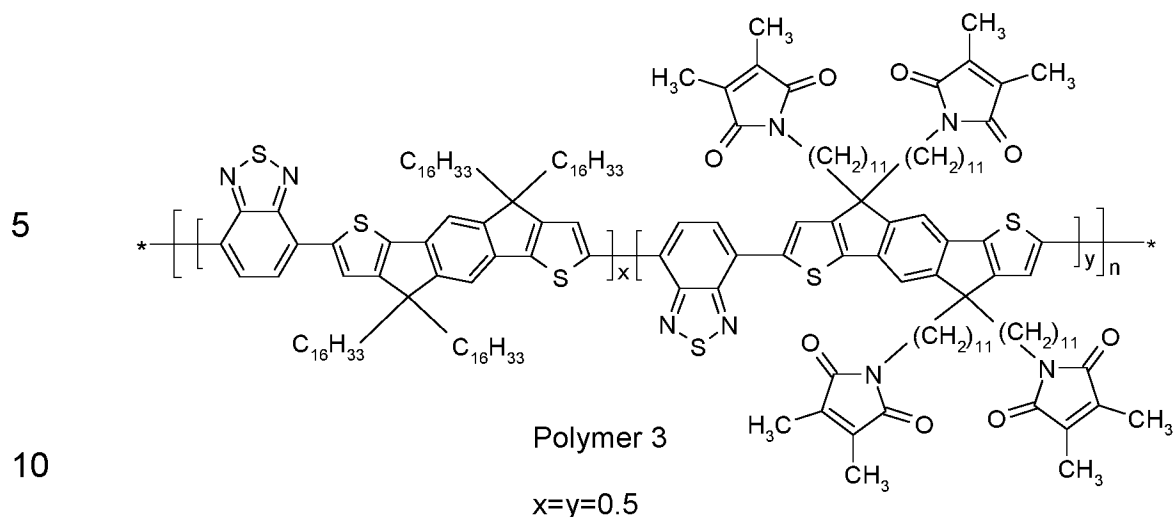
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Polymer 3

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To a degassed mixture of 2,7-dibromo-4,4,9,9-tetrahexadecyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (288.8 mg, 0.218 mmol), Monomer 1 (335.1 mg; 0.218 mmol), 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole (169.6 mg, 0.437 mmol), anhydrous tetrahydrofuran (5.0 cm³), aqueous sodium carbonate solution (0.87 cm³, 1.8 mmol, 2.0 M) and Aliquat 336 (10 mg) was added

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tris(dibenzylideneacetone)di-palladium(0) (8.0 mg, 0.009 mmol) and tri(o-tolyl)phosphine (10.6 mg, 0.035 mmol) and the mixture degassed for an additional 10 minutes. The mixture was heated at reflux for 15 minutes. Anhydrous toluene (5.0 cm³) was added and the mixture heated at reflux for 2 hours. Toluene (5 cm³) was added, the solution cooled briefly then precipitated into methanol (150 cm³). The solid was collected by suction

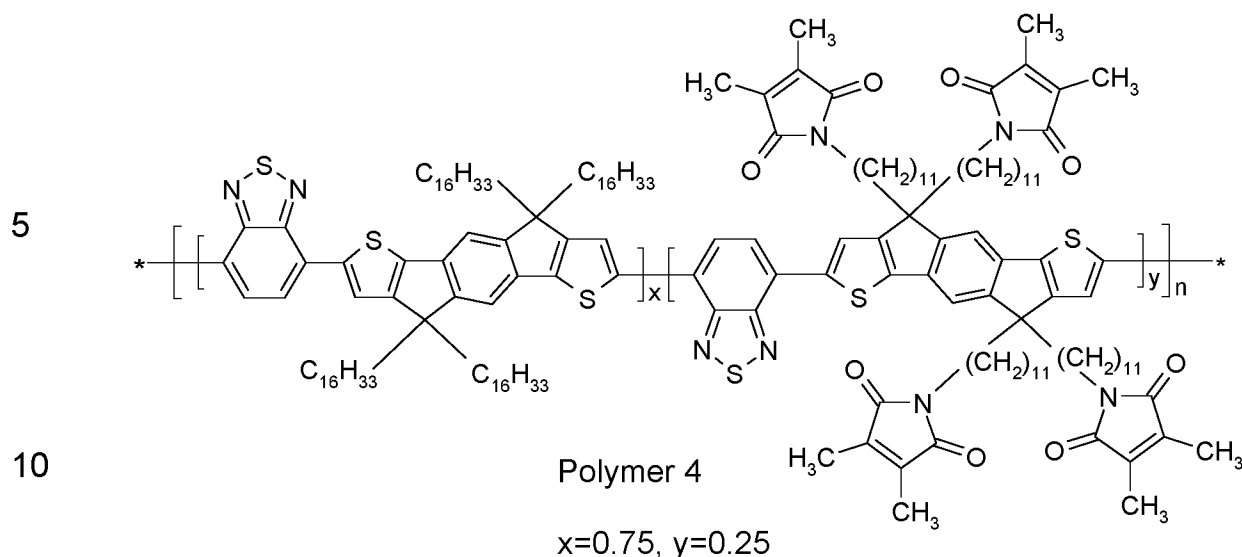
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filtration, washed with water and acetone. The solid was subjected to Soxhlet extraction (acetone, petroleum ether (80-100 °C) and chloroform). The chloroform solution was concentrated *in vacuo* before precipitation in methanol. The solid was collected by filtration to give Polymer 3 (570 mg, 93%) as a brown/blue solid. GPC (chlorobenzene, 50 °C) $M_n = 148,000$ g/mol, $M_w = 447,000$ g/mol. PDI = 3.02

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Polymer 4



15 To a degassed mixture of 2,7-dibromo-4,4,9,9-tetrahexadecyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (446.5 mg, 0.338 mmol), Monomer 1 (172.7 mg, 0.113 mmol), 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole (174.8 mg, 0.450 mmol), anhydrous tetrahydrofuran (5.0 cm³), aqueous sodium carbonate solution (0.90 cm³, 1.8 mmol, 2.0 M) and Aliquat 336 (10 mg) was added

20 tris(dibenzylideneacetone)di-palladium(0) (8.2 mg, 0.009 mmol) and tri(o-tolyl)phosphine (10.9 mg, 0.036 mmol) and the mixture degassed for an additional 10 minutes. The mixture was heated at reflux for 15 minutes. Anhydrous toluene (5.0 cm³) was added and the mixture was heated at reflux for 2 hours. Toluene (5 cm³) was added, the solution cooled briefly then precipitated into methanol (150 cm³). The solid was collected by

25 suction filtration, washed with water and acetone. The solid was subjected to Soxhlet extraction (acetone, petroleum ether (80-100 °C) and chloroform). The chloroform solution was concentrated *in vacuo* before precipitation in methanol. The solid was collected by filtration to give

30 Polymer 4 (530 mg, 85%) as a brown/blue solid. GPC (chlorobenzene, 50 °C) $M_n = 120,000$ g/mol, $M_w = 243,000$ g/mol.

Use Example 1

35 Field-effect transistor fabrication and measurements

Top-gate thin-film organic field-effect transistors (OFETs) were fabricated on glass substrates with thermally evaporated Au source-drain electrodes at the thickness of 40 nm. A planarization layer was deposited prior to the electrodes evaporation. The electrodes were then treated with Merck Lisicon® M001 using a standard procedure. 7 mg/cm³ solution of the organic semiconductor in dichlorobenzene was spin-coated on top (an optional annealing of the film was carried out at 100 °C, 150 °C or 200 °C for between 1 and 5 minutes followed by a spin-coated fluoropolymer dielectric material (Lisicon® D139 from Merck, Germany). Finally, a thermally evaporated Ag gate electrode was deposited. The electrical characterization of the transistor devices was carried out in ambient air atmosphere using computer controlled Agilent 4155C Semiconductor Parameter Analyser. Charge carrier mobility in the saturation regime (μ_{sat}) was calculated for the compound. Field-effect mobility was calculated in the saturation regime ($V_d > (V_g - V_0)$) using equation (1):

$$\left(\frac{dI_d^{\text{sat}}}{dV_g} \right)_{V_d} = \frac{WC_i}{L} \mu^{\text{sat}} (V_g - V_0) \quad (1)$$

where W was the channel width, L the channel length, C_i the capacitance of insulating layer, V_g the gate voltage, V_0 the turn-on voltage, and μ_{sat} was the charge carrier mobility in the saturation regime. Turn-on voltage (V_0) was determined as the onset of source-drain current.

The field effect transistor device characteristics for a device using Polymer 4 as the active OSC material in top gate bottom contact configuration is shown in **Fig. 1**. Therein the mobility was calculated based on the first derivative of the linear regime and second derivative for the saturation regime. The dimensions of the device are 500 μm (W) and 20 μm (L).

Use Example 2

Demonstration of photopatterning of the polymers

A solution of Polymer 4 in chloroform containing 0.15% Omnipol TX was spin-coated on glass substrate to prepare a film. The film was covered

with a shadow mask and exposed to UV light of 254 nm at 1.536 J/cm² for 2 minutes. Mesitylene was then puddled for 30 seconds and spun off. The resulting film thickness left is 28.67 nm. The smallest feature size is 10 μm (gap of transistor pattern).

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Fig. 2 shows a microscopic image of the directly patterned film of Polymer 4 on bare glass.

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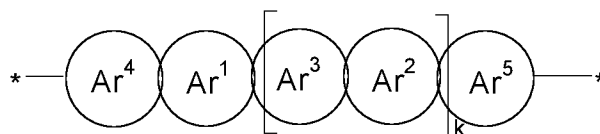
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Claims

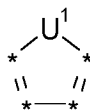
1. A conjugated polymer comprising one or more repeating units of formula I



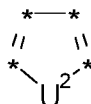
and/or one or more divalent repeating units Ar^6 ,

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

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



A1



A2

U^1 , U^2 CR^1R^2 , SiR^1R^2 , GeR^1R^2 , $C=CR^1R^2$ or NR^1 ,

Ar^3 , Ar^4 , Ar^5 fused aryl or heteroaryl ring which has from 5 to 20 ring atoms, is mono- or polycyclic, optionally contains fused rings, and is unsubstituted or substituted by one or more identical or different groups L,

Ar^6 arylene or heteroarylene which has from 5 to 20 ring atoms, is mono- or polycyclic, optionally contains fused rings, and is unsubstituted or substituted by one or more identical or different groups L or R^1 ,

R^1 , R^2 H, F, Cl, CN, $-Sp-R^C$, or straight-chain, branched or cyclic alkyl with 1 to 30, preferably 1 to 20, C atoms, in which

- one or more CH₂ groups are each optionally replaced by -O-, -S-, -C(=O)-, -C(=S)-, -C(=O)-O-, -O-C(=O)-, -NR⁰-, -SiR⁰R⁰⁰-, -CF₂-, -CR⁰=CR⁰⁰-, -CY¹=CY²- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, and in which one or more H atoms are each optionally replaced by F, Cl, Br, I or CN, and in which one or more CH₂ or CH₃ groups are each optionally replaced by a cationic or anionic group, or aryl, heteroaryl, arylalkyl, heteroarylalkyl, aryloxy or heteroaryloxy, wherein each of the aforementioned cyclic groups has 5 to 20 ring atoms, is mono- or polycyclic, optionally contains fused rings, and is unsubstituted or substituted by one or more identical or different groups L,
- and the pair of R¹ and R², together with the C, Si or Ge atom to which they are attached, may also form a spiro group with 5 to 20 ring atoms which is mono- or polycyclic, optionally contains fused rings, and is unsubstituted or substituted by one or more identical or different groups L,
- Sp a spacer group,
- R^C a maleimide or maleimide containing group that is unsubstituted or substituted, preferably by C₁₋₄ alkyl, very preferably by methyl,
- L F, Cl, -NO₂, -CN, -NC, -NCO, -NCS, -OCN, -SCN, R⁰, OR⁰, SR⁰, -C(=O)X⁰, -C(=O)R⁰, -C(=O)-OR⁰, -O-C(=O)-R⁰, -NH₂, -NHR⁰, -NR⁰R⁰⁰, -C(=O)NHR⁰, -C(=O)NR⁰R⁰⁰, -SO₃R⁰, -SO₂R⁰, -OH, -CF₃, -SF₅, or optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 30, preferably 1 to 20 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, preferably F, -CN, R⁰, -OR⁰, -SR⁰, -C(=O)-R⁰, -C(=O)-OR⁰, -O-C(=O)-R⁰, -O-C(=O)-OR⁰, -C(=O)-NHR⁰, or -C(=O)-NR⁰R⁰⁰,

R^0, R^{00} H or straight-chain or branched alkyl with 1 to 20, preferably 1 to 12, C atoms that is optionally fluorinated,

X^0 halogen, preferably F or Cl,

k 0 or an integer from 1 to 10, preferably 0, 1, 2, 3, 4, 5, 6 or 7, very preferably 0, 1, 2 or 3, most preferably 1,

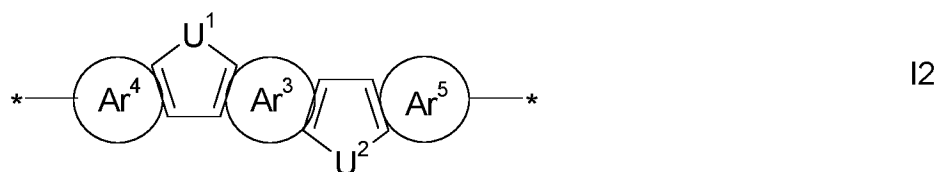
wherein the conjugated polymer comprises

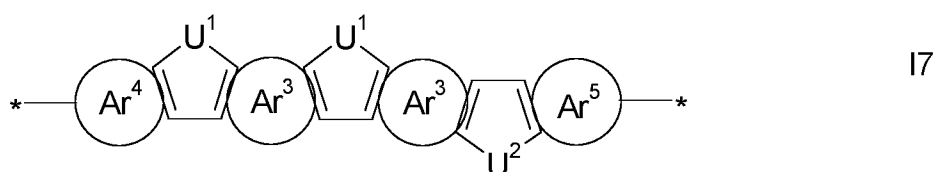
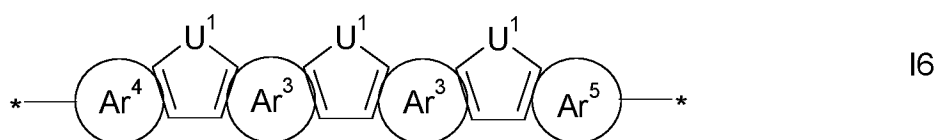
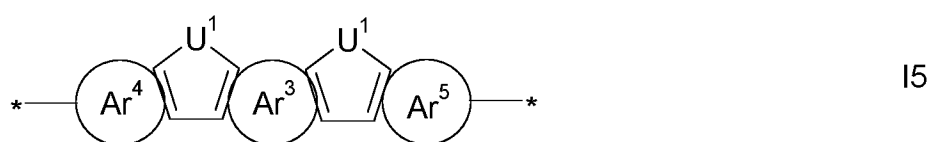
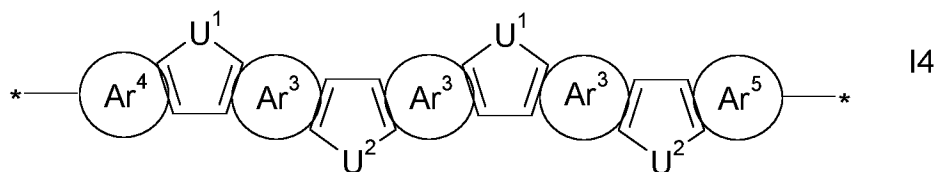
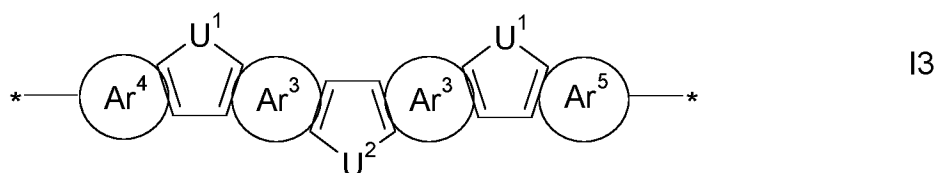
a) at least one unit of formula I wherein at least two groups R^1 and R^2 that are attached to the same C, Si or Ge atom denote each $-Sp-R^C$, or wherein at least one group R^1 that is attached to an N atom denotes $-Sp-R^C$, or

b) at least one unit Ar^6 which is substituted by at least one group R^1 that denotes $-Sp-R^C$,

or both a) and b).

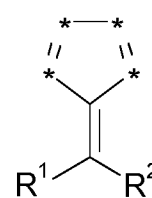
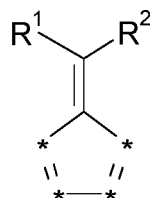
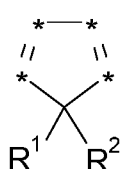
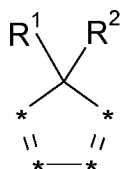
2. The conjugated polymer according to claim 1, characterized in that the repeating units of formula I are selected from the following subformulae





wherein U^1 , U^2 , Ar^3 , Ar^4 and Ar^5 , independently of each other and on each occurrence identically or differently, have the meanings given in claim 1

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



A1a

A2a

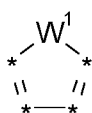
A1b

A2b

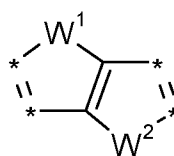
wherein R^1 and R^2 have the meanings given in claim 1.

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

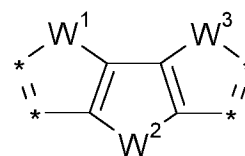
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A3a

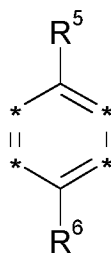


A3b

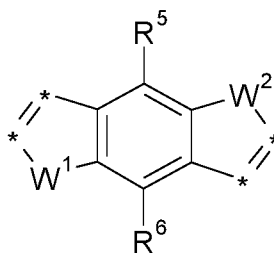


A3c

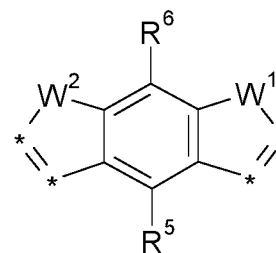
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A3d

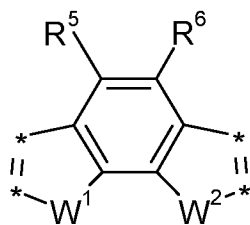


A3e

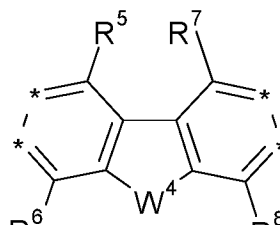


A3f

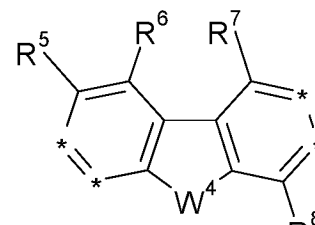
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A3g

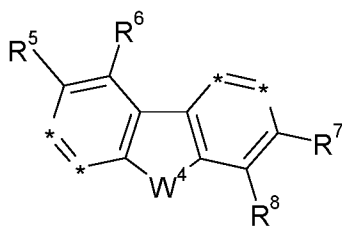


A3h

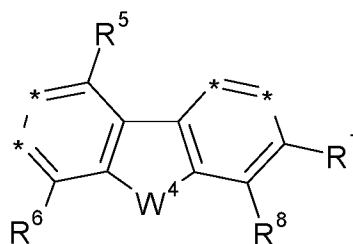


A3i

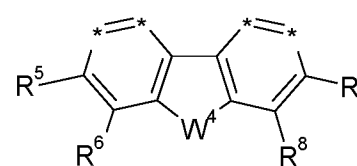
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A3j



A3k

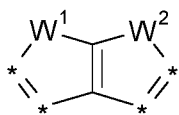


A3l

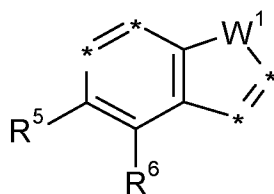
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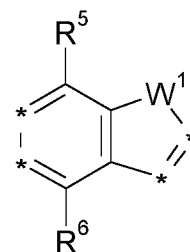
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A3m

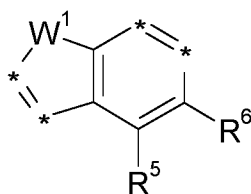


A3n

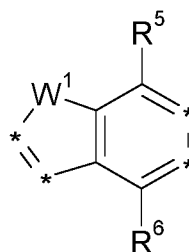


A3o

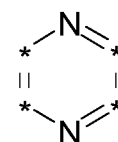
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A3p

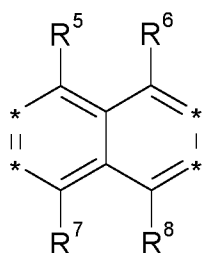


A3q

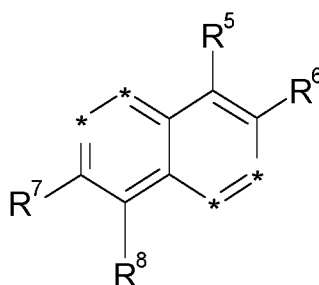


A3r

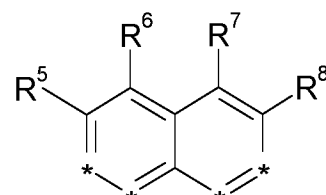
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A3s



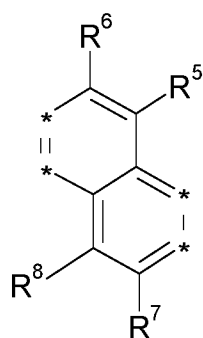
A3t



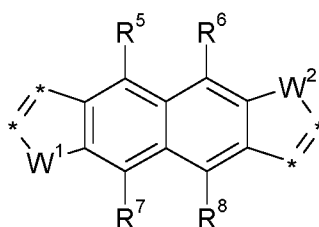
A3u

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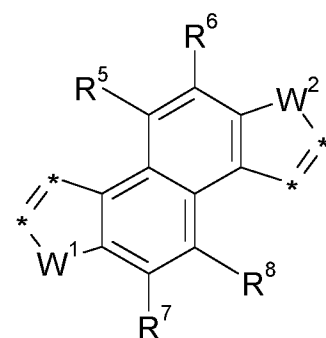
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A3v



A3w



A3x

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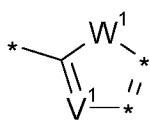
wherein the individual radicals, independently of each other and on each occurrence identically or differently, have the following meanings

W^1, W^2, W^3 S, O, Se or C=O, preferably S,

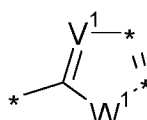
W^4 S, O, Se, C=O or NR^5 ,

5 R^{5-8} one of the meanings given for R^1 in claim 1.

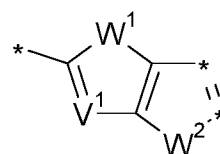
10 5. The conjugated polymer according to one or more of claims 1 to 4, characterized in that the groups Ar^4 are on each occurrence identically or differently selected from the following formulae and their mirror images



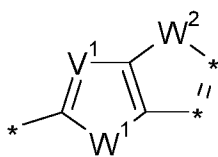
A4a



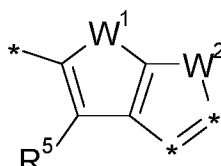
A4b



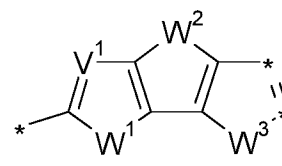
A4c



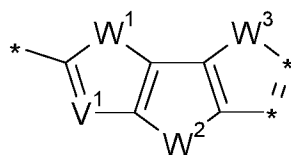
A4d



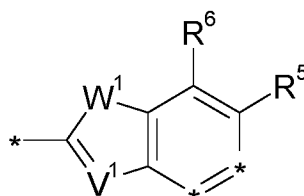
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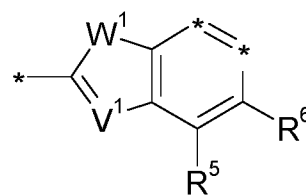
A4f



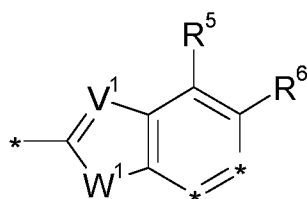
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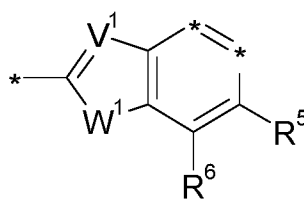
A4h



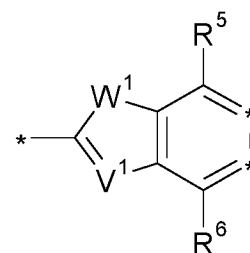
A4i



A4j

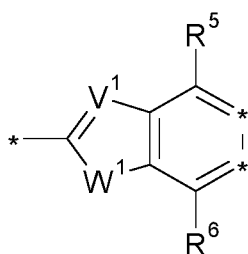


A4k

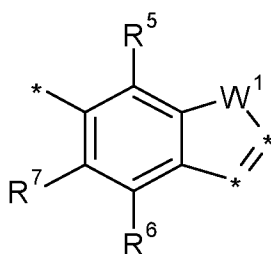


A4l

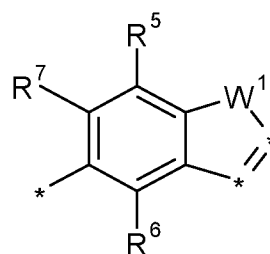
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A4m

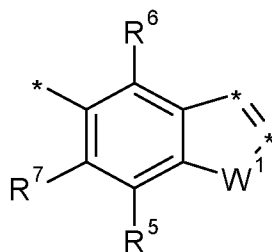


A4n

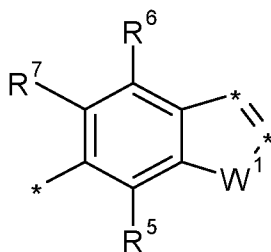


A4o

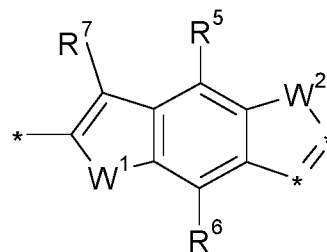
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A4p

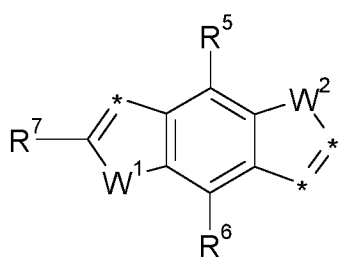


A4q

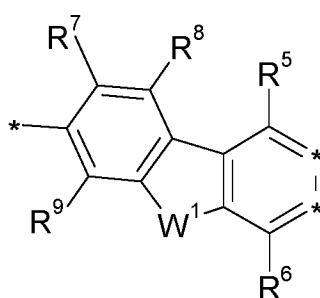


A4r

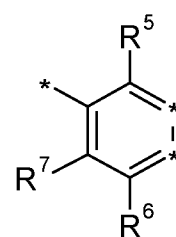
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A4s



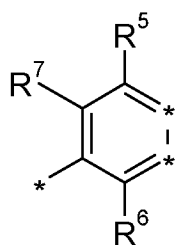
A4t



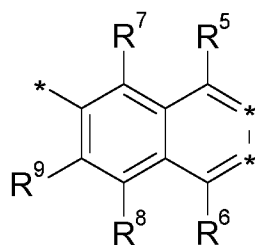
A4u

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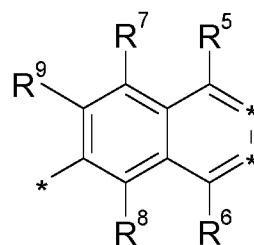
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A4v



A4w



A4x

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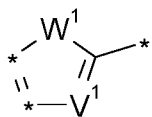
wherein W^1 , W^2 , W^3 and R^{5-8} have the meanings given in claim 4, V^1 denotes CR^5 or N, and R^9 has one of the meanings given for R^5 .

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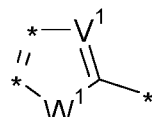
6. The conjugated polymer according to one or more of claims 1 to 5, characterized in that the groups Ar^5 are on each occurrence

identically or differently selected from the following formulae and their mirror images

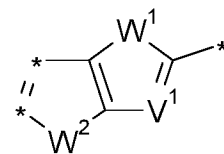
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A5a

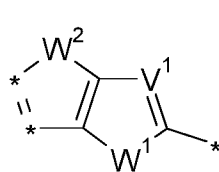


A5b

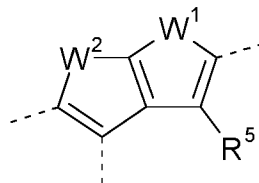


A5c

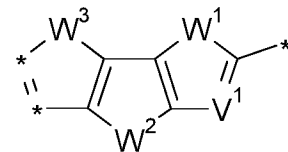
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A5d

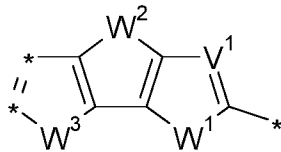


A5e

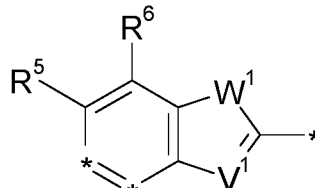


A5f

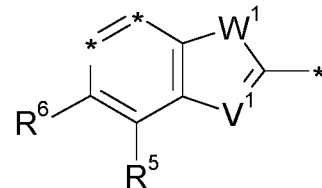
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A5g

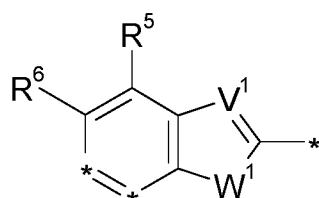


A5h

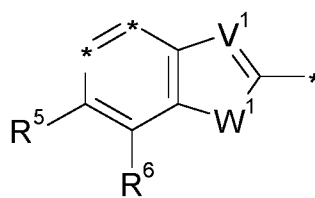


A5i

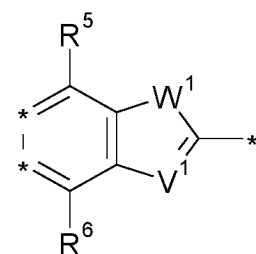
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A5j



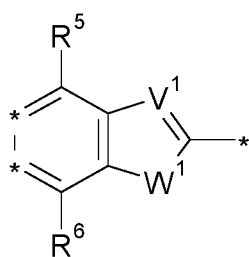
A5k



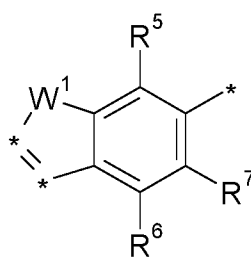
A5l

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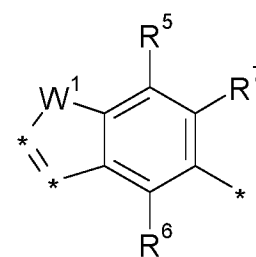
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A5m

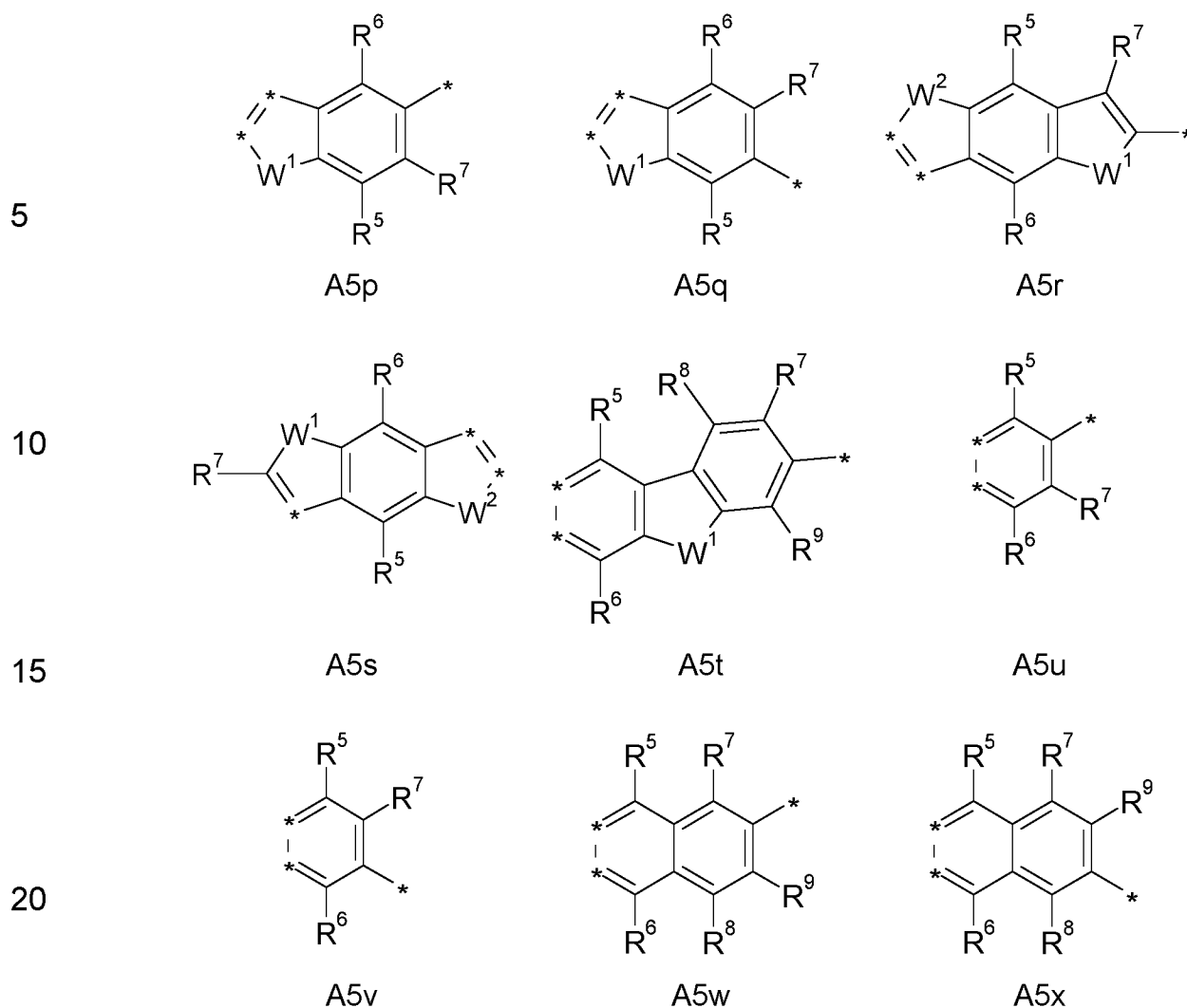


A5n



A5o

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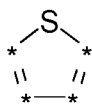
wherein V^1 , W^1 , W^2 , W^3 and R^{5-9} have the meanings given in claim 5 and 6.

