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- **FRANCISCO OTON ET AL: "Benzodicarbomethoxytetrathiafulvalene Derivatives as Soluble Organic Semiconductors", THE JOURNAL OF ORGANIC CHEMISTRY, vol. 76, no. 1, 7 January 2011 (2011-01-07), pages 154-163, XP055363250, ISSN: 0022-3263, DOI: 10.1021/jo101817j**
- **ZHENG ZHAO ET AL: "Tetracyanodibenzotetrathiafulvalene Diimides: Design, Synthesis, and Property Study", THE JOURNAL OF ORGANIC CHEMISTRY, vol. 78, no. 23, 6 December 2013 (2013-12-06), pages 12214-12219, XP055317021, ISSN: 0022-3263, DOI: 10.1021/jo401916f**

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Description

Technical Field

[0001] The invention relates to novel compounds containing one or more 1,3-dithiolo[4,5-d]phthalimide ("DTPI") units, to methods for their preparation and educts or intermediates used therein, to mixtures and formulations containing them, to the use of the compounds, mixtures and formulations as organic semiconductors in organic electronic (OE) devices, especially in organic photovoltaic (OPV) devices and organic photodetectors (OPD), and to OE, OPV and OPD devices comprising these compounds, mixtures or formulations.

Background

[0002] In recent years, there has been development of organic semiconducting (OSC) materials in order to produce more versatile, lower cost electronic devices. Such materials find application in a wide range of devices or apparatus, including organic thin film transistors (OTFTs), organic light emitting diodes (OLEDs), organic photodetectors (OPDs), organic photovoltaic (OPV) cells, sensors, memory elements and logic circuits to name just a few. The organic semiconducting materials are typically present in the electronic device in the form of a thin layer.

[0003] Organic semiconducting (OSC) materials are receiving ever-growing attention mostly due to their lucrative commercial prospects in organic electronics manufactured by cost effective solution processing technology at low temperature. It is generally believed that OSCs have a number of advantage over their inorganic counterparts, such as the potential of fabricating lightweight flexible backplanes, the opportunity to make large area displays using low-cost, high speed solution based fabrication techniques, and their optical and electronic properties being fine-tuneable via rational chemical structure modifications.

[0004] The main disadvantages of the OSC materials currently known in prior art are their relatively low device performance and their modest thermal, photo and electrical stability. Over the past two decades a wide range of new π-conjugated polymers have been made available, and have shown improved performance in OE devices like OTFTs such as high charge carrier mobility, reaching or even surpassing that of amorphous silicon. In the meantime, power conversion efficiencies of OPV cells fabricated using low bandgap π-conjugated polymers as active electron donor materials have exceeded 10%.

[0005] The performance of OTFTs is principally based upon the charge carrier mobility of the semiconducting material and the current on/off ratio. Thus, for use in OTFTs the OSC should have a low conductivity in the off state and a high charge-carrier mobility, enabling a high on/off ratio in the OTFT. In addition, the OSC, if n-type, should be stable to oxidation i.e. have a high ionisation potential, as oxidative doping leads to reduced device performance, for example increased off current and threshold voltage shift. Further requirements for the OSC are good processability, especially for large-scale production of thin-film layers and desired patterns, and high stability, thin-film uniformity and integrity of the OSC layer.

[0006] In OPV cells, π-conjugated polymers and organic small molecules have found use as OSC in the photoactive layer, as they allow devices to be manufactured by solution-processing techniques such as spin casting, dip coating or ink jet printing. Solution processing can be carried out cheaper and on a larger scale, compared to the evaporative techniques used to make inorganic thin film devices. In photoactive layers containing a blend of an n-type OSC and a p-type OSC, typically a π-conjugated polymer, forming a bulk-heterojunction (BHJ), the π-conjugated polymer serves as the main absorber of the solar energy. Therefore a low band gap is a basic requirement for the polymer to absorb the maximum of the solar spectrum. Thus, for use in OPV cells and OPDs, the OSC should have a low bandgap, which enables improved light harvesting by the photoactive layer and can lead to higher power conversion efficiency.

[0007] Polymerising π-π-donor-acceptor (D-A) monomers to synthesize D-A copolymers through transition metal catalysed polycondensation is a known strategy to achieve low bandgap semiconducting polymers for OPV and OPD applications. Conjugated D-A copolymers have also been found to demonstrate high charge carrier mobilities in OTFTs. It is generally accepted that the alternating D-A structure facilitates stronger intermolecular interactions, leading to smaller π-π-stacking distance and efficient intermolecular charge transfer due to static attractions between the donor and the acceptor monomer units.

[0008] To date, a large number of conjugated π-structures have been synthesized which can be used as monomers for preparing conjugated OSC polymers. However, electron donor units remain overwhelmingly dominant in the pool of monomers mainly due to the relative ease of synthetic accessibility of building blocks and precursors. In contrast, there is only a limited number of electron acceptor units or monomers available.

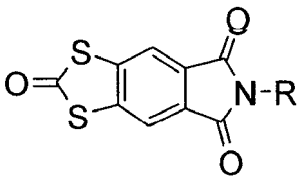
[0009] Therefore, it is desired to increase the pool of electron acceptors by adding electron deficient π-units to make further promising D-A copolymers available.

[0010] Thus, there is still a need for OSC compounds which are suitable for use in OE devices like OTFTs, OPDs and OPV cells, and which show one or more of the above-mentioned desired properties.

[0011] It was an aim of the present invention to provide OSC compounds for use in OE devices like OTFTs, OPDs and OPV devices, which are easy to synthesize, especially by methods suitable for mass production, which show especially good processibility, high stability, good solubility in organic solvents, high charge carrier mobility, and a low bandgap. Another aim of the invention was to extend the pool of OSC materials having electron acceptor property. Other aims of the present invention are immediately evident to the expert from the following detailed description.

[0012] The inventors of the present invention have found that one or more of the above aims can be achieved by providing compounds having a divalent unit derived from π-extended phthalimide, like the 1,3-dithiolo[4,5-d]phthalimide ("DTPI") units as disclosed and claimed hereinafter.

[0013] X. Gao, et al., Adv. Mater., 2007, 19 (19), 3037 and F. Octón et al., Chem. Mater., 2011, 23 (3), 851) disclose dibenzotetrathiafulvalene (DBTTF) bisimides. F. Octón et al., J. Org. Chem., 2011, 76 (1), 154 discloses tetrathiafulvalene (TTF) dicarboxylic diesters with fluorinated alkyl chains. In the synthesis routes to these compounds as disclosed in the above-mentioned documents the following intermediate is used

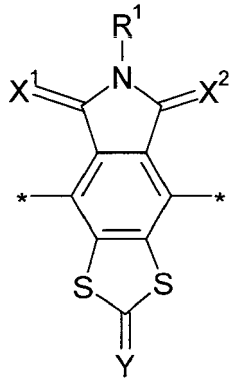


wherein R is an alkyl or fluoroalkyl group. However, these documents do neither disclose nor suggest compounds or their uses as described and claimed hereinafter

[0014] CN101161656 (A), FRANCISCO OTON ET AL: "Benzodicarbomethoxytetrathiafulvalene Derivatives as Soluble Organic Semiconductors", THE JOURNAL OF ORGANIC CHEMISTRY, vol. 76, no. 1, 7 January 2011 (2011-01-07), pages 154-163, and ZHENG ZHAO ET AL: "Tetracyanodibenzotetrathiafulvalene Diimides: Design, Synthesis, and Property Study", THE JOURNAL OF ORGANIC CHEMISTRY, vol. 78, no. 23, 6 December 2013 (2013-12-06), pages 12214-12219 disclose tetrathiafulvalene derivatives.

Summary

[0015] The invention relates to a compound according to the claims comprising one or more divalent units of formula I



I

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

X^1, X^2 O or S,

Y O, S or CU^1U^2,

U^1, U^2 an electron withdrawing group, preferably selected from CN, C(=O)R or C(=O)OR, or U^1 and U^2 together form a carbocyclic, heterocyclic, aromatic or heteroaromatic ring having 4 to 15 ring atoms that is optionally substituted by one or more groups L, preferably by one or more groups F, Cl, -CN, $-C(=O)-R^0$, $-C(=O)-OR^0$, $-O-C(=O)-R^0$, $-O-C(=O)-OR^0$, $-C(=O)-NHR^0$ or $-C(=O)-NR^0R^{00}$,

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

R straight-chain, branched or cyclic alkyl with 1 to 30, preferably 1 to 20, C atoms, in which one or more CH_2 groups are optionally replaced by -O-, -S-, -C(=O)-, -C(=S)-, -C(=O)-O-, -O-C(=O)-,-NR^0-, -SiR^0R^{00}-, -CF_2-, -CR^0=CR^{00}-, -Cy^1=Cy^2- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, and in which one or more H atoms are optionally replaced by F, Cl, Br, I or CN, and in which one or more CH_2 or CH_3 groups are optionally replaced by a cationic or anionic group, or aryl, heteroaryl, arylalkyl or heteroarylalkyl, 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,

L F, Cl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, R^0, OR^0, SR^0,-C(=O)X^0, -C(=O)R^0, -C(=O)-OR^0, -O-C(=O)-R^0, -NH_2, -NHR^0,-NR^0R^{00}, -C(=O)NHR^0, -C(=O)NR^0R^{00}, -SO_3R^0, -SO_2R^0, -OH, -NO_2, -CF_3, -SF_5, or optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 20 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, preferably F, -CN, R^0, -OR^0, -SR^0, -C(=O)-R^0, -C(=O)-OR^0, -O-C(=O)-R^0, -O-C(=O)-OR^0,-C(=O)-NHR^0, -C(=O)-NR^0R^{00},

Y^1, Y^2 H, F, Cl or CN,

X^0 halogen, preferably F or Cl,

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, and

with the proviso that, if X^1, X^2 and Y are O, the unit of formula I is bonded via the 1- or 4-position of the benzene ring to at least one group that is different from H (*i.e.* the unit of formula I is not bonded to two H atoms).

[0016] The compound as described above and below is a conjugated polymer. The conjugated polymer comprises, preferably consists of, one or more units of formula I and one or more arylene or heteroarylene units that have from 5 to 20 ring atoms, are mono- or polycyclic, do optionally contain fused rings, are unsubstituted or substituted by one or more identical or different groups L, and are either selected of formula I or are structurally different from formula I, and wherein all the aforementioned units are directly connected to each other.

[0017] The invention further relates to a compound according to the claims as described above and below which is a small molecule or an oligomer.

[0018] The invention further relates to the use of the units of formula I in or as repeating units in conjugated polymers.

[0019] The invention further relates to the use of units of formula I in or as repeating units having electron acceptor property in conjugated polymers.

[0020] The invention further relates to a conjugated polymer comprising one or more electron acceptor repeating units comprising a unit of formula I, and preferably further comprising one or more repeating units having electron donor property.

[0021] The invention further relates to a monomer according to the claims containing a unit of formula I, and optionally containing one or more additional arylene or heteroarylene units, and further containing one or more reactive groups which can be reacted to form a conjugated polymer as described above and below.

[0022] The invention further relates to the use of a compound as described above and below as electron acceptor or n-type semiconductor.

[0023] The invention further relates to the use of a conjugated polymer as described above and below as semiconductor, preferably as electron donor or p-type semiconductor.

[0024] The invention further relates to the use of a compound as described above and below as electron donor or electron acceptor component in a semiconducting material, formulation, polymer blend, device or component of a device.

[0025] The invention further relates to a semiconducting material, formulation, polymer blend, device or component of a device comprising a compound as described above and below as electron donor component, and preferably further comprising one or more compounds having electron acceptor properties.

[0026] The invention further relates to a mixture, which may also be a polymer blend, comprising one or more com-

pounds as described above and below, 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.

[0027] The invention further relates to a mixture comprising one or more compounds as described above and below, and further comprising one or more n-type organic semiconductors, preferably selected from fullerenes or substituted fullerenes.

[0028] The invention further relates to a formulation comprising one or more compounds or mixtures as described above and below, and further comprising one or more solvents, preferably selected from organic solvents.

[0029] The invention further relates to an organic semiconducting formulation comprising one or more compounds as described above and below, 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.

[0030] The invention further relates to an optical, electrooptical, electronic, electroluminescent or photoluminescent device, or a component thereof, or an assembly comprising it, which is prepared using a formulation according to the present invention.

[0031] The invention further relates to the use of a compound or mixture as described above and below as semiconducting, charge transport, electrically conducting, photoconducting or light emitting material, or in an optical, electrooptical, electronic, electroluminescent or photoluminescent device, or in a component of such a device or in an assembly comprising such a device or component

[0032] The invention further relates to a semiconducting, charge transport, electrically conducting, photoconducting or light emitting material comprising a compound or mixture as described above and below.

[0033] The invention further relates to an optical, electrooptical, electronic, electroluminescent or photoluminescent device, or a component thereof, or an assembly comprising it, which comprises a compound or mixture as described above and below, or comprises a semiconducting, charge transport, electrically conducting, photoconducting or light emitting material as described above and below.

[0034] The optical, electrooptical, electronic, electroluminescent and photoluminescent device includes, without limitation, organic thin film transistors (OTFT), 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, laser diodes, Schottky diodes, photoconductors and photodetectors.

[0035] Preferred devices are OTFTs, OTFTs, OPVs, OPDs and OLEDs, in particular bulk heterojunction (BHJ) OPVs or inverted BHJ OPVs.

[0036] Further preferred is the use of a compound or mixture as described above and below as dye in a DSSC or a perovskite-based solar cell. Further preferred is a DSSC or perovskite-based solar cells comprising a compound or mixture as described above and below.

[0037] 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.

[0038] 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 containg them, flat panel displays or backlights thereof, electrophotographic devices, electrophotographic recording devices, organic memory devices, sensor devices, biosensors and biochips.

[0039] In addition the compounds, mixtures 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.

[0040] The invention further relates to a bulk heterojunction which comprises, or is being formed from, a mixture comprising one or more compounds according to the present invention and one or more n-type organic semiconductors that are preferably selected from fullerenes or substituted fullerenes. The invention further relates to a bulk heterojunction (BHJ) OPV device or inverted BHJ OPV device, comprising such a bulk heterojunction.

Terms and Definitions

[0041] As used herein, the term "polymer" will be understood to mean a molecule of high relative molecular mass, the structure of which essentially comprises multiple repetitions of units derived, actually or conceptually, from molecules of low relative molecular mass (Pure Appl. Chem., 1996, 68, 2291). The term "oligomer" will be understood to mean a molecule of intermediate relative molecular mass, the structure of which essentially comprises a small plurality of units derived, actually or conceptually, from molecules of lower relative molecular mass (Pure Appl. Chem., 1996, 68, 2291). In a preferred meaning as used herein present invention a polymer will be understood to mean a compound having > 1, i.e. at least 2 repeat units, preferably $\geq$ 5 repeat units, and an oligomer will be understood to mean a compound with

> 1 and < 10, preferably < 5, repeat units.

[0042] Further, as used herein, the term "polymer" will be understood to mean a molecule that encompasses a backbone (also referred to as "main chain") of one or more distinct types of repeat units (the smallest constitutional unit of the molecule) and is inclusive of the commonly known terms "oligomer", "copolymer", "homopolymer", "random polymer" and the like. Further, it will be understood that the term polymer is inclusive of, in addition to the polymer itself, residues from initiators, catalysts and other elements attendant to the synthesis of such a polymer, where such residues are understood as not being covalently incorporated thereto. Further, such residues and other elements, while normally removed during post polymerization purification processes, are typically mixed or comingled with the polymer such that they generally remain with the polymer when it is transferred between vessels or between solvents or dispersion media.

[0043] As used herein, in a formula showing a polymer or a repeat unit, like for example a unit of formula I or a polymer of formula III or IV or their subformulae, an asterisk (*) will be understood to mean a chemical linkage 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.

[0044] As used herein, the terms "repeat unit", "repeating unit" and "monomeric unit" are used interchangeably and will be understood to mean the constitutional repeating unit (CRU), which is the smallest constitutional unit the repetition of which constitutes a regular macromolecule, a regular oligomer molecule, a regular block or a regular chain (Pure Appl. Chem., 1996, 68, 2291). As further used herein, the term "unit" will be understood to mean a structural unit which can be a repeating unit on its own, or can together with other units form a constitutional repeating unit.

[0045] 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 polymerisation reaction, like for example a group having the meaning of R^5 or R^6 as defined below.

[0046] As used herein, the term "endcap group" will be understood to mean a group that is attached to, or replacing, a terminal group of the polymer backbone. The endcap group can be introduced into the polymer by an endcapping process. Endcapping can be carried out for example by reacting the terminal groups of the polymer backbone with a monofunctional compound ("endcapper") like for example an alkyl- or arylhalide, an alkyl- or arylstannane or an alkyl- or arylboronate. The endcapper can be added for example after the polymerisation reaction. Alternatively the endcapper can be added in situ to the reaction mixture before or during the polymerisation reaction. In situ addition of an endcapper can also be used to terminate the polymerisation reaction and thus control the molecular weight of the forming polymer. Typical endcap groups are for example H, phenyl and lower alkyl.

[0047] As used herein, the term "small molecule" will be understood to mean a monomeric compound which typically does not contain a reactive group by which it can be reacted to form a polymer, and which is designated to be used in monomeric form. In contrast thereto, the term "monomer" unless stated otherwise will be understood to mean a monomeric compound that carries one or more reactive functional groups by which it can be reacted to form a polymer.

[0048] 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.

[0049] As used herein, the term "n-type" or "n-type semiconductor" will be understood to mean an extrinsic semiconductor in which the conduction electron density is in excess of the mobile hole density, and the term "p-type" or "p-type semiconductor" will be understood to mean an extrinsic semiconductor in which mobile hole density is in excess of the conduction electron density (see also, J. Thewlis, Concise Dictionary of Physics, Pergamon Press, Oxford, 1973).

[0050] 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 part of the molecule taking part in a specified reaction (see also Pure Appl. Chem., 1994, 66, 1134).

[0051] 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-hybridisation (or optionally also sp-hybridisation), and wherein these C atoms may also be replaced by hetero atoms. In the simplest case this is for example a compound with alternating C-C single and double (or triple) bonds, but is also inclusive of compounds with aromatic units like for example 1,4-phenylene. The term "mainly" in this connection will be understood to mean that a compound with naturally (spontaneously) occurring defects, or with defects included by design, which may lead to interruption of the conjugation, is still regarded as a conjugated compound.

[0052] As used herein, unless stated otherwise the molecular weight is given as the number average molecular weight M_n or weight average molecular weight M_W, which is determined by gel permeation chromatography (GPC) against polystyrene standards in eluent solvents such as tetrahydrofuran, trichloromethane (TCM, chloroform), chlorobenzene

or 1,2,4-trichlorobenzene. Unless stated otherwise, chlorobenzene is used as solvent. The degree of polymerization, also referred to as total number of repeat units, n, will be understood to mean the number average degree of polymerization given as $n = M_n/M_U$, wherein M_n is the number average molecular weight and Mu is the molecular weight of the single repeat unit, see J. M. G. Cowie, Polymers: Chemistry & Physics of Modern Materials, Blackie, Glasgow, 1991.

[0053] As used herein, the term "carbyl group" will be understood to mean any monovalent or multivalent organic moiety which comprises at least one carbon atom either without any non-carbon atoms (like for example -C≡C-), or optionally combined with at least one non-carbon atom such as B, N, O, S, P, Si, Se, As, Te or Ge (for example carbonyl etc.).

[0054] As used herein, the term "hydrocarbyl group" will be understood to mean a carbyl group that does additionally contain one or more H atoms and optionally contains one or more hetero atoms like for example B, N, O, S, P, Si, Se, As, Te or Ge.

[0055] As used herein, the term "hetero atom" will be understood to mean an atom in an organic compound that is not an H- or C-atom, and preferably will be understood to mean B, N, O, S, P, Si, Se, As, Te or Ge.

[0056] A carbyl or hydrocarbyl group comprising a chain of 3 or more C atoms may be straight-chain, branched and/or cyclic, and may include spiro-connected and/or fused rings.