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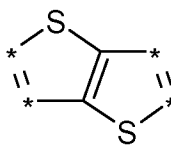
7. The conjugated polymer according to one or more of claims 1 to 6, characterized in that the groups Ar^3 are on each occurrence identically or differently selected from the following formulae and their mirror images

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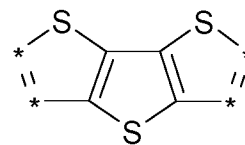
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A3a1

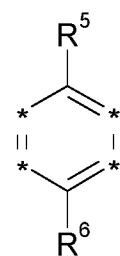


A3b1

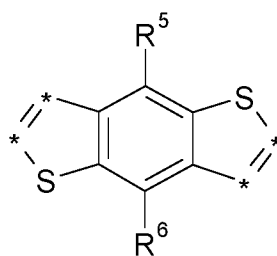


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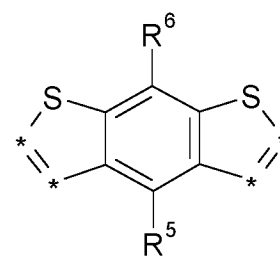
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A3d1

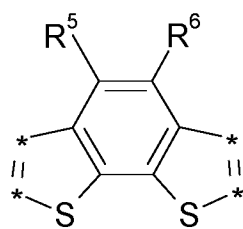


A3e1

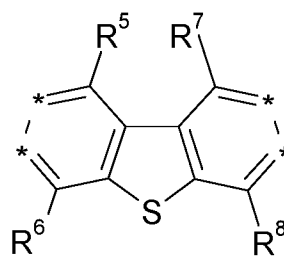


A3f1

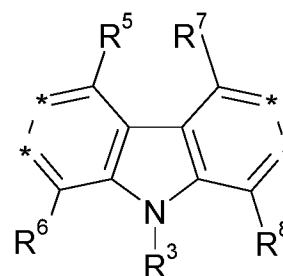
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A3g1

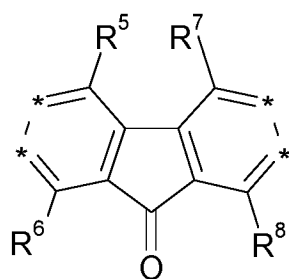


A3h1

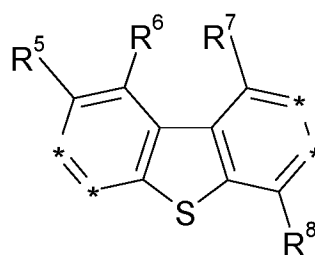


A3h2

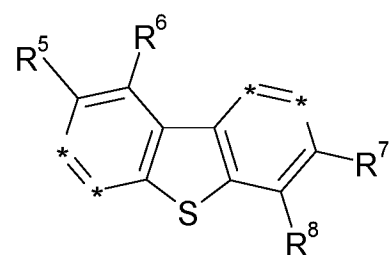
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A3h3



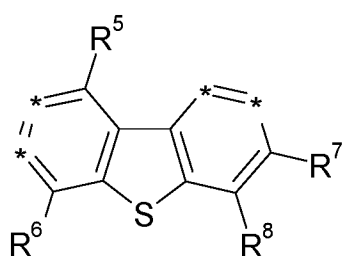
A3i1



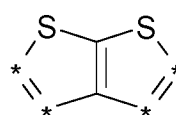
Arj1

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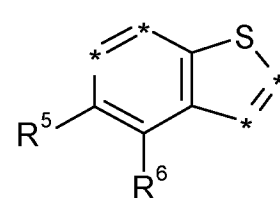
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A3k1



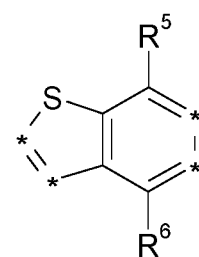
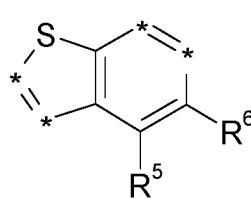
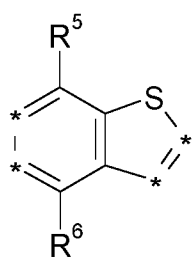
A3m1



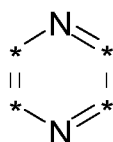
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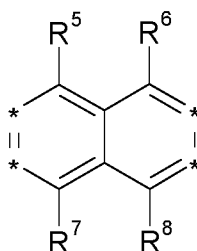
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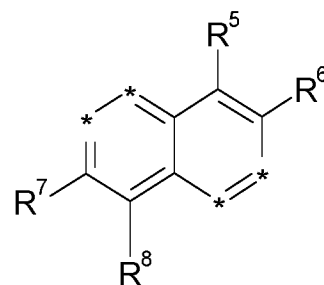
A3o1



A3p1



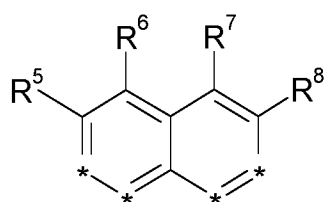
A3q1



A3r1

A3s1

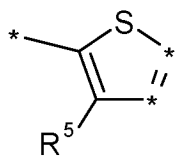
A3t1



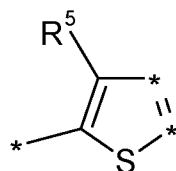
A3u1

wherein R^{5-8} have the meanings given in claim 4.

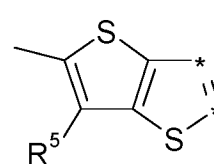
8. The conjugated polymer according to one or more of claims 1 to 7, characterized in that the groups Ar^4 are on each occurrence identically or differently selected from the following formulae and their mirror images



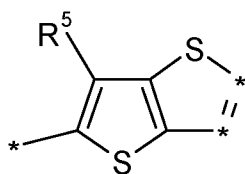
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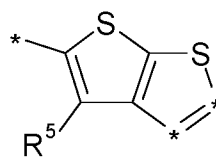
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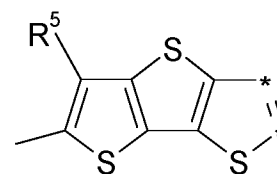
A4c1



A4d1

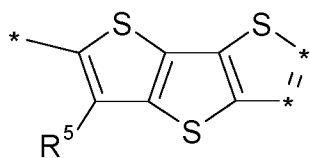


A4e1

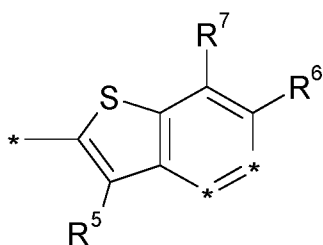


A4f1

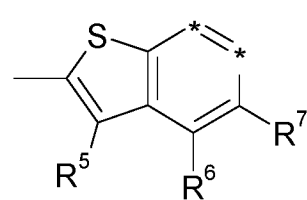
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A4g1

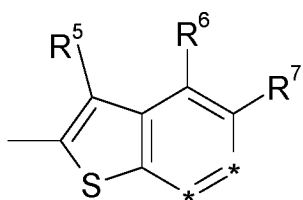


A4h1

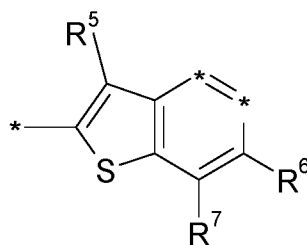


A4i1

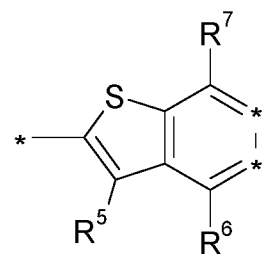
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A4j1

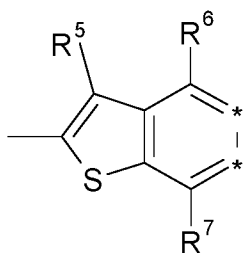


A4k1

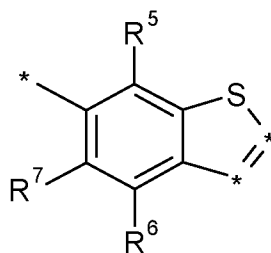


A4l1

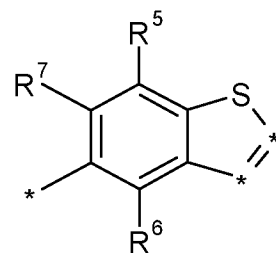
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A4m1

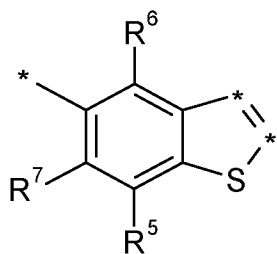


A4n1

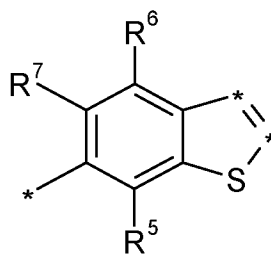


A4o1

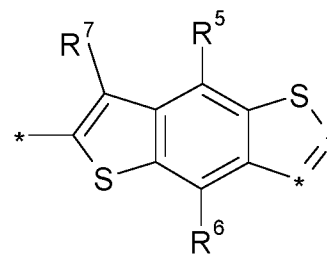
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A4p1



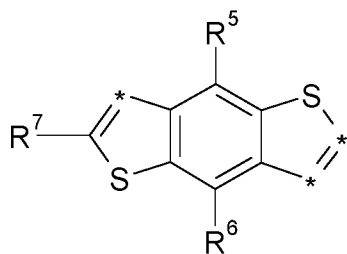
A4q1



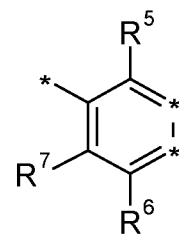
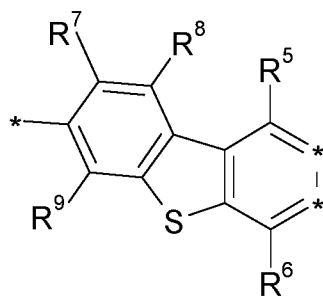
A4r1

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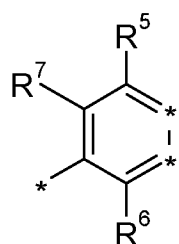
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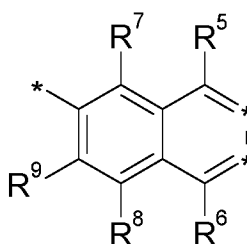


A4s1



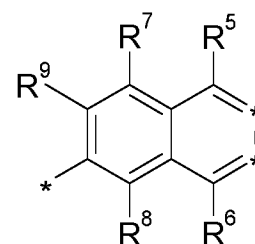
A4v1

A4t1



A4w1

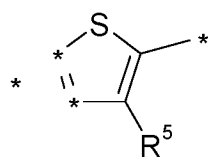
A4u1



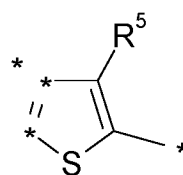
A4x1

wherein R^{5-9} have the meanings given in claim 4 and 5.

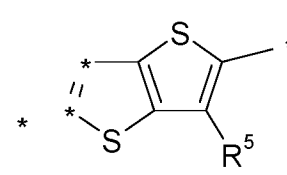
9. The conjugated polymer according to one or more of claims 1 to 8, characterized in that the groups Ar^5 are on each occurrence identically or differently selected from the following formulae and their mirror images



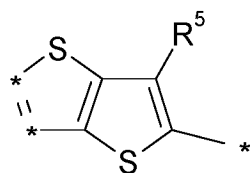
A5a1



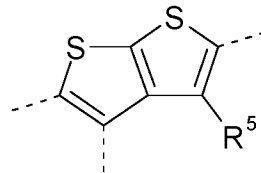
A5b1



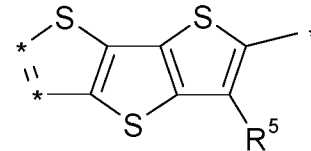
A5c1



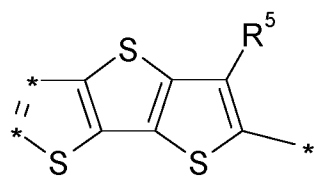
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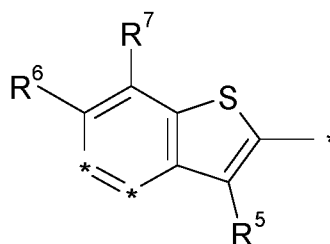
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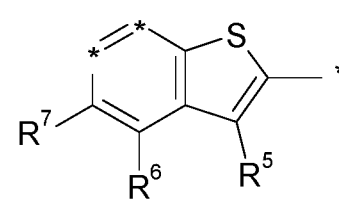
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A5g1

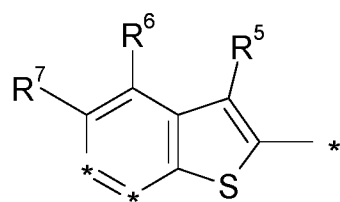


A5h1

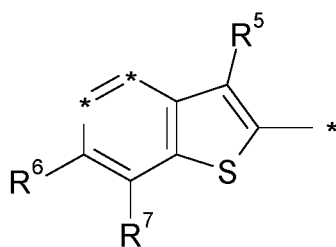


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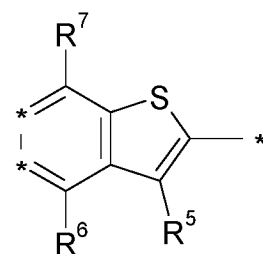
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A5j1

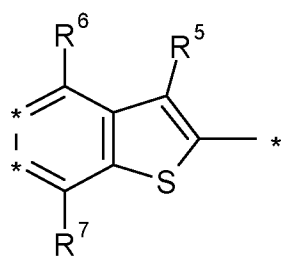


A5k1

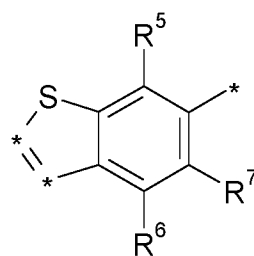


A5l1

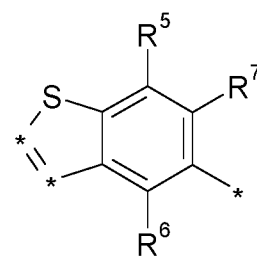
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A5m1

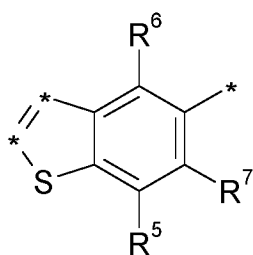


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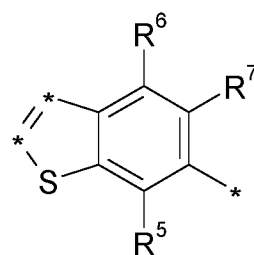


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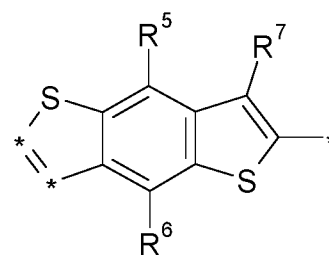
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A5p1

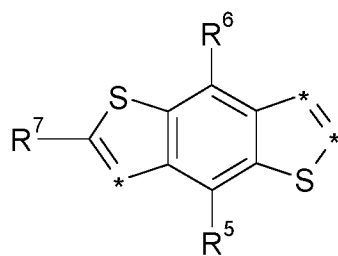


A5q1

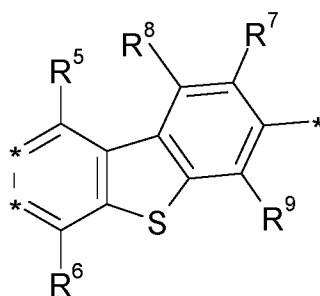


A5r1

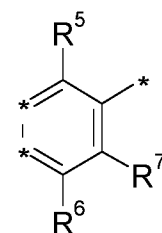
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A5s1



A5t1

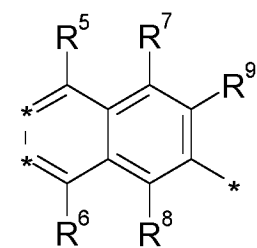
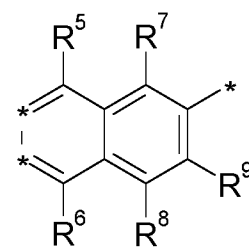
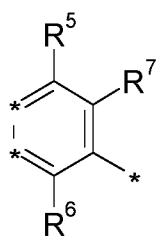


A5u1

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A5v1

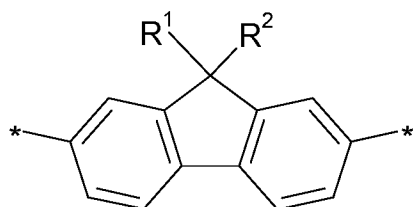
A5w1

A5x1

wherein R^{5-9} have the meanings given in claim 4 and 5.

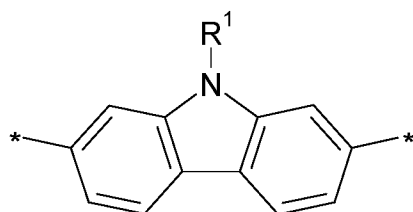
- 5 10. The conjugated polymer according to one or more of claims 1 to 9, characterized in that the units of formula I are selected from the following subformulae

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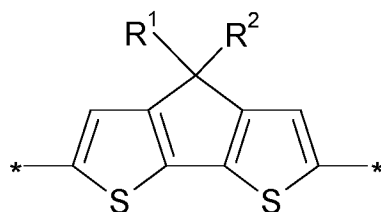
I1-1

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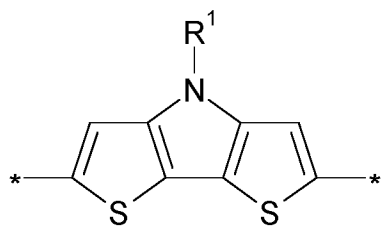
I1-2

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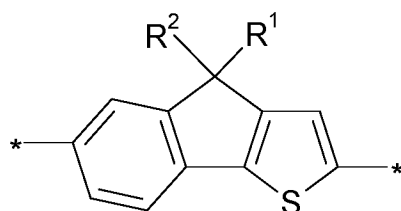
I1-3

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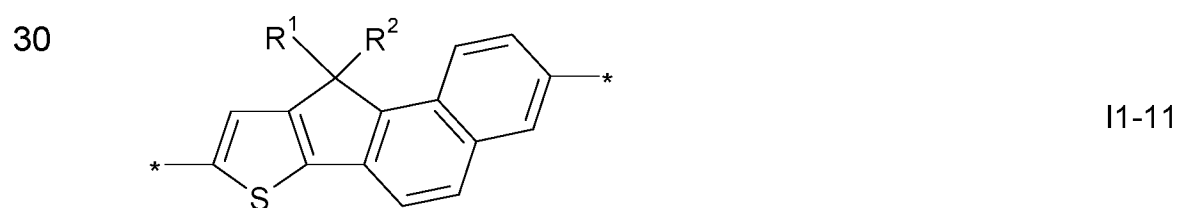
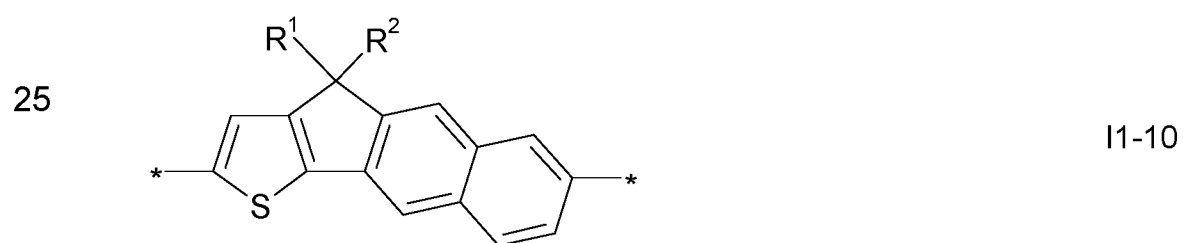
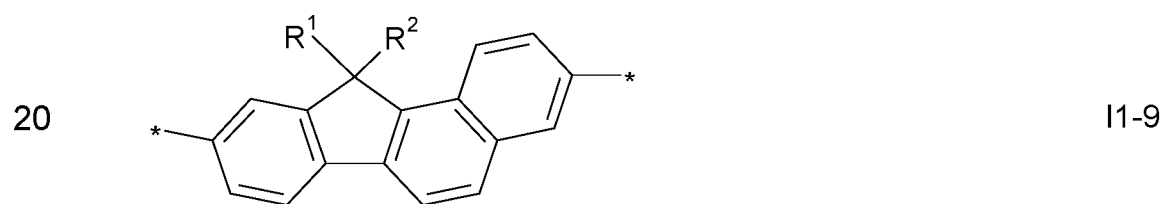
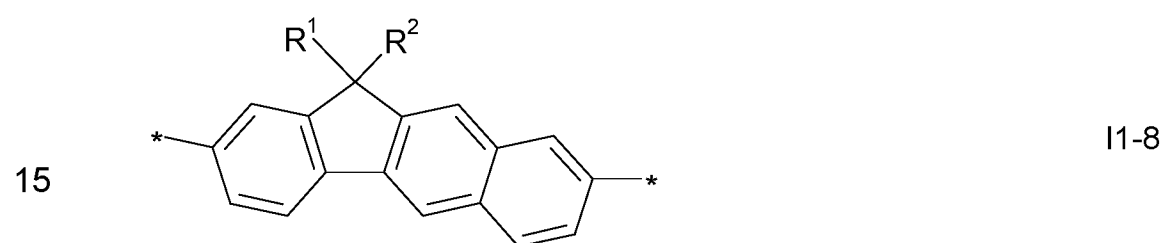
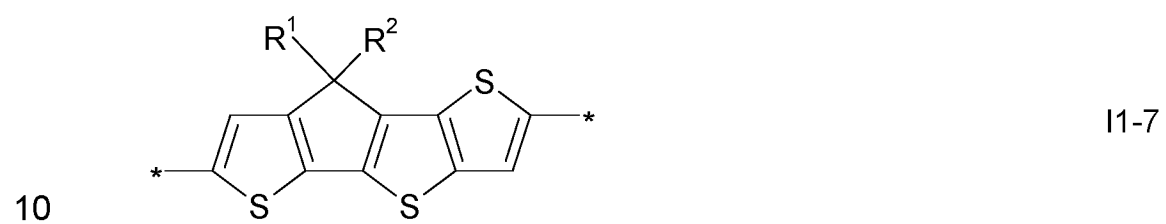
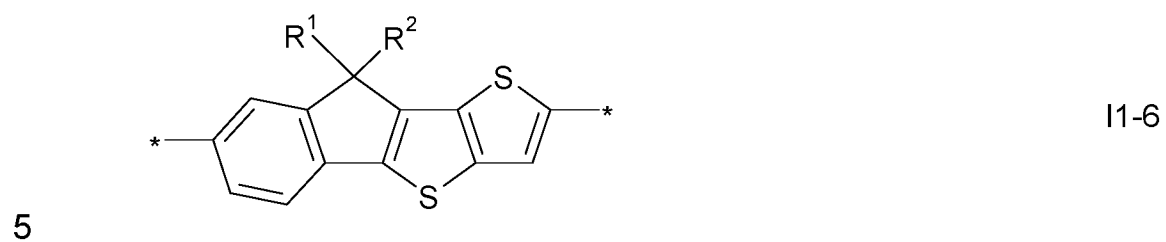
I1-4

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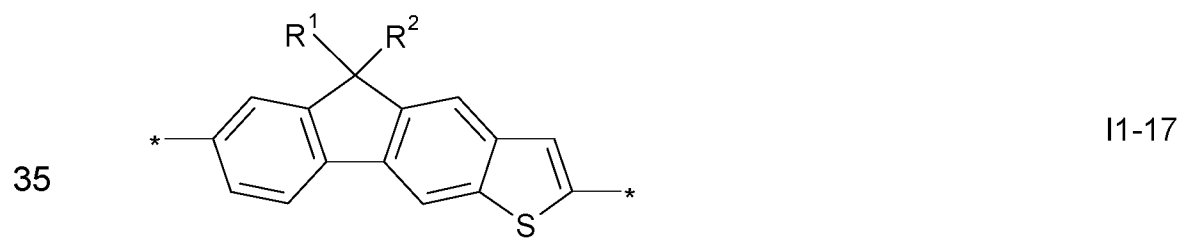
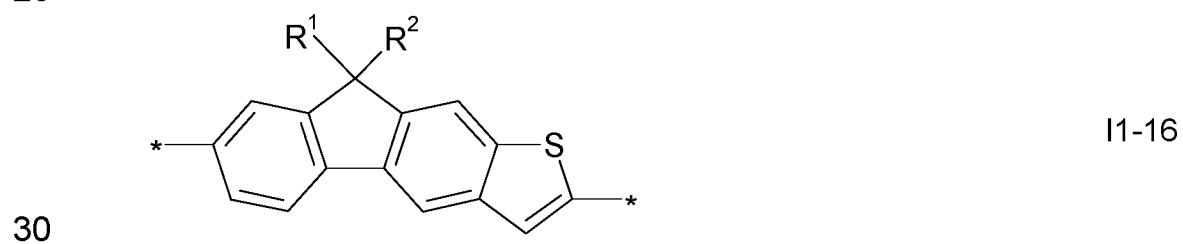
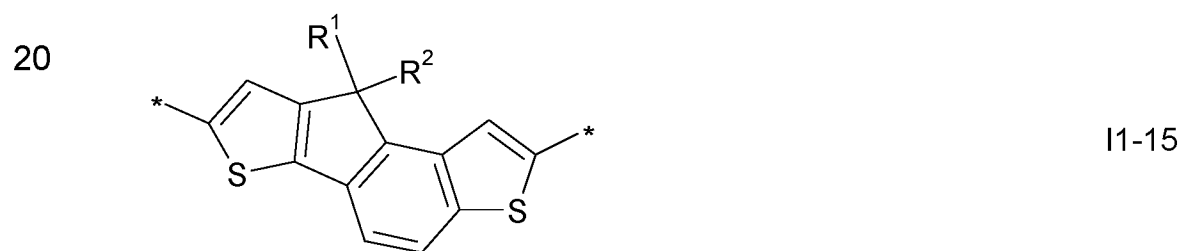
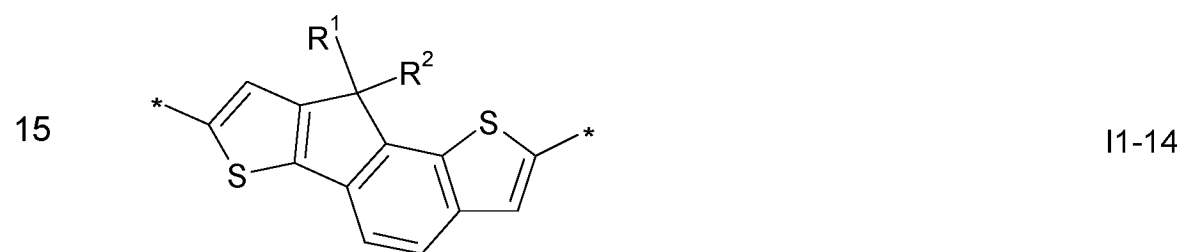
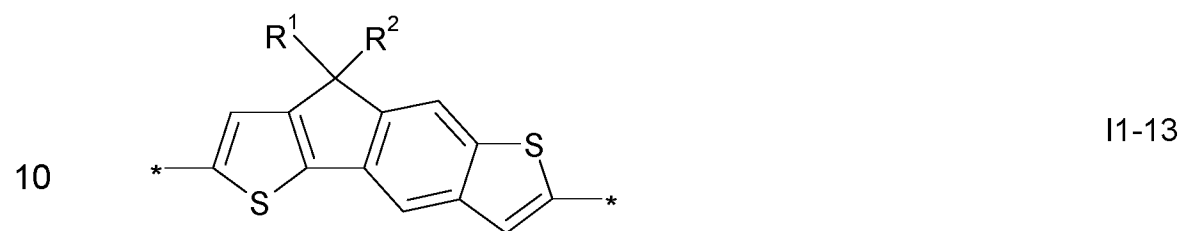
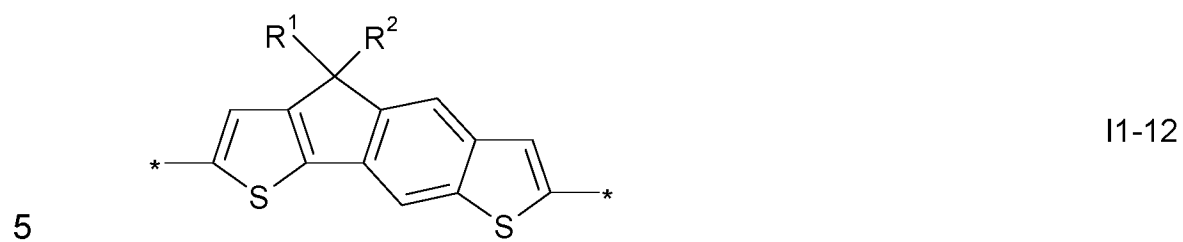


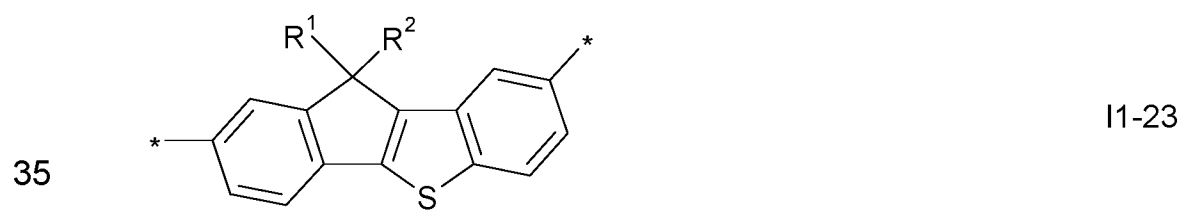
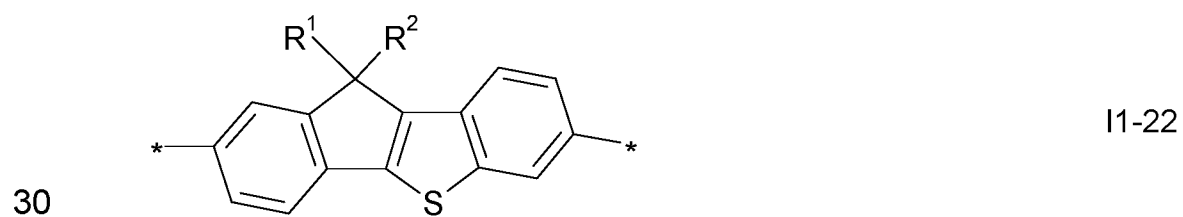
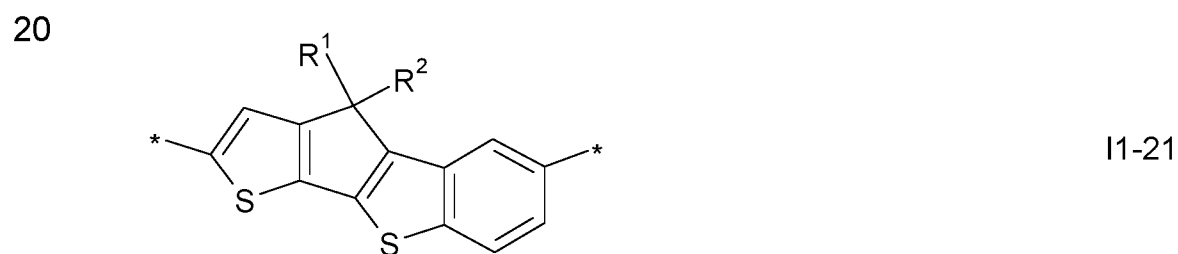
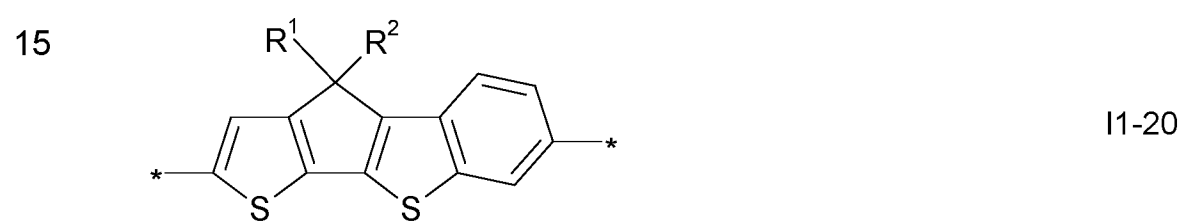
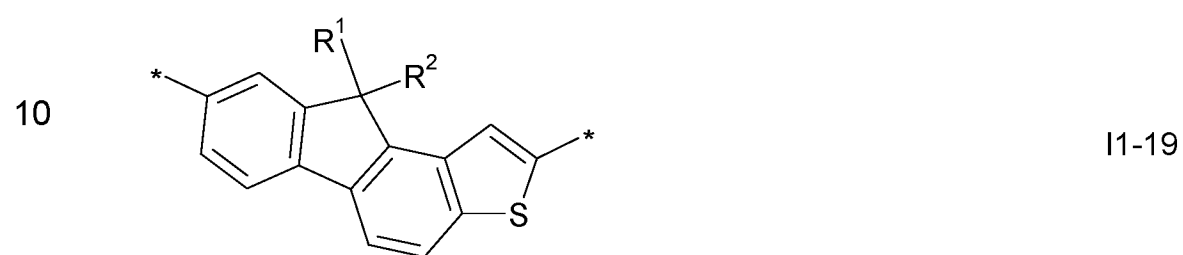
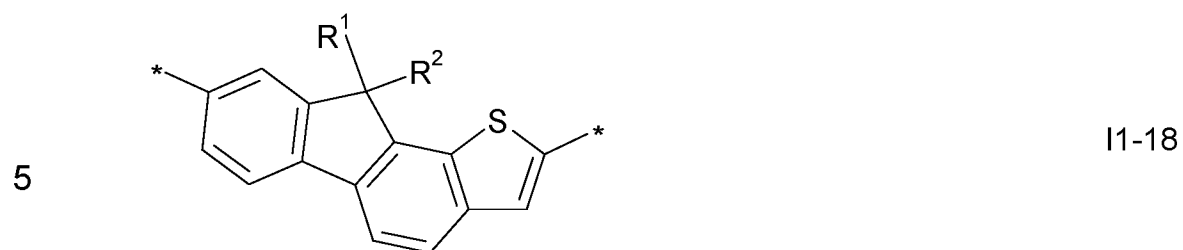
I1-5