[0057] Preferred carbyl and hydrocarbyl groups include alkyl, alkoxy, thioalkyl, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy and alkoxycarbonyloxy, each of which is optionally substituted and has 1 to 40, preferably 1 to 25, very preferably 1 to 18 C atoms, furthermore optionally substituted aryl or aryloxy having 6 to 40, preferably 6 to 25 C atoms, furthermore alkylaryloxy, arylcarbonyl, aryloxycarbonyl, arylcarbonyloxy and aryloxycarbonyloxy, each of which is optionally substituted and has 6 to 40, preferably 7 to 40 C atoms, wherein all these groups do optionally contain one or more hetero atoms, preferably selected from B, N, O, S, P, Si, Se, As, Te and Ge.

[0058] Further preferred carbyl and hydrocarbyl group include for example: a C_1-C_{40} alkyl group, a C_1-C_{40} fluoroalkyl group, a C_1-C_{40} alkoxy or oxaalkyl group, a C_2-C_{40} alkenyl group, a C_2-C_{40} alkynyl group, a C_3-C_{40} allyl group, a C_4-C_{40} alkyldienyl group, a C_4-C_{40} polyenyl group, a C_2-C_{40} ketone group, a C_2-C_{40} ester group, a C_6-C_{18} aryl group, a C_6-C_{40} alkylaryl group, a C_6-C_{40} arylalkyl group, a C_4-C_{40} cycloalkyl group, a C_4-C_{40} cycloalkenyl group, and the like. Preferred among the foregoing groups are a C_1-C_{20} alkyl group, a C_1-C_{20} fluoroalkyl group, a C_2-C_{20} alkenyl group, a C_2 -C_{20} alkynyl group, a C_3-C_{20} allyl group, a C_4-C_{20} alkyldienyl group, a C_2-C_{20} ketone group, a C_2-C_{20} ester group, a C_6-C_{12} aryl group, and a C_4-C_{20} polyenyl group, respectively.

[0059] 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.

[0060] 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.

[0061] 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 optionally replaced by a hetero atom, preferably selected from N, O, 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, wherein

[0062] L is selected from F, Cl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, -R^0, -OR^0,-SR°, -C(=O)X^0, -C(=O)R^0, -C(=O)-OR^0, -O-C(=O)-R^0, -NH_2, -NHR^0,-NR^0R^{00}, -C(=O)NHR^0, -C(=O)NR^0R0^{00}, -SO_3R^0, -SO_2R^0, -OH, -NO_2, -CF_3,-SF_5, or optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 20 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, wherein X^0 is halogen, preferably F or Cl, and R^0, R^{00} denote H or straight-chain or branched alkyl with 1 to 20, preferably 1 to 12 C atoms that is optionally fluorinated.

[0063] Preferably L. is selected from F, -CN, R^0, -OR^0, -SR^0, -C(=O)-R^0, -C(=O)-OR^0, -O-C(=O)-R^0, -O-C(=O)-OR^0, -C(=O)-NHR^0 and -C(=O)-NR^0R^{00}.

[0064] Further preferably L is selected from F or alkyl, alkoxy, oxaalkyl, thioalkyl, fluoroalkyl, fluoroalkoxy, alkylcarbonyl, alkoxycarbonyl, with 1 to 12 C atoms, or alkenyl or alkynyl with 2 to 12 C atoms.

[0065] Preferred non-aromatic carbocyclic or heterocyclic groups are tetrahydrofuran, indane, pyran, pyrrolidine, piperidine, cyclopentane, cyclohexane, cycloheptane, cyclopentanone, cyclohexanone, dihydro-furan-2-one, tetrahydropyran-2-one and oxepan-2-one.

[0066] An aryl group as referred to above and below preferably has 4 to 30 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.

[0067] A heteroaryl 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 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.

[0068] An arylalkyl or heteroarylalkyl group as referred to above and below preferably denotes -$(CH_2)_a$-aryl or -$(CH_2)_a$-heteroaryl, wherein a is an integer from 1 to 6, preferably 1, and "aryl" and "heteroaryl" have the meanings given above and below. A preferred arylalkyl group is benzyl which is optionally substituted by L.

[0069] 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.

[0070] Preferred aryl and heteroaryl groups are phenyl in which, in addition, one or more CH groups may 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 pyrrole, preferably N-pyrrole, furan, pyridine, preferably 2- or 3-pyridine, pyrimidine, pyridazine, pyrazine, triazole, tetrazole, pyrazole, imidazole, isothiazole, thiazole, thiadiazole, isoxazole, oxazole, oxadiazole, thiophene, preferably 2-thiophene, selenophene, preferably 2-selenophene, 2,5-dithiophene-2',5'-diyl, thieno[3,2-b]thiophene, thieno[2,3-b]thiophene, furo[3,2-b]furan, furo[2,3-b]furan, seleno[3,2-b]selenophene, seleno[2,3-b]selenophene, thieno[3,2-b]selenophene, thieno[3,2-b]furan, indole, isoindole, benzo[b]furan, benzo[b]thiophene, benzo[1,2-b;4,5-b']dithiophene, benzo[2,1-b;3,4-b']dithiophene, quinole, 2- methylquinole, isoquinole, quinoxaline, quinazoline, benzotriazole, benzimidazole, benzothiazole, benzisothiazole, benzisoxazole, benzoxadiazole, benzoxazole, benzothiadiazole, 4H-cyclopenta[2,1-b;3,4-b']dithiophene, 7H-3,4-dithia-7-sila-cyclopenta[a]pentalene, all of which can be unsubstituted, mono- or polysubstituted with L as defined above. Further examples of aryl and heteroaryl groups are those selected from the groups shown hereinafter.

[0071] An alkyl group or an alkoxy group, *i.e.,* where the terminal CH_2 group is replaced by -O-, can be straight-chain or branched. It is preferably straight-chain, has 2, 3, 4, 5, 6, 7, 8, 12 or 16 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, dodecyl or hexadecyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, octoxy, dodecoxy or hexadecoxy, furthermore methyl, nonyl, decyl, undecyl, tridecyl, tetradecyl, pentadecyl, nonoxy, decoxy, undecoxy, tridecoxy or tetradecoxy, for example.

[0072] An alkenyl group, *i.e.*, wherein one or more CH_2 groups are 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.

[0073] Especially preferred alkenyl groups are C_2-C_7-1E-alkenyl, C_4-C_7-3E-alkenyl, C_5-C_7-4-alkenyl, C_6-C_7-5-alkenyl and C_7-6-alkenyl, in particular C_2-C_7-1E-alkenyl, C_4-C_7-3E-alkenyl and C_5-C_7-4-alkenyl. Examples for particularly preferred alkenyl groups are vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 1E-heptenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-heptenyl, 4-pentenyl, 4Z-hexenyl, 4E-hexenyl, 4Z-heptenyl, 5-hexenyl, 6-heptenyl and the like. Groups having up to 5 C atoms are generally preferred.

[0074] An oxaalkyl group, *i.e.*, where one CH_2 group is replaced by -O-, is preferably straight-chain 2-oxapropyl (=methoxymethyl), 2-(=ethoxymethyl) or 3-oxabutyl (=2-methoxyethyl), 2-, 3-, or 4-oxapentyl, 2-, 3-, 4-, or 5-oxahexyl, 2-, 3-, 4-, 5-, or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-,7-, 8- or 9-oxadecyl, for example.

[0075] In an alkyl group wherein one CH_2 group is replaced by -O- and one CH_2 group is replaced by -C(O)-, these radicals are preferably neighboured. Accordingly these radicals together form a carbonyloxy group -C(O)-O- or an oxycarbonyl group -O-C(O)-. Preferably this group is straight-chain and has 2 to 6 C atoms. It is accordingly preferably acetyloxy, propionyloxy, butyryloxy, pentanoyloxy, hexanoyloxy, acetyloxymethyl, propionyloxymethyl, butyryloxymethyl, pentanoyloxymethyl, 2-acetyloxyethyl, 2-propionyloxyethyl, 2-butyryloxyethyl, 3-acetyloxypropyl, 3-propionyloxypropyl, 4-acetyloxybutyl, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, butoxycarbonyl, pentoxycarbonyl, methoxycarbonylmethyl, ethoxycarbonylmethyl, propoxycarbonylmethyl, butoxycarbonylmethyl, 2-(methoxycarbonyl)ethyl, 2-(ethoxycarbonyl)ethyl, 2-(propoxycarbonyl)ethyl, 3-(methoxycarbonyl)propyl, 3-(ethoxycarbonyl)propyl, 4-(methoxycarbonyl)-butyl.

[0076] An alkyl group wherein two or more CH_2 groups are replaced by -O- and/or -C(O)O- can be straight-chain or branched. It is preferably straight-chain and has 3 to 12 C atoms. Accordingly, it is preferably bis-carboxy-methyl, 2,2-bis-carboxy-ethyl, 3,3-bis-carboxy-propyl, 4,4-bis-carboxy-butyl, 5,5-bis-carboxy-pentyl, 6,6-bis-carboxy-hexyl, 7,7-bis-carboxy-heptyl, 8,8-bis-carboxy-octyl, 9,9-bis-carboxy-nonyl, 10,10-bis-carboxy-decyl, bis-(methoxycarbonyl)-methyl, 2,2-bis-(methoxycarbonyl)-ethyl, 3,3-bis-(methoxycarbonyl)-propyl, 4,4-bis-(methoxycarbonyl)-butyl, 5,5-bis-(methoxycarbonyl)-pentyl, 6,6-bis-(methoxycarbonyl)-hexyl, 7,7-bis-(methoxycarbonyl)-heptyl, 8,8-bis-(methoxycarbonyl)-octyl, bis-(ethoxycarbonyl)-methyl, 2,2-bis-(ethoxycarbonyl)-ethyl, 3,3-bis-(ethoxycarbonyl)-propyl, 4,4-bis-(ethoxycarbonyl)-butyl, 5,5-bis-(ethoxycarbonyl)-hexyl.

[0077] A thioalkyl group, *i.e.,* where one CH_2 group is replaced by -S-, is preferably straight-chain thiomethyl (-SCH_3), 1-thioethyl (-SCH_2CH_3), 1-thiopropyl (= -$SCH_2CH_2CH_3$), 1- (thiobutyl), 1-(thiopentyl), 1-(thiohexyl), 1-(thioheptyl), 1-(thiooctyl), 1-(thiononyl), 1-(thiodecyl), 1-(thioundecyl) or 1-(thiododecyl), wherein preferably the CH_2 group adjacent to the sp^2 hybridised vinyl carbon atom is replaced.

[0078] A fluoroalkyl group is perfluoroalkyl C_iF_{2i+1}, wherein i is an integer from 1 to 15, in particular CF_3, C_2F_5, C_3F_7,

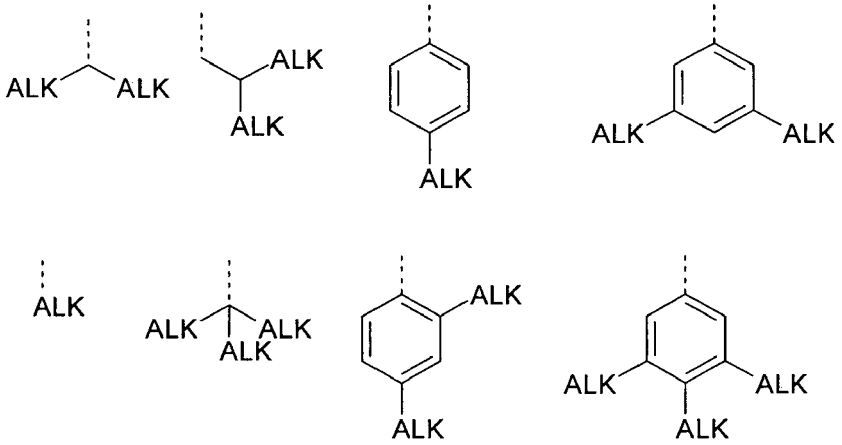
C_4F_9, C_5F_{11}, C_6F_{13}, C_7F_{15} or C_8F_{17}, very preferably C_6F_{13}, or partially fluorinated alkyl, preferably with 1 to 15 C atoms, in particular 1,1-difluoroalkyl, all of the aforementioned being straight-chain or branched.

[0079] Preferably "fluoroalkyl" means a partially fluorinated (i.e. not perfluorinated) alkyl group.

[0080] 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, 2-propylpentyl, in particular 2-methylbutyl, 2-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethyl-hexoxy, 2-butyloctoxyo, 2-hexyldecoxy, 2-octyldodecoxy, 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, 2-fluoromethyloctyloxy for example. Very preferred are 2-ethylhexyl, 2-butyloctyl, 2-hexyldecyl, 2-octyldodecyl, 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.

[0081] Preferred achiral branched groups are isopropyl, isobutyl (=methylpropyl), isopentyl (=3-methylbutyl), tert. butyl, isopropoxy, 2-methyl-propoxy and 3-methylbutoxy.

[0082] In a preferred embodiment, the alkyl groups are independently of each other selected from primary, secondary or tertiary alkyl or alkoxy with 1 to 30 C atoms, wherein one or more H atoms are optionally replaced by F, or aryl, aryloxy, heteroaryl or heteroaryloxy that is optionally alkylated or alkoxylated and has 4 to 30 ring atoms. Very preferred groups of this type are selected from the group consisting of the following formulae

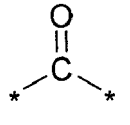


wherein "ALK" denotes optionally fluorinated, preferably linear, alkyl or alkoxy with 1 to 20, preferably 1 to 12 C-atoms, in case of tertiary groups very preferably 1 to 9 C atoms, and the dashed line denotes the link to the ring to which these groups are attached. Especially preferred among these groups are those wherein all ALK subgroups are identical.

[0083] As used herein, if an aryl(oxy) or heteroaryl(oxy) group is "alkylated or alkoxylated", this means that it is substituted with one or more alkyl or alkoxy groups having from 1 to 20 C-atoms and being straight-chain or branched and wherein one or more H atoms are optionally substituted by an F atom.

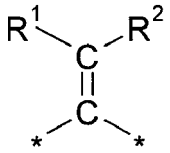
[0084] Above and below, Y^1 and Y^2 are independently of each other H, F, Cl or CN.

[0085] As used herein. -CO- -C=O- and -CO- will be understood to mean a carbonyl group, i.e. a group having the structure



.

[0086] As used herein. $C=CR^1 R^2$ will be understood to mean a group having the structure



[0087] 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 is preferably Br or I.

Detailed Description

[0088] The compounds of the present invention comprise the structural feature of a phthalimide moiety fused with a 1,3-dithiol ring (DTPI) bearing electron withdrawing substituents at the 2-position.

[0089] The compounds of the present invention are easy to synthesize and exhibit advantageous properties. They show good processability for the device manufacture process, high solubility in organic solvents, and are especially suitable for large scale production using solution processing methods.

[0090] Co-polymers derived from monomers of the present invention and electron donor monomers show low band-gaps, high charge carrier mobilities, high external quantum efficiencies in BHJ solar cells, good morphology when used in p/n-type blends e.g. with fullerenes, high oxidative stability, a long lifetime in electronic devices, and are promising materials for organic electronic OE devices, especially for OTFTs and OPV devices with high power conversion efficiency.

[0091] The compounds of the present invention are also suitable as p-type semiconductors for the preparation of blends of p-type and n-type semiconductors which are suitable for use in BHJ photovoltaic devices.

[0092] Besides, the compounds of the present invention show the following advantageous properties:

i) Additional solubility can be introduced into the compound by inclusion of solubilising groups R^1, U^1 and/or U^2. Especially a solubilising alkyl chain R^1 on the imide N-atom facilitate synthesis and purification of the unit, and in addition facilitates fine-tuning the solution processibility of the resultant polymer.

ii) The S-atoms in the 1,3-dithiol ring enable stronger interchain interactions, compared for example to benzothiadiazole units.

iii) Additional fine-tuning of the electronic energies (HOMO/LUMO levels) by co-polymerisation with appropriate co-monomer(s) can afford attractive candidate materials for OPV applications.

iv) The DTPI units have planar structures that enable strong pi-pi stacking in the solid state leading to improved charge transport properties in the form of higher charge carrier mobility.

v) Using the DTPI unit together with electron donating units, it is possible to create a donor-acceptor polymer, optionally with spacer units like thiophene, bithiophene or thienothiophene to keep the backbone flat. Such polymers are expected to have a high Voc.

[0093] Very preferably R^1 and R in the units of formula I denote 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.

[0094] If R^1 or R denote an aryl(oxy) or heteroaryl(oxy) group, it is preferably selected from phenyl, pyrrole, furan, pyridine, thiazole, thiophene, thieno[3,2-b]thiophene or thieno[2,3-b]thiophene, each of which is unsubstituted or substituted with F or alkyl, alkoxy or thioalkyl each having from 1 to 20 C atoms and being optionally fluorinated.

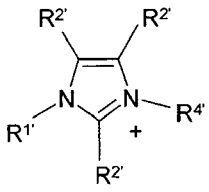
[0095] In another preferred embodiment of the present invention, R^1 and/or R denote straight-chain, branched or cyclic alkyl with 1 to 20 C-atoms wherein one or more CH_2 or CH_3 groups are substituted by a cationic or anionic group.

[0096] 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.

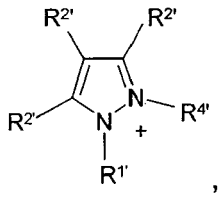
[0097] Preferred cationic groups are selected from the group consisting of tetraalkylammonium, tetraalkylphosphonium, N-alkylpyridinium, N,N-dialkylpyrrolidinium, 1,3-dialkylimidazolium, wherein "alkyl" preferably denotes a straight-chain or branched alkyl group with 1 to 12 C atoms.

[0098] Further preferred cationic groups are selected from the group consisting of the following formulae

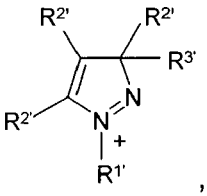
imidazolium



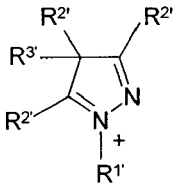
1H-pyrazolium



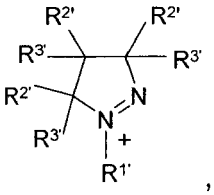
3H-pyrazolium



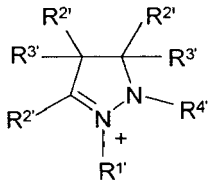
4H-pyrazolium



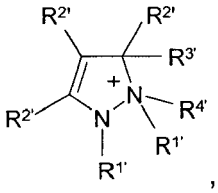
1-pyrazolinium



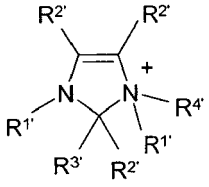
2-pyrazolinium



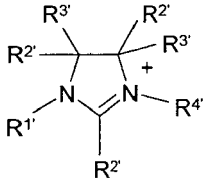
3-pyrazolinium



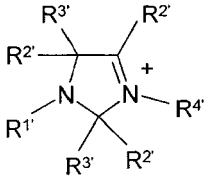
2,3-dihydroimidazolinium



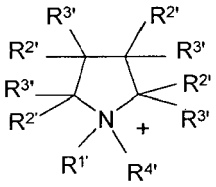
4,5-dihydroimidazolinium



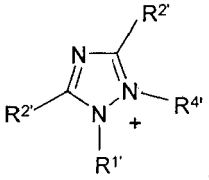
2,5-dihydroimidazolinium



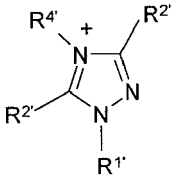
pyrrolidinium



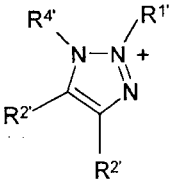
1,2,4-triazolium



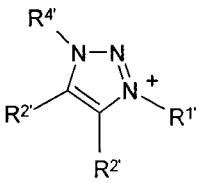
1,2,4-triazolium



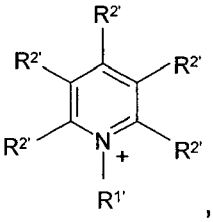
1,2,3-triazolium



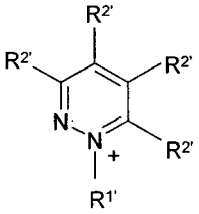
1,2,3-triazolium



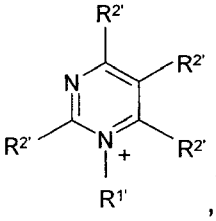
pyridinium



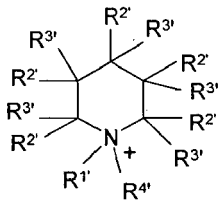
pyridazinium



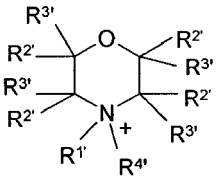
pyrimidinium



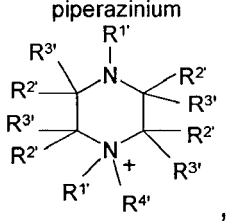
piperidinium



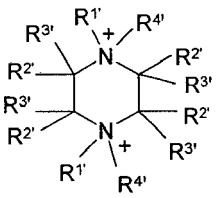
morpholinium



piperazinium

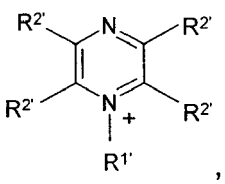


piperazinium

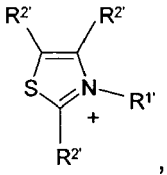


indolium

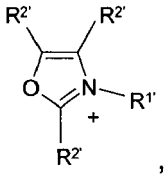
pyrazinium

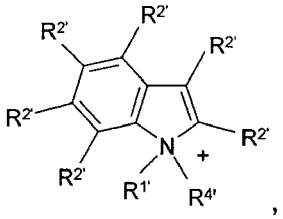


thiazolium

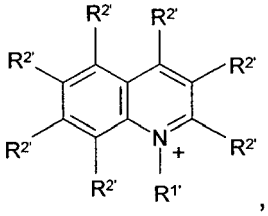


oxazolium

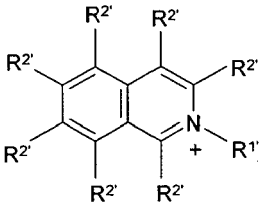




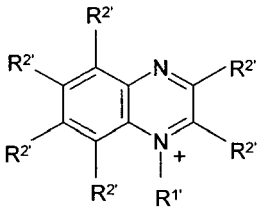
quinolinium



isoquinolinium

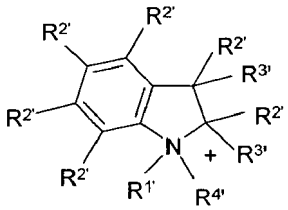


quinoxalinium



or

indolinium



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 below, or denote a link to the respective group R^{1-4}.