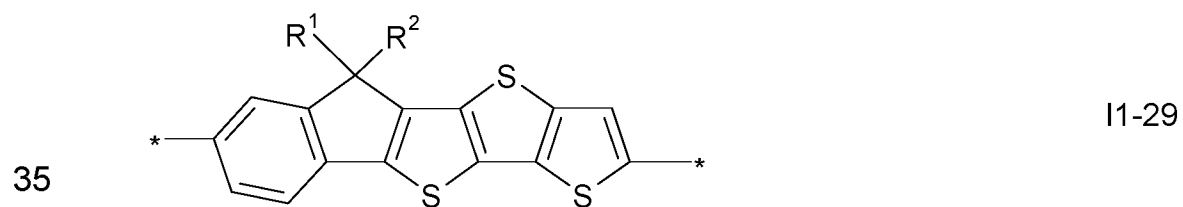
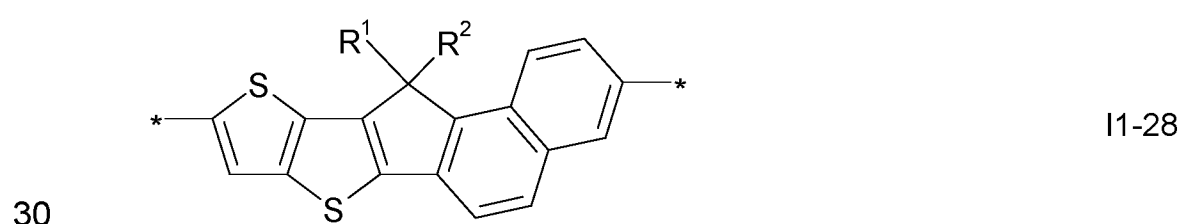
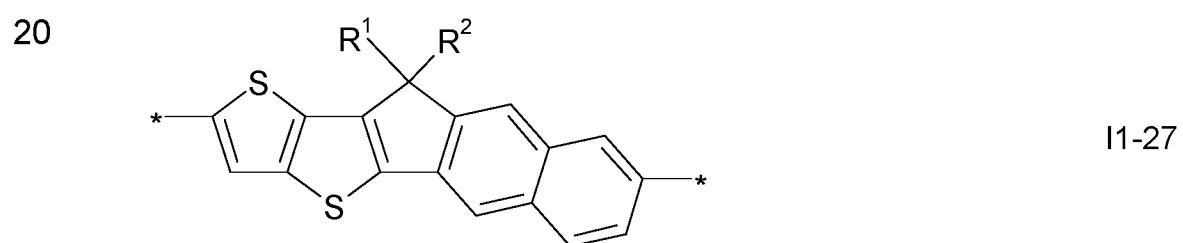
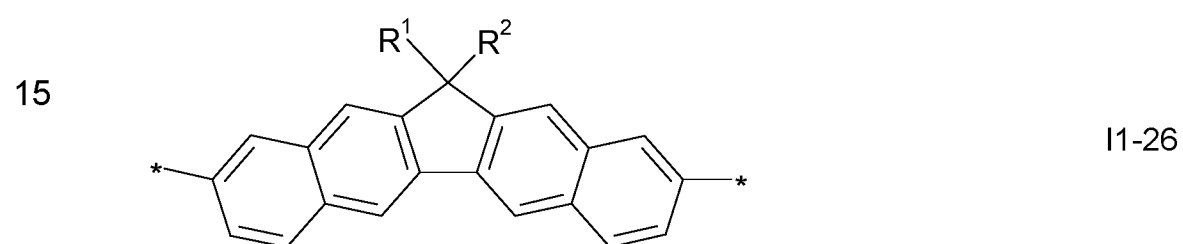
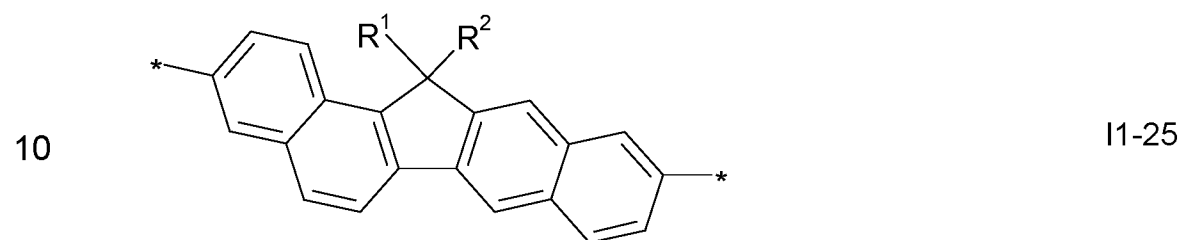
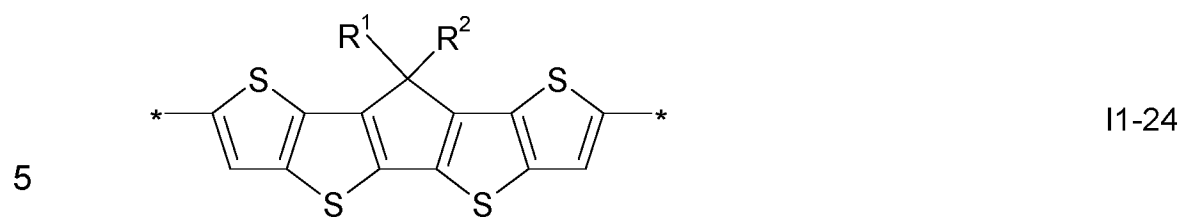
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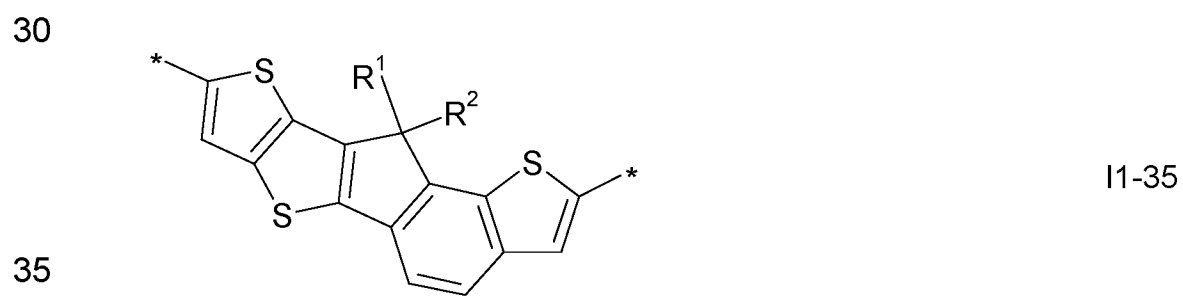
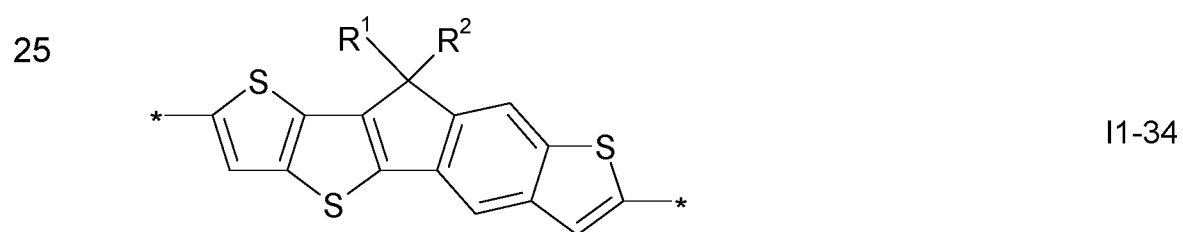
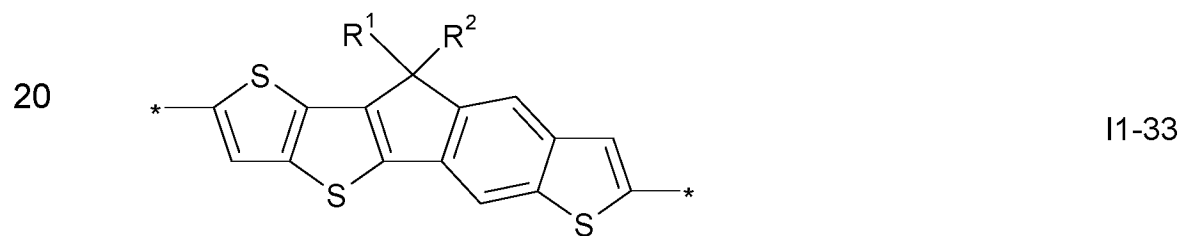
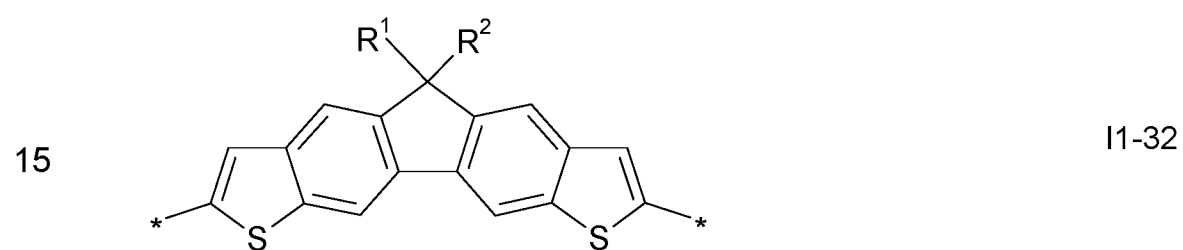
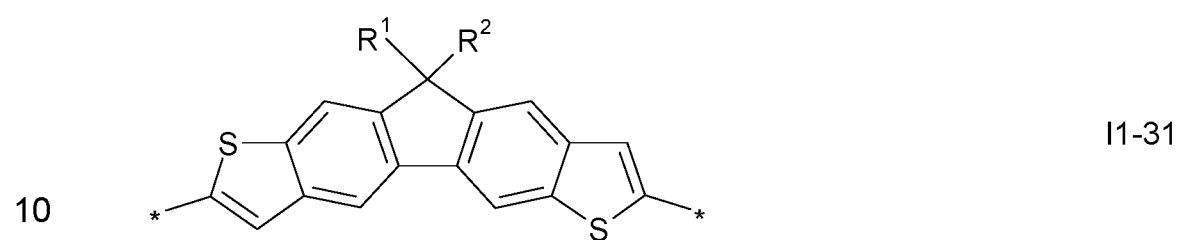
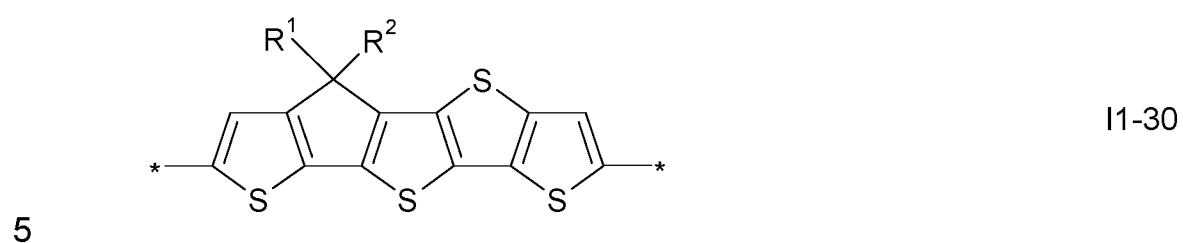


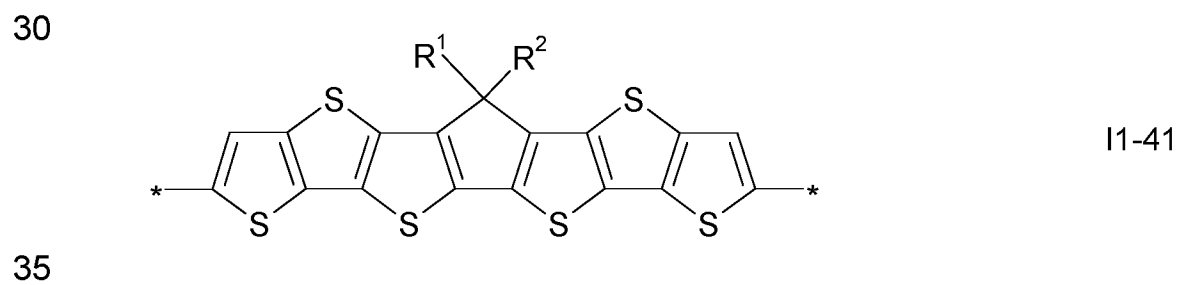
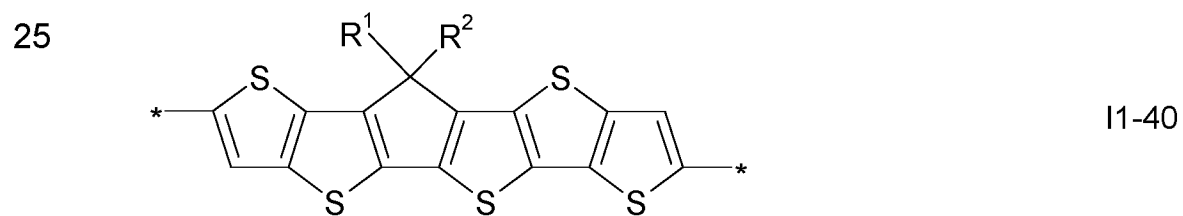
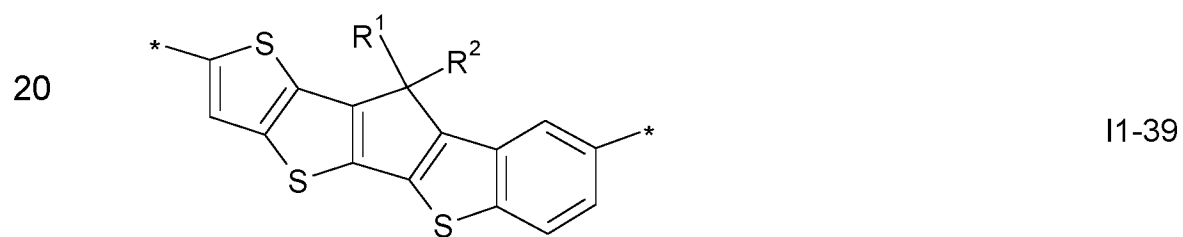
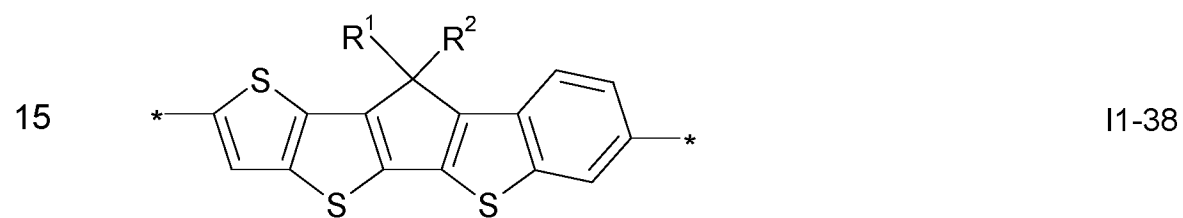
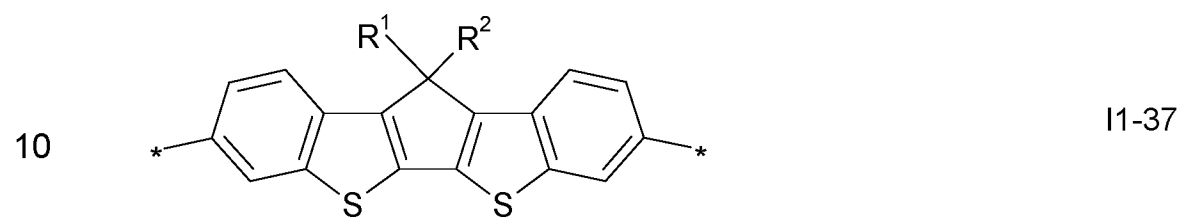
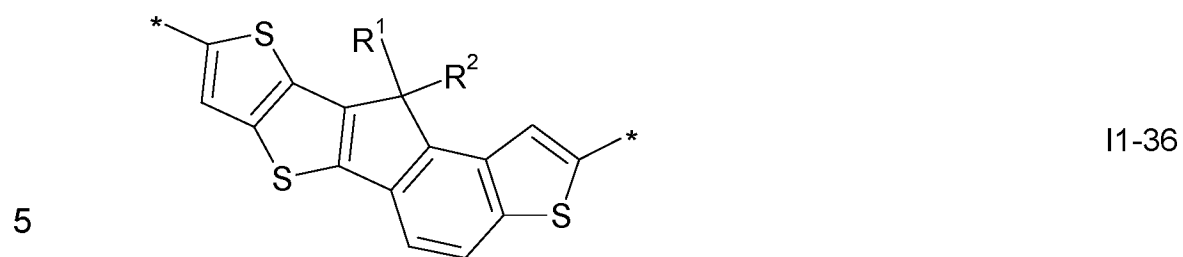
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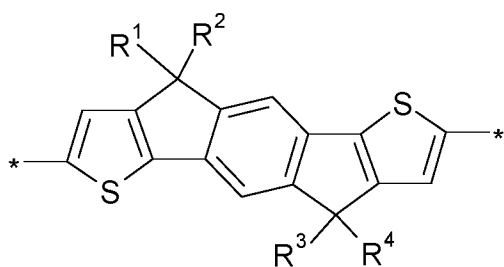






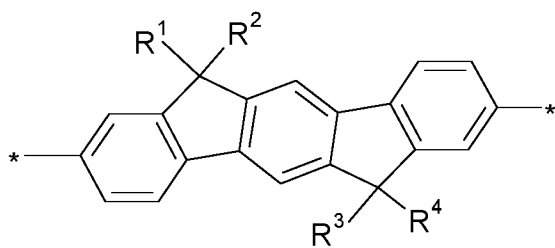


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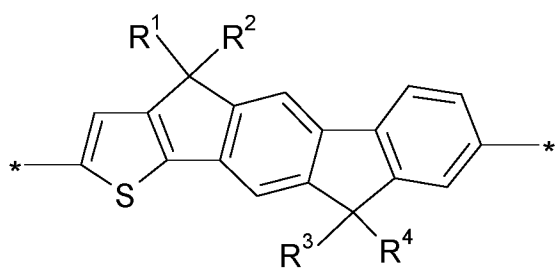
I2-1

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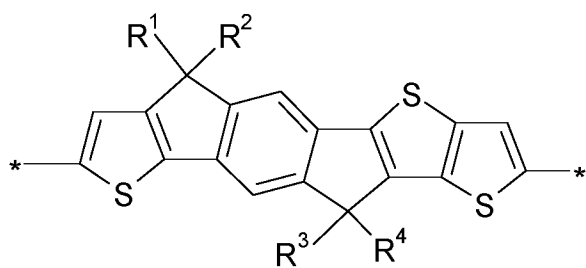
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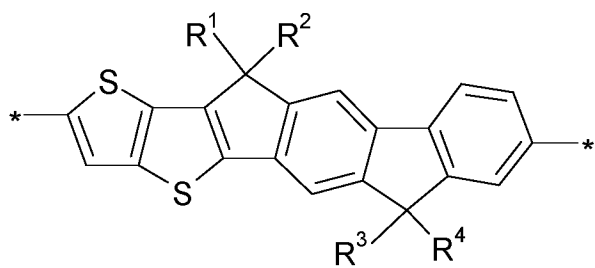
I2-3

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I2-4

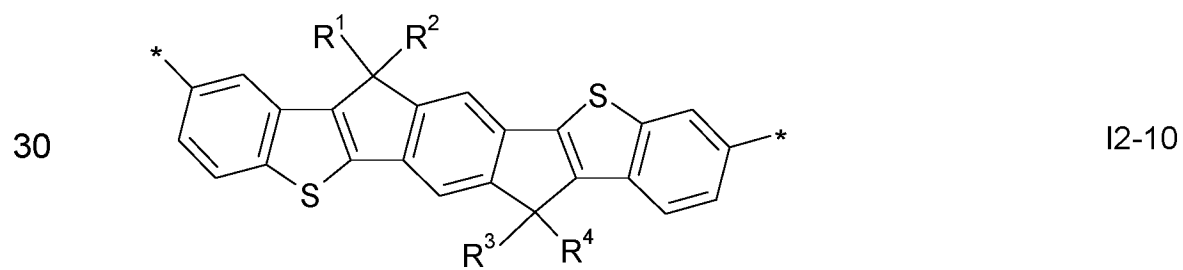
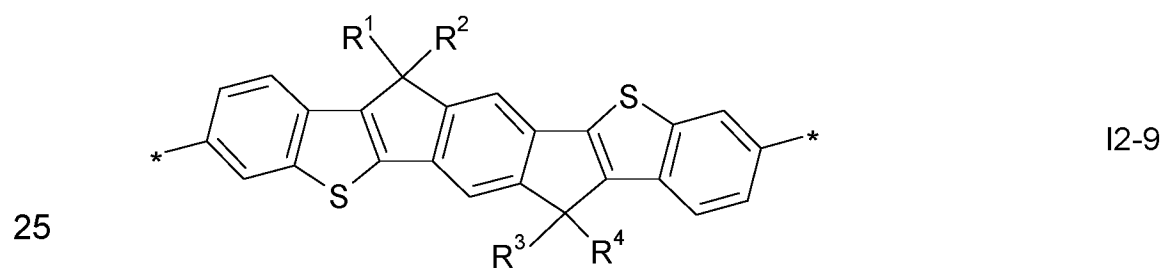
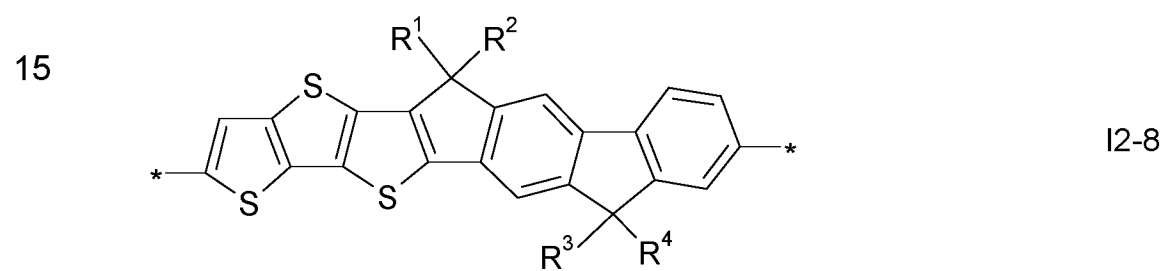
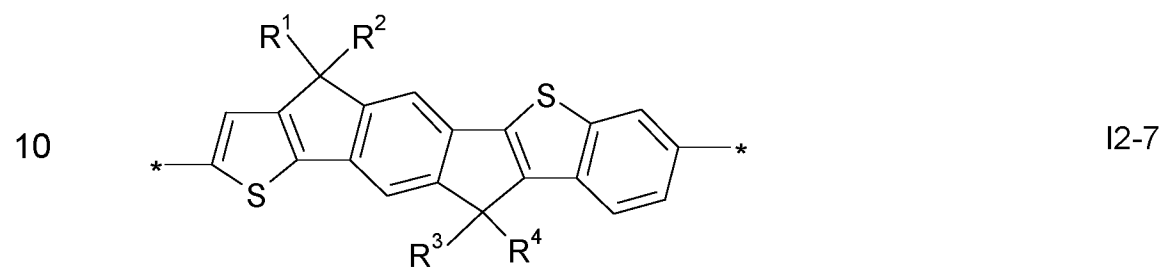
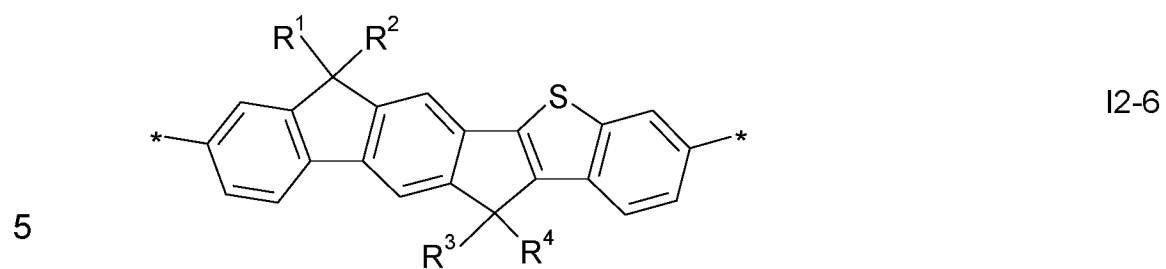
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I2-5

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The chemical structure shows a fluorene core. At the 9-position, there are two substituents, R^1 and R^2 . At the 2-position, there is a substituent R^3 and a thienyl group (a benzene ring fused to a thiophene ring) with an asterisk (*) at the 5-position. At the 6-position, there is a substituent R^4 and another thienyl group with an asterisk (*) at the 5-position.

12-12

The chemical structure shows a fluorene core. At the 9-position, there are two substituents, R^1 and R^2 . At the 2-position, there are two substituents, R^3 and R^4 . The fluorene is substituted at the 1 and 8 positions with thienyl groups. Each thienyl group is attached at its 2-position to the fluorene ring and has an asterisk (*) at its 5-position, indicating a point of attachment or a specific substituent.

12-13

The chemical structure shows a fluorene core substituted at the 1, 8, 9, and 10 positions with groups R^1 , R^2 , R^3 , and R^4 respectively. The fluorene is linked at its 2 and 7 positions to two thienyl rings. Each thienyl ring has an asterisk (*) at its 5-position, indicating a site for further substitution or a specific functional group.

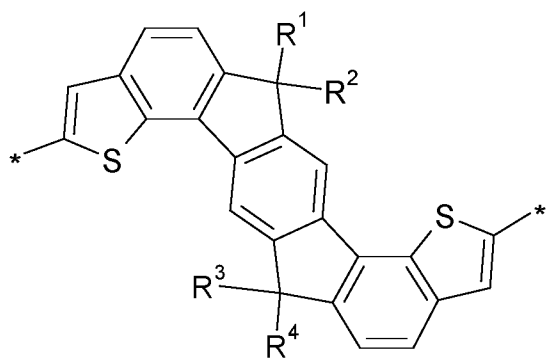
12-14

The chemical structure shows a fluorene core. At the 9-position, there are two substituents, R^1 and R^2 . At the 2-position, there is a substituent R^3 and a thienyl group (a benzene ring fused to a thiophene ring, with an asterisk $*$ on the thiophene ring). At the 7-position, there is a substituent R^4 and another thienyl group (also marked with an asterisk $*$).

12-15

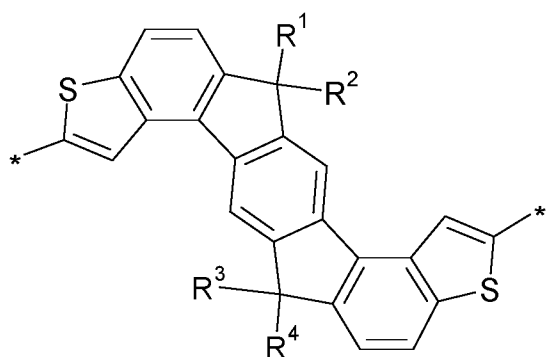
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I2-16

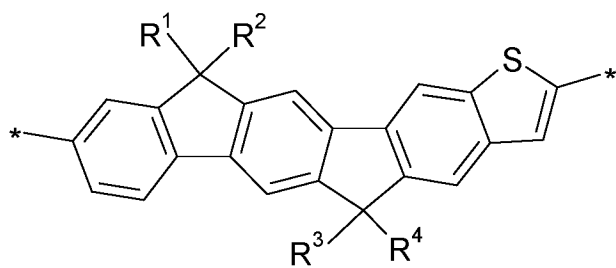
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I2-17

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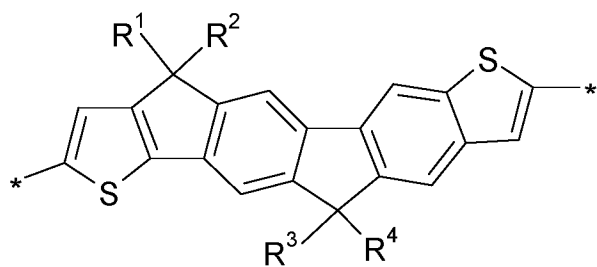
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I2-18

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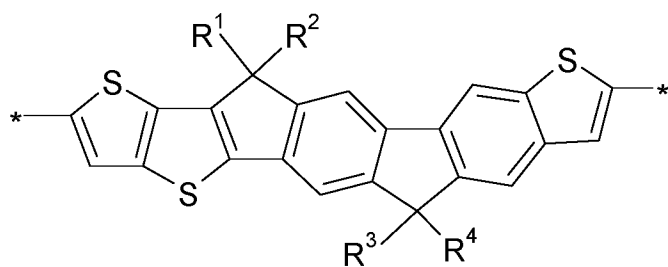
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I2-19

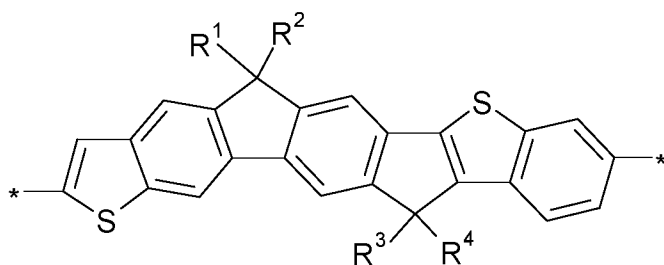
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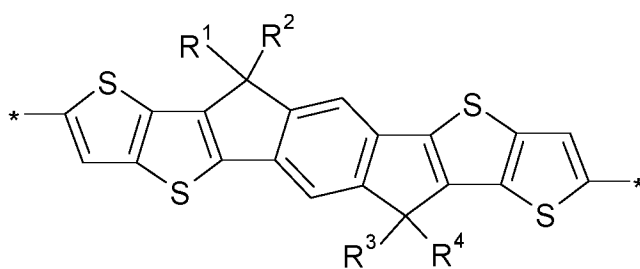
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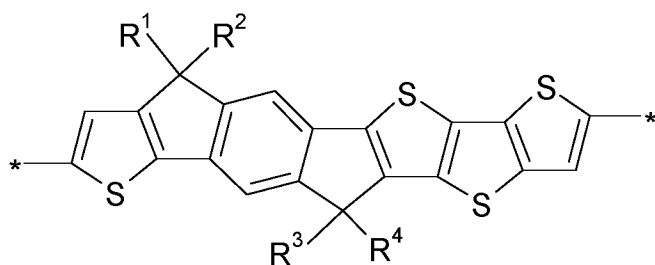
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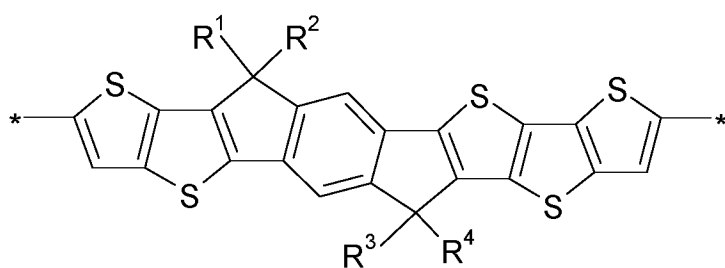
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12-23

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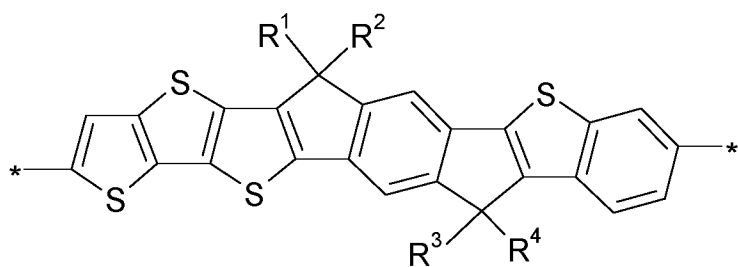


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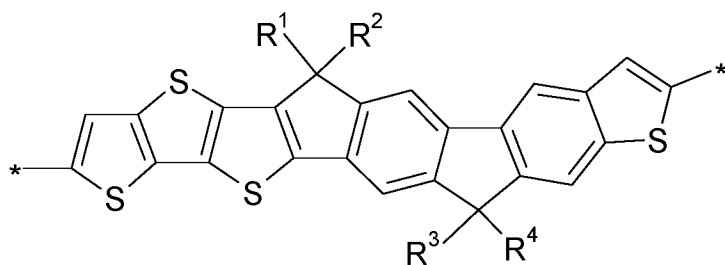
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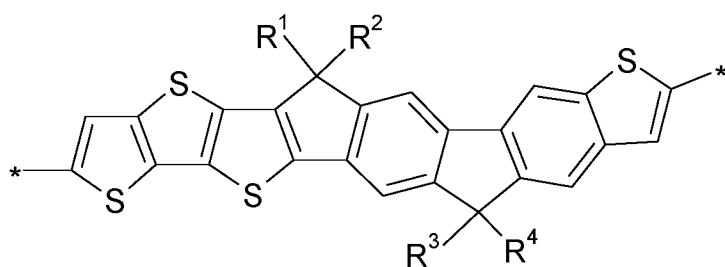
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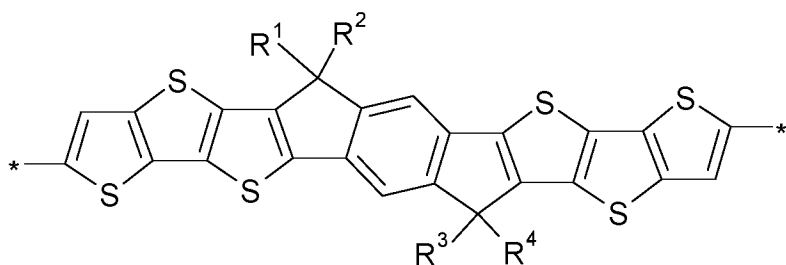
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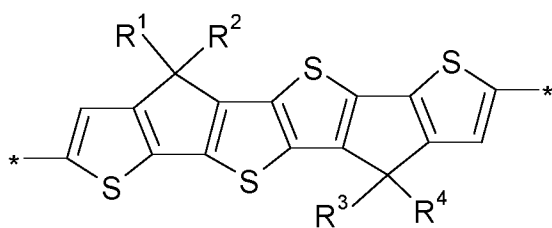
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12-28

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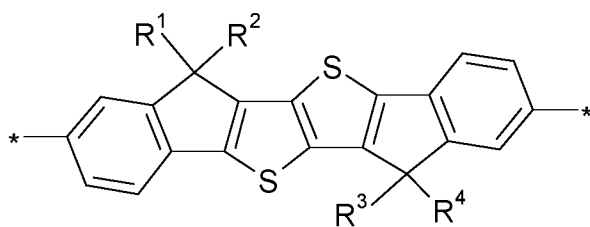


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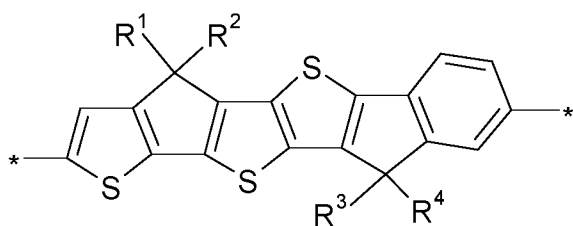
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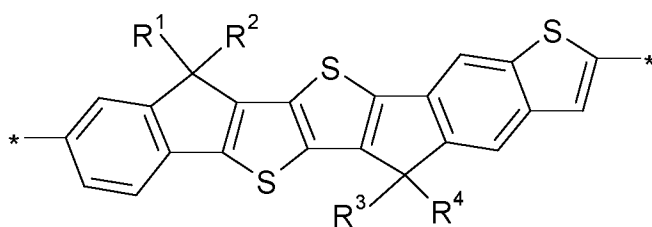
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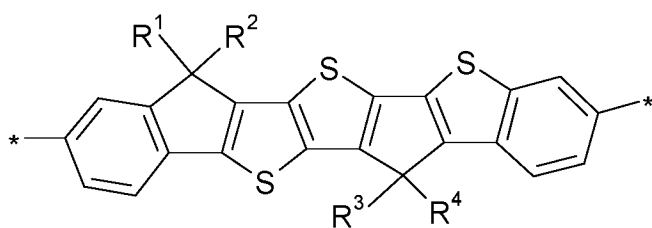
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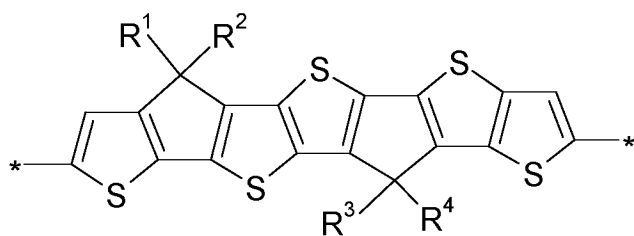
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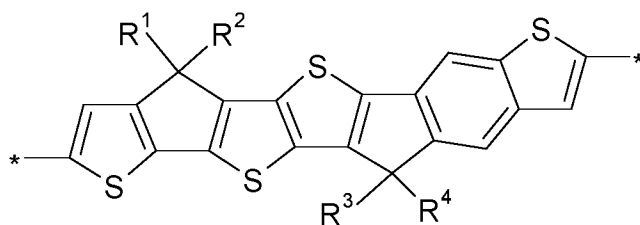
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12-34

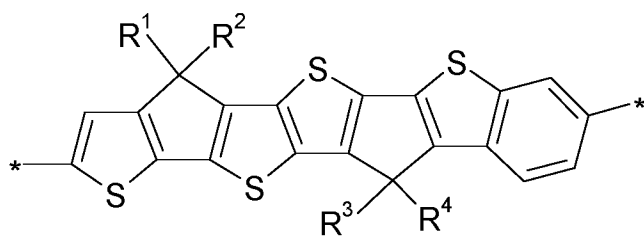
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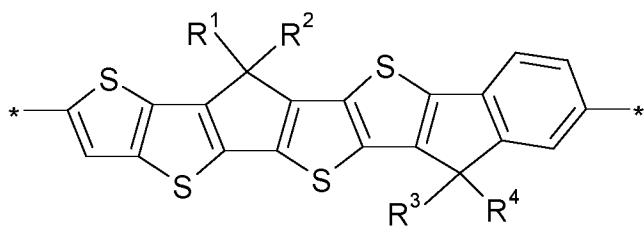
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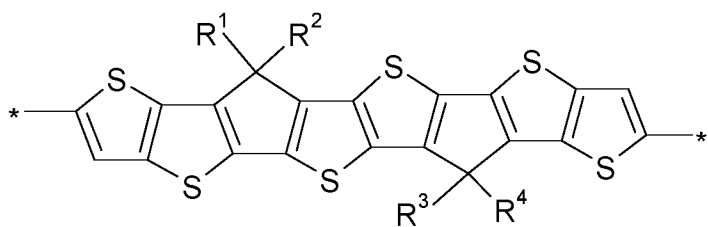
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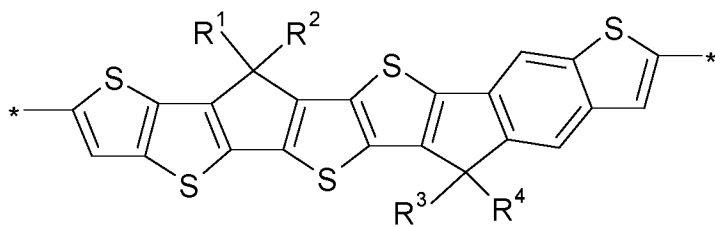
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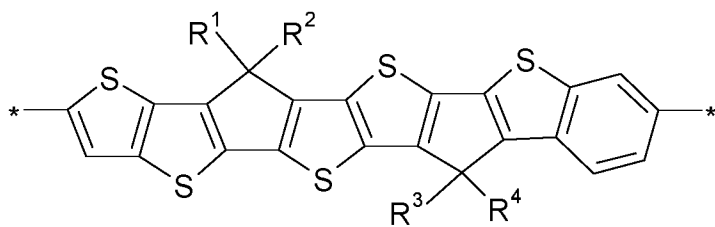
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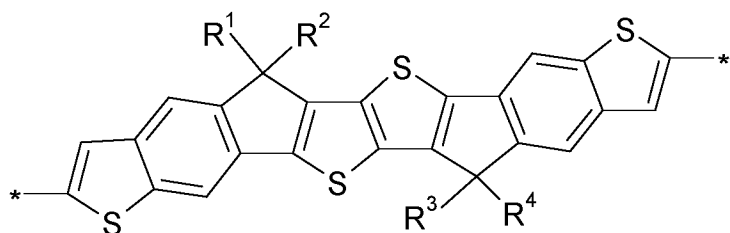
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12-40

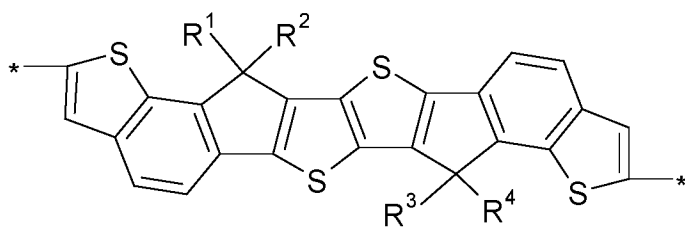
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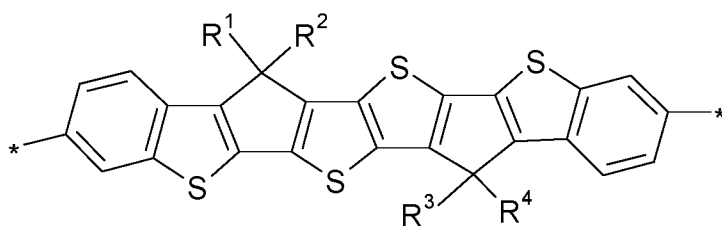
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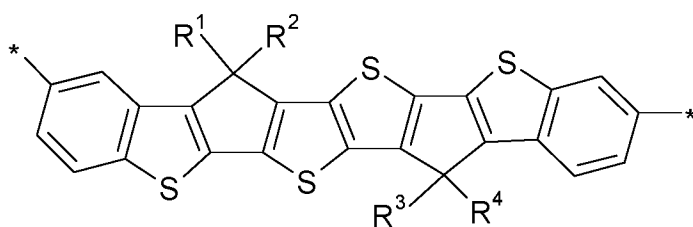
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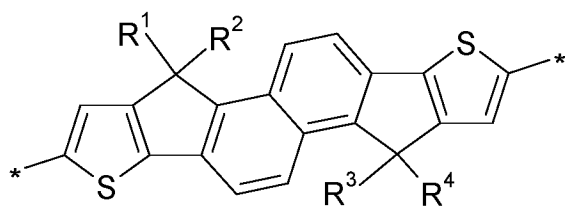
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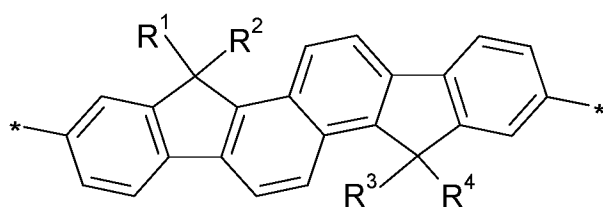
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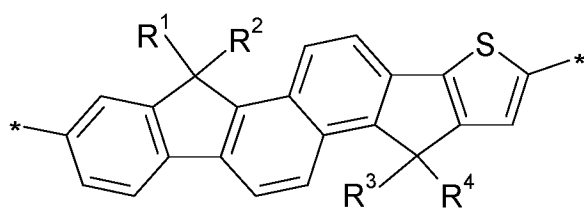
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12-46

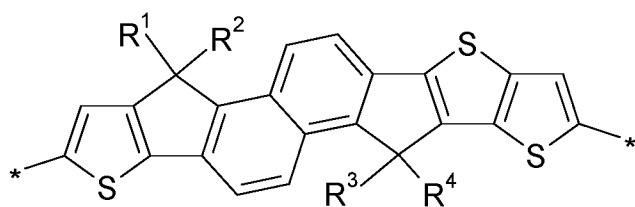
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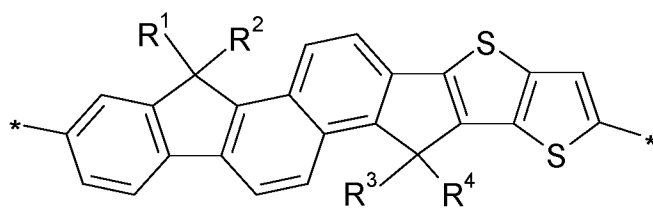
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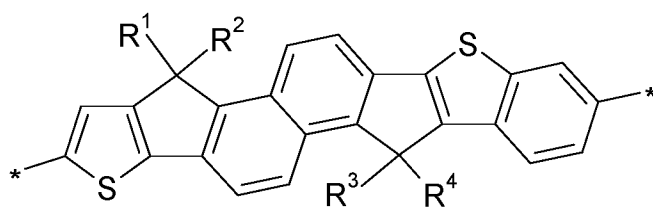
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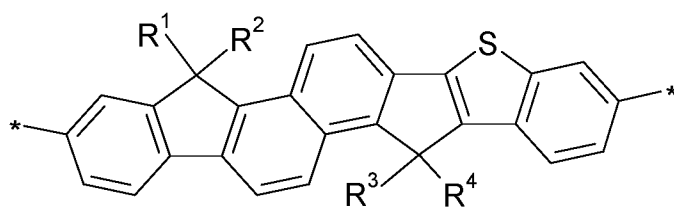
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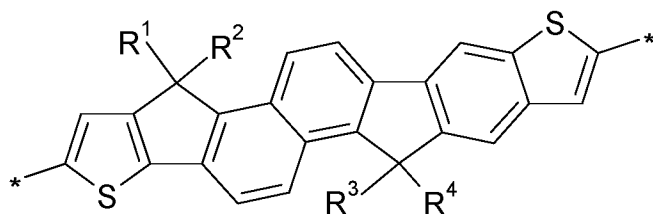
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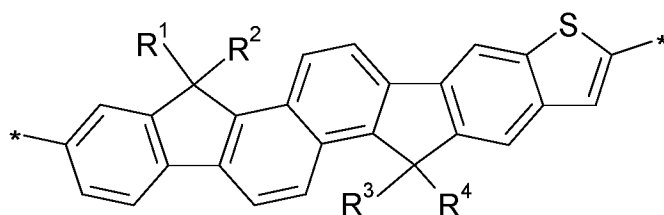
I2-51

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I2-52

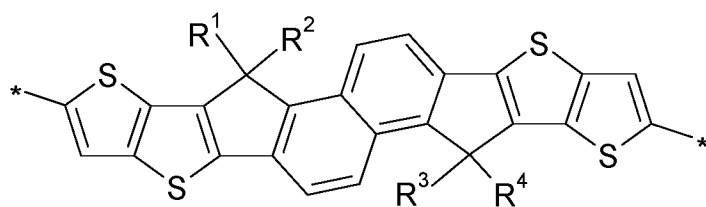
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I2-53

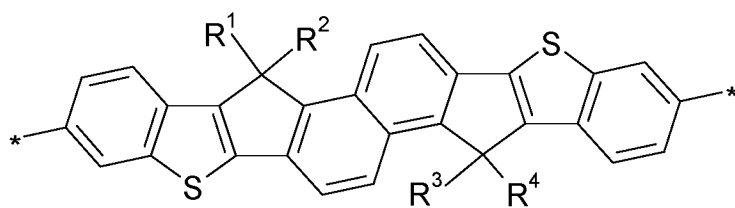
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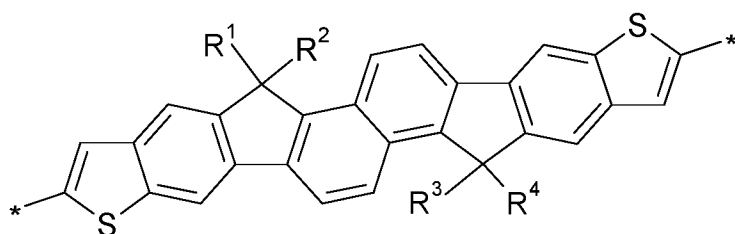
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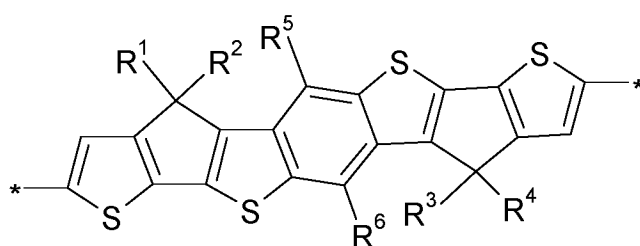
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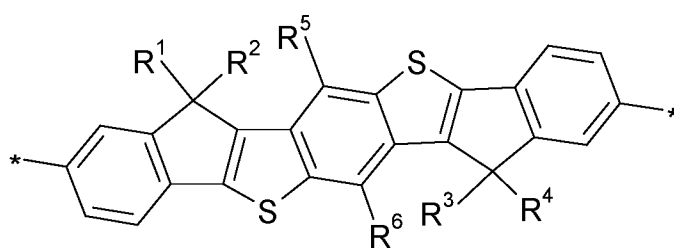
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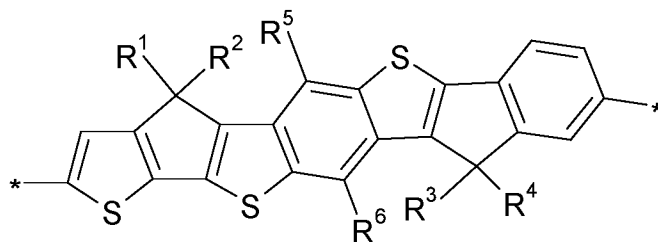
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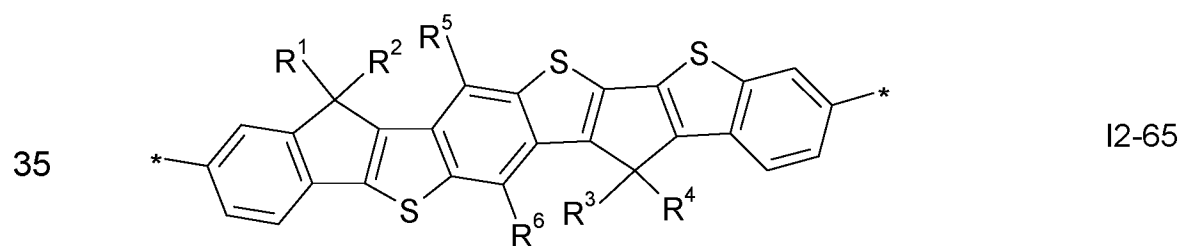
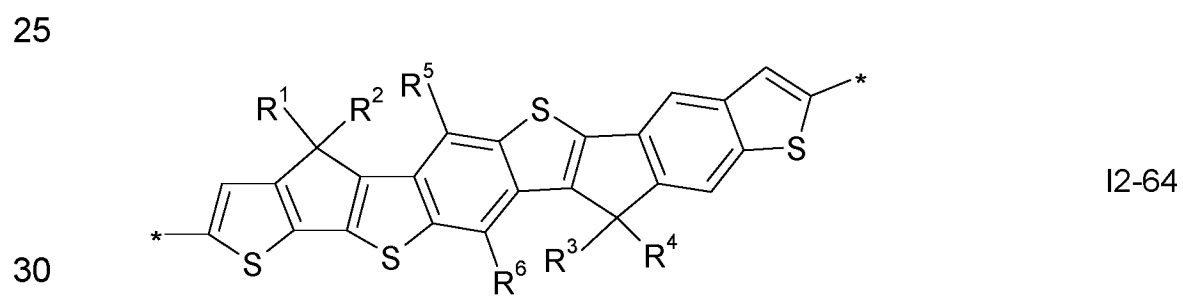
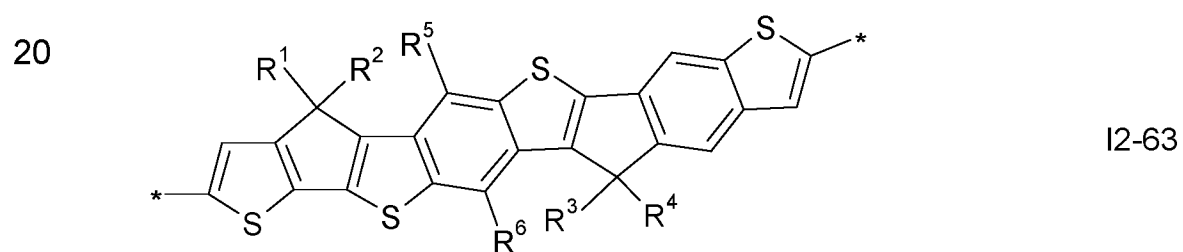
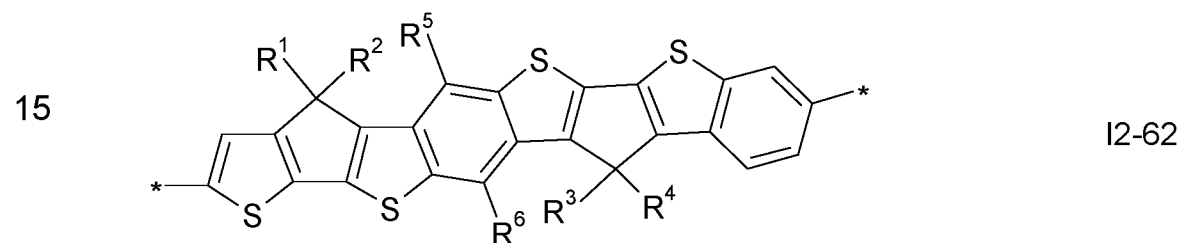
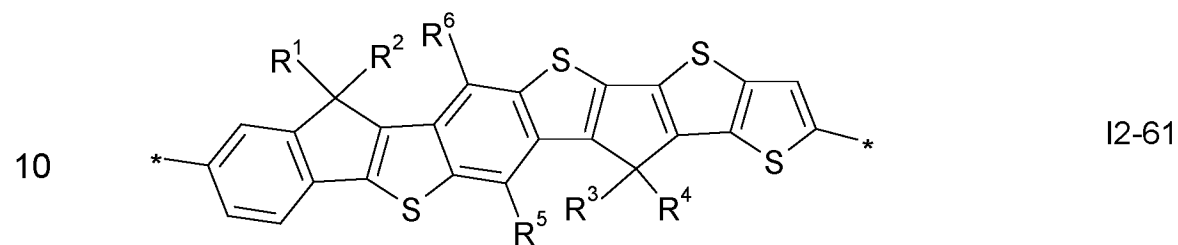
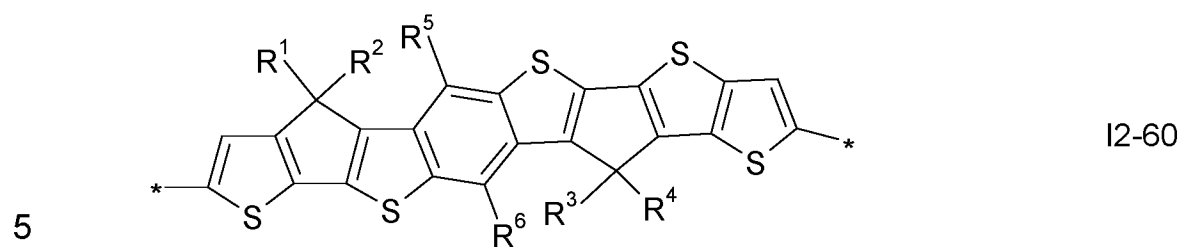
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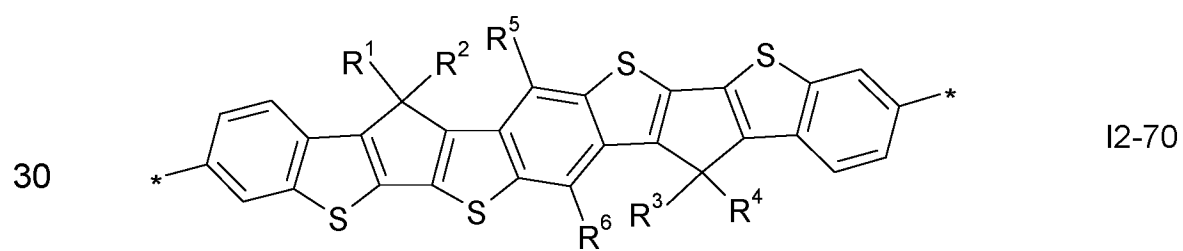
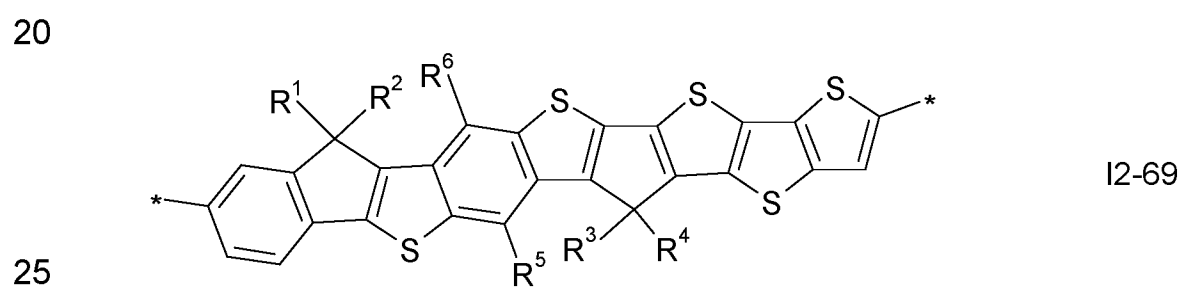
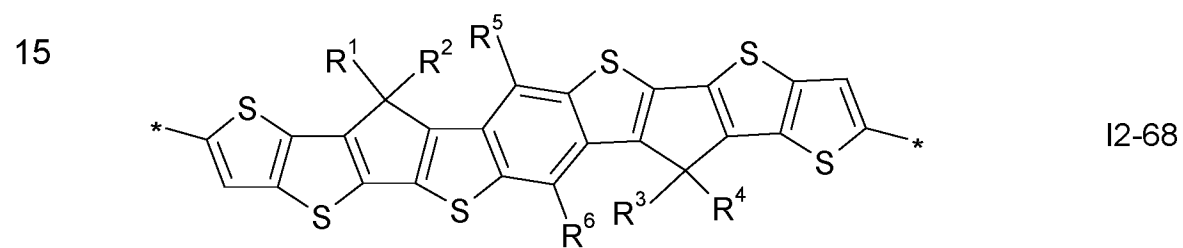
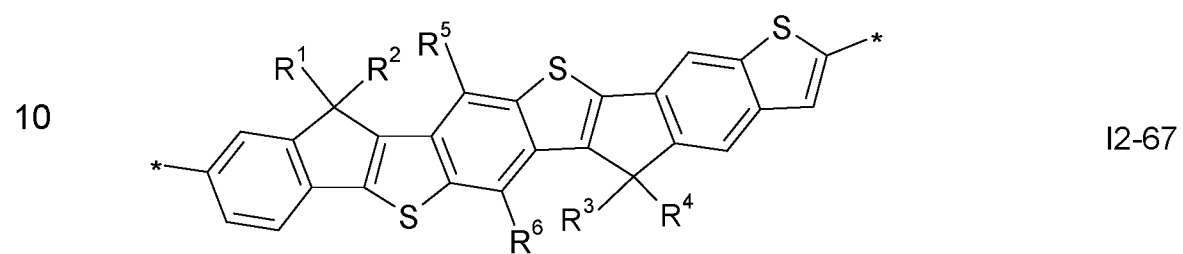
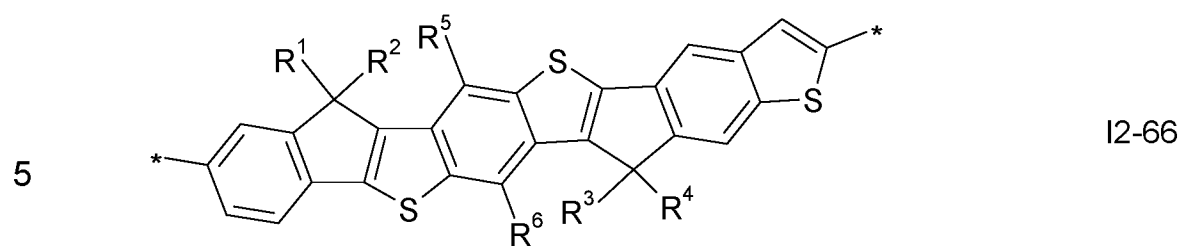
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12-59

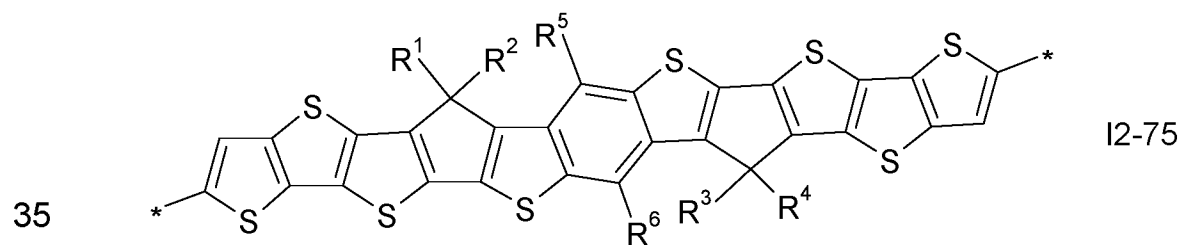
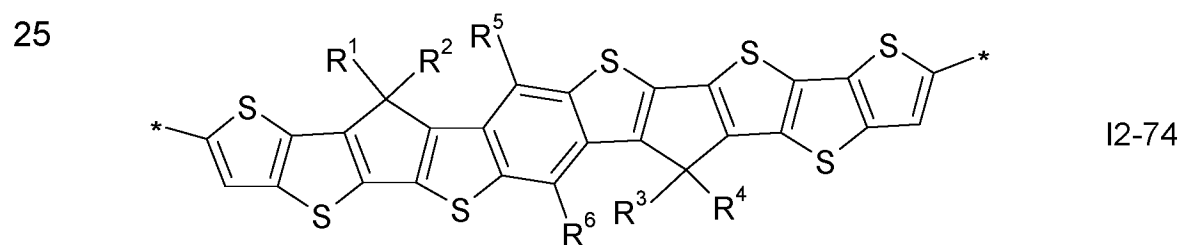
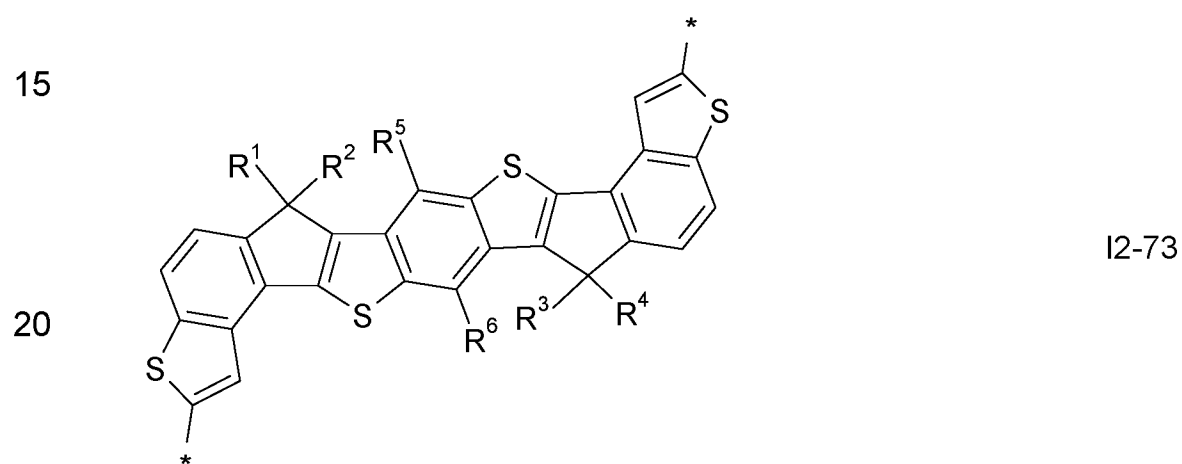
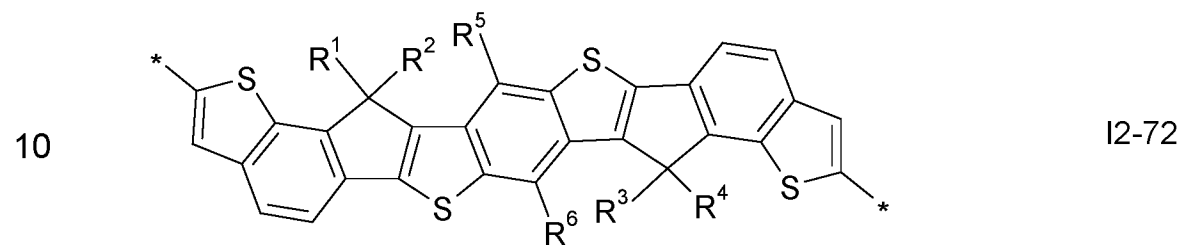
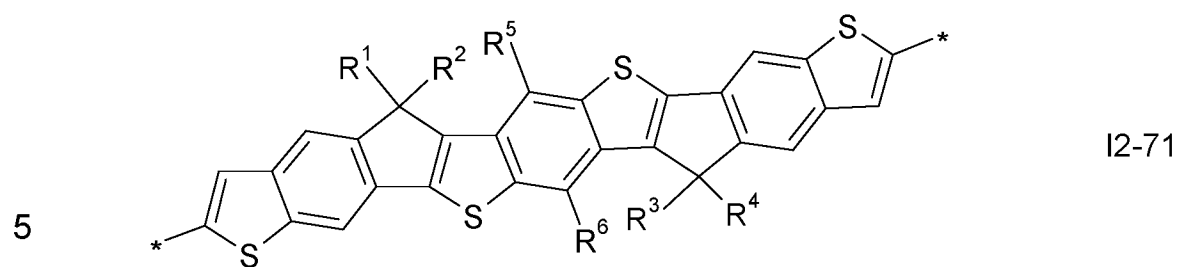
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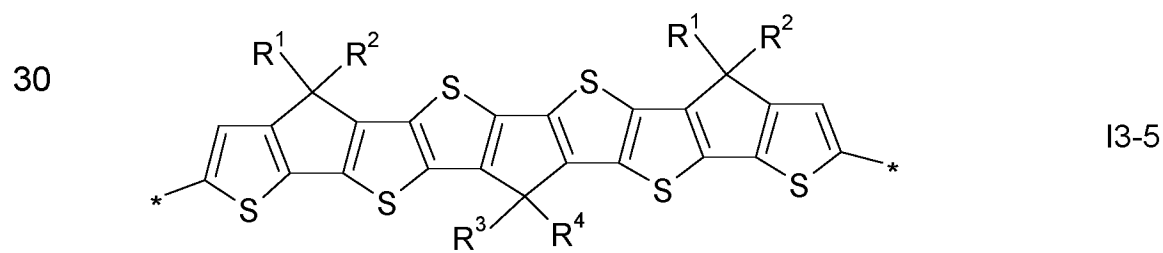
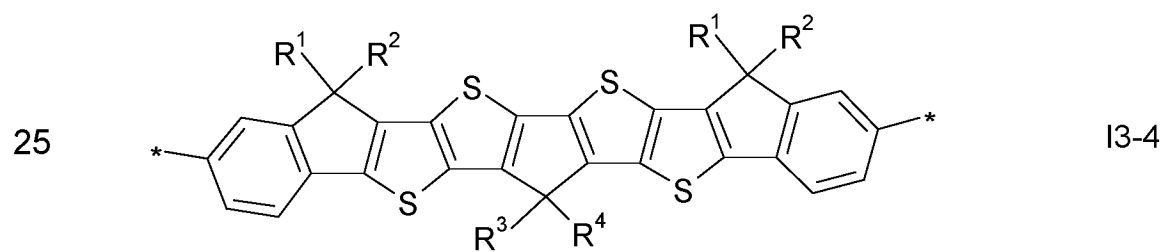
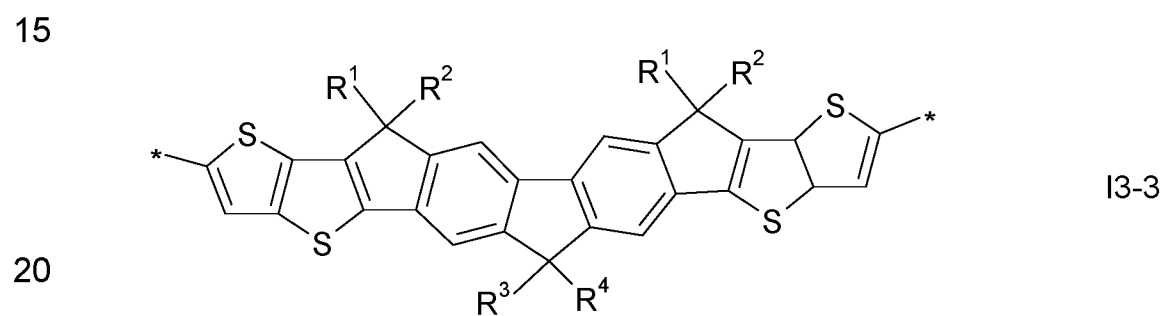
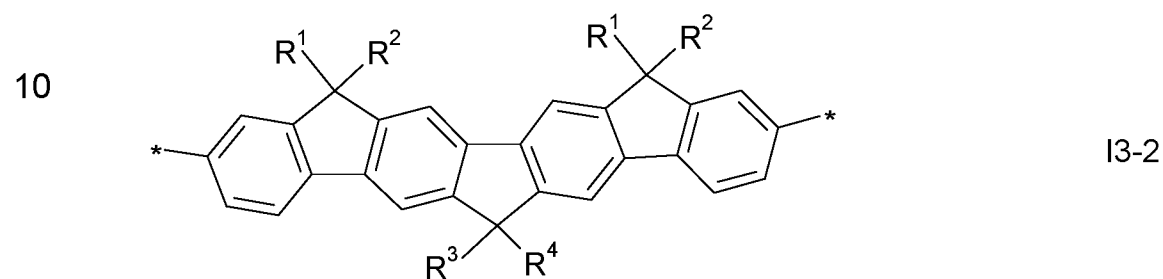
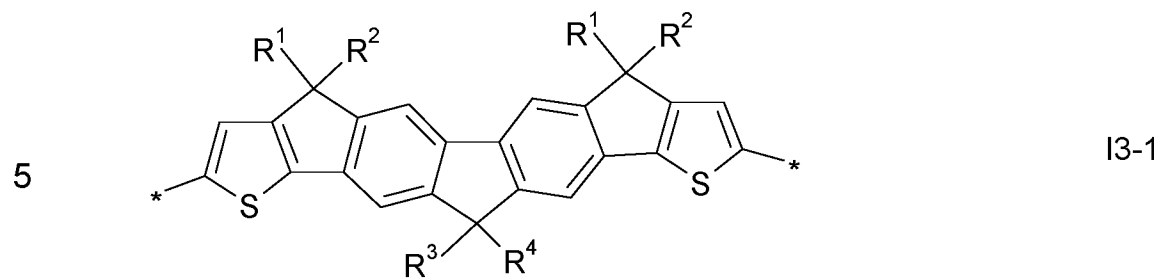