[0099] 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 group R^1, 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^{1-4}.

[0100] 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.

[0101] The compounds according to the present invention include small molecules, monomers, oligomers and polymers.

[0102] A preferred embodiment of the present invention relates to a conjugated polymer comprising, preferably consisting of, one or more units selected of formula I as defined above and below, and further comprising one or more arylene or heteroarylene units that have from 5 to 20 ring atoms, are mono- or polycyclic, do optionally contain fused rings, are unsubstituted or substituted by one or more identical or different groups L, and are either selected of formula I or are structurally different from formula I, and wherein all the aforementioned units are directly connected to each other.

[0103] Another preferred embodiment of the present invention relates to a conjugated polymer comprising, preferably consisting of, one or more repeating units of formula II1 or II2, and optionally one or more repeating units of formula II3:

$$-(Ar^1)_a\text{-}U\text{-}(Ar^2)_b\text{-}(Ar^3)_c\text{-}(Ar^4)_d- \qquad II1$$

$$-(Ar^1)_a\text{-}(Ar^2)_b\text{-}U\text{-}(Ar^3)_c\text{-}(Ar4)_d- \qquad II2$$

$$-(Ar^1)_a\text{-}(Ar^2)_b\text{-}(Ar^3)_c\text{-}(Ar^4)_d- \qquad II3$$

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

U a unit of formula I as defined above and below,

Ar^{1-4} arylene or heteroarylene that has 5 to 20 ring atoms, is mono- or polycyclic, does optionally contain fused rings, is unsubstituted or substituted by one or more identical or different groups L, and is different from formula I,

a, b, c, d 0 or 1, wherein in formula II3 a+b+c+d≥1.

[0104] Preferred units of formula 111 and II2 are those wherein a+b+c+d≥1.

[0105] Preferably the conjugated polymer comprises one or more repeating units of formula II1 or II2 wherein a+b+c+d≥1.

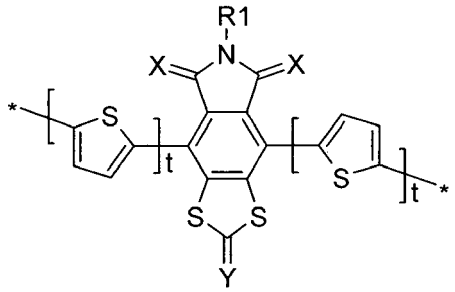
[0106] Further preferably the conjugated polymer comprises one or more repeating units of formula II1 wherein b=1 and a=c=d=0 and one or more repeating units of formula II3 wherein a=b=1 and c=d=0.

[0107] Further preferably the conjugated polymer comprises two or more distinct repeating units of formula II1 wherein b=1 and a=c=d=0.

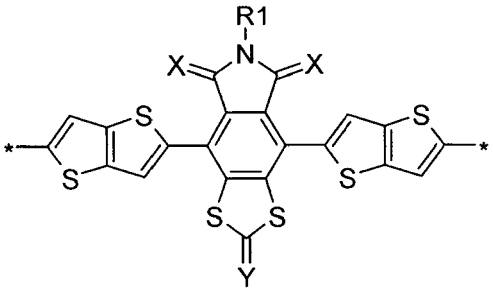
[0108] Further preferably the conjugated polymer consists of repeating units of formula II1 wherein a=b=c=d=0 (homopolymers of units U).

[0109] Further preferably at least one of Ar^1, Ar^2, Ar^3 and Ar^4 is an arylene or heteroarylene group as being defined in formula 111 and having electron donor property.

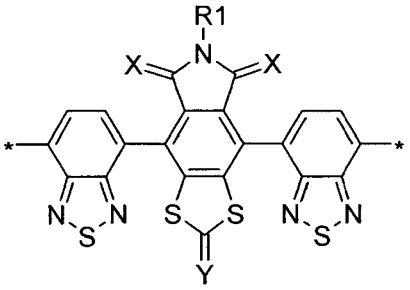
[0110] Very preferred are repeating units selected from the following formulae.



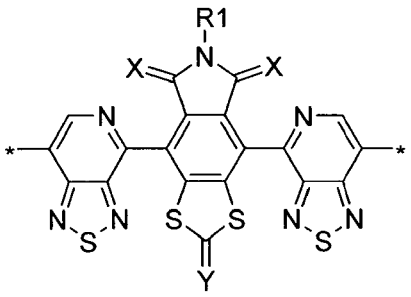
R1



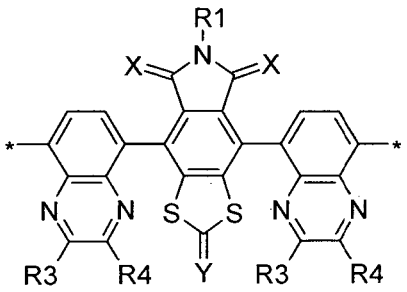
R2



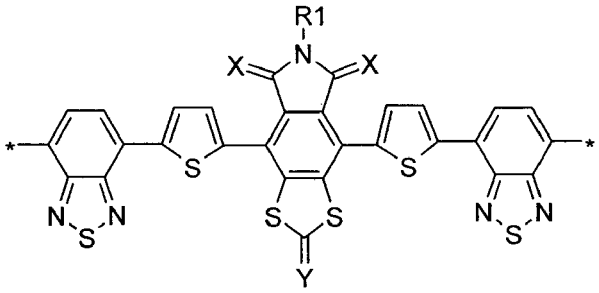
R3



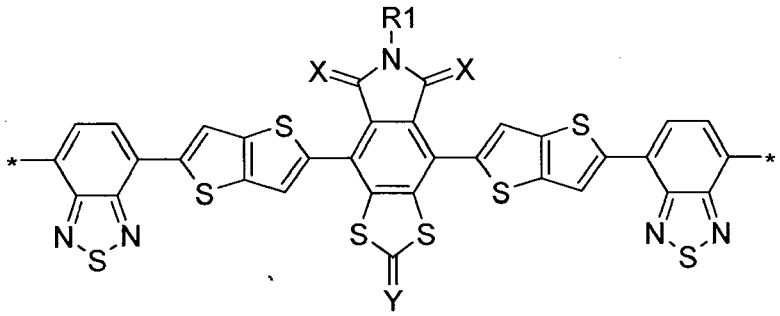
R4



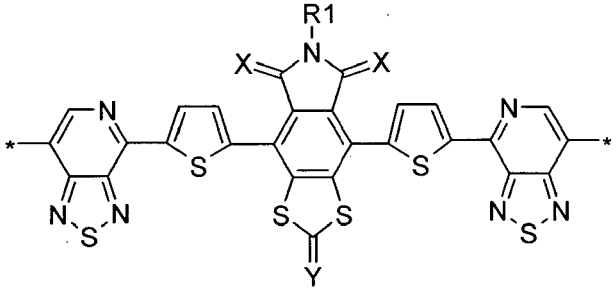
R5



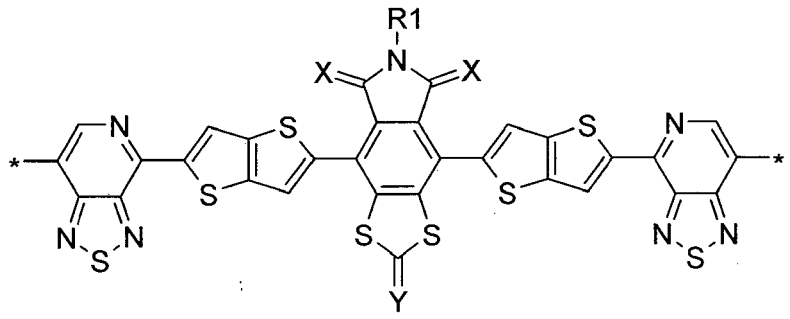
R6



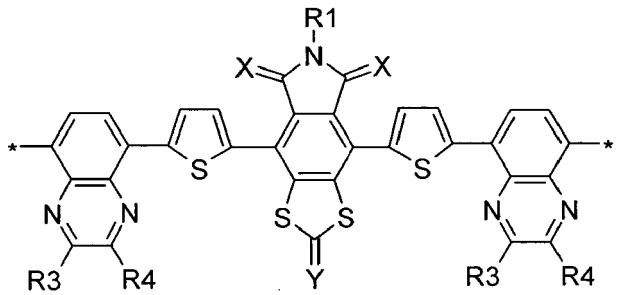
R7



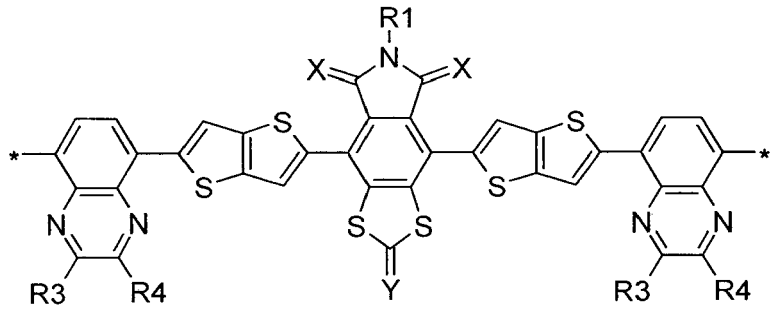
R8



R9



R10

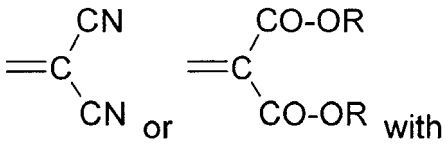


R11

wherein R^1 is as defined above and below, X has on each occurrence identically or differently one of the meanings of X^1 as given above and below, Y is as defined above and below, t is 1, 2, 3 or 4, preferably 1 or 2, and R^2, R^3 and R^4 have independently of each other and on each occurrence identically or differently one of the meanings given for L.

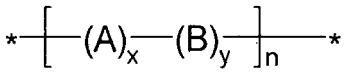
[0111] In formulae R1-R11 X is preferably O or S, very preferably O.

[0112] In formulae R1-R11 Y is preferably O, S or



R being as defined above.

[0113] Further preferably the conjugated polymer according to the present invention is selected of formula III:



III

wherein

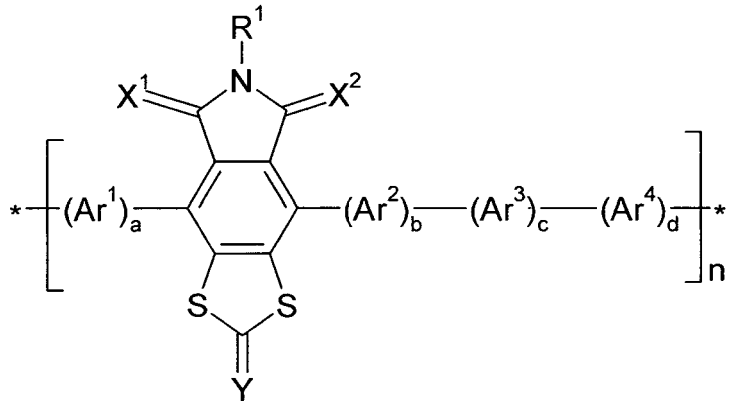
A is a unit of formula I, II1, II2 or R1-R11 as defined above and below,

B is a unit of formula I, II1, II2, II3 or R1-R11 as defined above and below which is different from A,

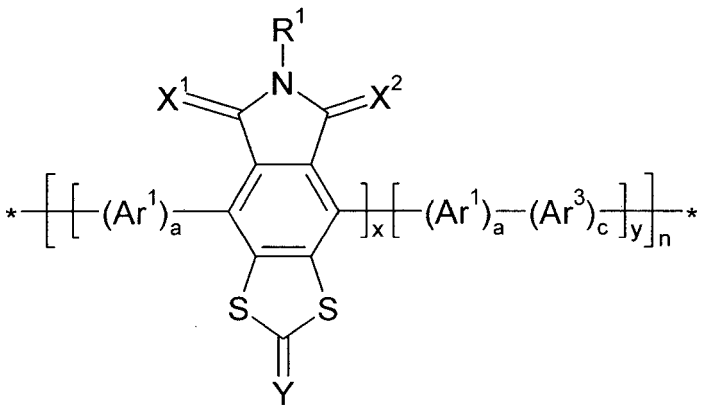
x is > 0 and ≤ 1,

y is ≥ 0 and < 1,
x+y is 1, and
n is an integer ≥5.

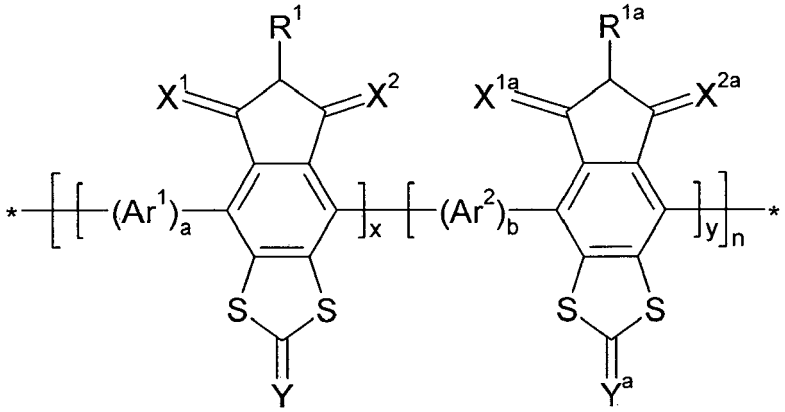
[0114] Further preferably the conjugated polymer according to the present invention is selected from the following formulae



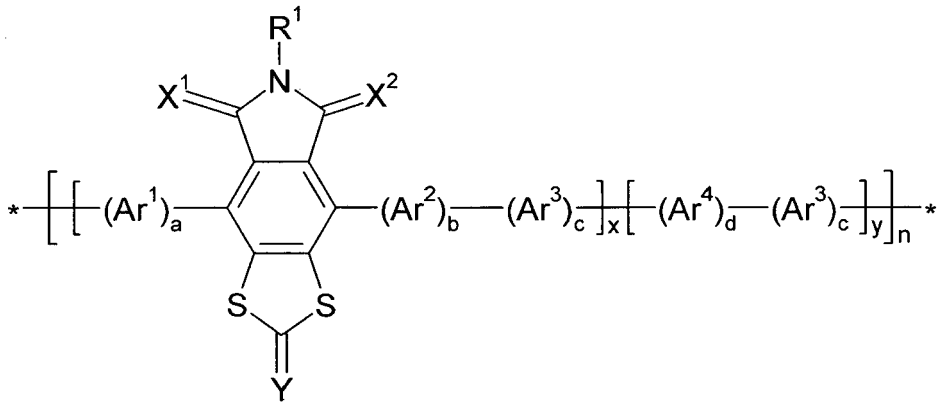
III1



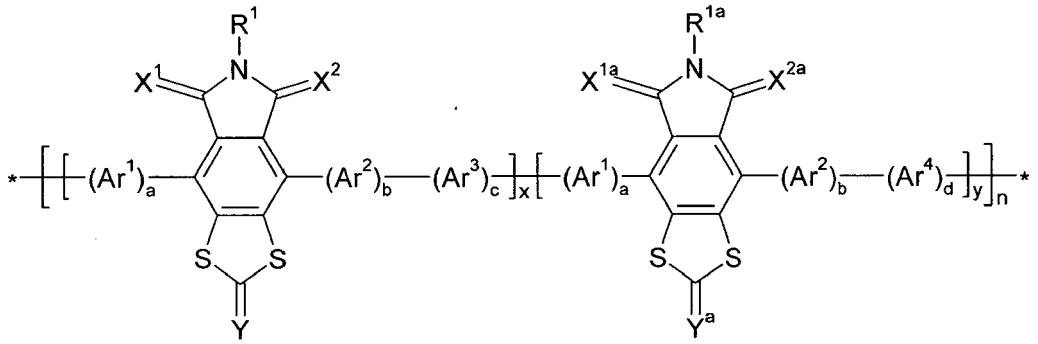
III2



III3



III4



III5

wherein

X^1, X^2, Y and R^1 have the meanings of formula I or one of the preferred meanings given above and below,
X^{1a} has one of the meanings given for X^1,
X^{2a} has one of the meanings given for X^1,
Y^a has one of the meanings given for Y,
R^{1a} has one of the meanings given for R^1,
Ar^2, Ar^3, Ar^4, a, b, c and d have the meanings of formula II1 or one of the preferred meanings given above and below,
x, y and n have the meanings of formula III or one of the preferred meanings given above and below,
preferably Ar^3 is selected from arylene or heteroarylene units as described above and below having electron donor properties, and
in formula III3 and III5 preferably at least one of X^1, X^2, Y and R^1 is different from its corresponding radical X^{1a}, X^{2a}, Y^a and R^{1a}, respectively.

[0115] In the polymers of formula III and III1-III5, x and y denote the mole fraction of repeating units A and B, respectively, and n denotes the degree of polymerisation or total number of repeating units A and B. These formulae include block copolymers, random or statistical copolymers and alternating copoymers of A and B, as well as homopolymers of A for the case when x>0 and y=0.

[0116] In the polymers of formula III and III1- III5, x is preferably from 0.1 to 0.9, very preferably from 0.3 to 0.7.

[0117] In the polymers of formula III and III1-III5, y is preferably from 0.1 to 0.9, very preferably from 0.3 to 0.7.

[0118] In the polymers according to the present invention, the total number of repeating units n is preferably from 2 to 10,000. The total number of repeating units n is preferably ≥ 5, very preferably ≥ 10, most preferably ≥ 50, and preferably ≤ 500, very preferably ≤ 1,000, most preferably ≤ 2,000, including any combination of the aforementioned lower and upper limits of n.

[0119] 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.