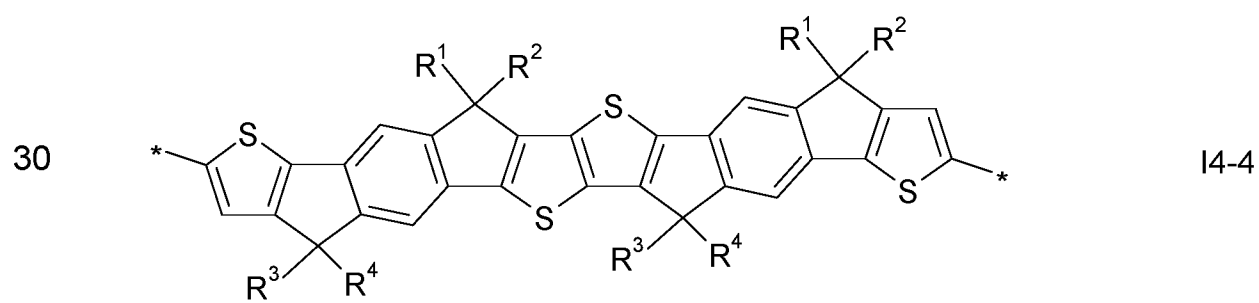
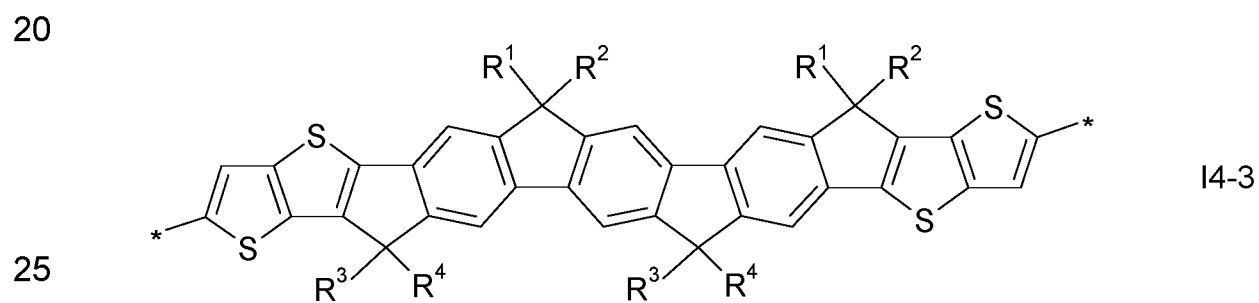
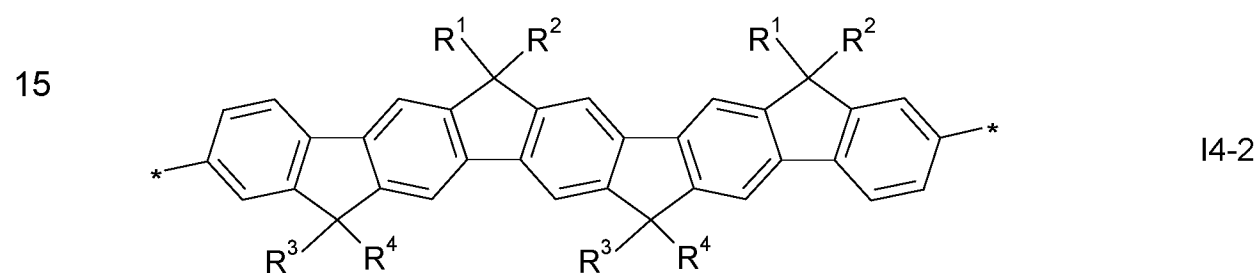
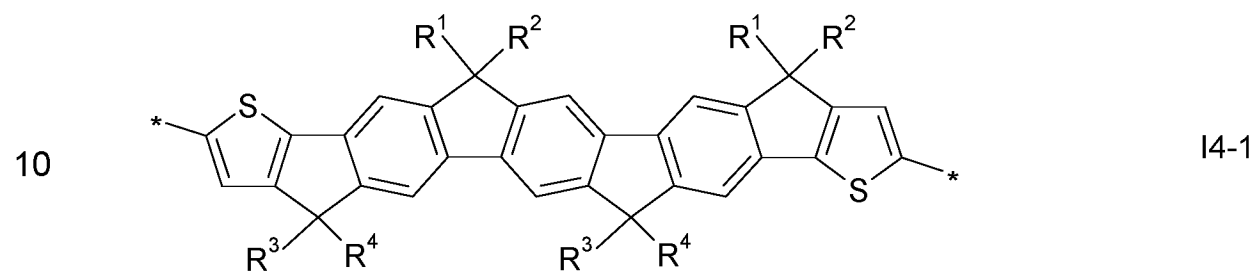
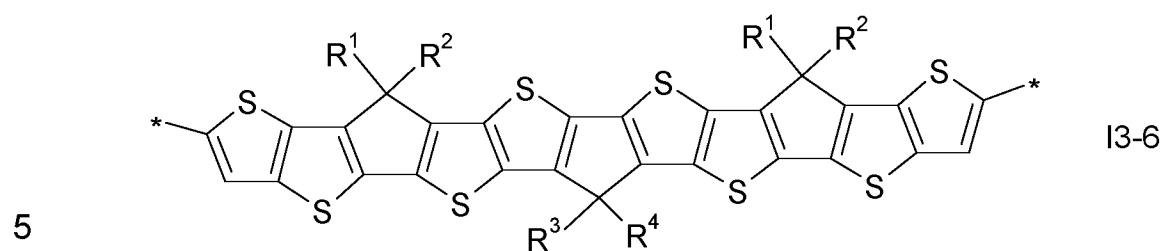
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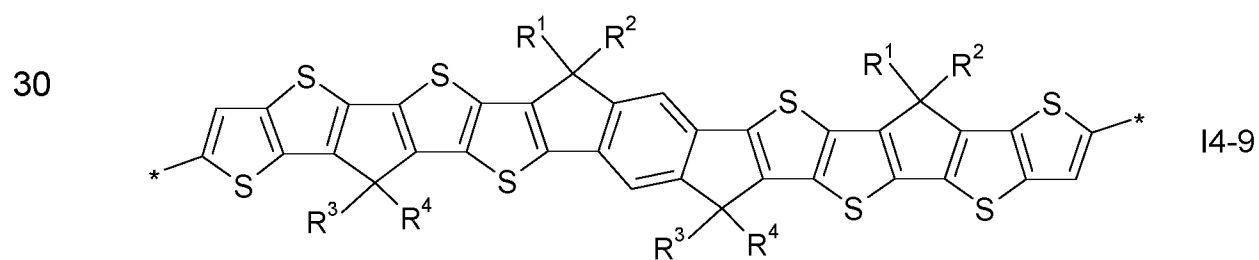
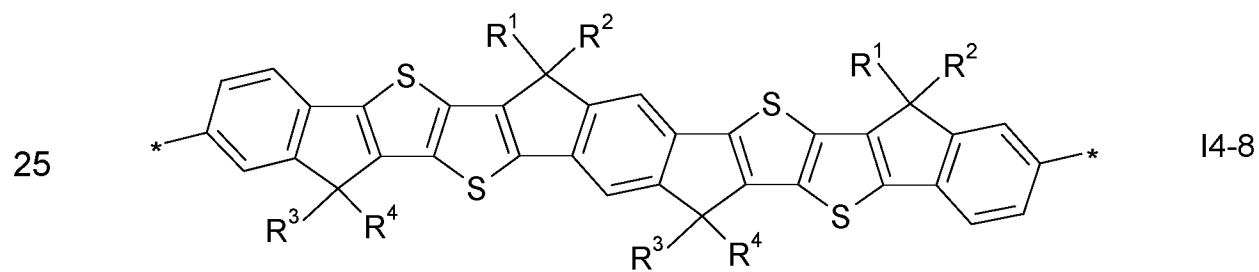
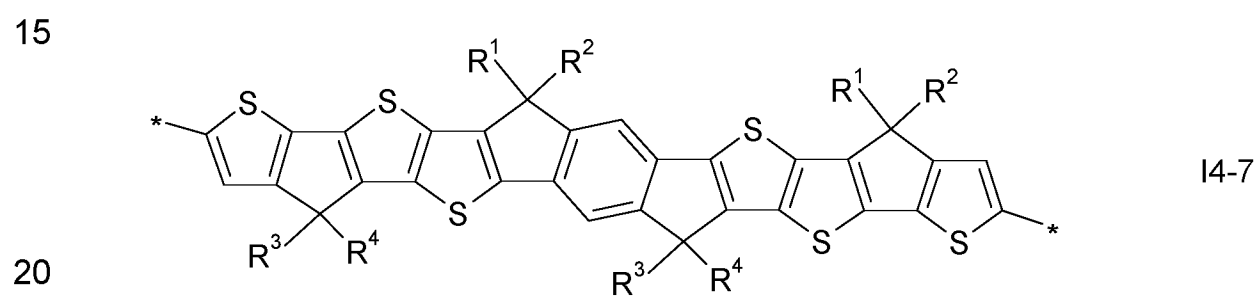
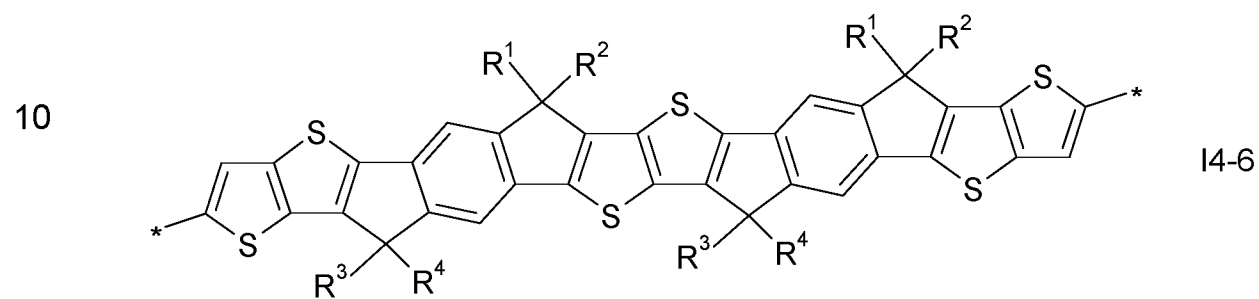
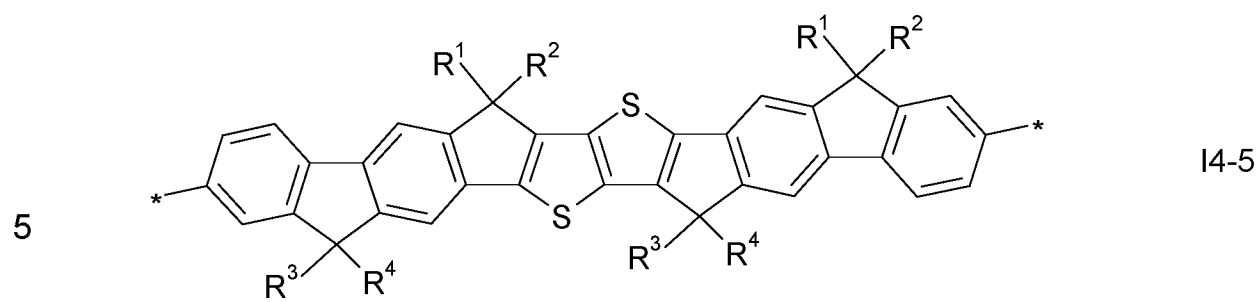


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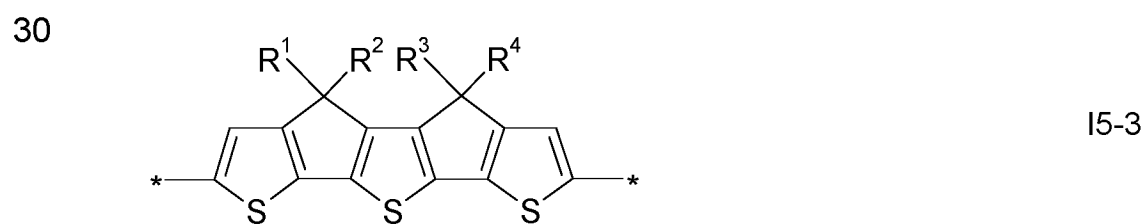
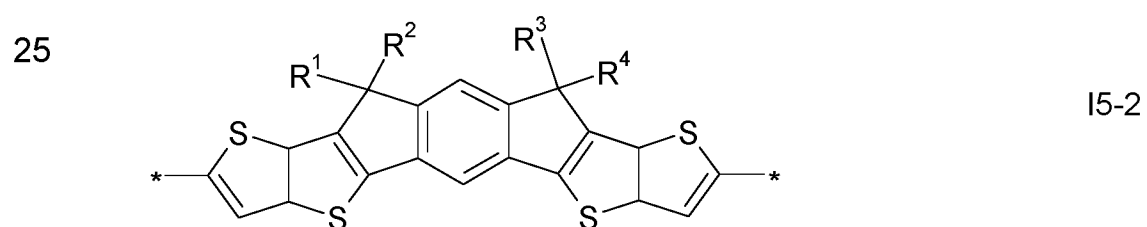
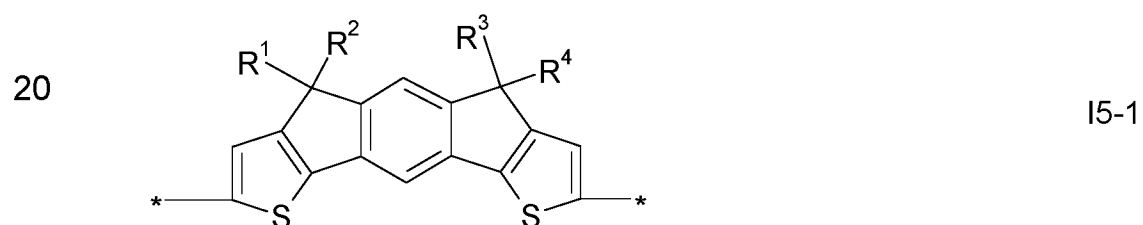
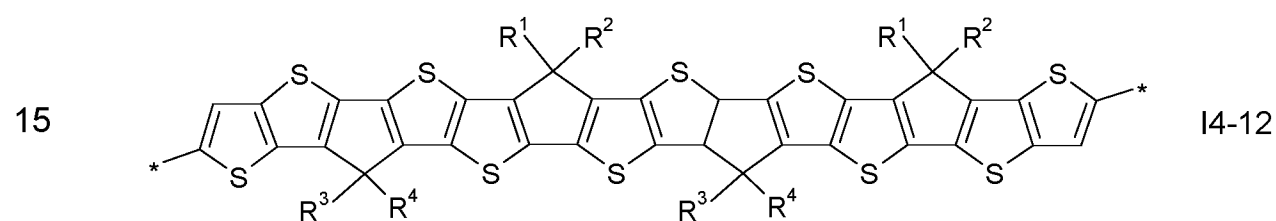
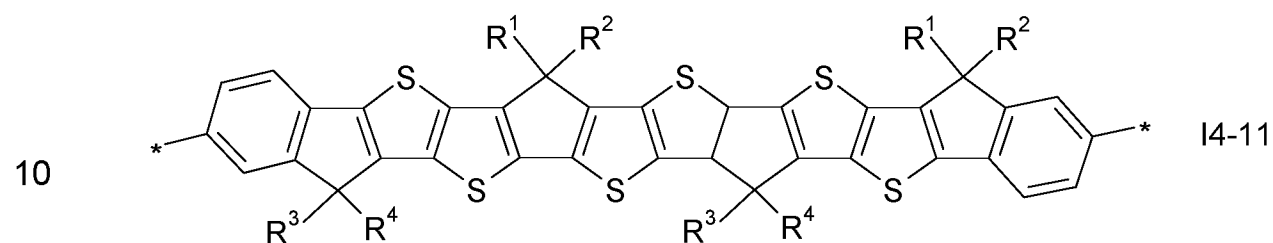
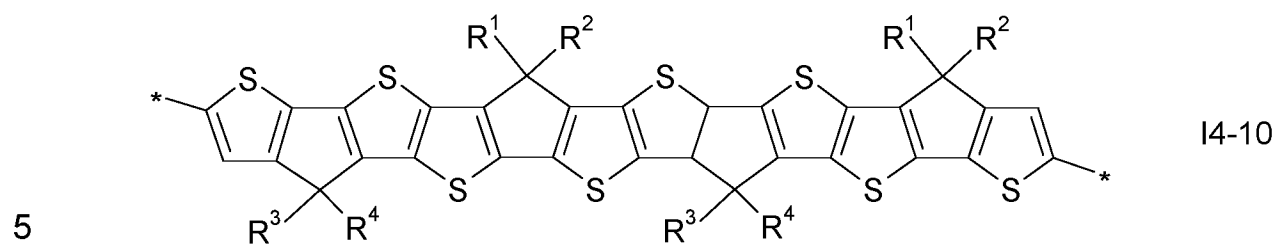


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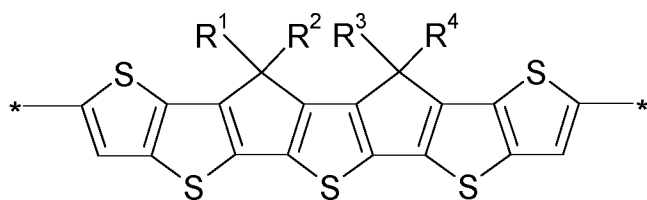
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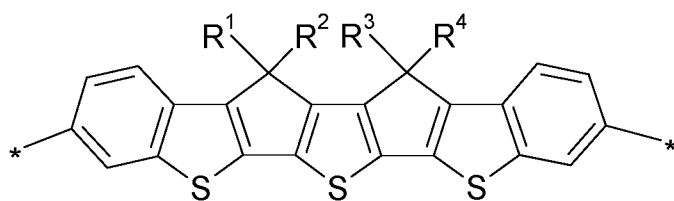


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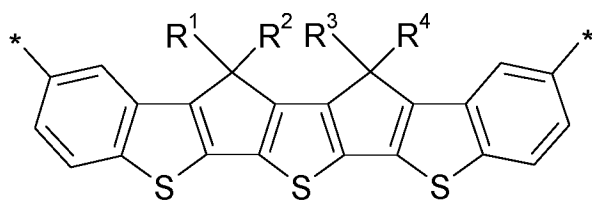
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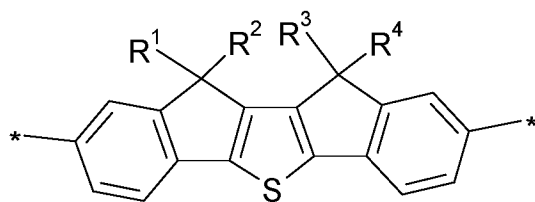
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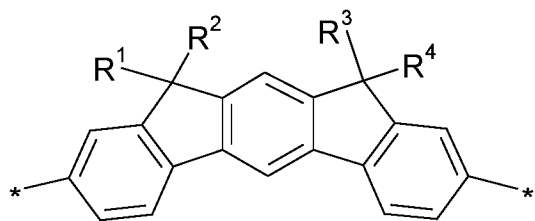
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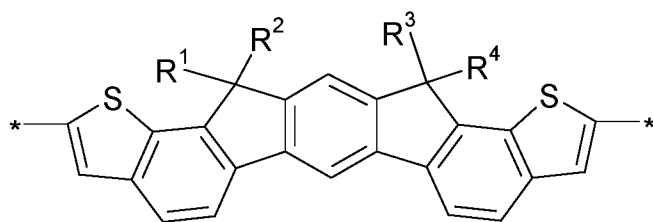
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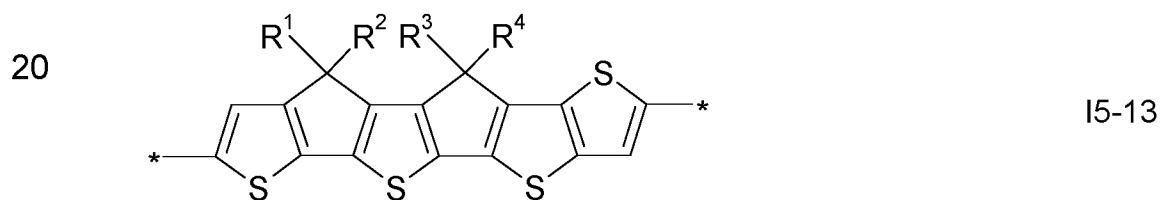
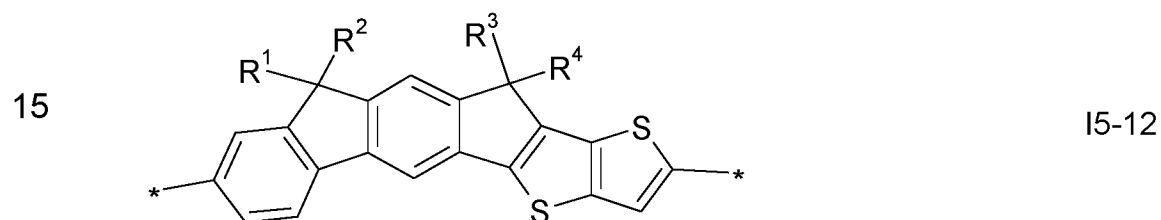
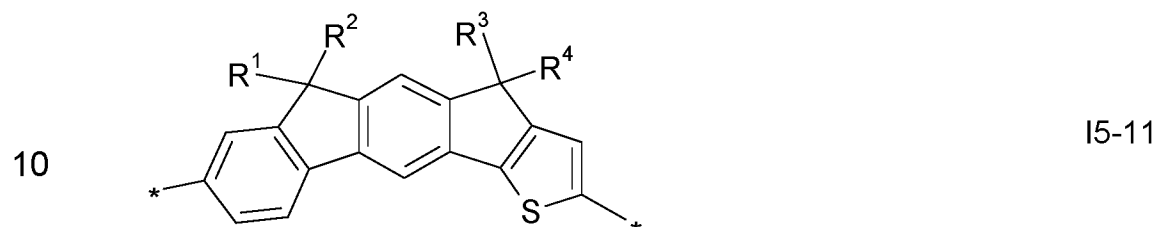
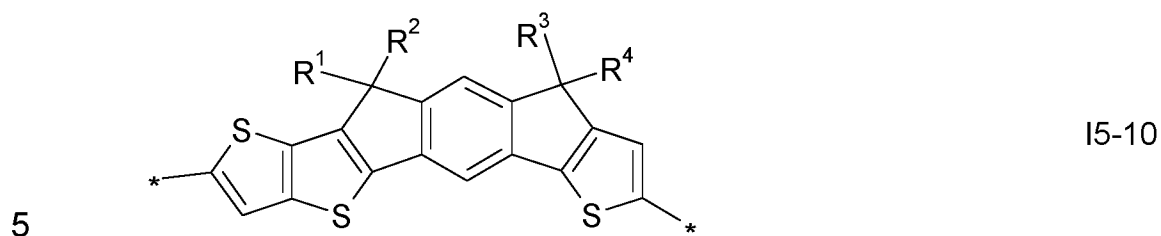
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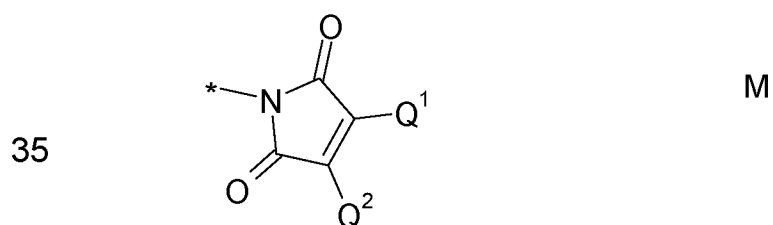
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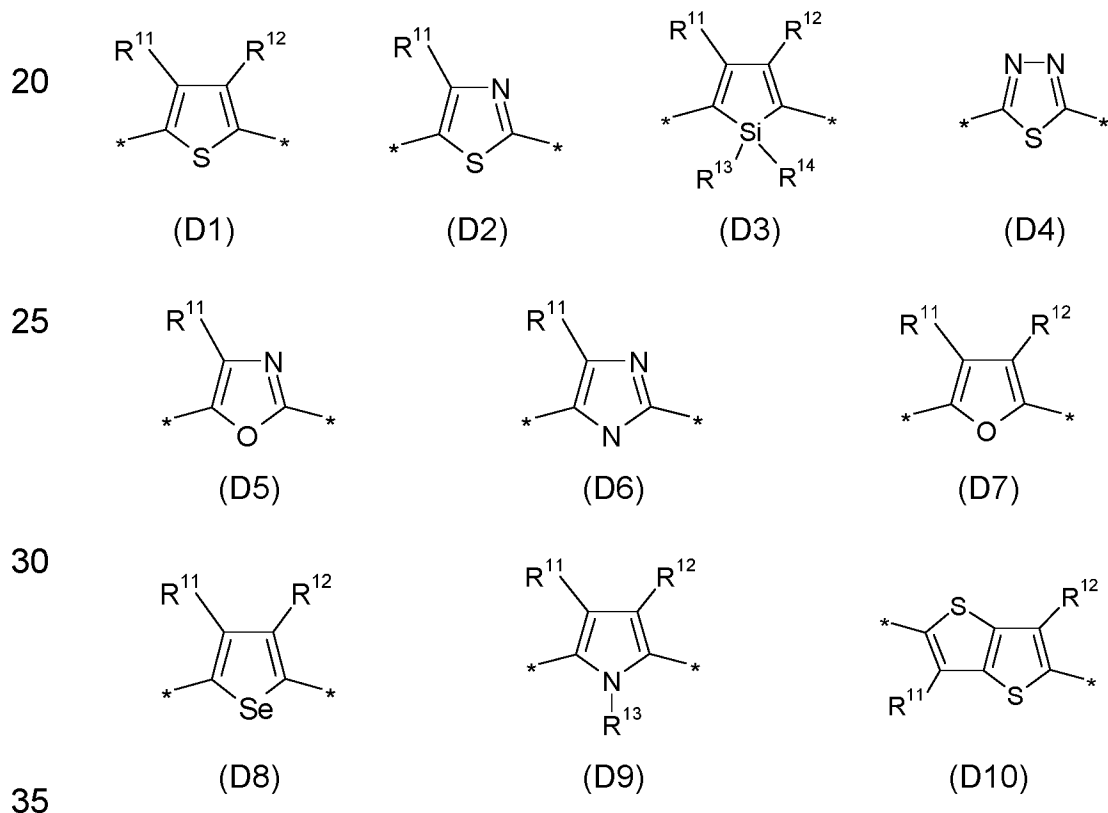
25 wherein R^1 , R^2 , R^5 and R^6 have the meanings given in claim 1 and 4, R^3 and R^4 have one of the meanings given for R^1 and R^2 , and the benzene and thiophene rings are optionally substituted in free positions by one or more groups R^5 .

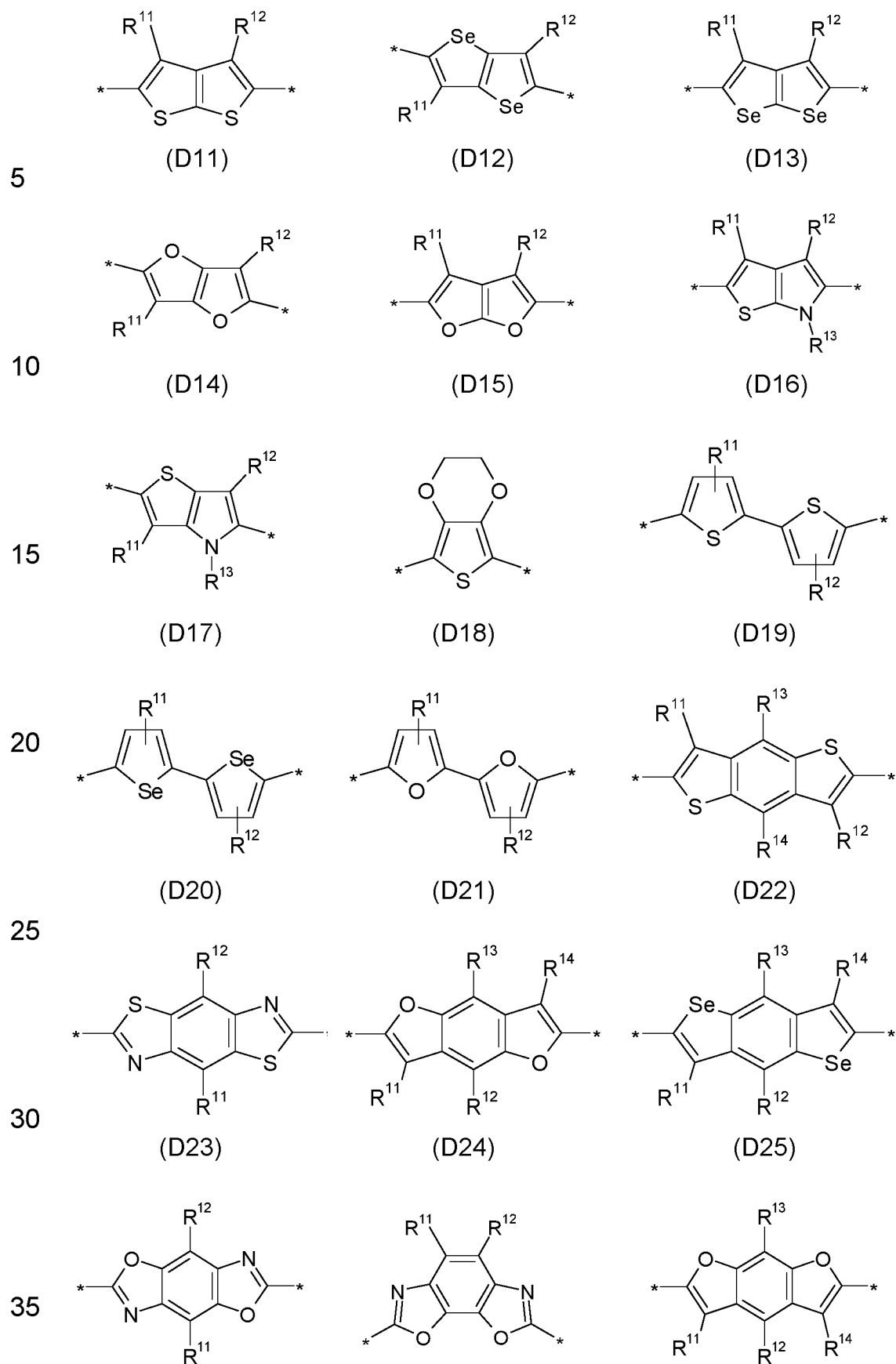
30 11. The conjugated polymer according to one or more of claims 1 to 10, characterized in that R^C is selected from formula M

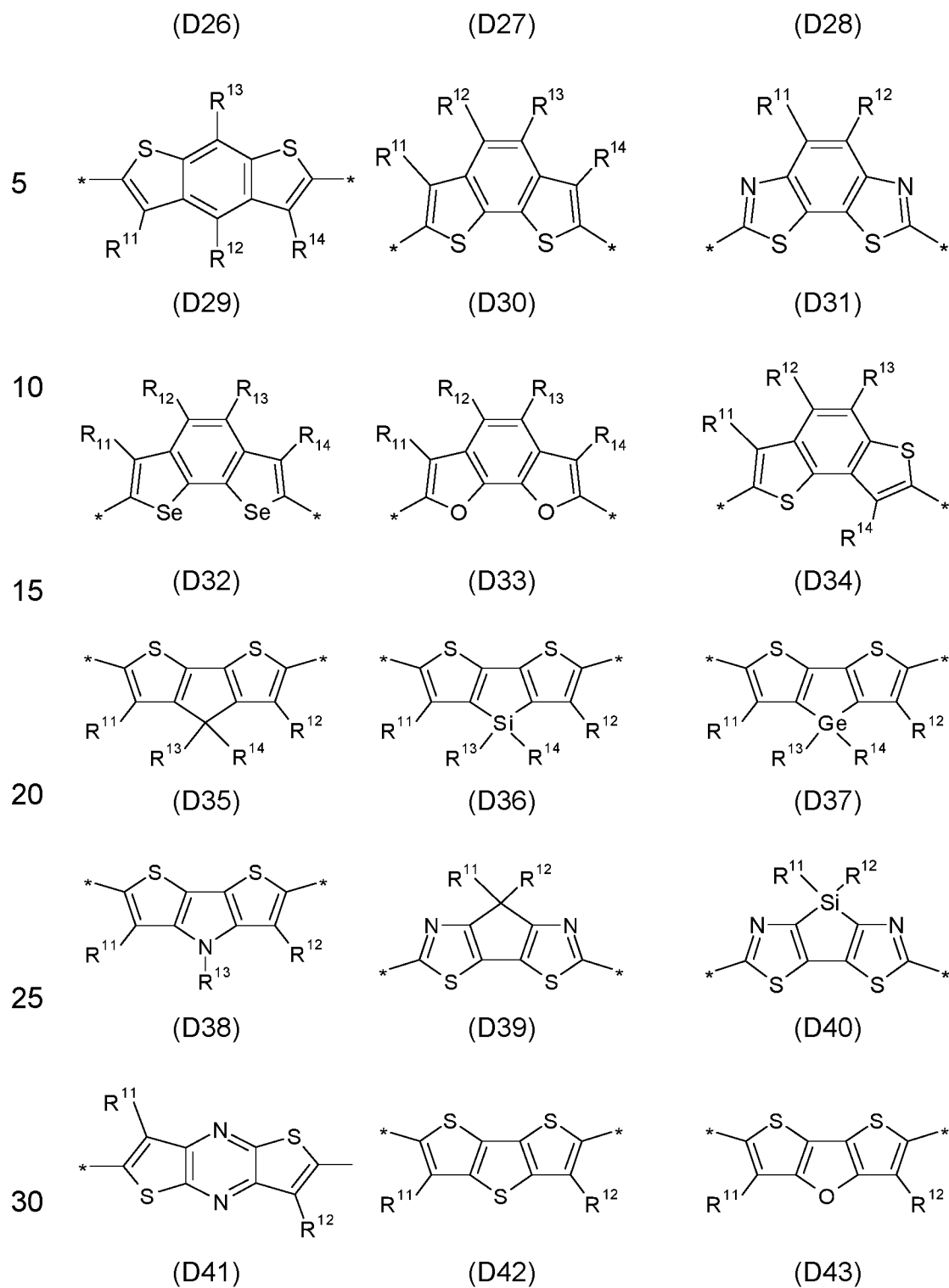


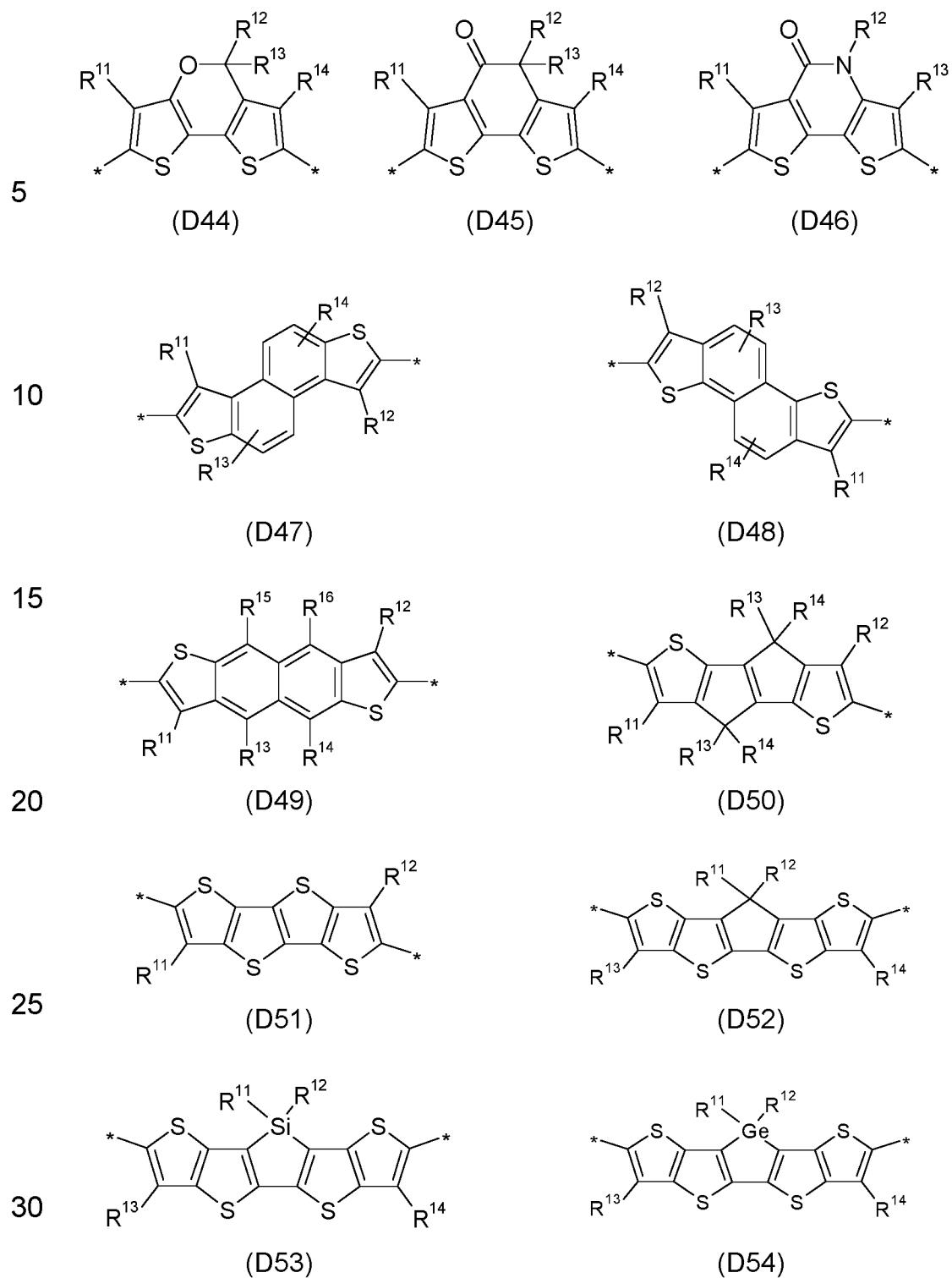
wherein Q^1 and Q^2 are each independently from one another H, CH_3 , C_2H_5 , C_3H_7 or C_4H_9 , very preferably H or CH_3 , most preferably CH_3 .