[0120] Further preferably the conjugated polymer according to the present invention is selected of formula IV

$$R^5\text{-chain-}R^6 \qquad \text{IV}$$

wherein "chain" denotes a polymer chain selected of formulae III, III1-III5,

and P1-P32, and R^5 and R^6 have independently of each other one of the meanings of R^1 or L as defined above, or denote, independently of each other, H, F, Br, Cl, I, $-CH_2Cl$, -CHO, $-CR'=CR''_2$, $-SiR'R''R'''$, $-SiR'X'X''$,$-SiR'R''X'$, $-SnR'R''R'''$, $-BR'R''$, $-B(OR')(OR'')$, $-B(OH)_2$, $-O-SO_2-R'$, $-C\equiv CH$,$-C\equiv C-SiR'_3$, -ZnX' or an endcap group, X' and X'' denote halogen, R', R'' and R''' have independently of each other one of the meanings of R^0 given in formula 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.

[0121] Preferred endcap groups R^5 and R^6 are H, C_{1-40} alkyl, or optionally substituted C_{6-12} aryl or C_{2-10} heteroaryl, very preferably H or phenyl.

[0122] A further preferred embodiment of the present invention relates to a monomer of formula V1 or V2

$$R^7\text{-}(Ar^1)_a\text{-}U\text{-}(Ar^2)_b\text{-}(Ar^3)_c\text{-}(Ar^4)_d\text{-}R^8 \qquad V1$$

$$R^7\text{-}(Ar^1)_a\text{-}(Ar^2)_b\text{-}U\text{-}(Ar^3)_c\text{-}(Ar^4)_d\text{-}R^8 \qquad V2$$

wherein U, Ar^{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^7 and R^8 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, $-SiMe_3$, $-SiMe_2F$, $-SiMeF_2$, $-O-SO_2Z^1$, $-B(OZ^2)_2$, $-CZ^3=C(Z^3)_2$, $-C\equiv CH$, $-C\equiv CSi(Z^1)_3$, $-ZnX^0$, $Mg-X^0$ and $-Sn(Z^4)_3$, wherein X^0 is halogen, preferably Cl, Br or I, 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^7 and R^8 is different from H, and preferably both of R^1 and R^2 are different from H.

[0123] Very preferred are monomers of formula V1 and V2 and their subformulae wherein a+b+c+d $\geq$1.

[0124] Further preferred are monomers of formula V1 and its subformulae wherein a+b+c+d=0.

[0125] Further preferred are monomers selected from the following formulae

$$R^7\text{-}Ar^1\text{-}U\text{-}Ar^2\text{-}R^8 \qquad V1a$$

$$R^7\text{-}U\text{-}R^8 \qquad V1b$$

$$R^7\text{-}Ar^1\text{-}U\text{-}R^8 \qquad V1c$$

$$R^7\text{-}U\text{-}Ar^2\text{-}R^8 \qquad V1d$$

wherein U, Ar^1, Ar^2, R^7 and R^8 are as defined in formula V1.

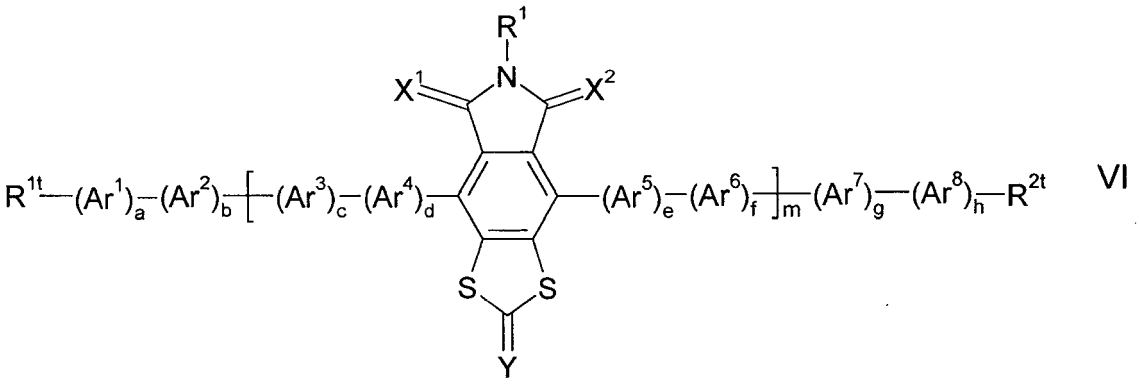
[0126] Further preferred are monomers of formula V3

$$R^7\text{-}U^*\text{-}R^8 \qquad V3$$

wherein U* is a unit selected from formula R1-R11 as defined above and R^7 and R^8 are as defined in formula V1.

[0127] Very preferred are monomers of formula V1, V2 and V3 and their subformulae wherein R^7 and R^8 are selected from Br, $B(OZ^2)_2$, $Mg-X^0$ and $Sn(Z^4)_3$.

[0128] The present invention relates to a small molecule or oligomer of formula VI

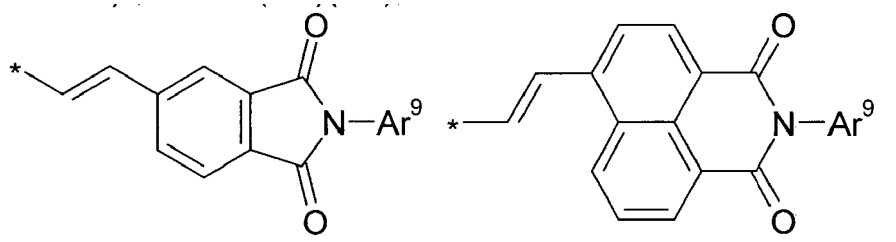


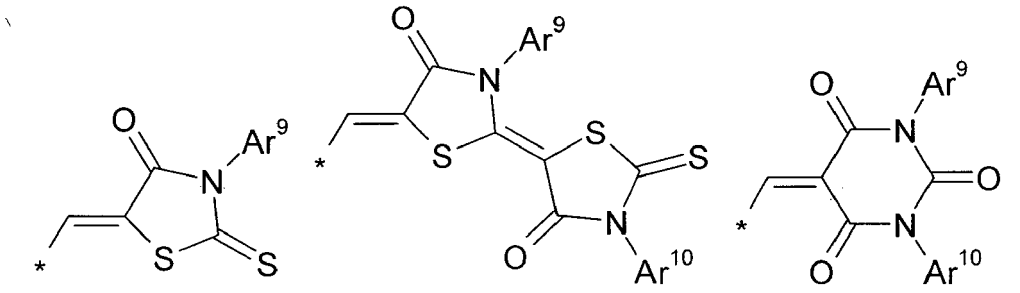
VI

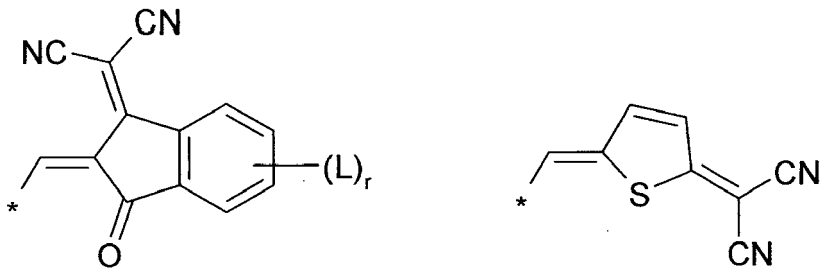
wherein the individual radicals, independently of each other and on each occurrence identically or differently, have the

following meanings

Ar^{1-8}	one of the meanings given for Ar^1 in formula 111 or one of its preferred meanings given above and below, or a unit of formula I as defined above and below, or $-CY^1=CY^2-$,
y^1, y^2	H, F, Cl or CN,
$R^{1t, 2t}$	H, F, Cl, Br, -CN, $-CF_3$, R*, $-CF_2-R^*$, -O-R*, -S-R*, $-SO_2-R^*$,$-SO_3-R^*$,-C(=O)-R*, -C(=S)-R*, $-C(=O)-CF_2-R^*$, -C(=O)-OR*,-C(=S)-OR*, -O-C(=O)-R*, -O-C(=S)-R*, -C(=O)-SR*, -S-C(=O)-R*, -C(=O)NR*R**, -NR*-C(=O)-R*, -NHR*,-NR*R**,-CR*=CR*R**, -C≡C-R*, -C≡C-SiR*R**R***, -SiR*R**R***,-CH=C(CN)-C(=O)-OR*, $-CH=C(CO-OR^*)_2$, $-CH=C(CO-NR^*R^{**}_2$ -CH=C(CN)(Ar^9),







$Ar^{9,10}$	aryl or heteroaryl, each having from 4 to 30 ring atoms, optionally containing fused rings and being unsubstituted or substituted with one or more groups L as defined in formula I,
R*, R**, R***	alkyl with 1 to 20 C atoms which is straight-chain, branched or cyclic, and is unsubstituted, or substituted with one or more F or Cl atoms or CN groups, or perfluorinated, and in which one or more C atoms are optionally replaced by -O-, -S-, -C(=O)-,-C(=S)-, $-SiR^0R^{00}-$, $-NR^0R^{00}-$, $-CHR^0=CR^{00}-$ or -C≡C- such that O- and/or S-atoms are not directly linked to each other,
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,
a-h	0 or 1, with at least one of a-h being 1,
m	1, 2 or 3,

L one of the meanings given above and below,

r 0, 1, 2, 3 or 4,

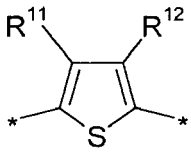
with the proviso that if a+b+c+d+e+f+g+h=0 and X^1, X^2 and Y are O, then at least one of R^{1t} and R^{2t} is different from H.

[0129] Especially preferred are small molecules of formula VI1

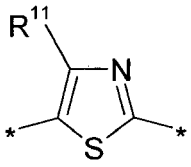
$$R^{1t}\text{-}U^*\text{-}R^{2t} \qquad \text{VI1}$$

wherein U* is a unit selected from formulae R1-R11 as defined above, and R^{1t} and R^{2t} have the meanings given in formula VI, and preferably denote H, F, R* or OR*.

[0130] Further preferred are repeating units, monomers, oligomers, polymers and small molecules of formulae II1, II2, III, III1-III5, IV, V1, V2, V1a-V1d, VI and their subformulae wherein one or more of Ar^1, Ar^2, Ar^3 and Ar^4 denote arylene or heteroarylene, preferably having electron donor properties, selected from the group consisting of the following formulae



(D1)



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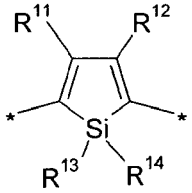

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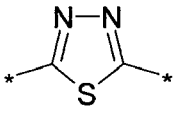

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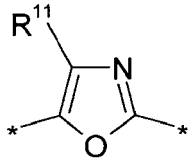

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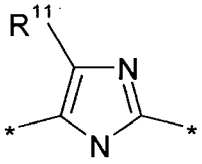

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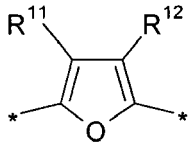

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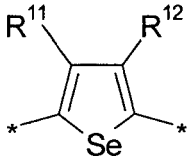

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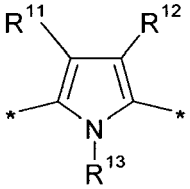

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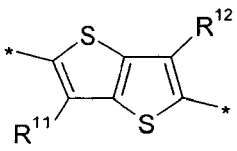

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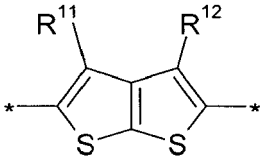

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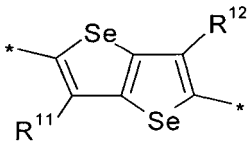

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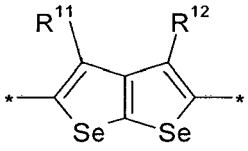

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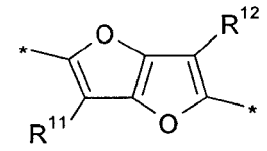

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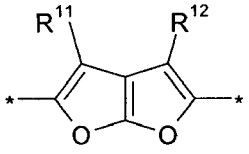

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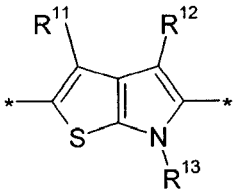

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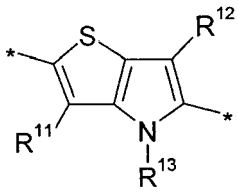

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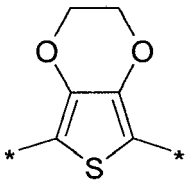

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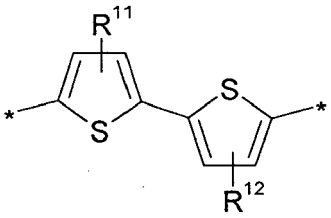

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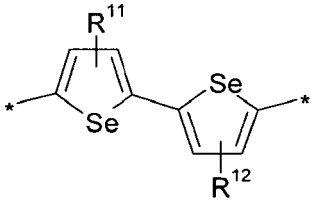

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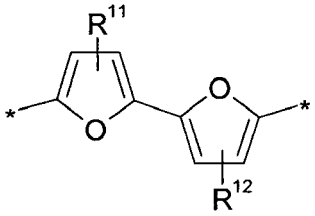

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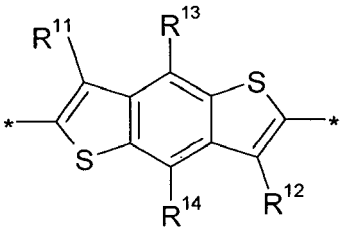

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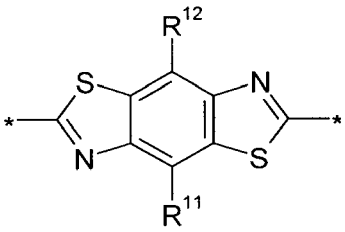

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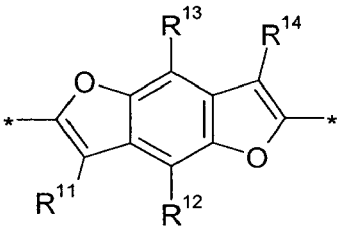

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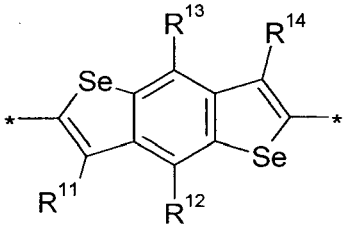

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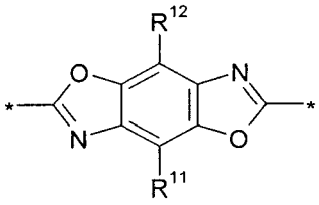

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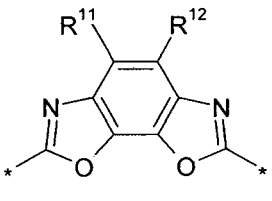

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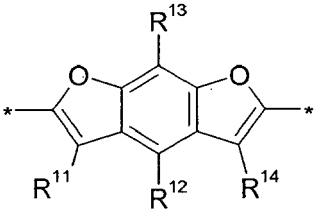

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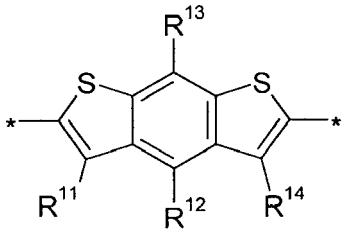

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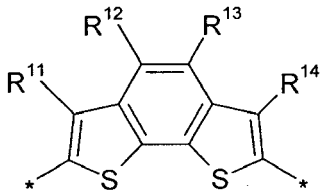

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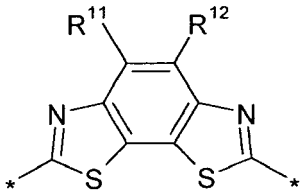

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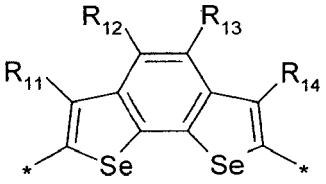

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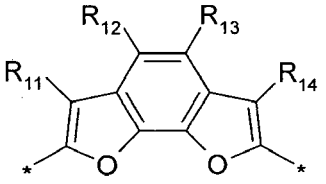

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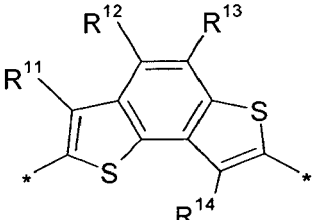

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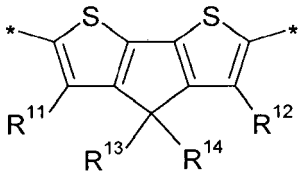

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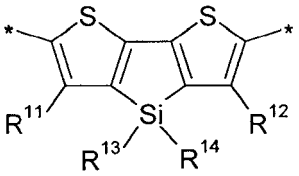

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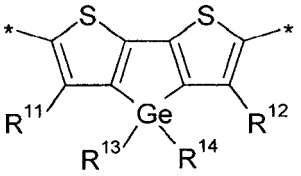

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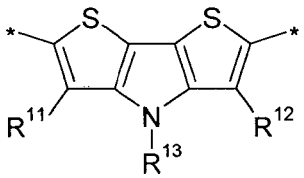

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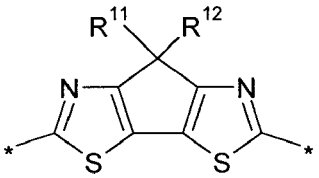

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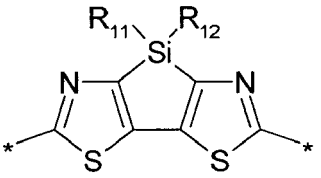

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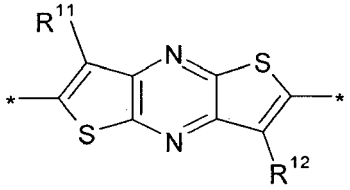

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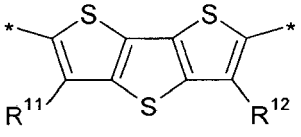

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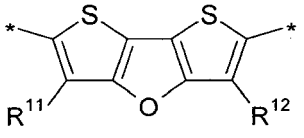

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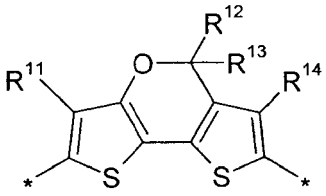

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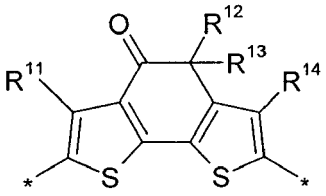

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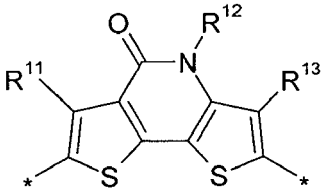

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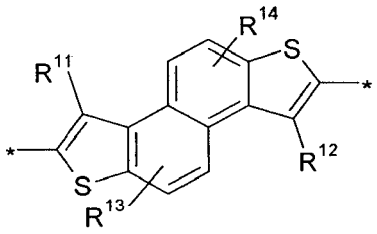

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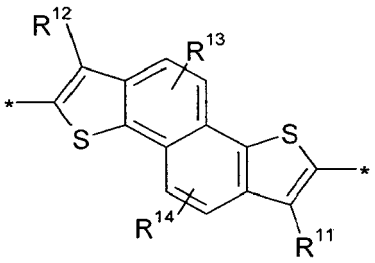

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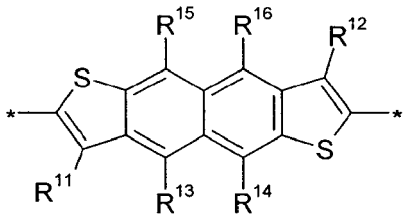

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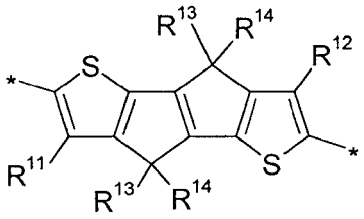

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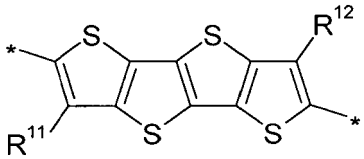

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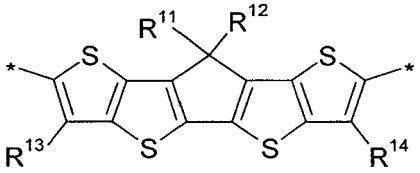

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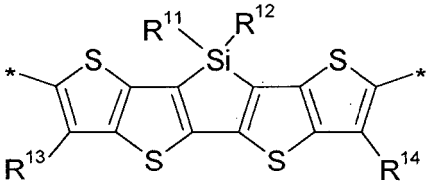

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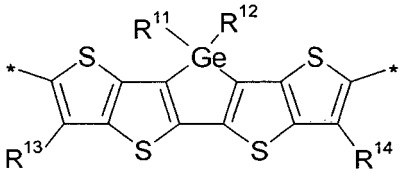

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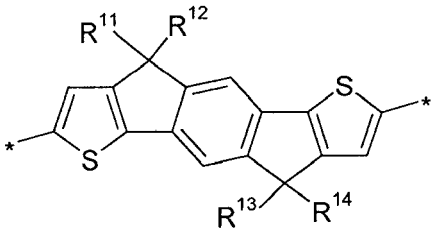

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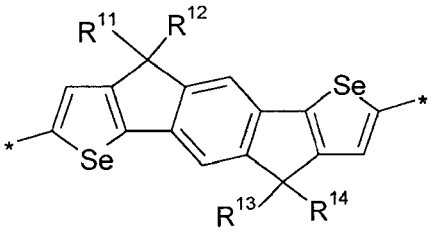

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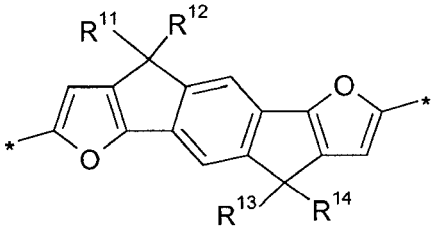

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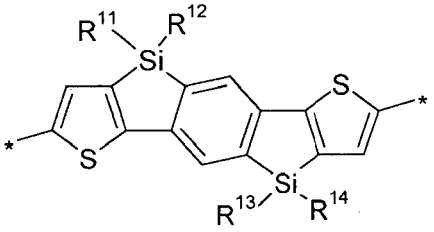

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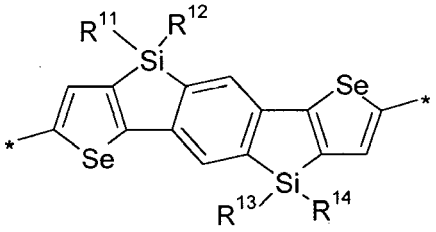

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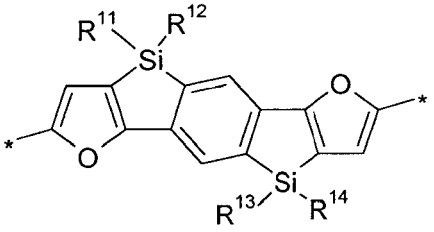

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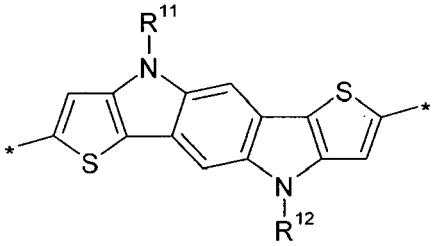

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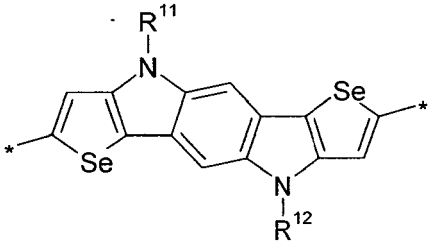

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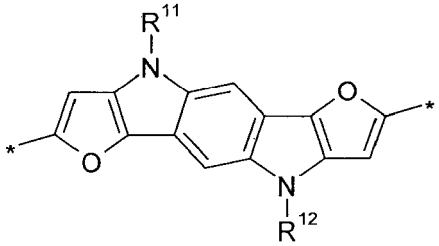

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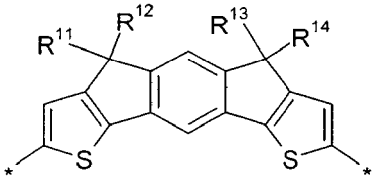

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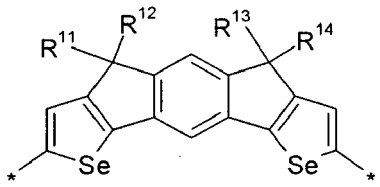

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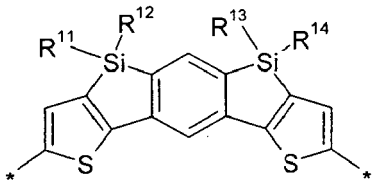

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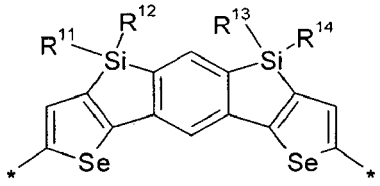

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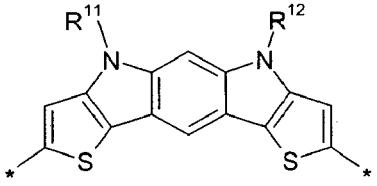

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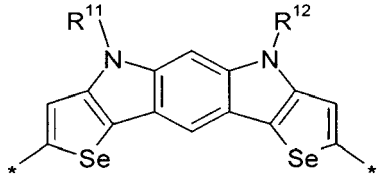

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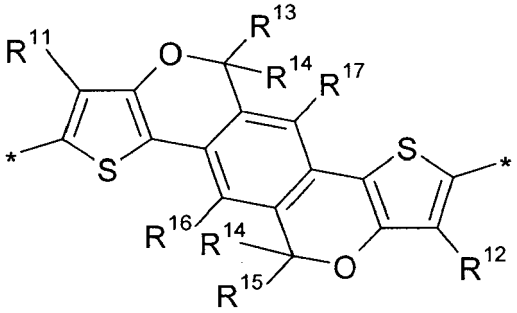

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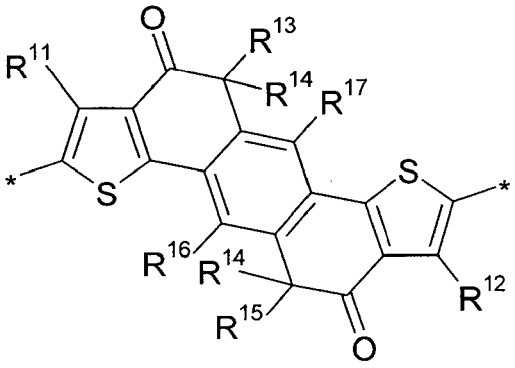

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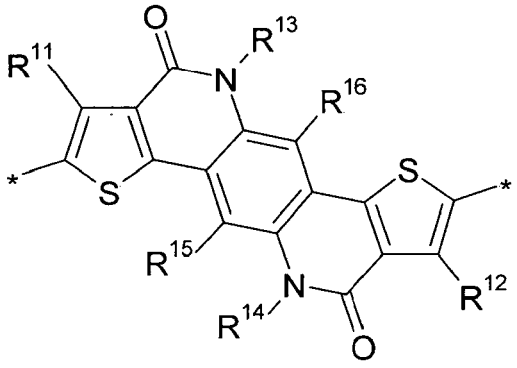

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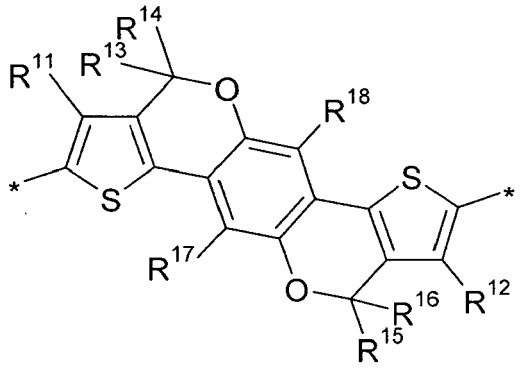

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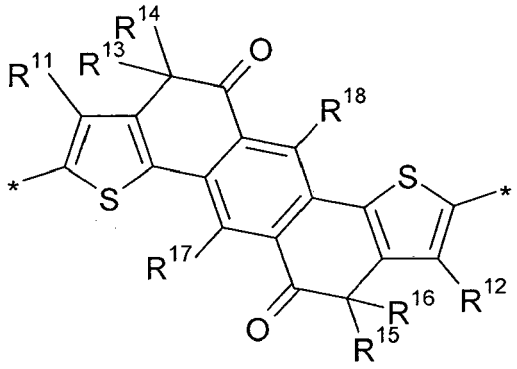

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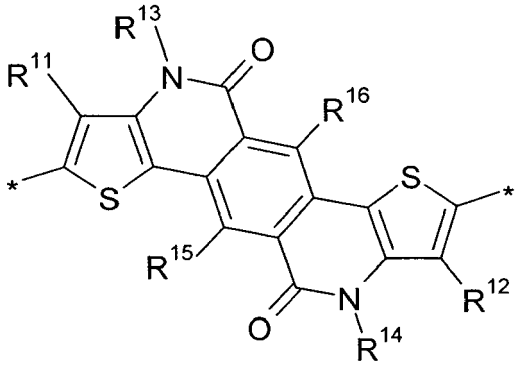

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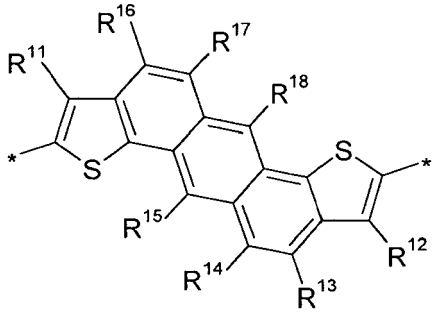

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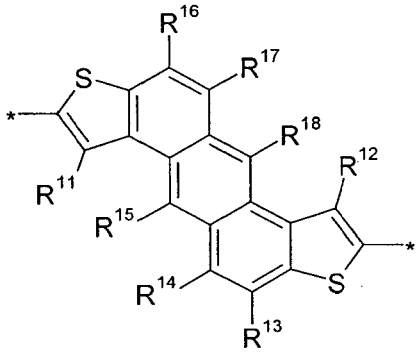

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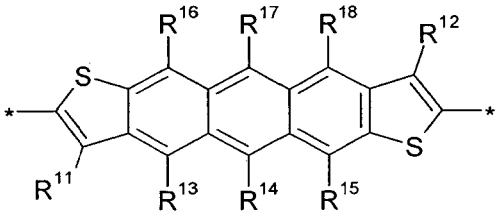

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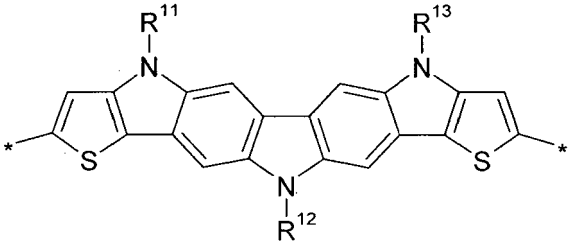

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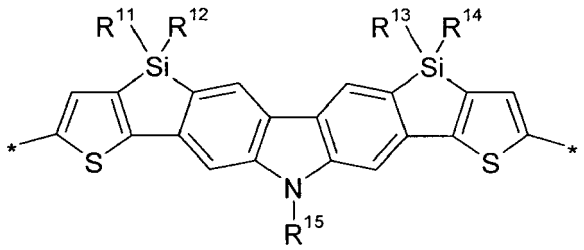

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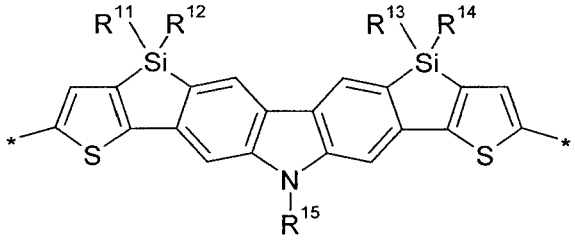

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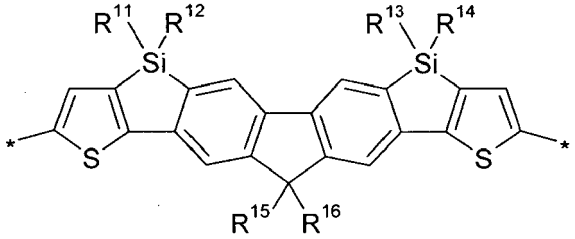

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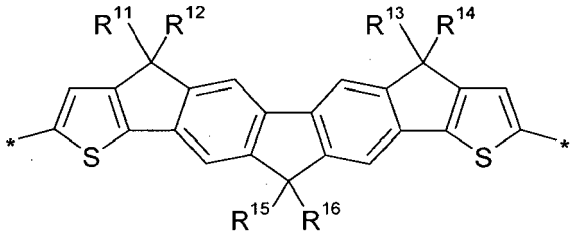

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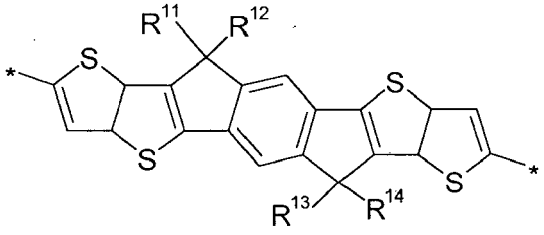

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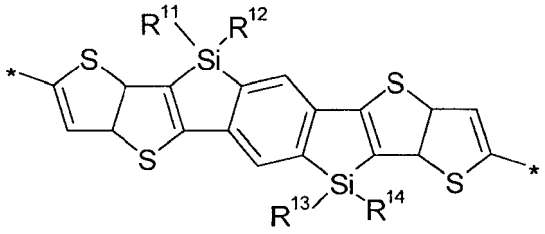

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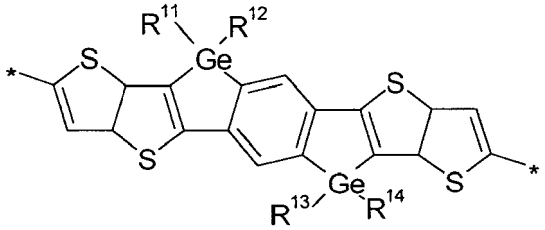

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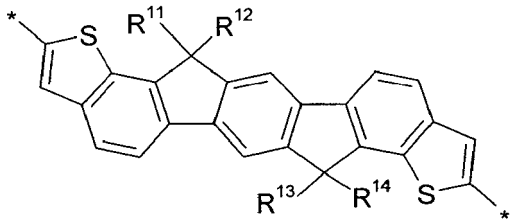

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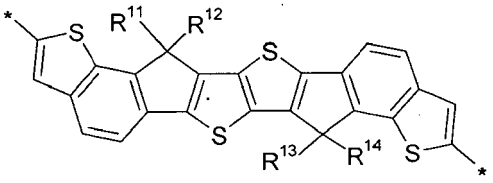

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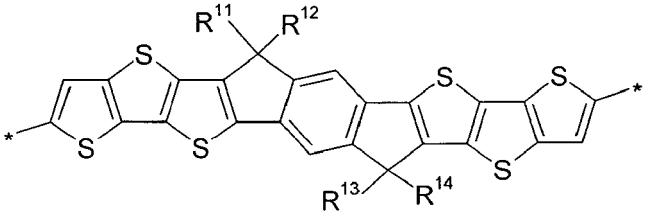

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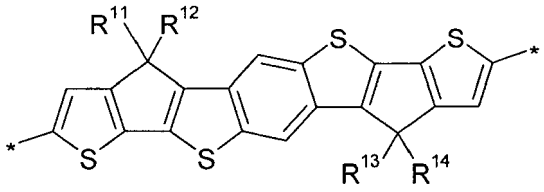

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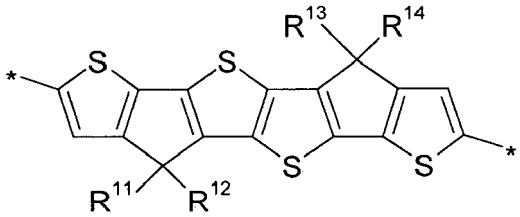

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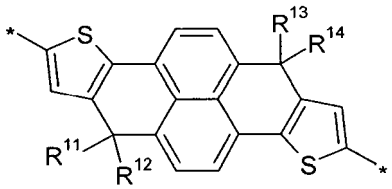

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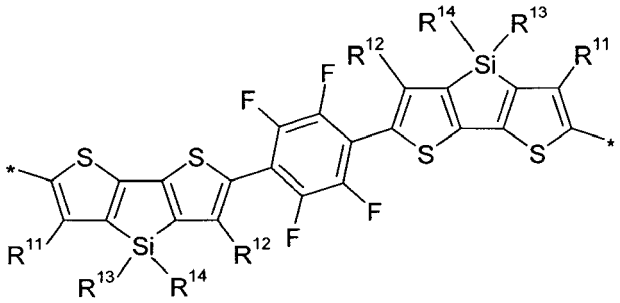

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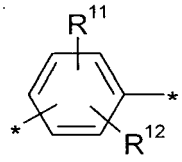

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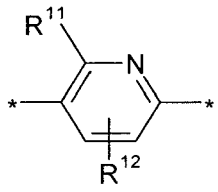

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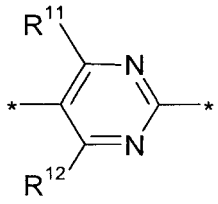

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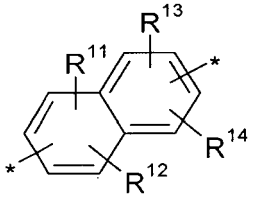

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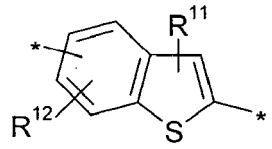

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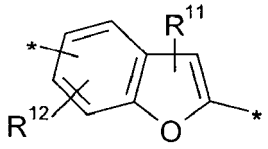

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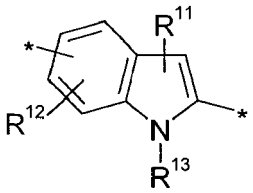

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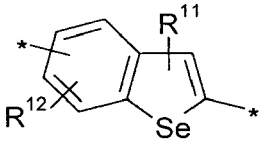

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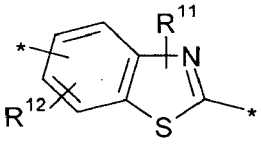

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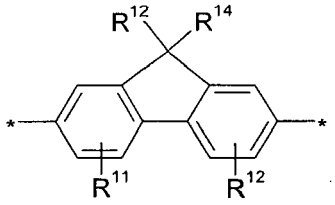

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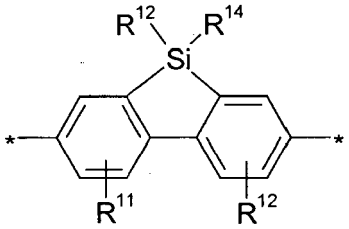

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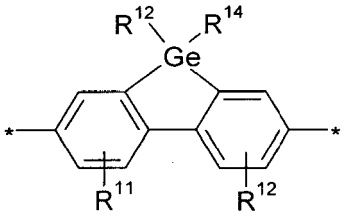

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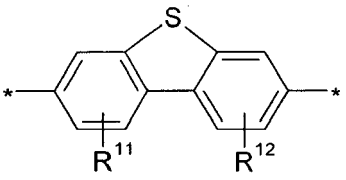

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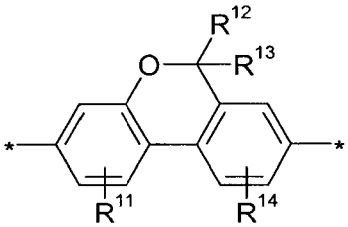

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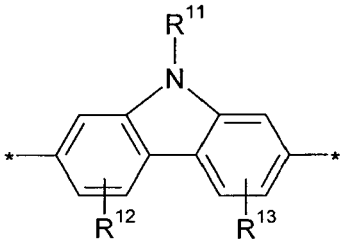