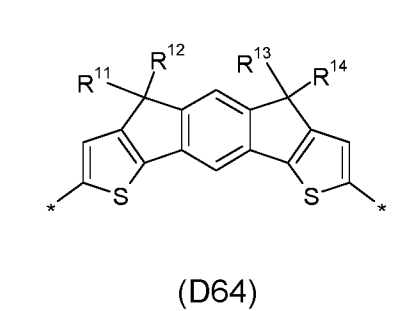
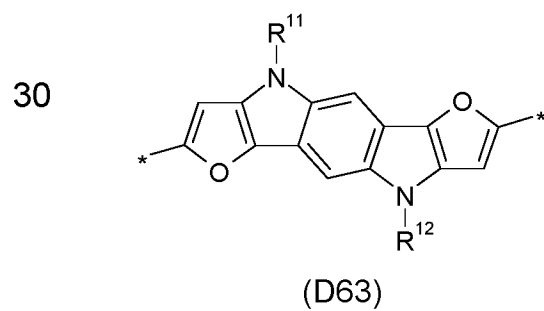
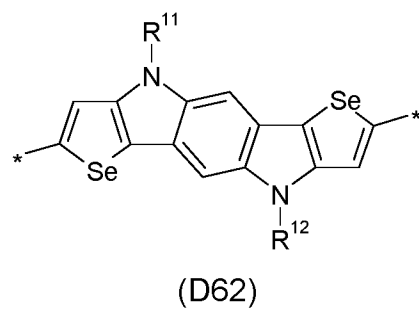
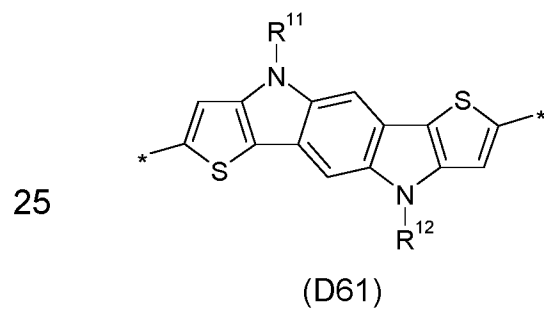
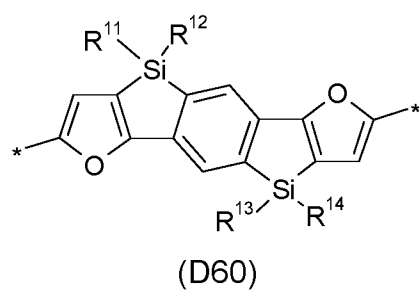
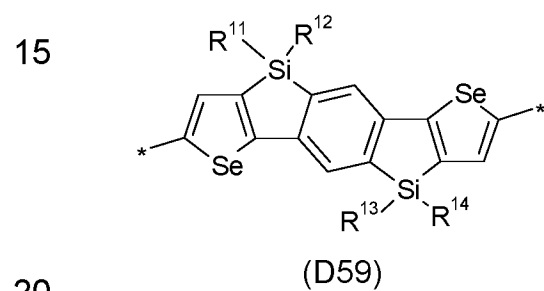
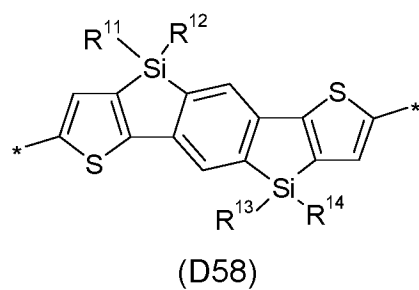
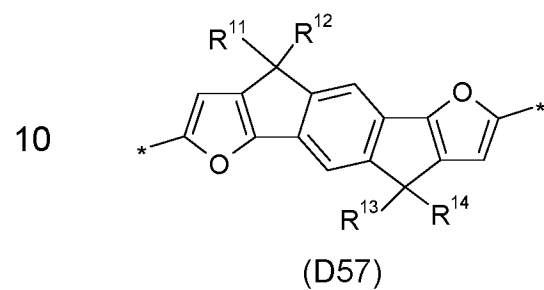
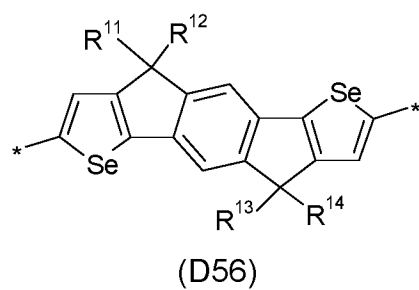
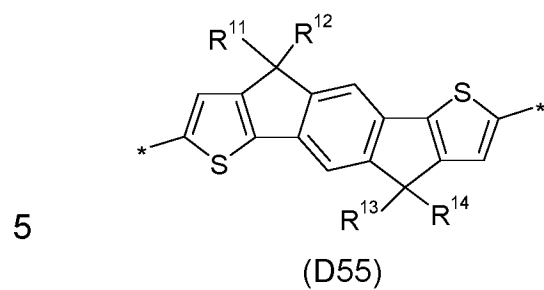
- 5 12. The conjugated polymer according to one or more of claims 1 to 11, characterized in that Sp is selected from alkylene with 1 to 30, preferably 1 to 20, C atoms, wherein one or more, but not all, CH_2 groups are each optionally replaced by $-O-$, $-S-$, $-C(=O)-$, $-C(=S)-$, $-C(=O)-O-$, $-O-C(=O)-$, $-NR^0-$, $-SiR^0R^{00}-$, $-CF_2-$, $-CR^0=CR^{00}-$, $-CY^1=CY^2-$ or $-C\equiv C-$ in such a manner that O and/or S atoms are not linked directly to one another, and in which one or more H atoms are each optionally replaced by F, Cl, Br, I or CN.
- 10
13. The conjugated polymer according to one or more of claims 1 to 12, characterized in that it comprises one or more units Ar^6 , which preferably have electron donor properties, and are selected from the group consisting of the formulae D1-D151 and their mirror images
- 15

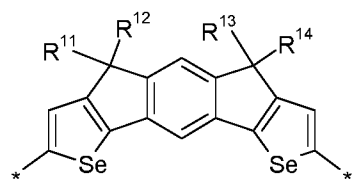




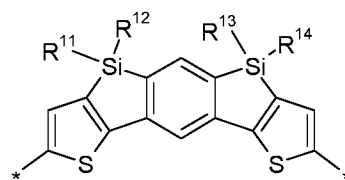




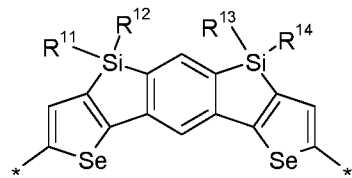




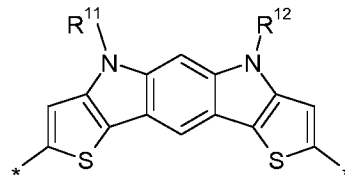
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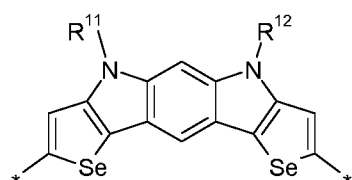
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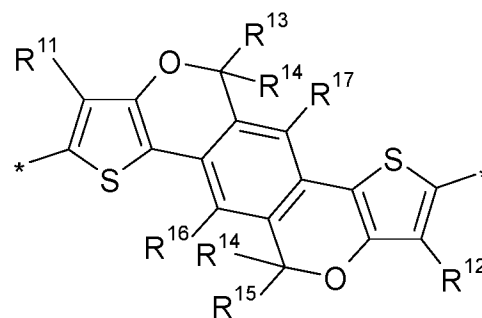
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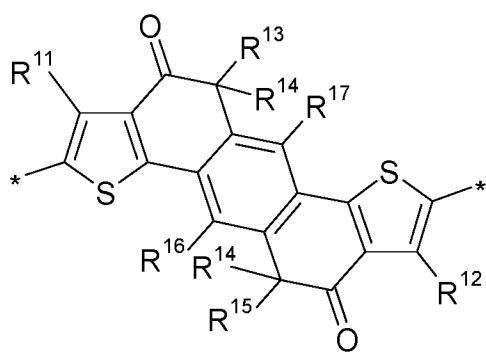
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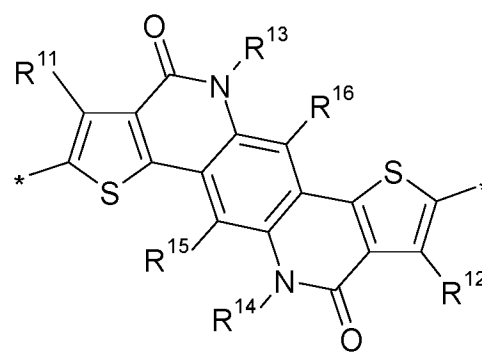
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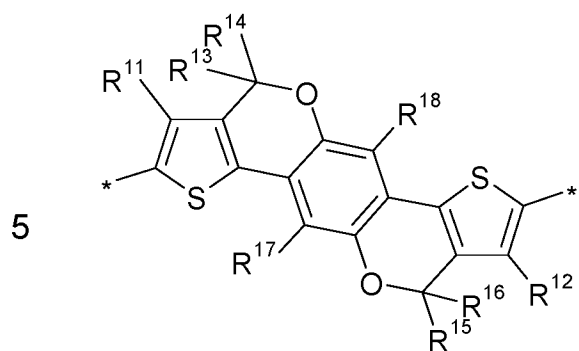
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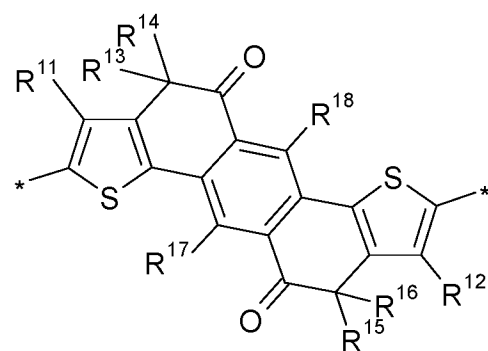
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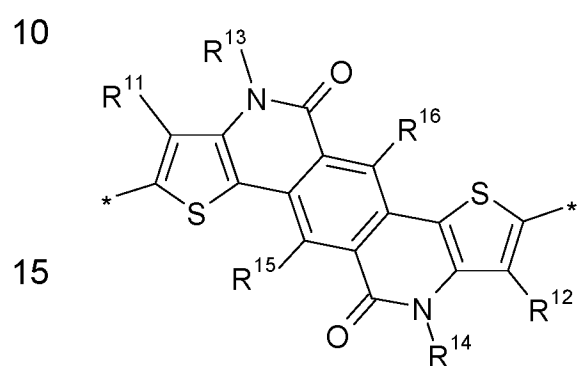
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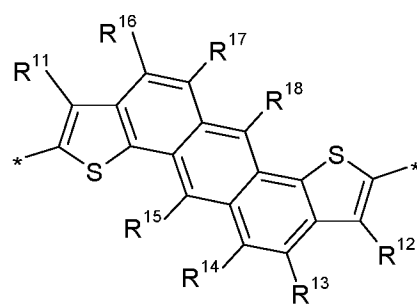
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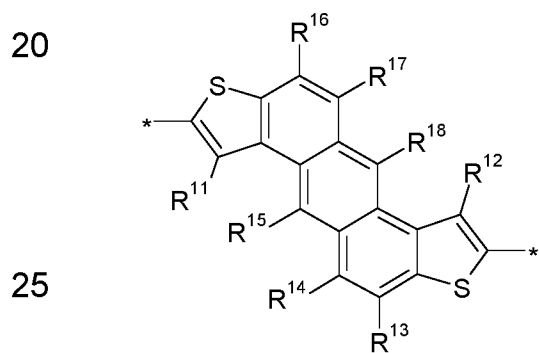
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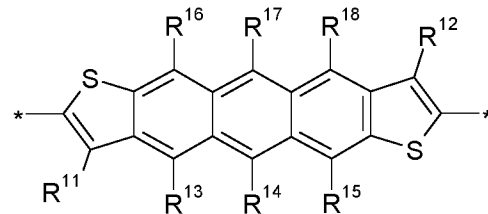
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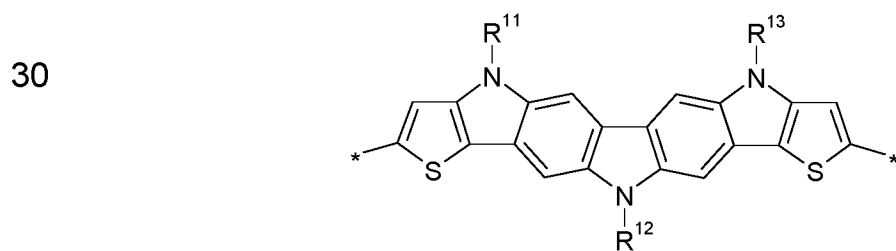
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(D77)



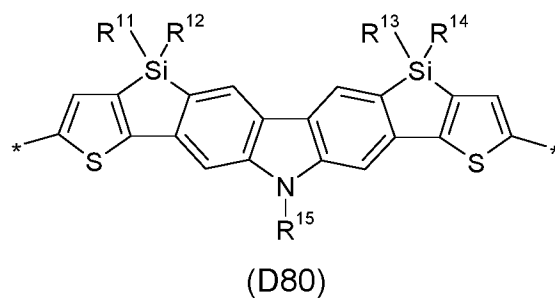
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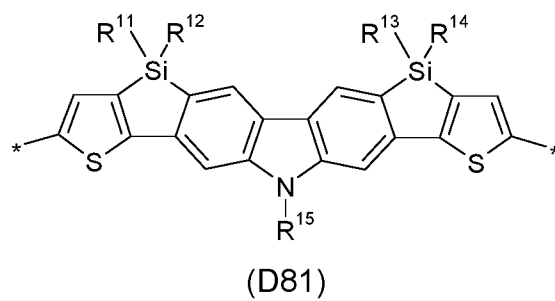
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- 235 -

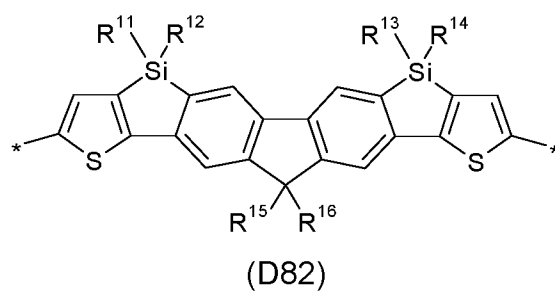
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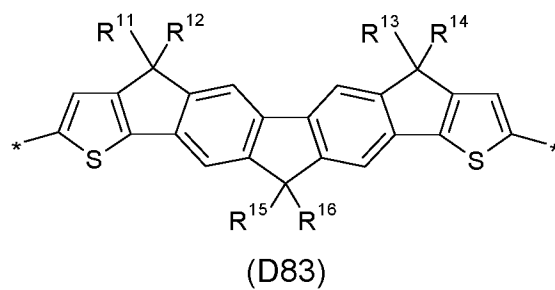
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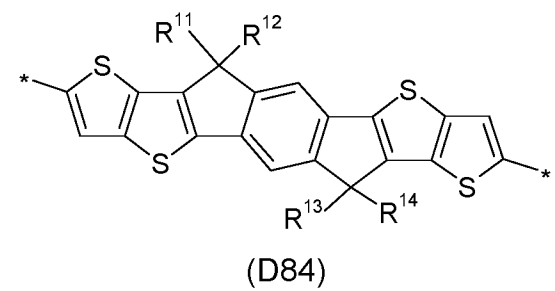
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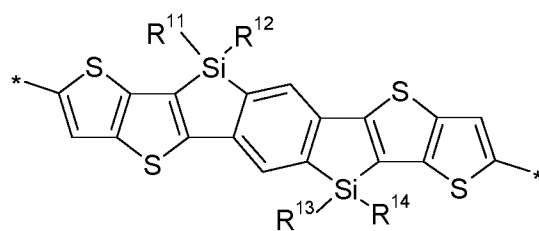
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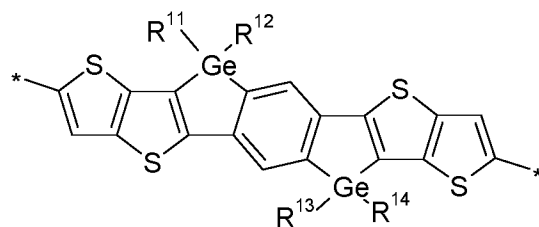
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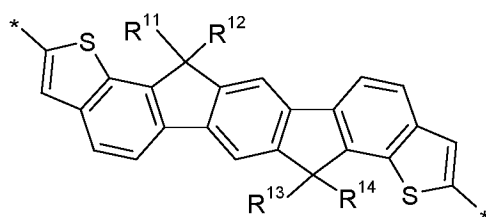
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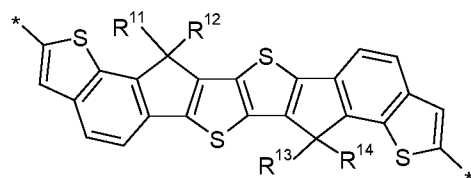
(D86)

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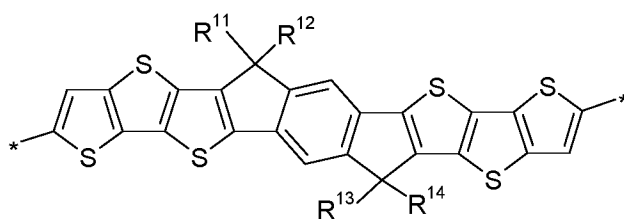
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(D88)

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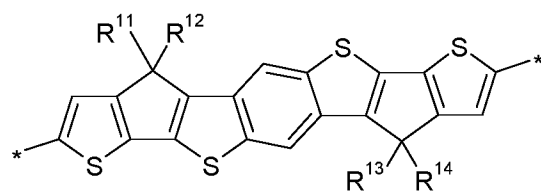


(D89)

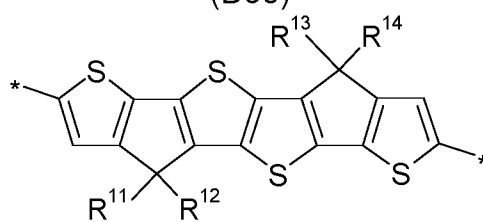
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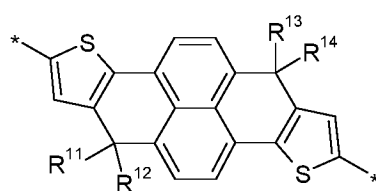
- 237 -



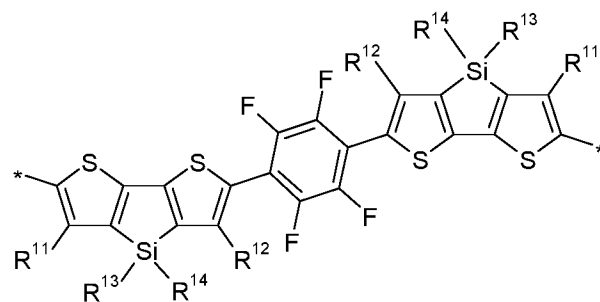
(D90)



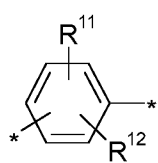
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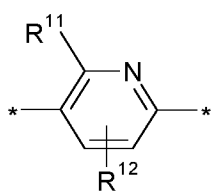
(D92)



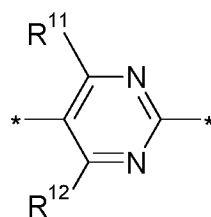
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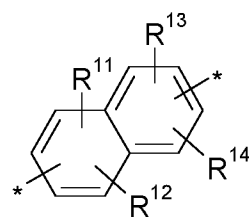
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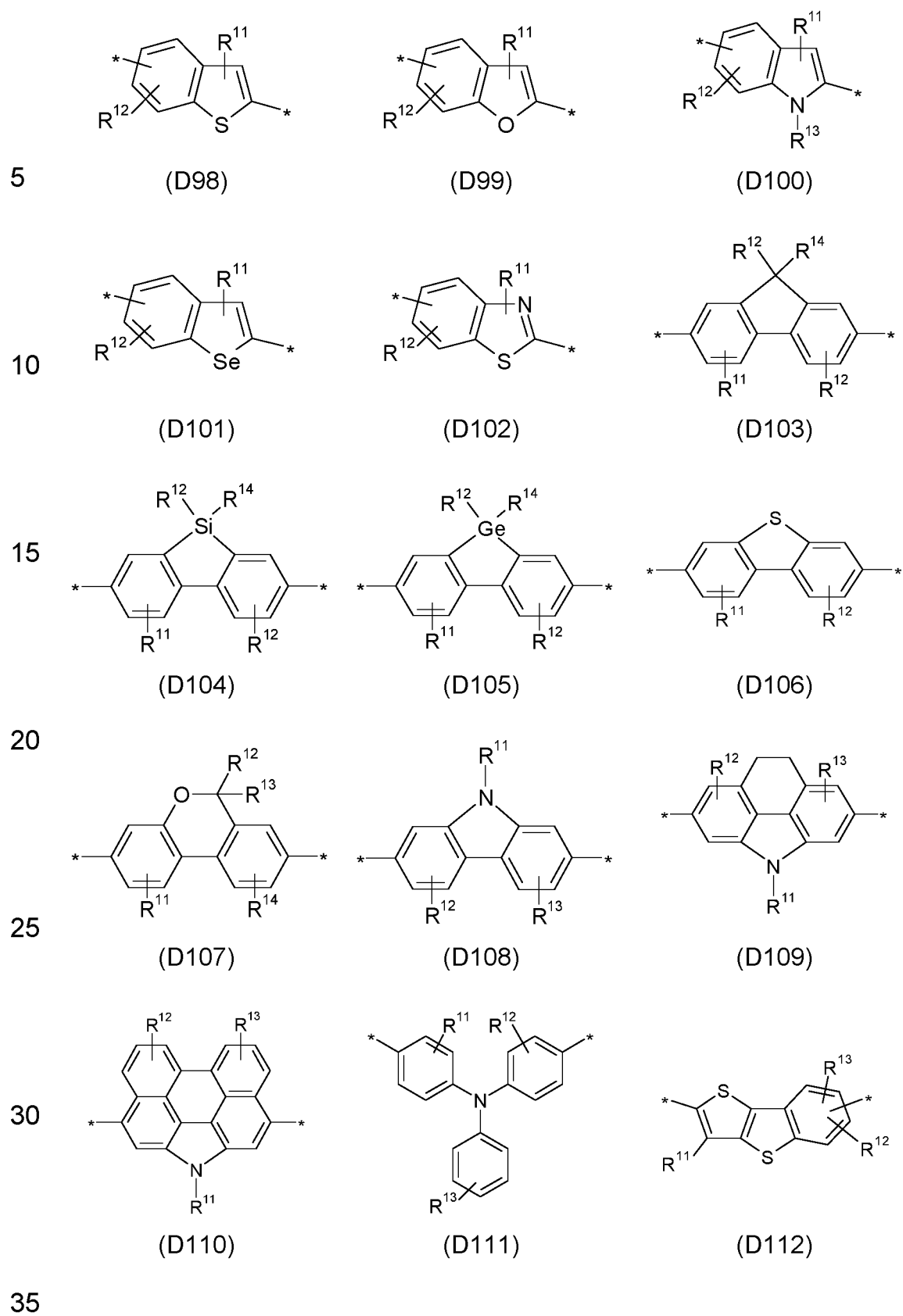
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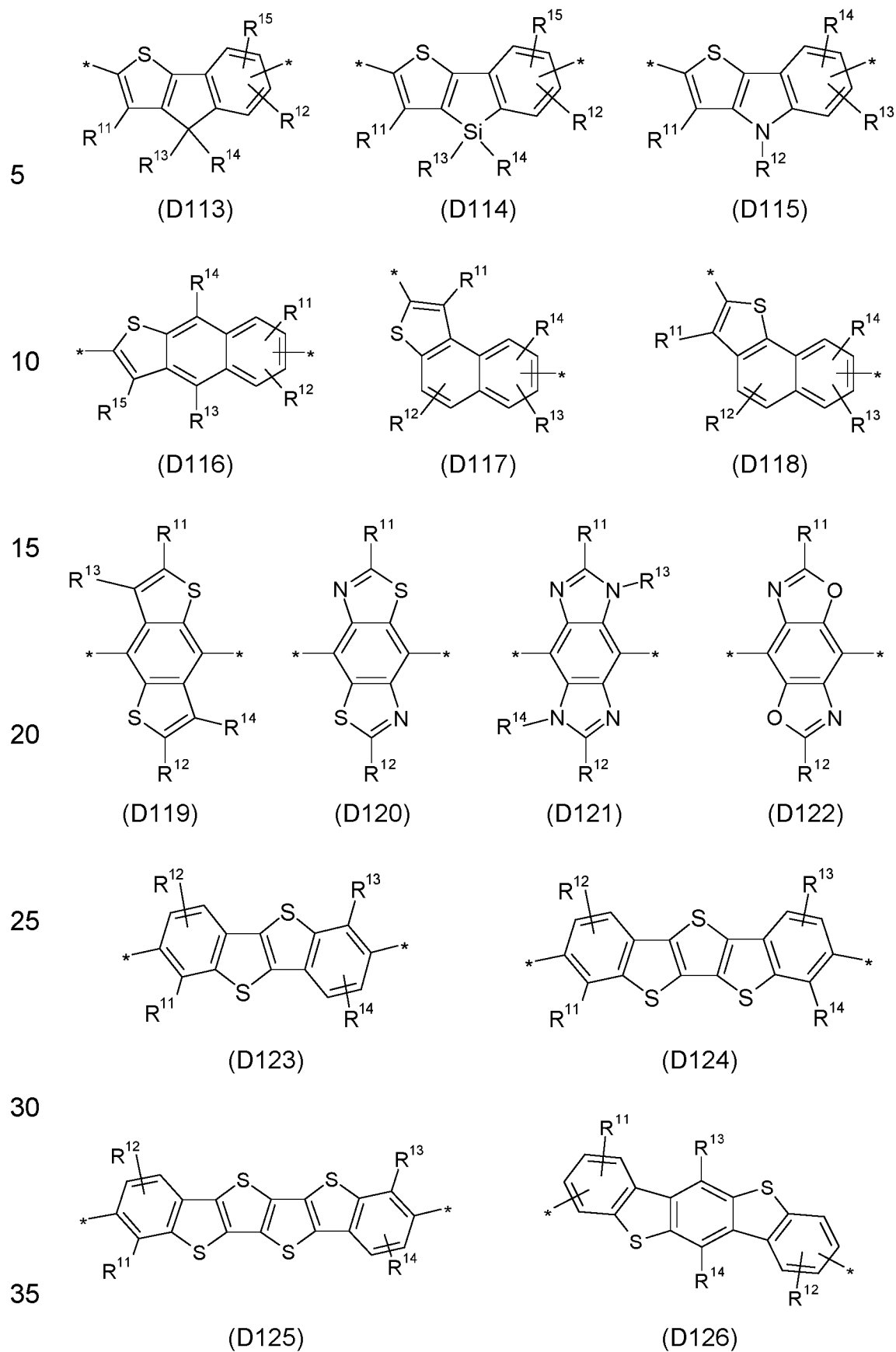


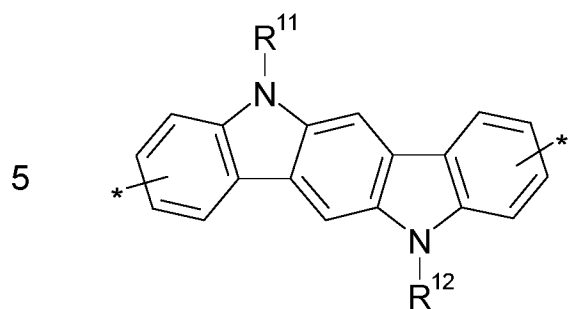
(D96)



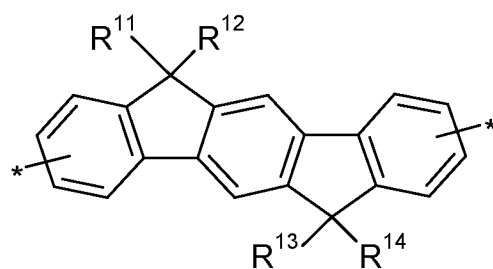
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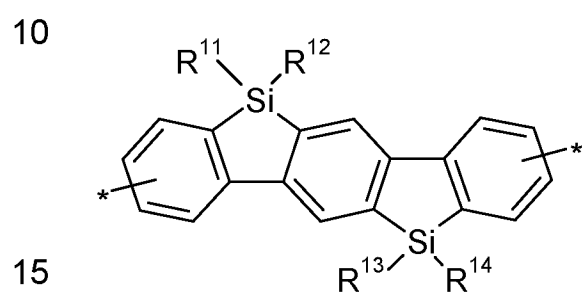




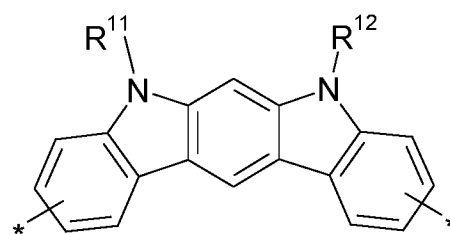
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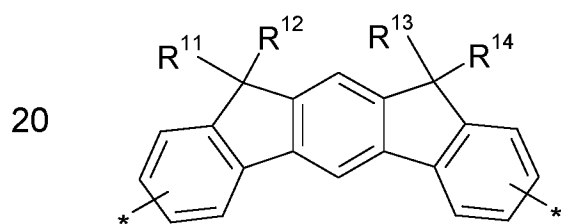
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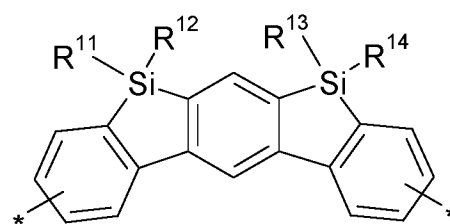
(D129)



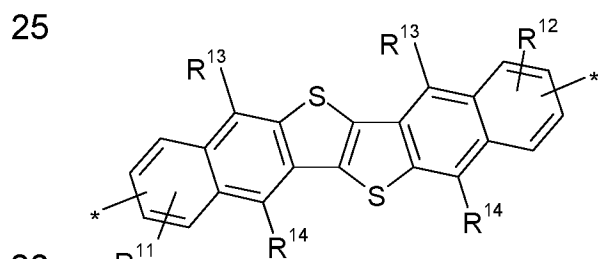
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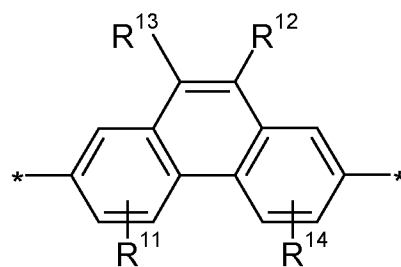
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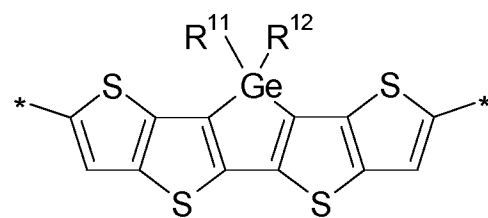
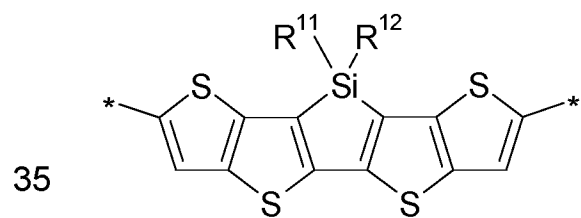
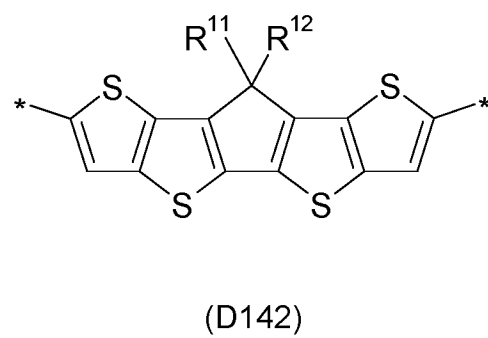
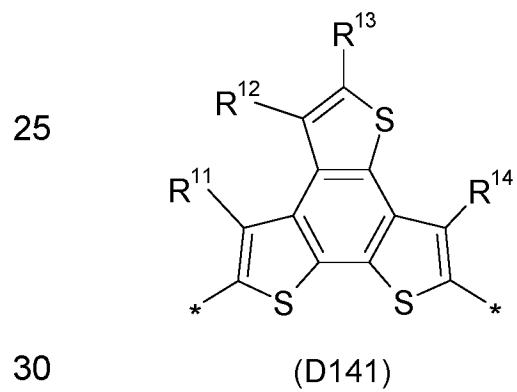
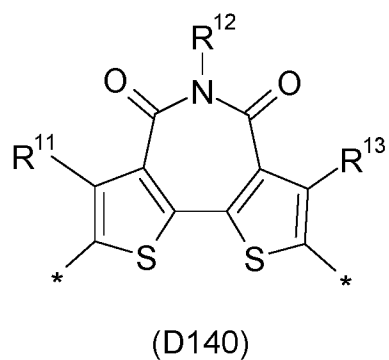
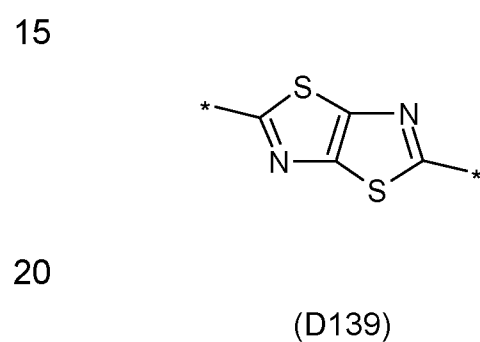
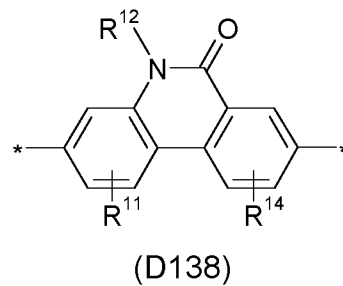
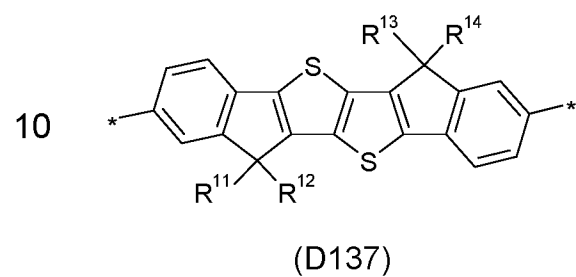
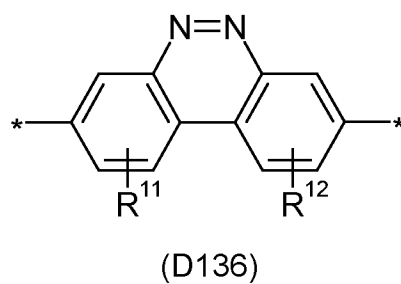
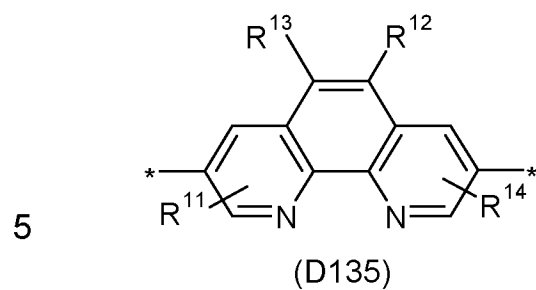
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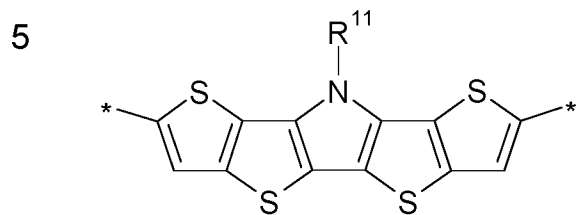
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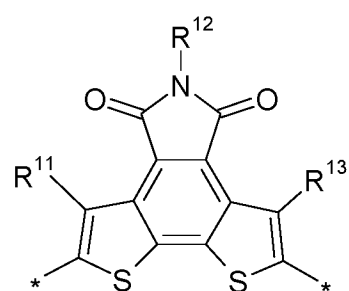
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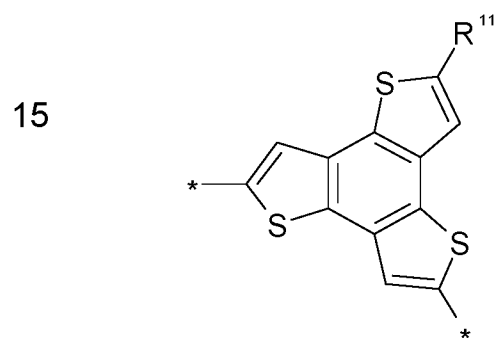
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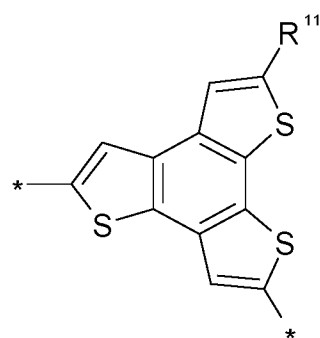
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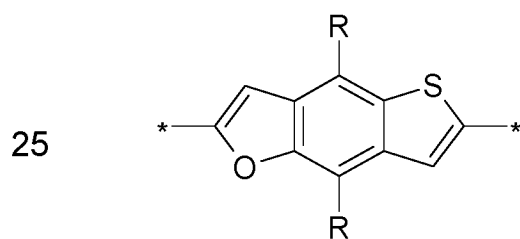
(D145)