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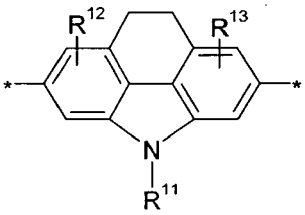

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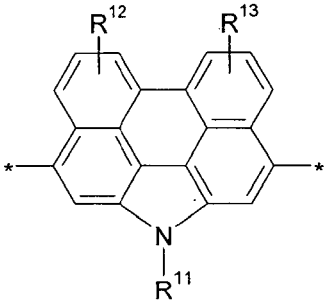

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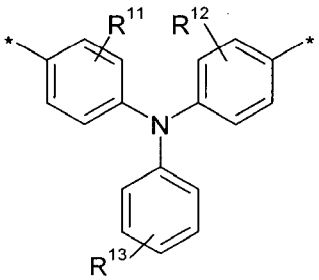

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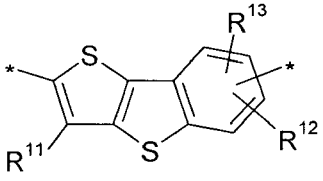

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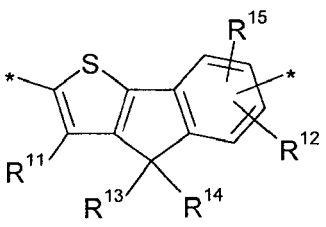

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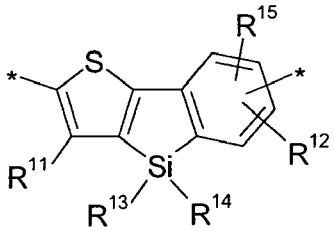

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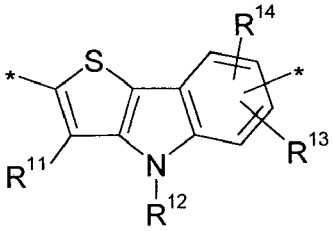

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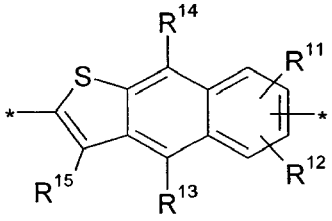
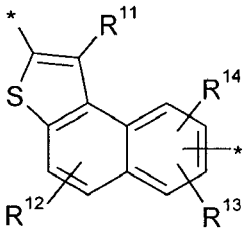


(D116)



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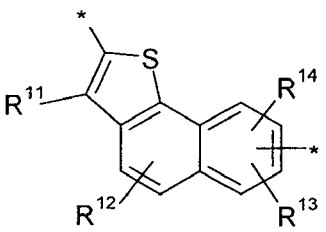

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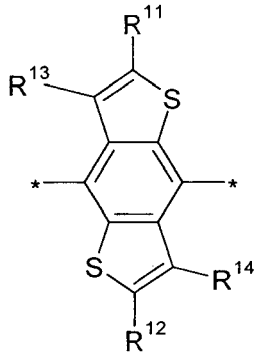

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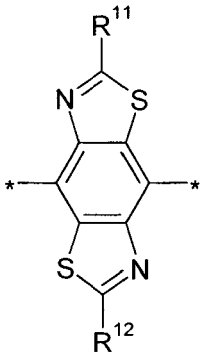

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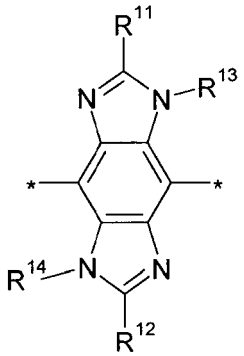

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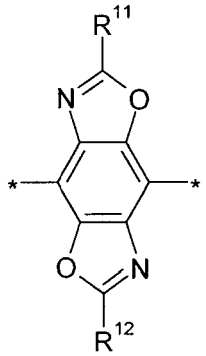

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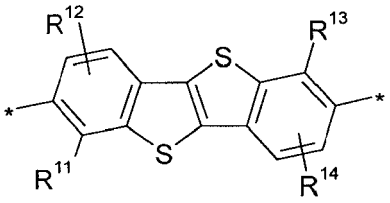

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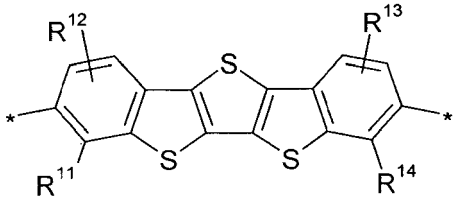

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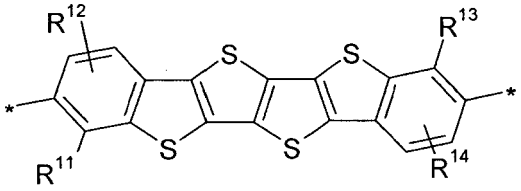

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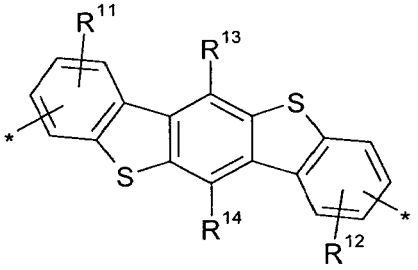

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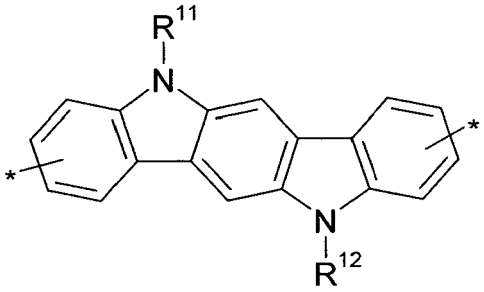

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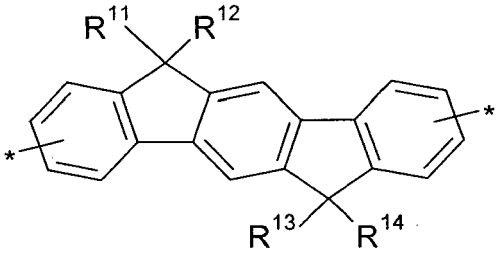
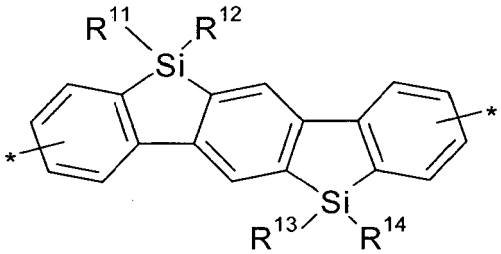


(D128)



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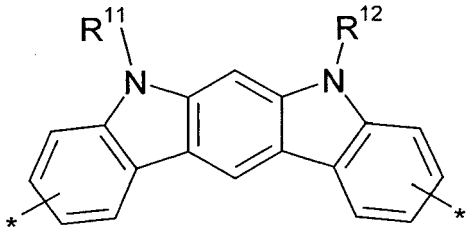

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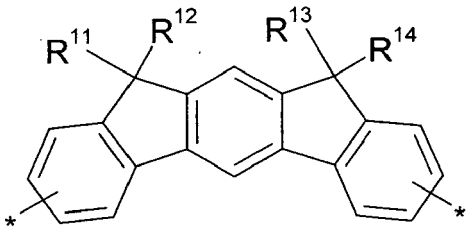

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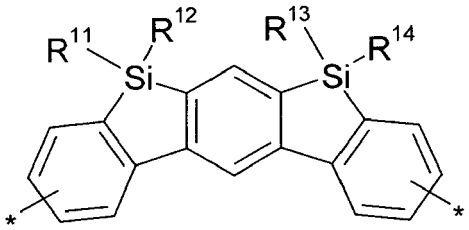

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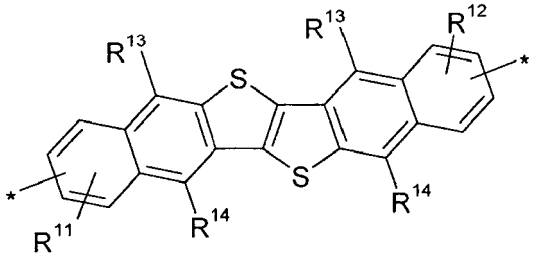

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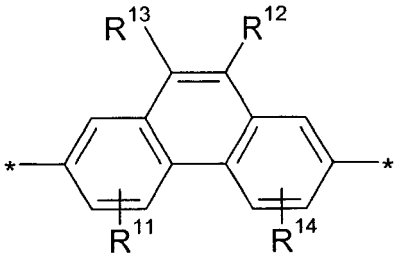

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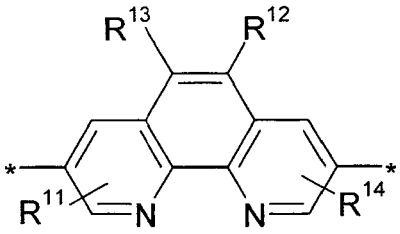

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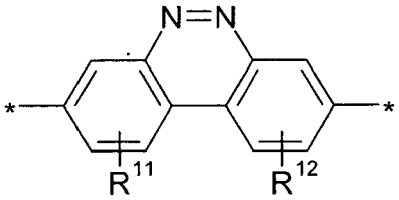

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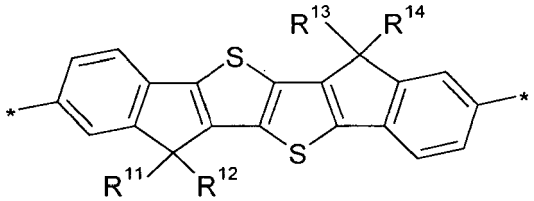
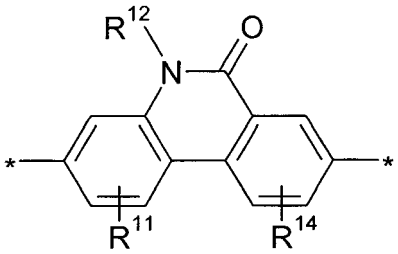


(D137)



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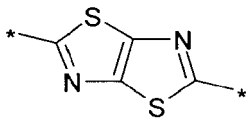

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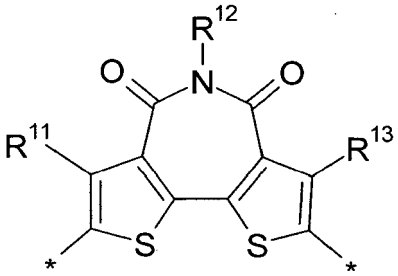

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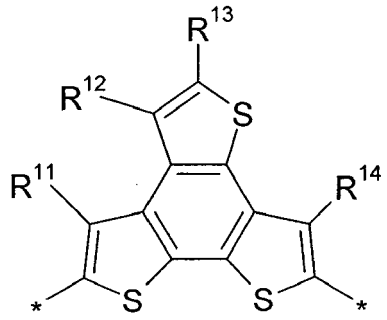

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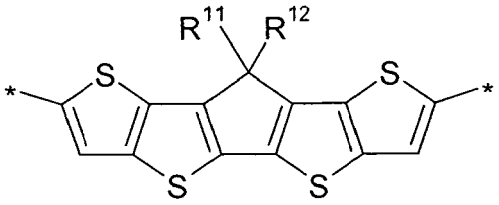

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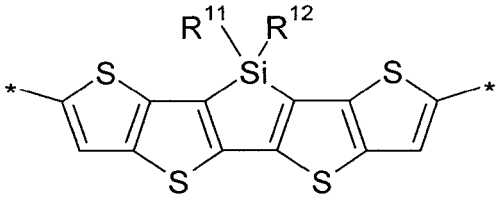

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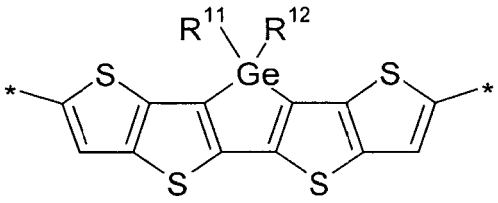
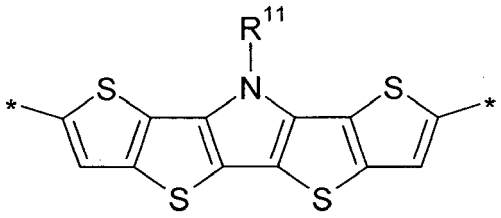
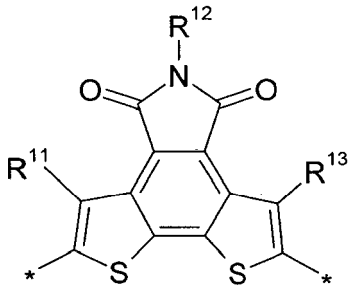


(D144)



(D145)

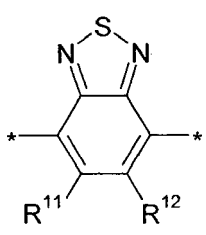


(D146)

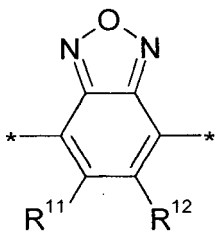
wherein R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17} and R^{18} independently of each other denote H or have one of the meanings of L as defined above and below.

[0131] Preferred donor units are selected from formulae D1, D7, D10, D11, D19, D22, D29, D30, D35, D36, D44, D55, D84, D87, D88, D89, D93, D106, D111, D140, D141 and D146, wherein preferably at least one of R^{11}, R^{12}, R^{13} and R^{14} is different from H.

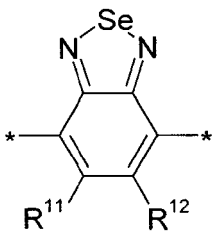
[0132] Further preferred are repeating units, monomers, oligomers, polymers and small molecules of formulae II1, II2, III, III1-III5, IV, V1, V2, V1a-V1d, VI and their subformulae wherein one or more of Ar^1, Ar^2, Ar^3 and Ar^4 denote arylene or heteroarylene, preferably having electron acceptor properties, selected from the group consisting of the following formulae



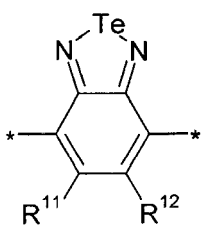
(A1)



(A2)



(A3)



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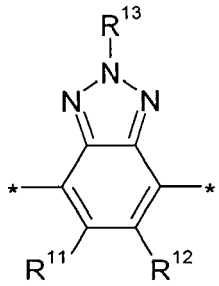
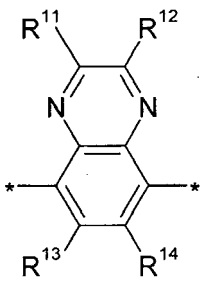
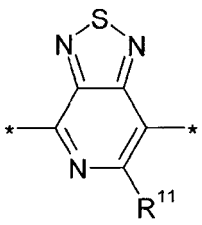


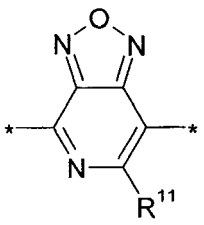
(A5)



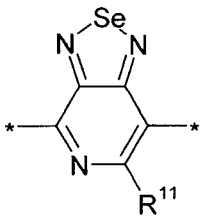
(A6)



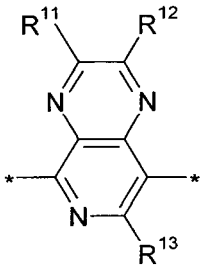
(A7)



(A8)



(A9)



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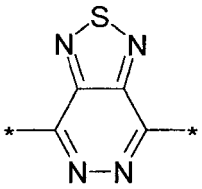
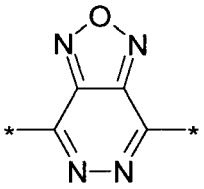
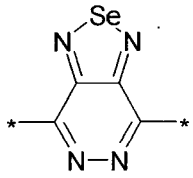


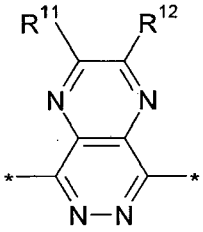
(A11)



(A12)



(A13)



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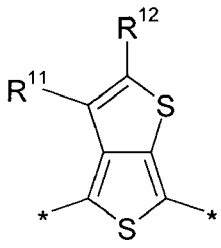

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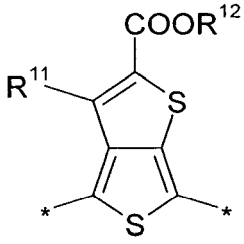
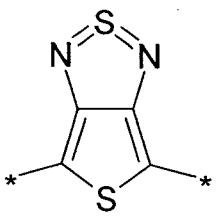
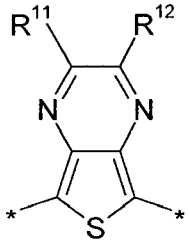


(A16)



(A17)



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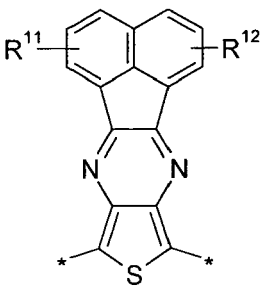
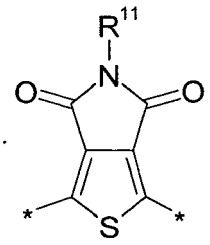
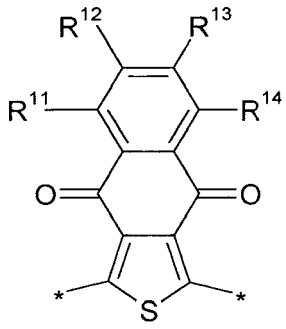


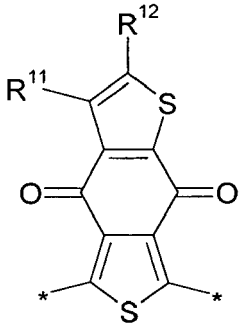
(A19)



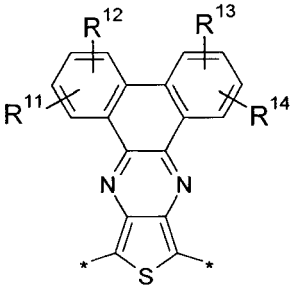
(A20)



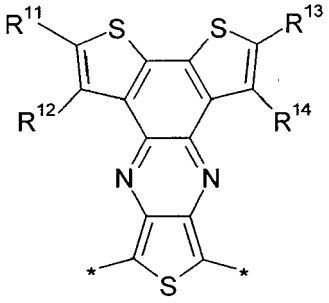
(A21)



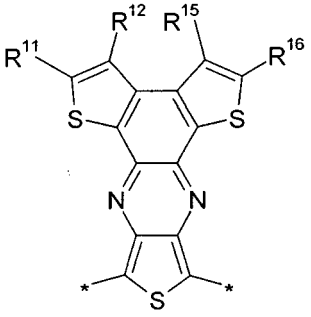
(A22)



(A23)



(A24)



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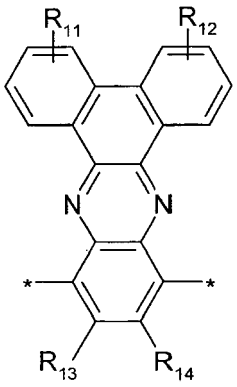

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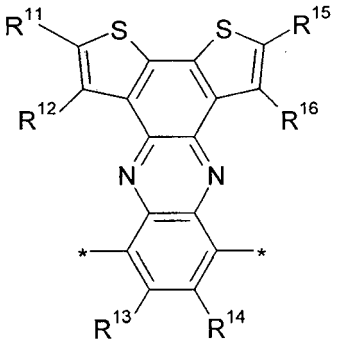

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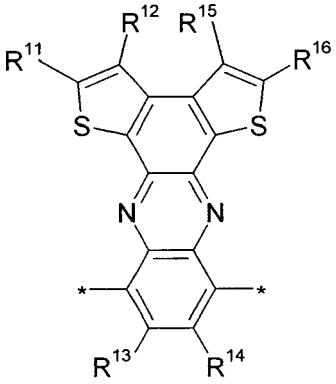

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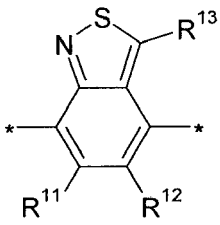

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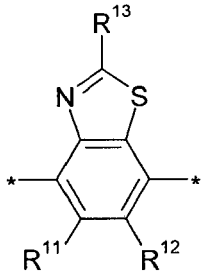

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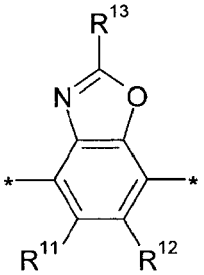

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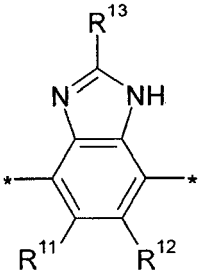

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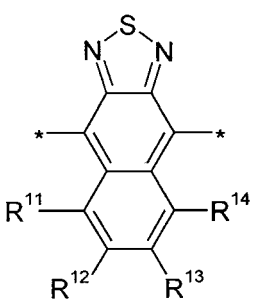

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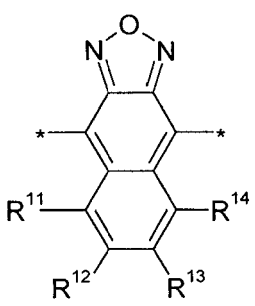

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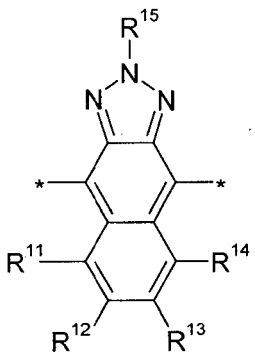

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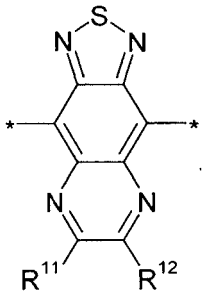

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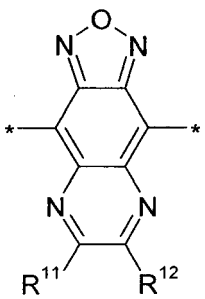

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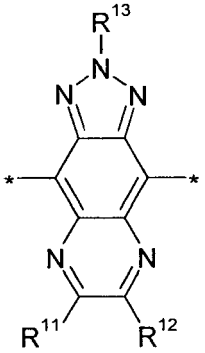

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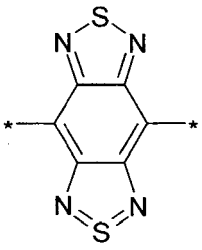

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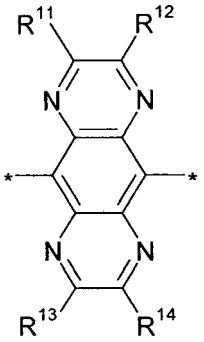

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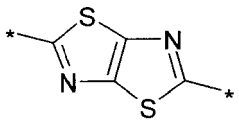

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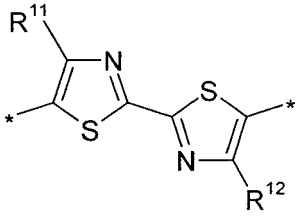

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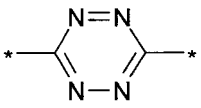

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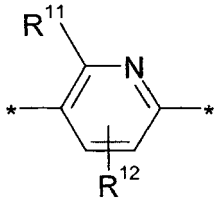

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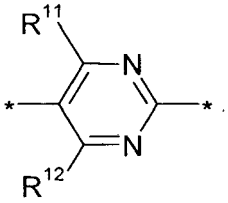

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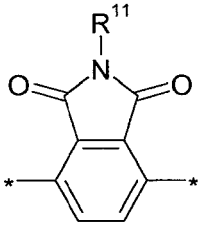

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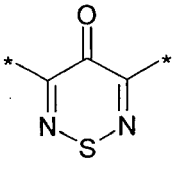

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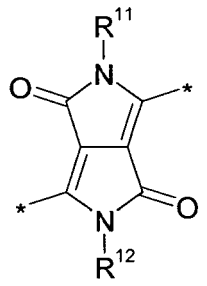

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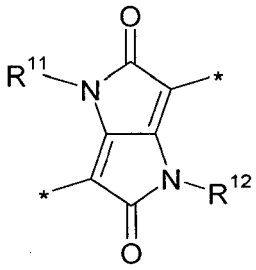

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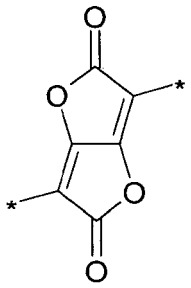

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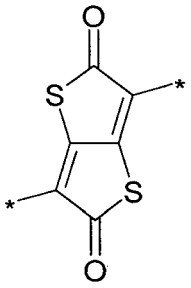

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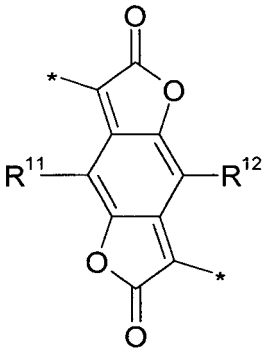

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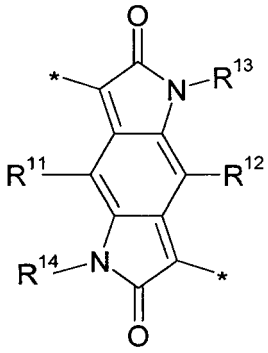

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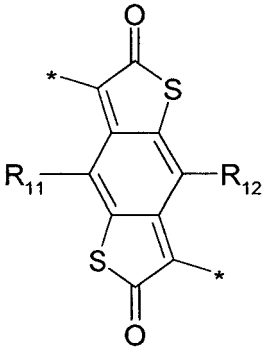

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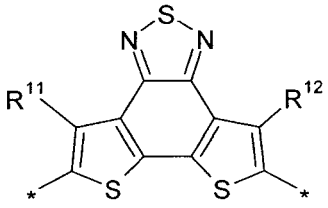

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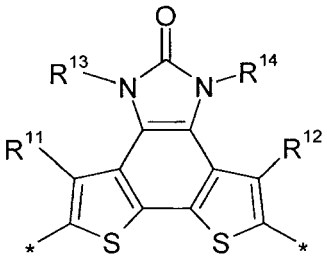

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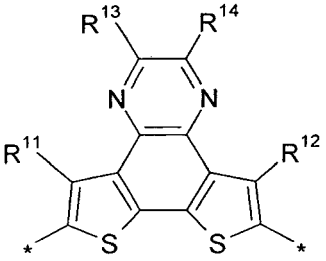

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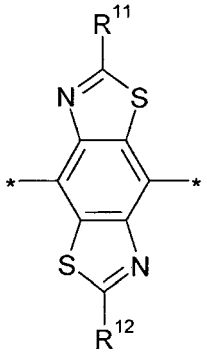

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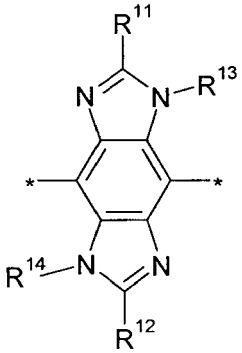

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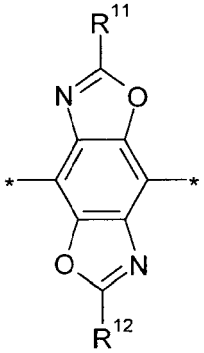

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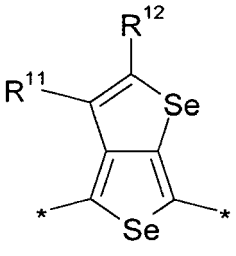

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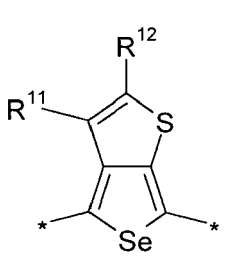

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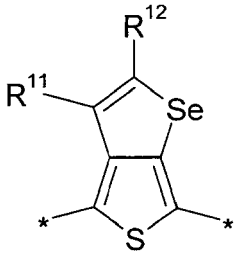

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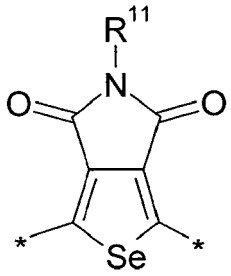

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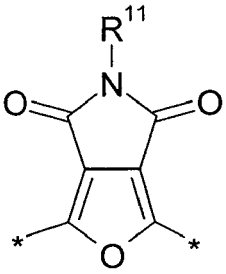

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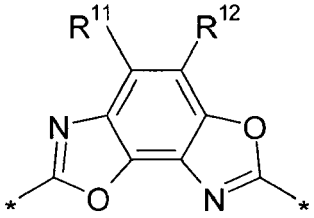

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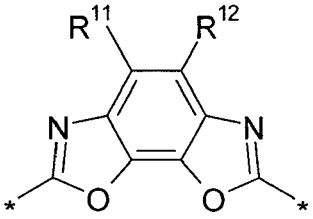

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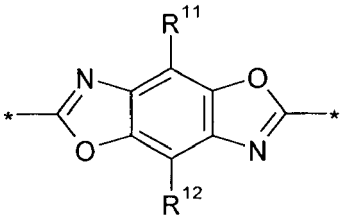

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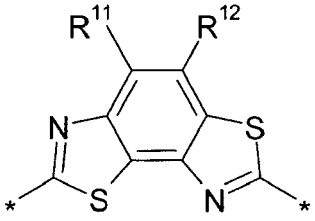

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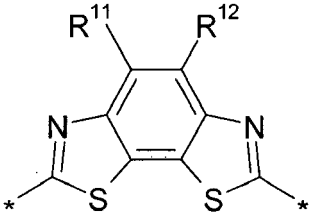

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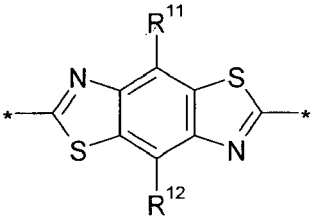

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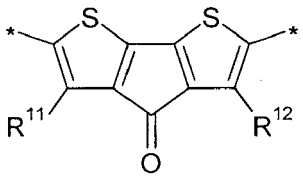

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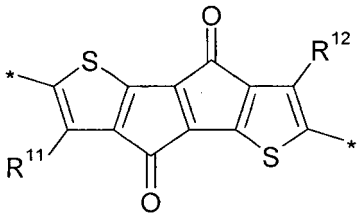

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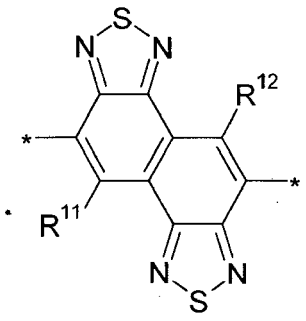

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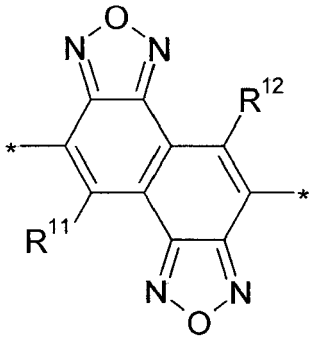

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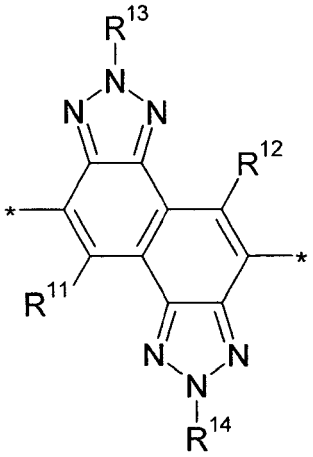

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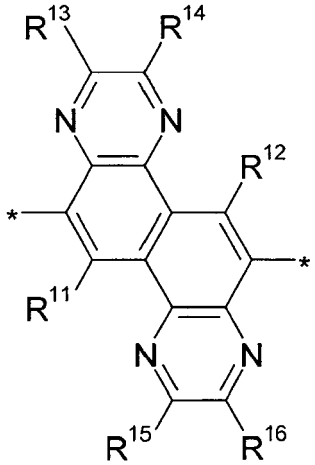

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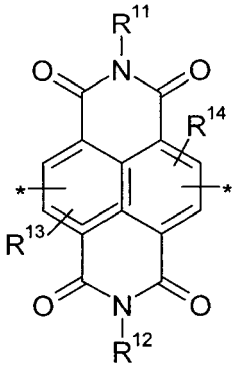

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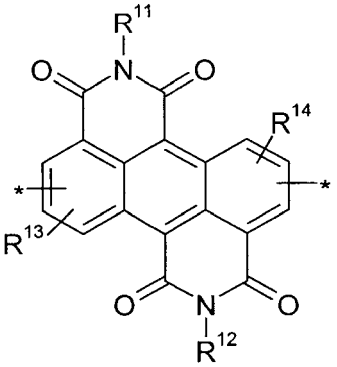

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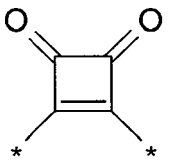

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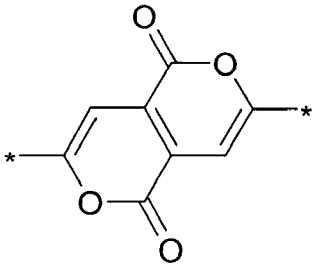

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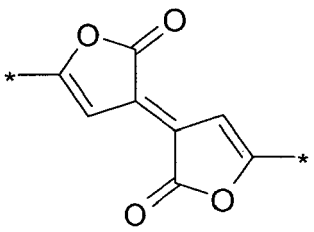

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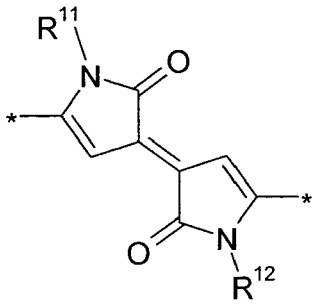

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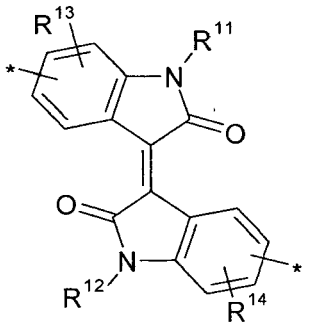

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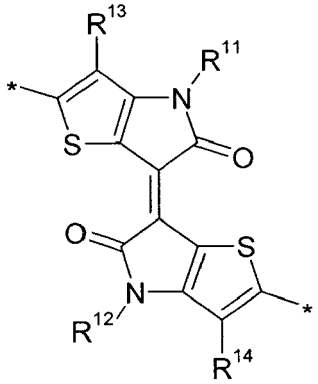

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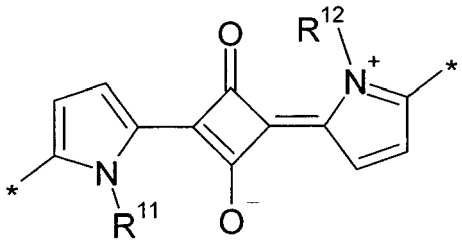
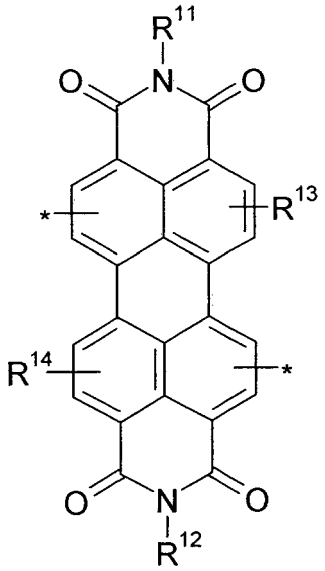


(A86)



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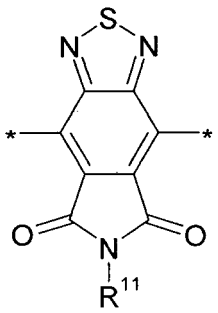

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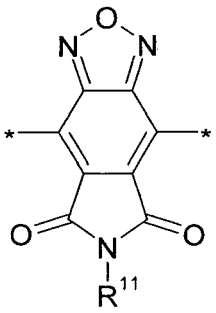

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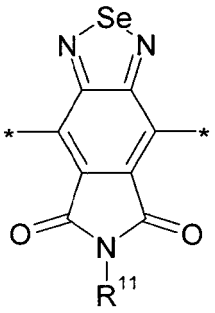

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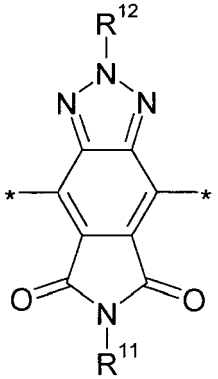

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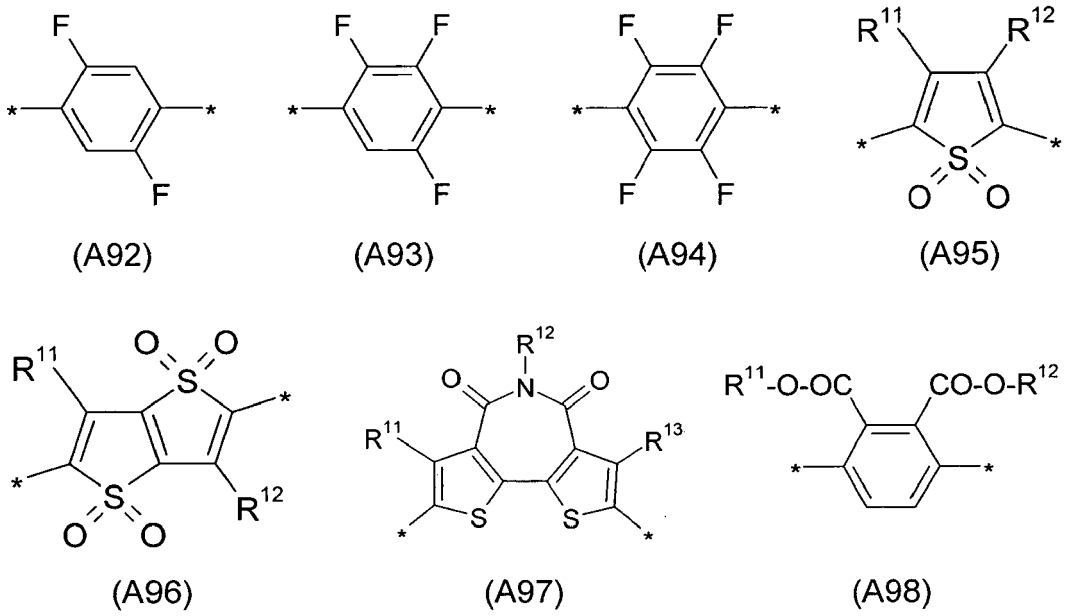
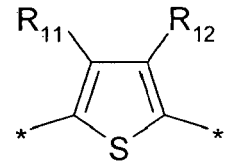
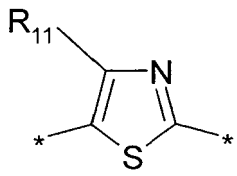


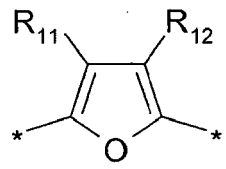
wherein R^{11}, R^{12}, R^{13}, R^{14}, R^{15} and R^{16} independently of each other denote H or have one of the meanings of L as defined above and below.

[0133] Preferred acceptor units are selected from formulae A1, A6, A7, A15, A16, A20, A74, A88, A92 or A98 wherein preferably at least one of R^{11}, R^{12}, R^{13} and R^{14} is different from H.