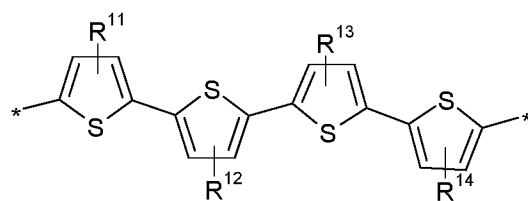
(D146)



(D147)

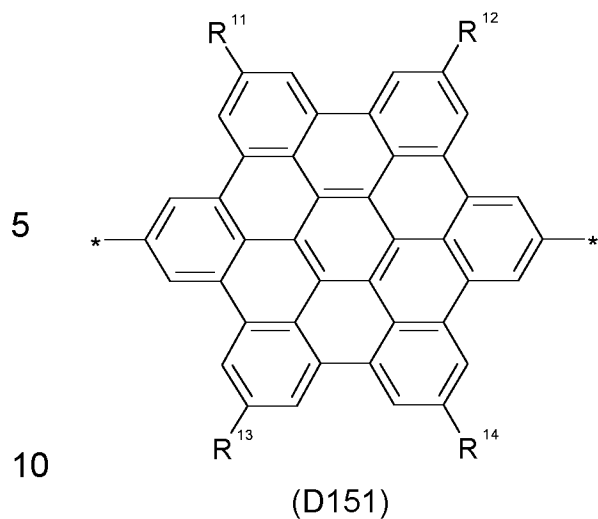


(D148)



(D149)

(D150)

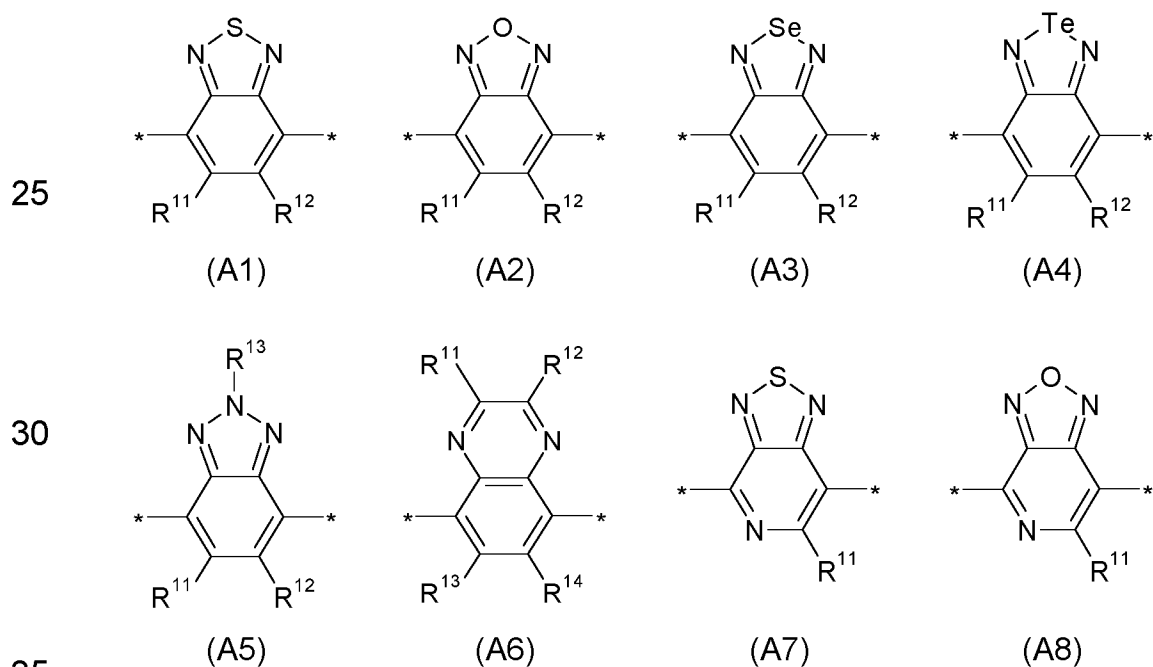


wherein R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} and R^{18} independently of each other have one of the meanings of R^1 as given in claim 1, and preferably at least one of the substituents R^{11-18} denotes $Sp-R^C$.

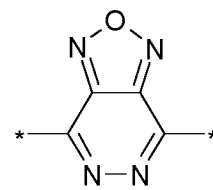
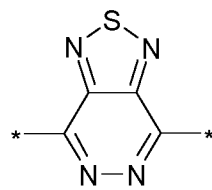
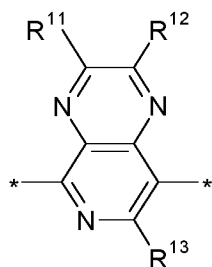
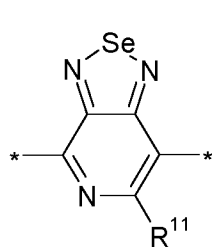
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14. The conjugated polymer according to one or more of claims 1 to 13, characterized in that it comprises one or more units Ar^6 , which preferably have electron acceptor properties, and are selected from the group consisting of the formulae A1-A103 and their mirror images

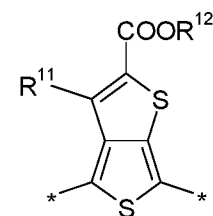
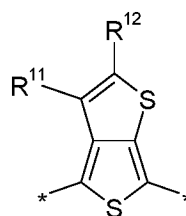
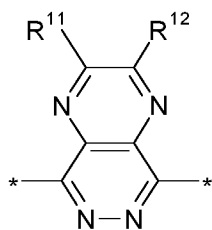
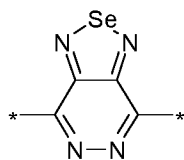
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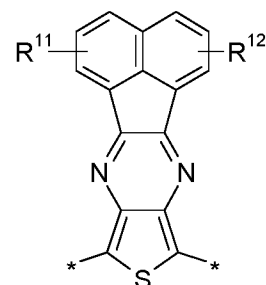
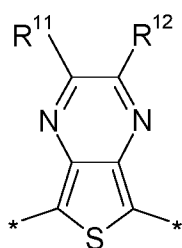
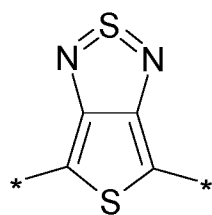
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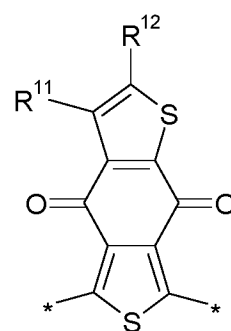
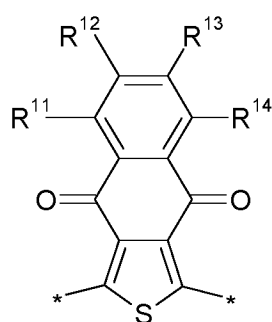
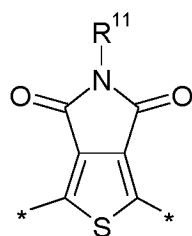
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(A17)

(A18)

(A19)

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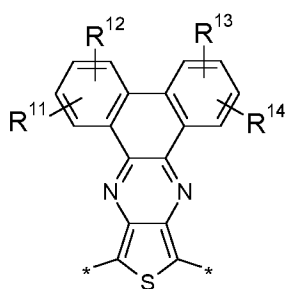
(A20)

(A21)

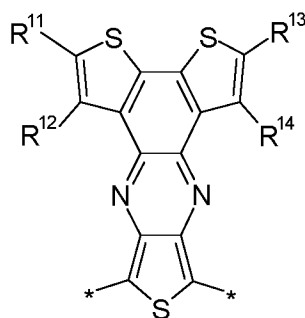
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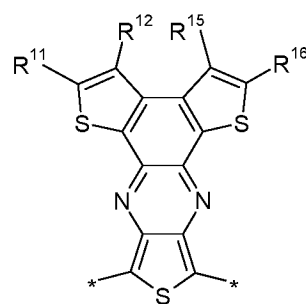
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(A23)

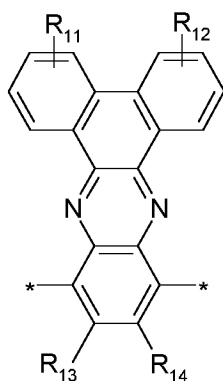


(A24)

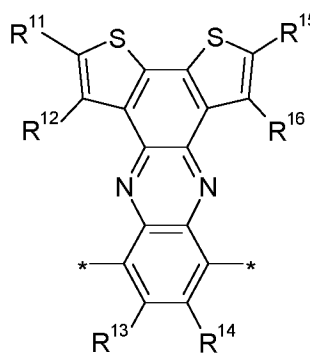


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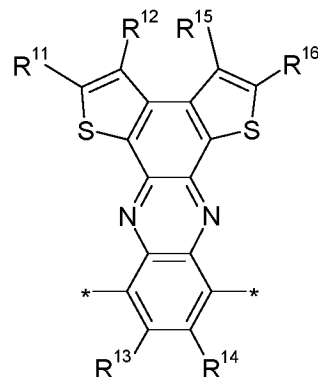
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(A26)



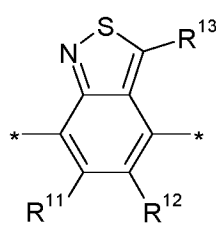
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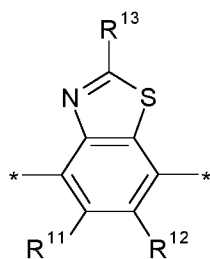
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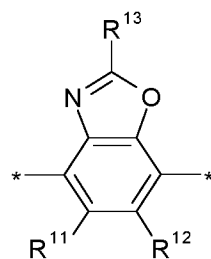
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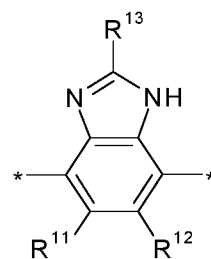
(A29)



(A30)



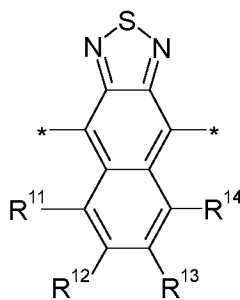
(A31)



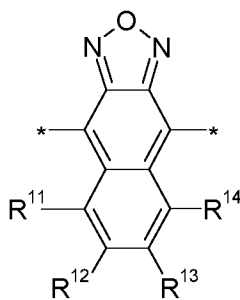
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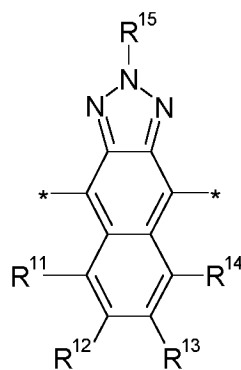
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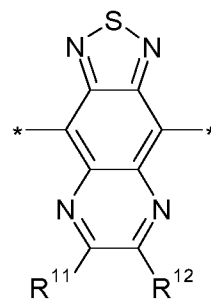
(A33)



(A34)



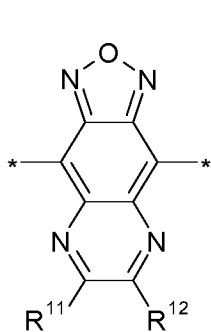
(A35)



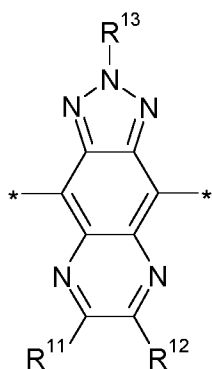
(A36)

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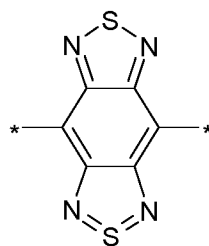
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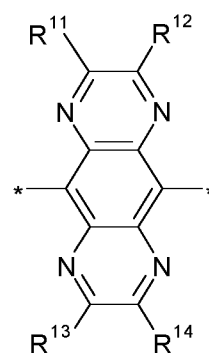
(A37)



(A38)

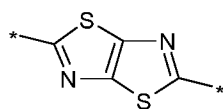


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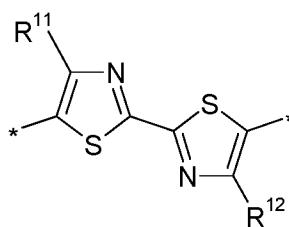


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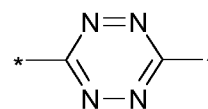
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(A41)

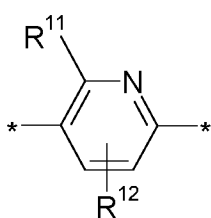


(A42)

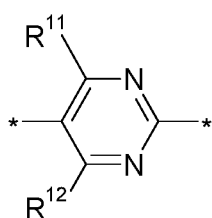


(A43)

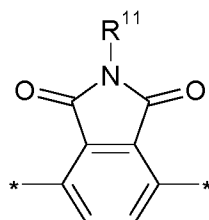
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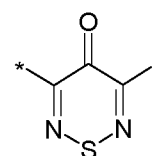
(A44)



(A45)



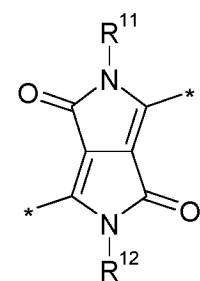
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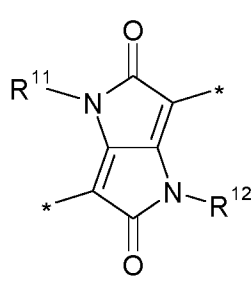
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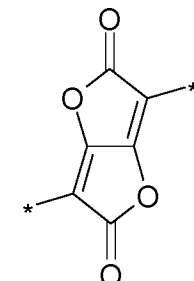
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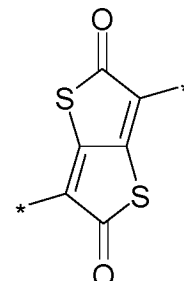
(A48)



(A49)



(A50)

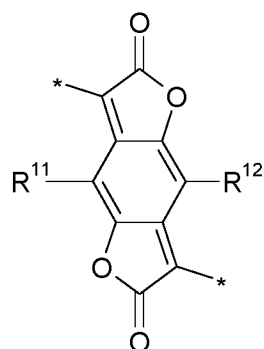


(A51)

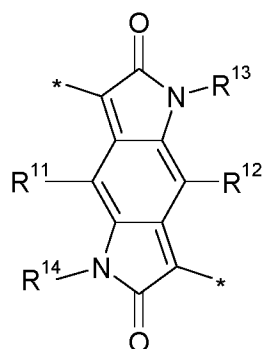
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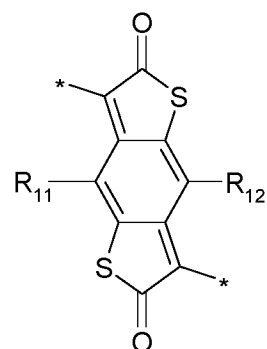
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(A52)

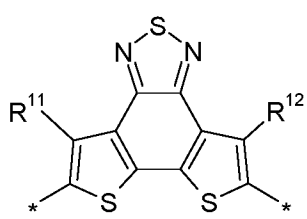


(A53)

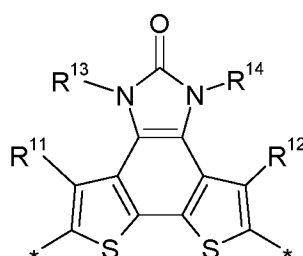


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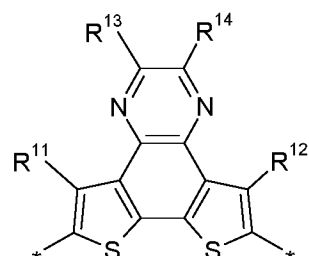
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(A55)



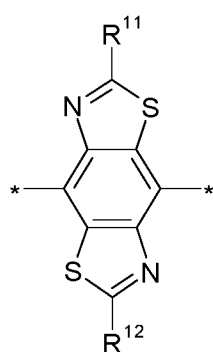
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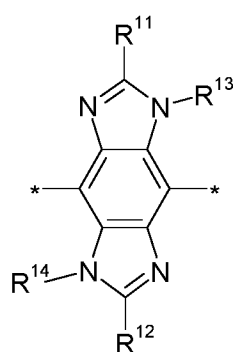
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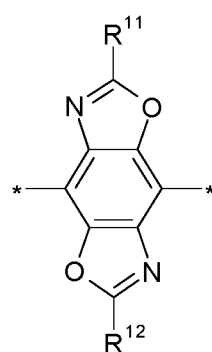
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(A58)

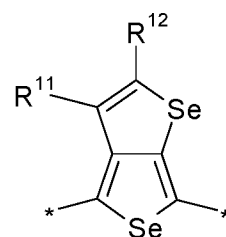


(A59)



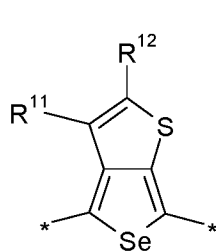
(A60)

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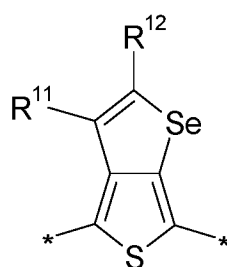


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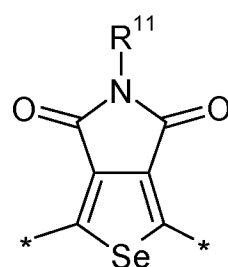
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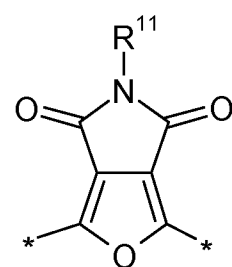
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(A63)



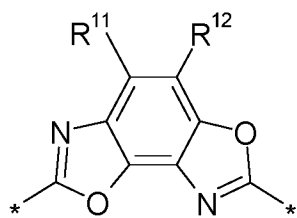
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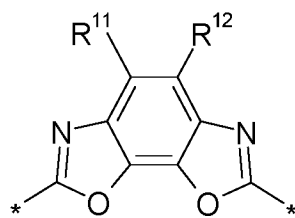
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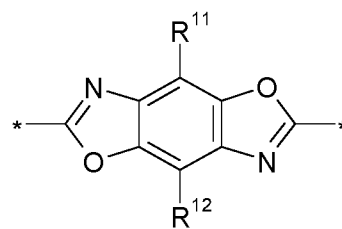
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(A66)

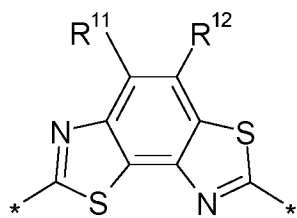


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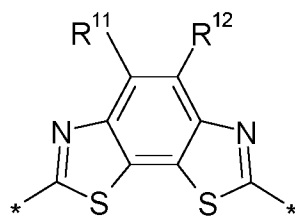


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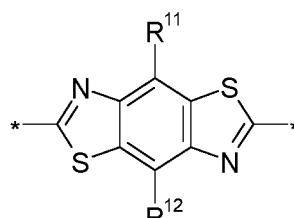
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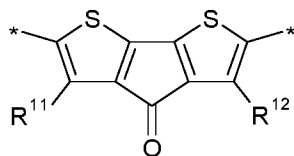


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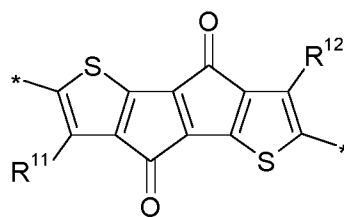


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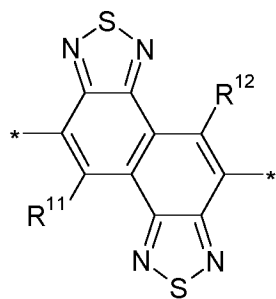
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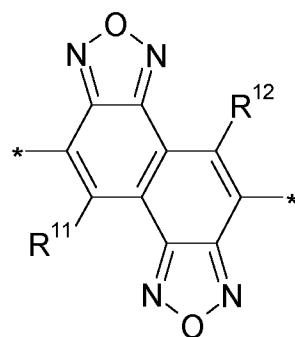
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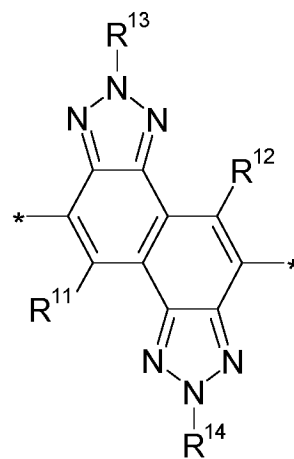
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(A74)



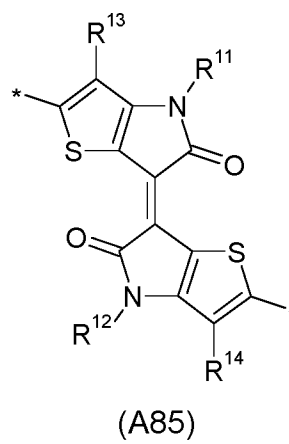
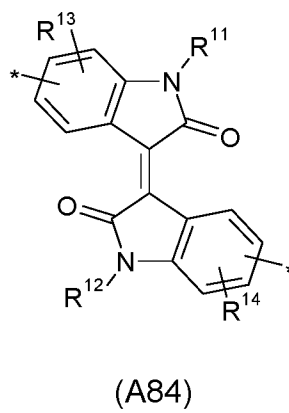
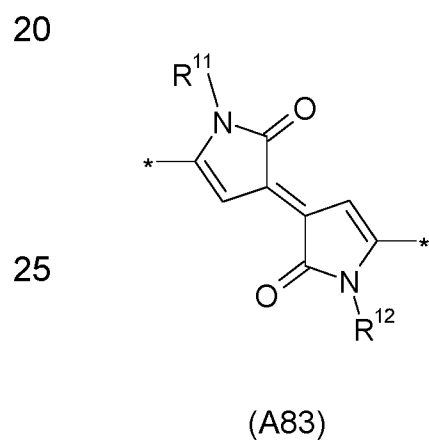
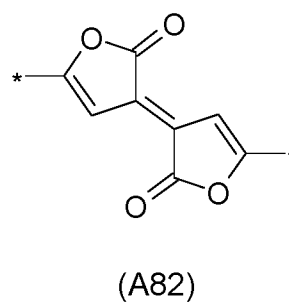
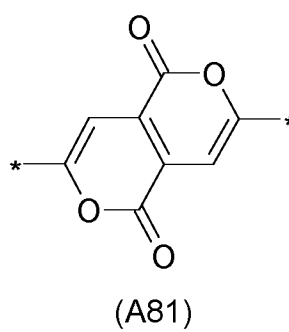
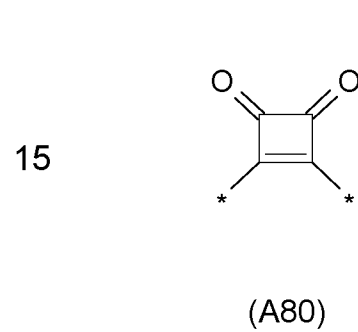
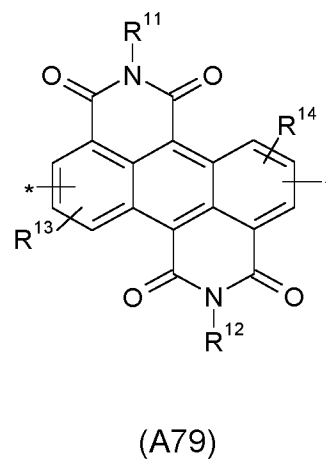
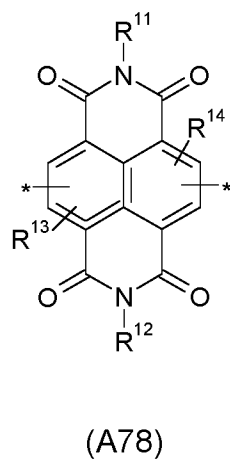
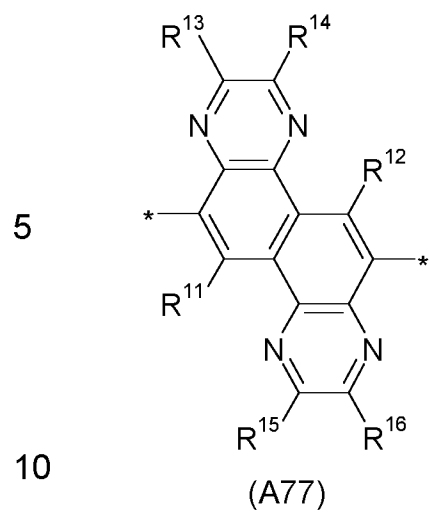
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(A76)

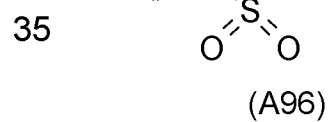
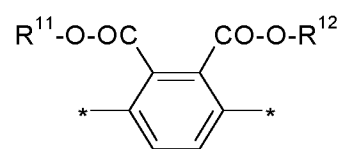
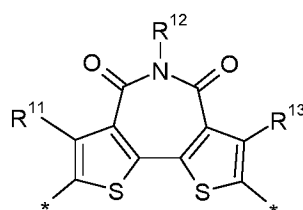
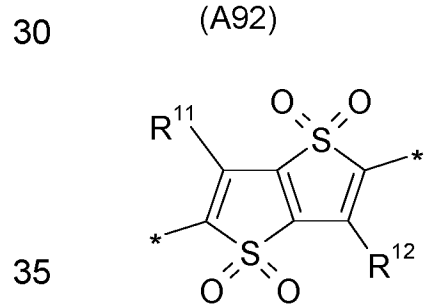
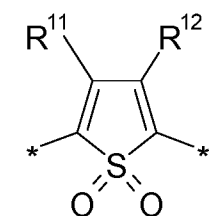
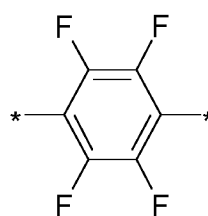
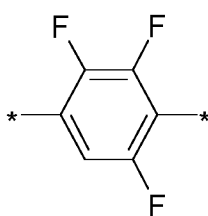
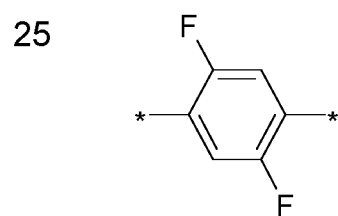
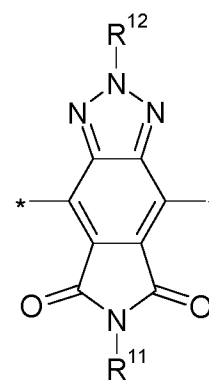
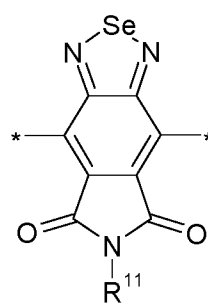
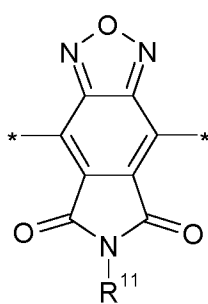
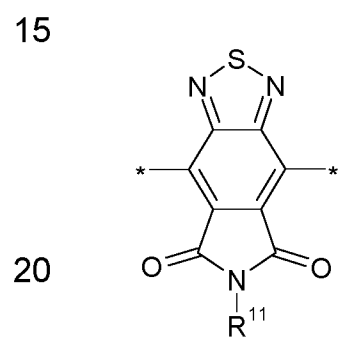
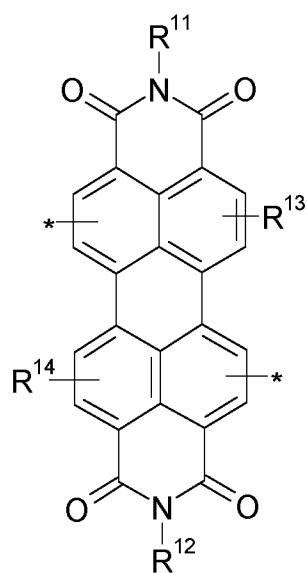
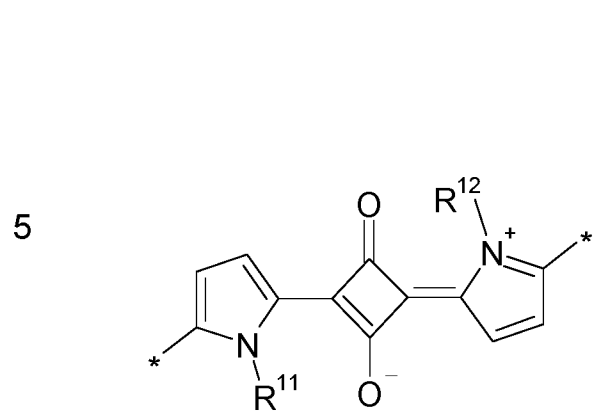
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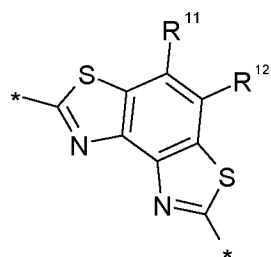
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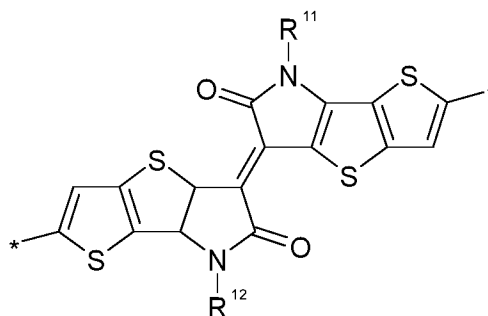
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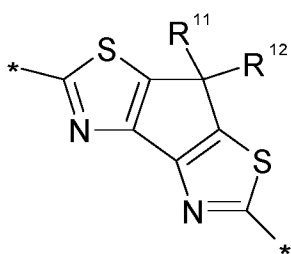
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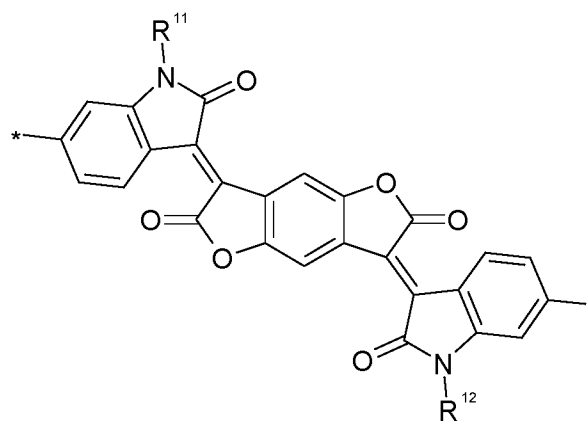
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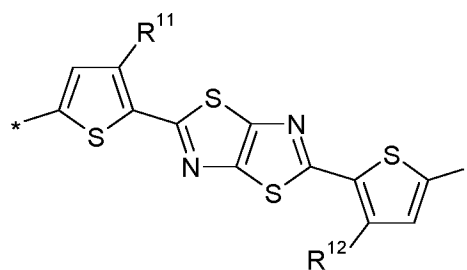
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(A102)

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(A103)

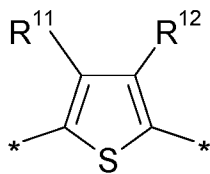
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wherein R^{11} , R^{12} , R^{13} , R^{14} , R^{15} and R^{16} independently of each other have one of the meanings of R^1 as given in claim 1, and preferably at least one of the substituents R^{11-16} denotes $Sp-R^C$.

35

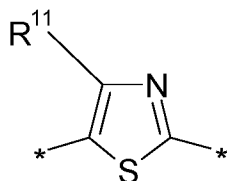
15. The conjugated polymer according to one or more of claims 1 to 14, characterized in that it comprises one or more units Ar^6 , which are selected from the group consisting of the formulae $Sp1$ - $Sp18$ and their mirror images

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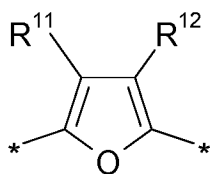
Sp1

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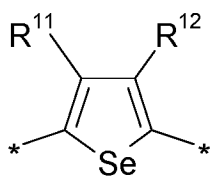
Sp2

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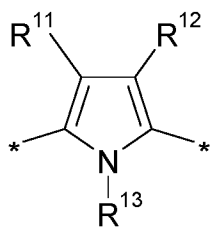
Sp3

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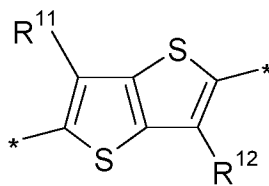
Sp4

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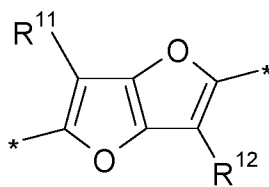
Sp5

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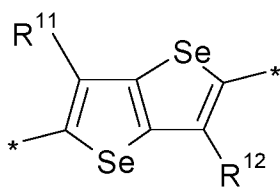
Sp6

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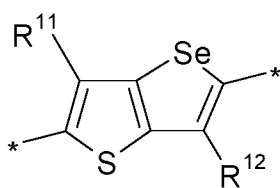
Sp7

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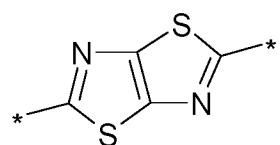
Sp8

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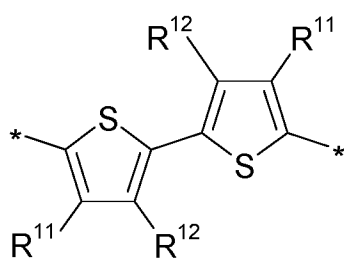
Sp9

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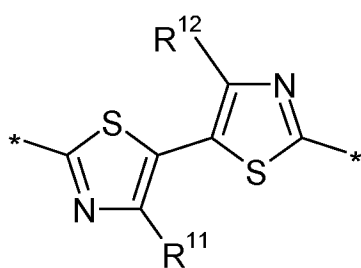
Sp10

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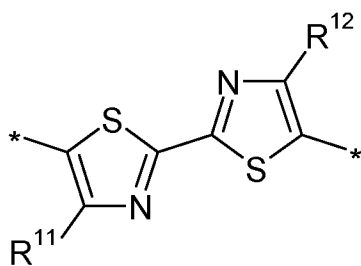
Sp11

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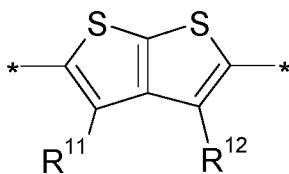
Sp12

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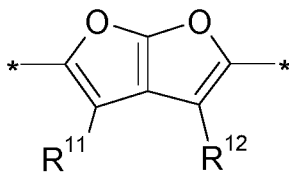
Sp13

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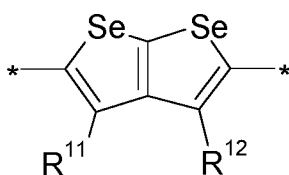
Sp14

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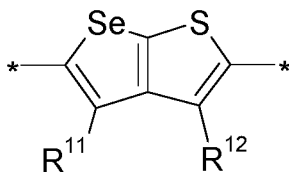
Sp15

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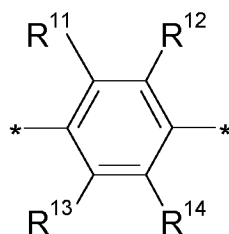
Sp16

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Sp17

20



Sp18

25

wherein R^{11} , R^{12} , R^{13} , R^{14} independently of each other have one of the meanings of R^1 as given in claim 1, and preferably at least one of R^{11-14} denotes $Sp-R^C$.

30

16. The conjugated polymer according to one or more of claims 1 to 15, characterized in that it comprises, preferably consists of, one or more, preferably two or more, units of formula I, I1-I7 or I1-1 to I5-13, and one or more units Ar^6 selected from the following groups

35

- A2) the group consisting of the formulae D1-D151, very preferably from the formulae D1, D7, D10, D11, D19, D22, D29, D30, D35,

D36, D37, D44, D55, D84, D87, D88, D89, D93, D94, D106,
D111, D139, D140, D141, D146 and D150,

and/or

- 5 B2) the group consisting of the formulae A1-A103, very preferably from the formulae A1, A6, A7, A15, A16, A20, A36, A49, A74, A78, A84, A88, A92, A94, A98, A102 and A103,

and/or

- 10 C2) the group consisting of the formulae Sp1-Sp18, very preferably of the formulae Sp1, Sp2, Sp6, Sp10, Sp11, Sp12, Sp13 and Sp14.

- 15 17. The conjugated polymer according to one or more of claims 1 to 16, characterized in that it comprises one or more units selected from -CY¹=CY²- and -C≡C-, wherein Y¹ and Y² are independently of each other H, F, Cl or CN.

- 20 18. The conjugated polymer according to one or more of claims 1 to 17, characterized in that it comprises one or more units, preferably consists of, one or more units selected from the following groups

1A) the group consisting of units of formula I, I1-I7 and I1-1 to I5-13 which are selected from electron acceptor units,

- 25 1D) the group consisting of formula I, I1-I7 and I1-1 to I5-13 which are selected from electron donor units,

2A) the group consisting of units Ar⁶ which are selected from electron acceptor units, preferably selected from the group consisting of formulae A1-A103,

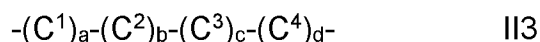
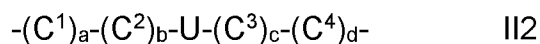
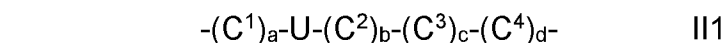
- 30 2D) the group consisting of units Ar⁶ which are selected from electron donor units, preferably selected from the group consisting of formulae D1-D151,

- 35 3) the group consisting of units Ar⁶ which are selected from spacer units, preferably selected from the group consisting of formulae Sp1-Sp18,

and wherein the polymer contains at least one unit selected from

groups 1A and 1D, and the polymer contains at least one unit of group 1A, 1D, 2A, 2D or 3 which is at least monosubstituted by $-Sp-R^C$.

- 5 19. The conjugated polymer according to one or more of claims 1 to 18, characterized in that it comprises, preferably consists of, one or more, preferably two or more, repeating units of formula II1 and/or II2, and optionally one or more repeating units of formula II3:



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

20 U a unit selected from formula I, I1-I7 or I1-1 to I5-13 as defined in any of claims 1 to 10, preferably selected from groups 1A and 1D,

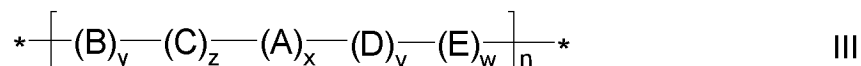
25 C^{1-4} distinct units having one of the meanings of Ar^6 as defined in any if claims 13 to 16, preferably selected from groups 2A, 2D and 3,

a, b, c, d 0 or 1, wherein in formula II3 $a+b+c+d \geq 1$,

30 and wherein the polymer contains at least one unit of formula II1, II2 or II3 wherein at least one of U and C^{1-4} is at least monosubstituted by $-Sp-R^C$.

20. The conjugated polymer according to one or more of claims 1 to 19, characterized in that it selected of formula III:

35



5

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

A a unit of formula II1 or II2,

10

B, C, D, E a unit of formula II1, II2 or II3,

x > 0 and ≤ 1,

15

v, w, y, z ≥ 0 and < 1,

v+w+x+y+z = 1, and

n an integer >1, preferably ≥5,

20

and wherein at least one of A-E is at least monosubstituted by -Sp-R^C.

25

21. The conjugated polymer according to one or more of claims 1 to 20, characterized in that it comprises, very preferably consists of, one or more units selected from the group consisting of the following formulae and their mirror images

-(U)- U1

30

-(U-Sp)- U2

-(Sp-U-Sp)- U3

-(D-Sp)- U4

35

-(A-Sp)- U5

	-(Sp-D-Sp)-	U6
5	-(Sp-A-Sp)-	U7
	-(A-D)-	U8
	-(D)-	U9
10	-(Sp-D-Sp-D)-	U10
	-(A)-	U11
15	-(Sp-A-Sp-A)-	U12

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

20 U the meaning given in claim 19,

D a donor unit selected from groups 1D and 2D as defined in claim 18,

25 A an acceptor unit selected from groups 1A and 2A as defined in claim 18,

Sp a spacer unit selected from the group 3 as defined in claim 18,

30 and wherein the polymer contains at least one unit U, D, A or Sp which is at least monosubstituted by -Sp-R^C.

22. The conjugated polymer according to one or more of claims 1 to 21, characterized in that it is selected from formulae Pi-Px

35 -[(U-Sp)_n- Pi

	$-\text{[(U-Sp)}_x\text{-(Ar}^6\text{-Sp)}_y\text{]}_n-$	Pii
5	$-\text{[(U-Sp)}_x\text{-(A-Sp)}_y\text{]}_n-$	Piii
	$-\text{[(U-Sp)}_x\text{-(D-Sp)}_y\text{]}_n-$	Piv
	$-\text{[(U-D)}_x\text{-(U-Sp)}_y\text{]}_n-$	Pv
10	$-\text{[(U-A)}_x\text{-(U-Sp)}_y\text{]}_n-$	Pvi
	$-\text{[(D)}_x\text{-(Sp-U-Sp)}_y\text{]}_n-$	Pvii
15	$-\text{[(A)}_x\text{-(Sp-U-Sp)}_y\text{]}_n-$	Pviii
	$-\text{[D-A]}_n-$	Pix
	$-\text{[(D-Sp)}_x\text{-(A-Sp)}_y\text{]}_n-$	Pviii
20	$-\text{[A-D-A]}_n-$	Pix
	$-\text{[Sp-U}^1\text{-Sp-U}^2\text{]}_n-$	Px

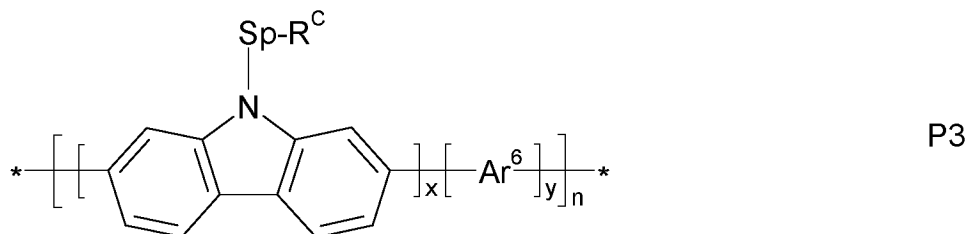
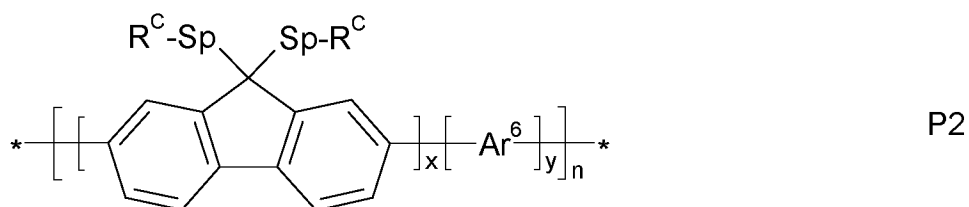
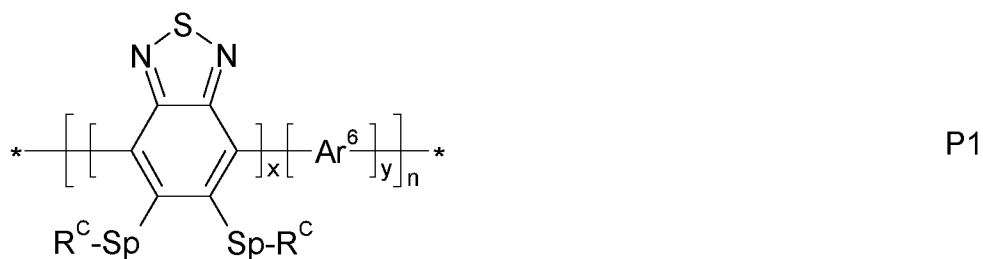
25 wherein A, D and Sp are as defined in formulae U2-U12, A, D and Sp can each, in case of multiple occurrence, also have different meanings, U¹ and U² have one of the meanings given for U and are different from each other, x and y denote the molar fractions of the corresponding units, x and y are each, independently of one another, a non-integer >0 and <1, with x+y=1, and n is an integer >1,

30 and wherein the polymer contains at least one unit U, D, A or Sp which is at least monosubstituted by -Sp-R^C.

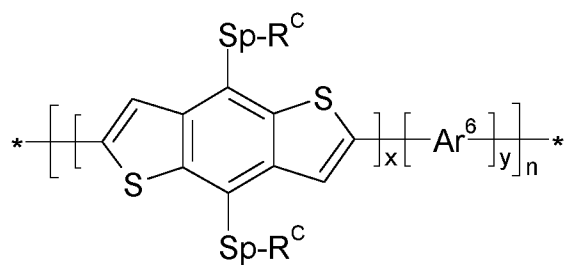
35 23. The conjugated polymer according to one or more of claims 1 to 22, characterized in that it in the formulae U2-U12 and Pi-Px

- a) the donor units D and 2D are selected from the group consisting of the formulae D1-D151, very preferably of the formulae D1, D7, D10, D11, D19, D22, D29, D30, D35, D36, D37, D44, D55, D84, D87, D88, D89, D93, D94, D106, D111, D139, D140, D141, D146 and D150,
- b) the acceptor units A and 2A are selected from the group consisting of the formulae A1-A103, very preferably of the formulae A1, A6, A7, A15, A16, A20, A36, A49, A74, A78, A84, A88, A92, A94, A98, A102 and A103,
- and
- c) the spacer units Sp are selected from the group consisting of the formulae Sp1-Sp18, very preferably of the formulae Sp1, Sp2, Sp6, Sp10, Sp11, Sp12, Sp13 and Sp14.

24. The conjugated polymer according to one or more of claims 1 to 23, it is selected from the following subformulae

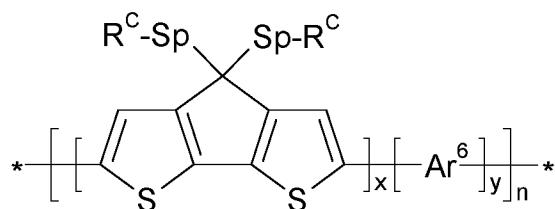


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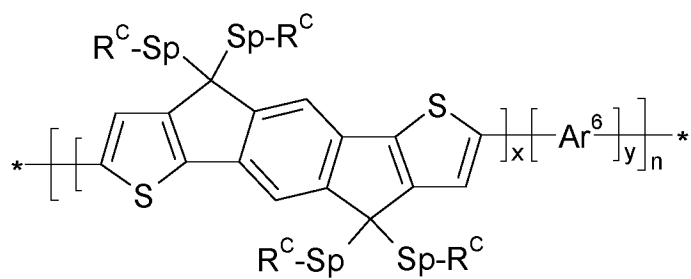
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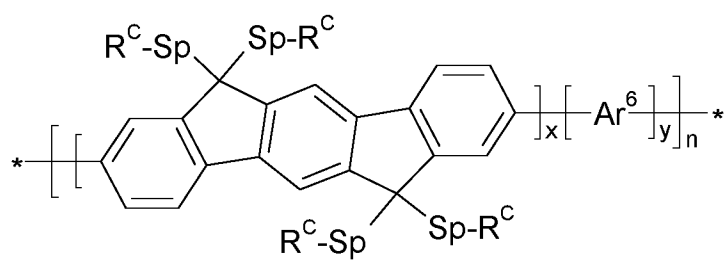
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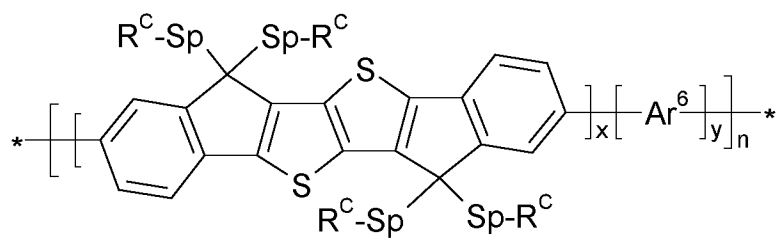
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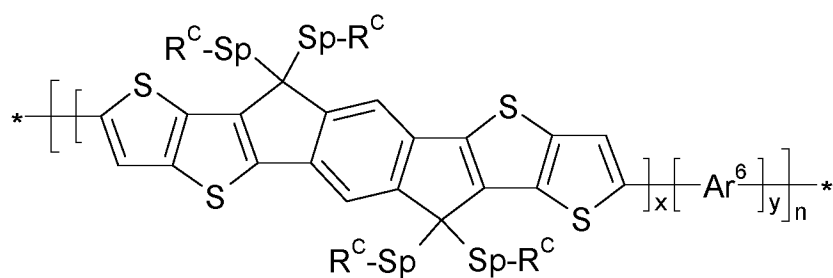


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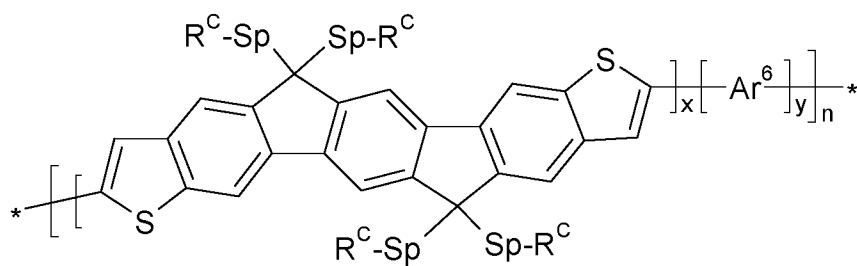
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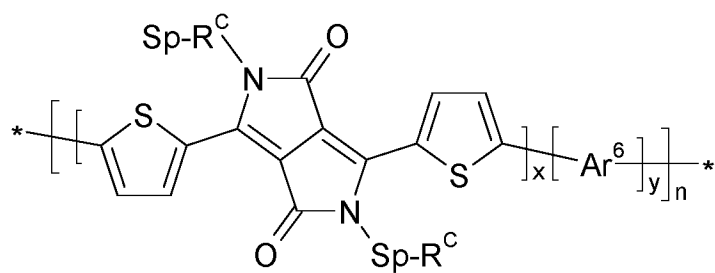
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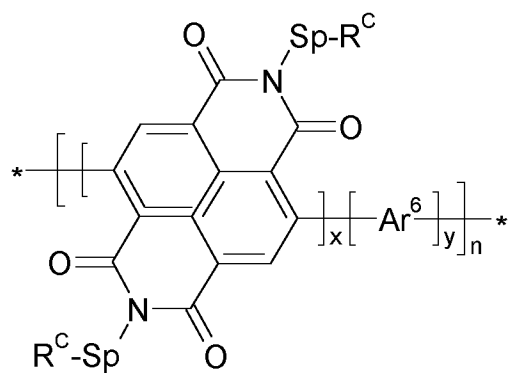
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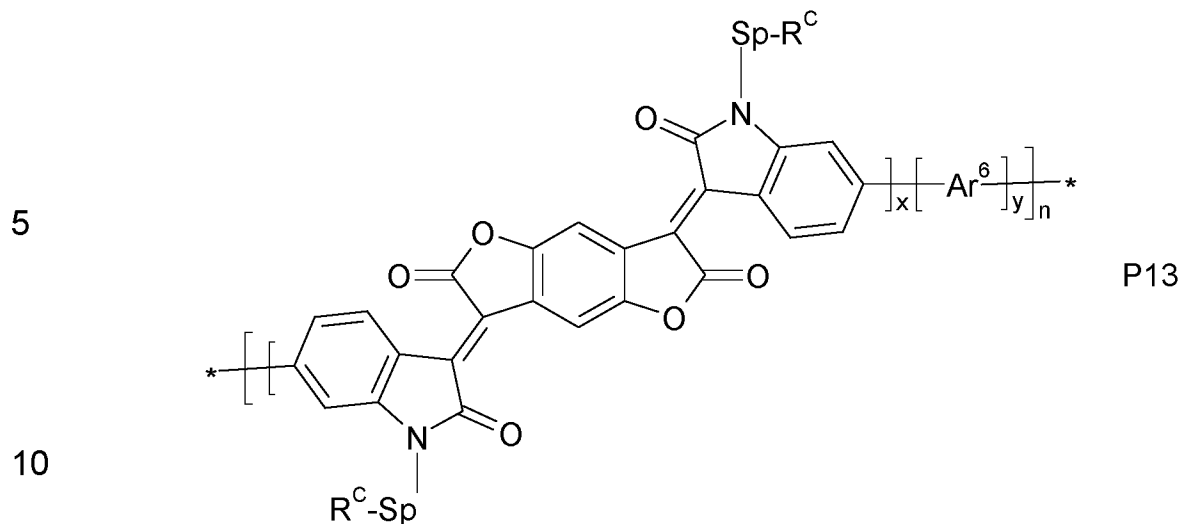


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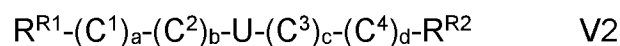
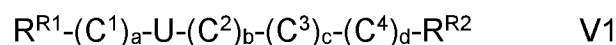
wherein R^C has the meanings given in claim 1 or 11, Sp has the meanings given in claim 1 or 12, Ar^6 has the meanings given in claim 1, 13, 14 or 15, x, y and n have the meanings given in claim 20.

25. The conjugated polymer according to one or more of claims 1 to 24, wherein the groups R^C are crosslinked.
26. A composition comprising one or more polymers according to one or more of claims 1 to 25, and further comprising one or more compounds having one or more of a semiconducting, hole or electron transporting, hole or electron blocking, electrically conducting, photoconducting, photoactive or light emitting property, and/or a binder.
27. Use of a polymer according to one or more of claims 1 to 25, or of a composition according to claim 25, in an electronic or optoelectronic device, or in a component of such a device or in an assembly comprising such a device.
28. A formulation comprising one or more polymers according to one or more of claims 1 to 24 or a composition according to claim 26, and further comprising one or more solvents selected from organic solvents.
29. A pattern or patterned film comprising a polymer according to one or

more of claims 1 to 25 or a composition according to claim 26 wherein the groups R^C are crosslinked.

- 5 30. An electronic or optoelectronic device, or a component thereof, or an assembly comprising it, which comprises a polymer, composition or patterned film according to one or more of claims 1 to 26.
- 10 31. The electronic or optoelectronic device according to claim 30, which is selected from organic field effect transistors (OFET), organic thin film transistors (OTFT), organic light emitting diodes (OLED), organic light emitting transistors (OLET), organic light emitting electro-chemical cells (OLEC), organic photovoltaic devices (OPV), organic photodetectors (OPD), organic solar cells, dye-sensitized solar cells (DSSC),
- 15 perovskite-based solar cells (PSC), organic photoelectrochemical cells (OPEC), laser diodes, Schottky diodes, photoconductors, photodetectors, thermoelectric devices and LC windows.
- 20 32. The component according to claim 30, which is selected from charge injection layers, charge transport layers, interlayers, planarizing layers, antistatic films, polymer electrolyte membranes (PEM), conducting substrates and conducting patterns.
- 25 33. The assembly according to claim 30, which is selected from integrated circuits (IC), radio frequency identification (RFID) tags, security markings, security devices, flat panel displays, backlights of flat panel displays, electrophotographic devices, electrophotographic recording devices, organic memory devices, sensor devices, biosensors and biochips.

- 30 34. A monomer of formula V1 or V2



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wherein U, C^{1-4} , a, b, c and d have the meanings of claim 19, and

5 R^{R1} and R^{R2} are independently of each other selected from the group consisting of H, an activated C-H bond, Cl, Br, I, O-tosylate, O-triflate, O-mesylate, O-nonaflate, $-\text{SiMe}_2\text{F}$, $-\text{SiMeF}_2$, $-\text{O}-\text{SO}_2\text{Z}^1$, $-\text{B}(\text{OZ}^2)_2$, $-\text{CZ}^3=\text{C}(\text{Z}^3)_2$, $-\text{C}\equiv\text{CH}$, $-\text{C}\equiv\text{CSi}(\text{Z}^1)_3$, $-\text{ZnX}^0$ and $-\text{Sn}(\text{Z}^4)_3$, wherein X^0 is halogen, Z^{1-4} are selected from the group consisting of alkyl and aryl, each being optionally substituted, and two groups Z^2 may also form a cycloboronate group having 2 to 20 C atoms together with the B- and O-atoms, and wherein at least one of R^{R1} and R^{R2} is different from H.

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35. The monomer of claim 34, which is selected from the following subformulae

15 $R^{R1}-U-R^{R2}$ V1a

$R^{R1}-C^1-U-C^2-R^{R2}$ V1b

$R^{R1}-C^1-U-R^{R2}$ V1c

20 $R^{R1}-U-C^2-R^{R2}$ V1d

wherein U, C^1 , C^2 , R^{R1} and R^{R2} are as defined in claim 34.

- 25 36. A process of preparing a polymer according to any of claims 1 to 24, by copolymerising one or more monomers of formula V1, V2 or V1a-d as defined in claim 34 and 35 with each other or with one or monomers of the following formulae in an aryl-aryl coupling reaction

$R^{R1}-C^1-R^{R2}$ MI

30 $R^{R1}-C^2-R^{R2}$ MII

$R^{R1}-C^3-R^{R2}$ MIII

$R^{R1}-C^4-R^{R2}$ MIV

35 wherein C^{1-4} , R^{R1} and R^{R2} have the meanings given in claim 34.

Fig. 1

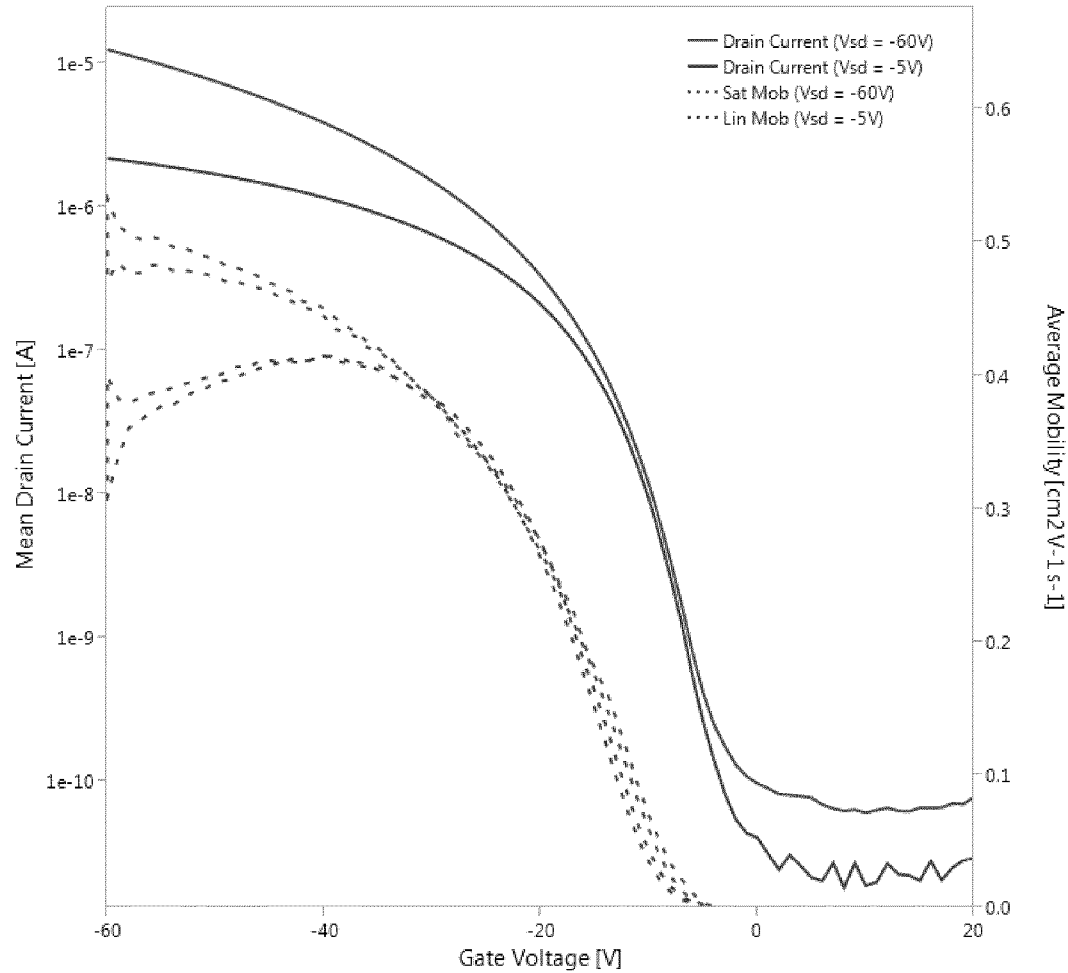
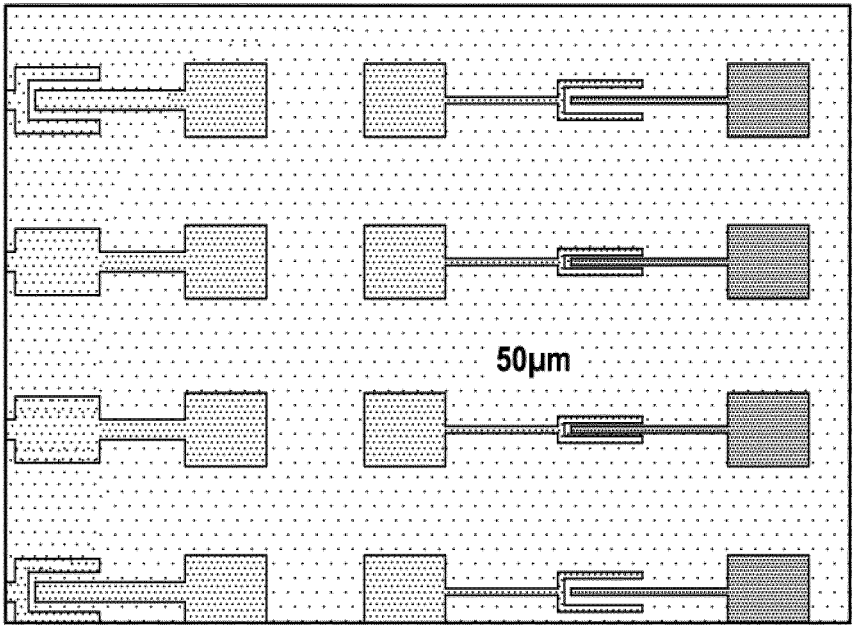


Fig. 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/052571

A. CLASSIFICATION OF SUBJECT MATTER INV. C08G61/12 C08L65/00 C09D165/00 C07D495/04 H01L51/00 H01L51/05 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) C08G C08L C09D C07D 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 <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category*</th> <th style="width: 70%;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 20%;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;"> WANG JINGWEI ET AL: "Single white polymers based on simple diarylmales: Polymeric structure and electroluminescent properties", SYNTHETIC METALS, vol. 230, 6 June 2017 (2017-06-06), pages 18-26, XP085113776, ISSN: 0379-6779, DOI: 10.1016/J.SYNTHMET.2017.05.017 schemes 1,2; abstract; figures 1,2 ----- </td> <td style="vertical-align: top;"> 1-10, 12-14, 16-33,36 </td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;"> US 2008/293164 A1 (GAYLORD BRENT S [US] ET AL) 27 November 2008 (2008-11-27) claims 93,99,110; figures 11,12,13,21,27b; examples 9,10 ----- -/-- </td> <td style="vertical-align: top;"> 1-33,36 </td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	WANG JINGWEI ET AL: "Single white polymers based on simple diarylmales: Polymeric structure and electroluminescent properties", SYNTHETIC METALS, vol. 230, 6 June 2017 (2017-06-06), pages 18-26, XP085113776, ISSN: 0379-6779, DOI: 10.1016/J.SYNTHMET.2017.05.017 schemes 1,2; abstract; figures 1,2 -----	1-10, 12-14, 16-33,36	X	US 2008/293164 A1 (GAYLORD BRENT S [US] ET AL) 27 November 2008 (2008-11-27) claims 93,99,110; figures 11,12,13,21,27b; examples 9,10 ----- -/--	1-33,36
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.									
X	WANG JINGWEI ET AL: "Single white polymers based on simple diarylmales: Polymeric structure and electroluminescent properties", SYNTHETIC METALS, vol. 230, 6 June 2017 (2017-06-06), pages 18-26, XP085113776, ISSN: 0379-6779, DOI: 10.1016/J.SYNTHMET.2017.05.017 schemes 1,2; abstract; figures 1,2 -----	1-10, 12-14, 16-33,36									
X	US 2008/293164 A1 (GAYLORD BRENT S [US] ET AL) 27 November 2008 (2008-11-27) claims 93,99,110; figures 11,12,13,21,27b; examples 9,10 ----- -/--	1-33,36									
☒ 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 12 May 2020		Date of mailing of the international search report 15/07/2020									
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 Meiners, Christian									

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EUGENE W. L. CHAN ET AL: "A Novel Layer-by-Layer Approach to Immobilization of Polymers and Nanoclusters", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 124, no. 41, 24 September 2002 (2002-09-24), pages 12238-12243, XP055692625, US ISSN: 0002-7863, DOI: 10.1021/ja026159o abstract scheme 1 text section "Introduction" on page 12238 -----	1-10,12, 13,15, 17-19, 21-23, 26,28,36
Y	CHARAS A ET AL: "Observation of field-effect in a cross-linked polyfluorene semiconductor", CHEMICAL PHYSICS LETTERS, ELSEVIER BV, NL, vol. 455, no. 4-6, 10 April 2008 (2008-04-10), pages 189-191, XP026052029, ISSN: 0009-2614, DOI: 10.1016/J.CPLETT.2008.02.087 [retrieved on 2008-03-02] cited in the application the whole document -----	1-33,36
X	US 2014/158949 A1 (WANG CHANGSHENG [GB] ET AL) 12 June 2014 (2014-06-12)	1-33,36
Y	paragraphs [0081], [0082], [0086], [0087], [0105] - [0108], [0198], [0199]; claims 1,3 -----	1-33,36
X	US 2015/207076 A1 (TIERNEY STEVEN [GB] ET AL) 23 July 2015 (2015-07-23)	1-33,36
Y	paragraphs [0016] - [0031], [0065] - [0067], [0080], [0081], [0174]; claims 1-3,9-14 -----	1-33,36
Y	US 5 202 221 A (IMAI MASANORI [US] ET AL) 13 April 1993 (1993-04-13) claim 1; table III -----	1-33,36
Y	US 2011/105711 A1 (INBASEKARAN MICHAEL [US] ET AL) 5 May 2011 (2011-05-05) paragraph [0032] - paragraph [0034]; claims 1,3 -----	1-33,36
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Y	paragraphs [0068] - [0075], [0082] - [0084], [0150]; claims 1-6,8-13 -----	1-33,36
	-/--	

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Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-33, 36

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-33, 36

Conjugated polymers of claims 1-25, compositions and formulations of claims 26 and 28, use of said polymers and compositions in accordance with claim 27, patterns and patterned films of claim 29, devices and components of claims 30-33, a process of preparing a polymer according to claims 1-24 in accordance with claim 36

2. claims: 34, 35

Monomers of claims 34 and 35

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2020/052571

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/270490 A1 (MITCHELL WILLIAM [GB] ET AL) 24 September 2015 (2015-09-24) paragraphs [0022], [0023], [0026], [0071], [0072], [0102], [0158], [0159]; claims 16,19,26-32 -----	1-12, 14-33,36

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