[0134] Further preferred are repeating units, monomers, oligomers, polymers and small molecules of formulae II1, II2, III, III1-III5, IV, V1, V2, V1a-V1d, VI and their subformulae wherein one or more of Ar^1, Ar^2, Ar^3 and Ar^4 denote arylene or heteroarylene selected from the group consisting of the following formulae


Sp1


Sp2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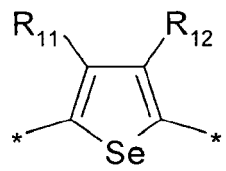
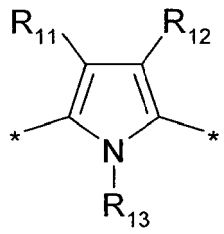
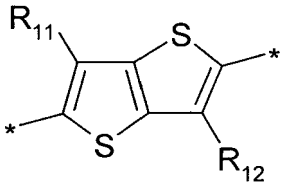

Sp4



Sp5



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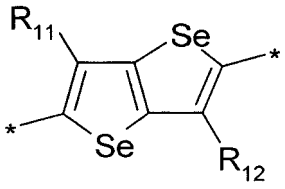

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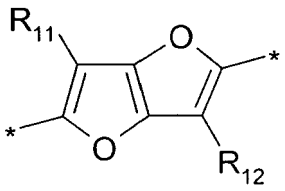
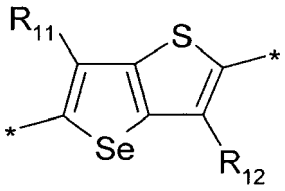
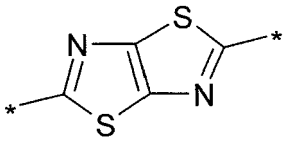


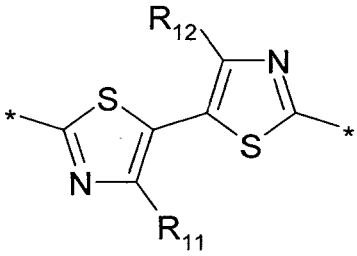
Sp8



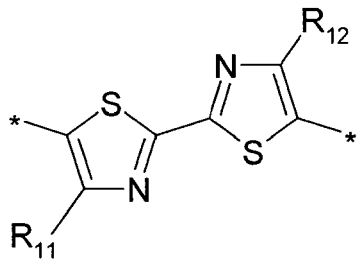
Sp9



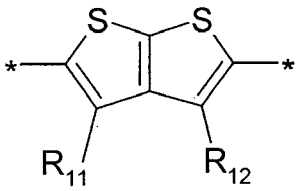
Sp10



Sp11



Sp12



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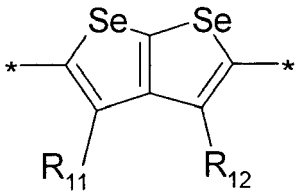

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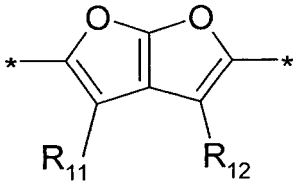

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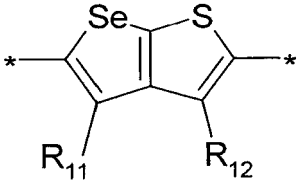


Sp16

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

[0135] Very preferred are units selected from formulae Sp1, Sp6, Sp13, wherein preferably one of R^{11} and R^{12} is H or both R^{11} and R^{12} are H.

[0136] Further preferred are repeating units, monomers and polymers of formulae II1, II2, III, III1-III5, IV, V1, V2, V1a-V1d and their subformulae wherein

a) one or more of Ar^1, Ar^2, Ar^3 and Ar^4 denote arylene or heteroarylene, preferably having electron donor properties, selected from the group consisting of the formulae D1-D145, very preferably of the formulae D1, D7, D10, D11, D19, D22, D29, D30, D35, D36, D44, D55, D84, D87, D88, D89, D93, D106, D111, D140, D141 and D146, and/or
b) one or more of Ar^1, Ar^2, Ar^3 and Ar^4 denote arylene or heteroarylene, preferably having electron accpetor properties, selected from the group consisting of the formulae A1-A98, very preferably of the formulae A1, A6, A7, A15, A16, A20, A74, A88, A92 and A98,
and
c) one or more of Ar^1, Ar^2, Ar^3 and Ar^4 denote arylene or heteroarylene selected from the group consisting of the formulae Sp1-Sp15, very preferably of the formulae Sp1, Sp6 and Sp13.

[0137] Further preferred are polymers of formula III3 and III5 wherein Ar^1 and Ar^2 have the same meaning and are

selected from formulae D1, D7, D10, D11, D19, D22, D29, D30, D35, D36, D44, D55, D84, D87, D88, D89, D93, D106, D111, D140, D141 and D146, and R^1 and R^2 denote R or -OR, and R^3 and R^4 denote C(=O)-R or C(=O)-OR with R being as defined above.

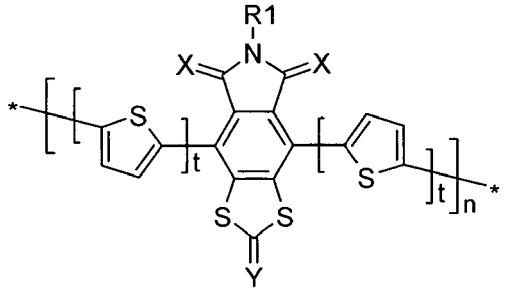
[0138] Further preferred are oligomers and small molecules of formula VI wherein Ar^{1-10} are selected from the following groups

a) the group consisting of the formulae D1-D145, very preferably of the formulae D1, D7, D10, D11, D19, D22, D29, D30, D35, D36, D44, D55, D84, D87, D88, D89, D93, D106, D111, D140, D141 and D146,

b) the group consisting of the formulae A1-A98, very preferably of the formulae A1, A6, A7, A15, A16, A20, A74, A88, A92 or A98,

c) the group consisting of the formulae Sp1-Sp15, very preferably of the formulae Sp1, Sp6 and Sp13.

[0139] Very preferred is a conjugated polymer selected from the following formulae:



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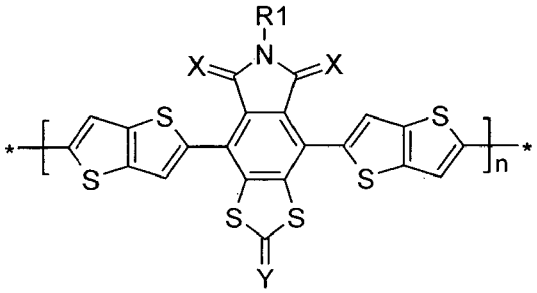

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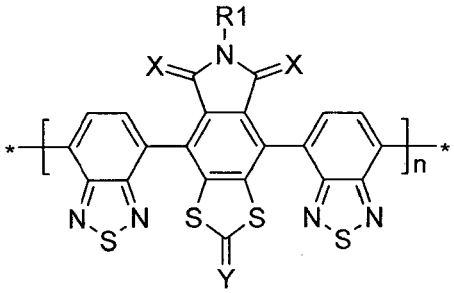

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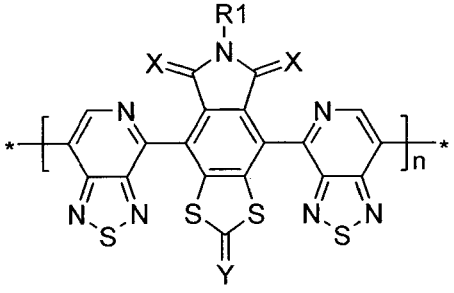

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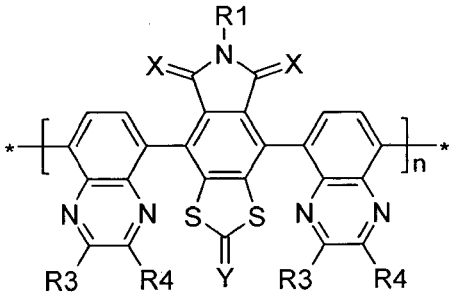

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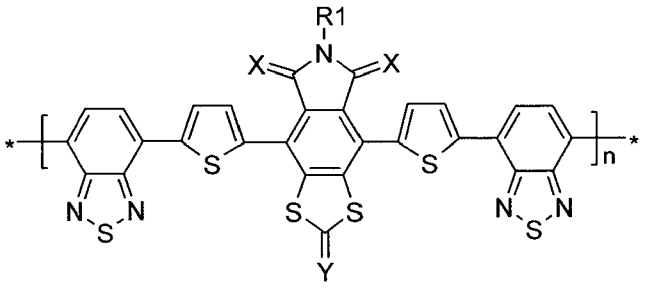

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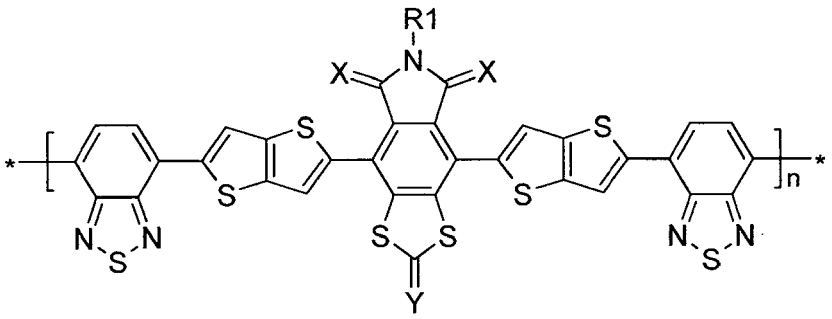

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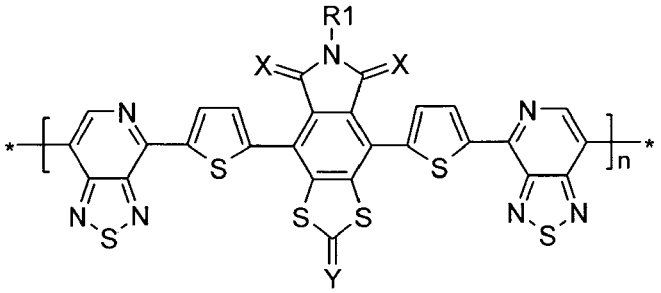

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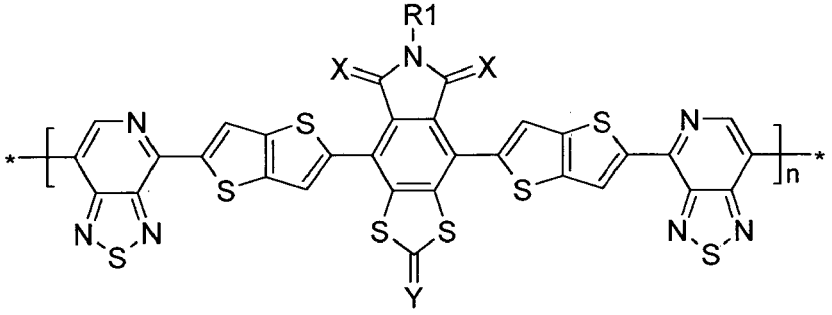

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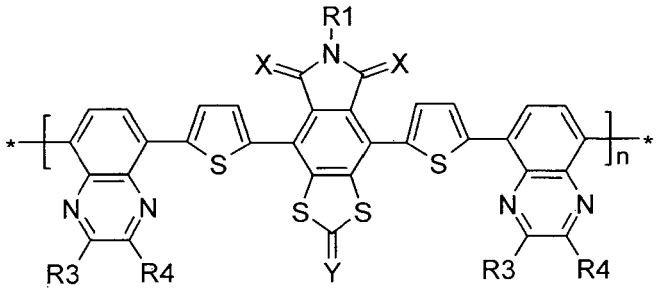

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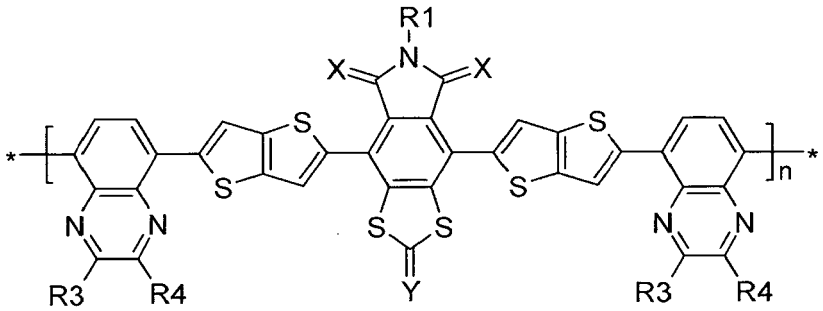

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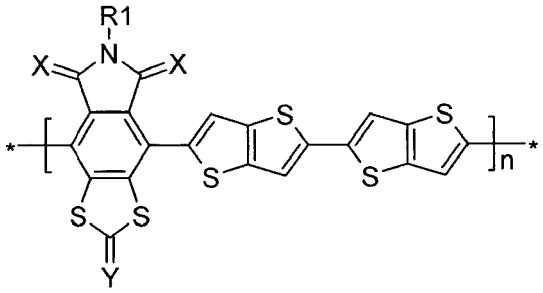

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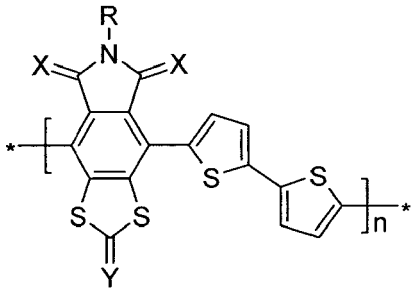

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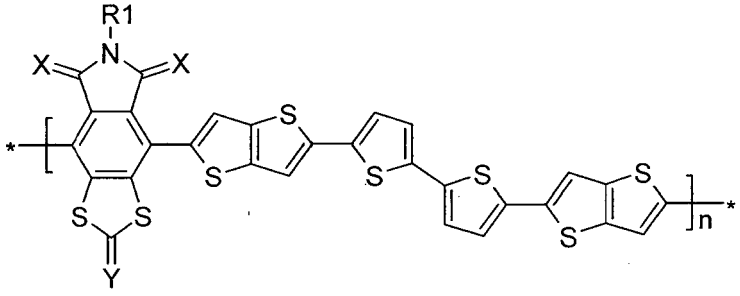

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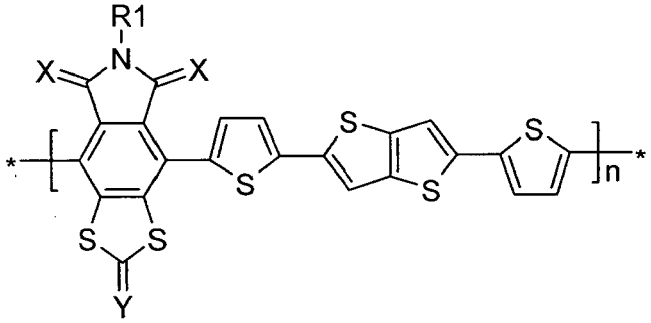

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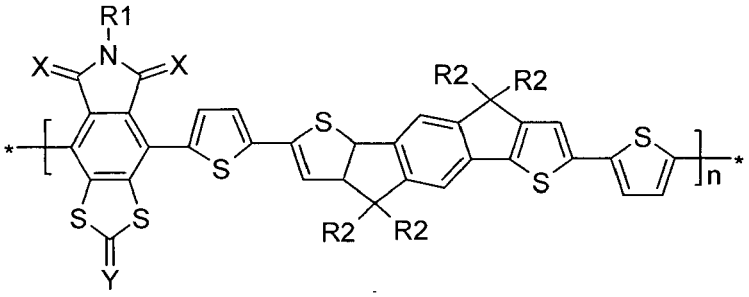

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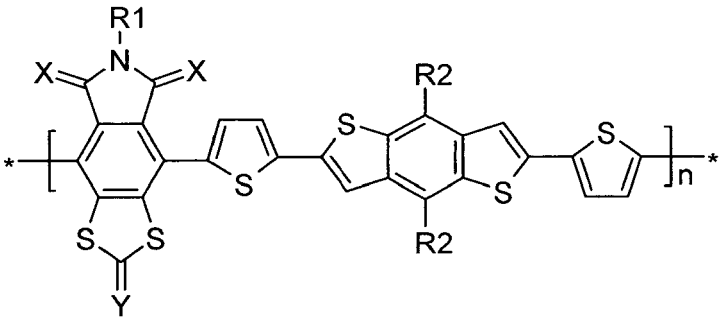

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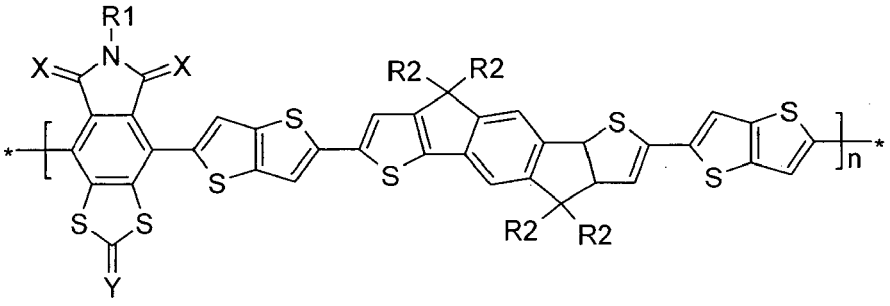

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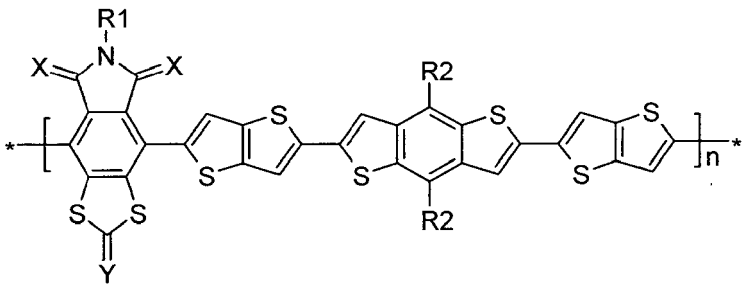

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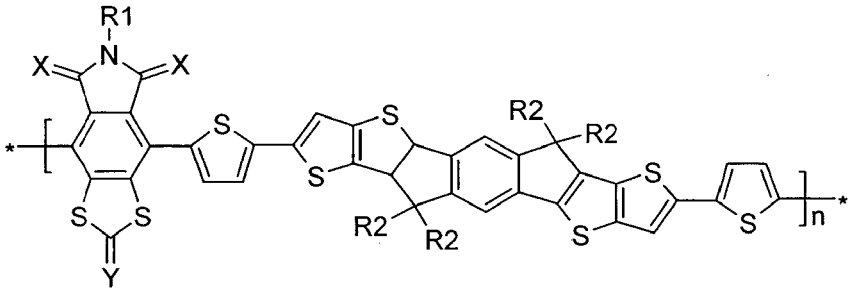

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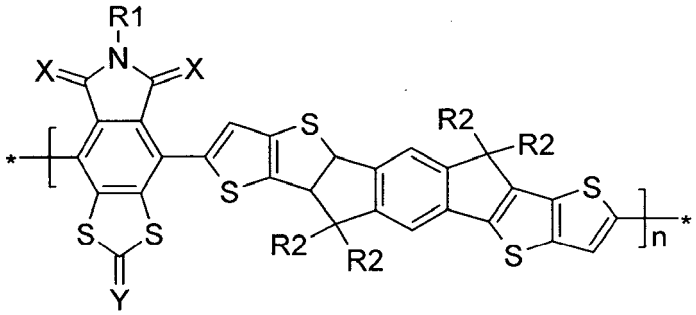

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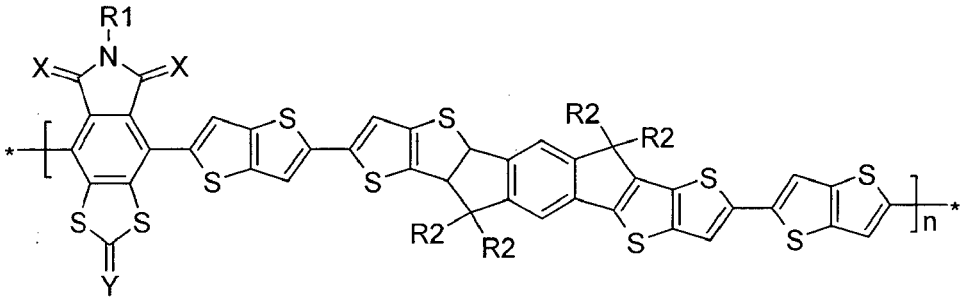

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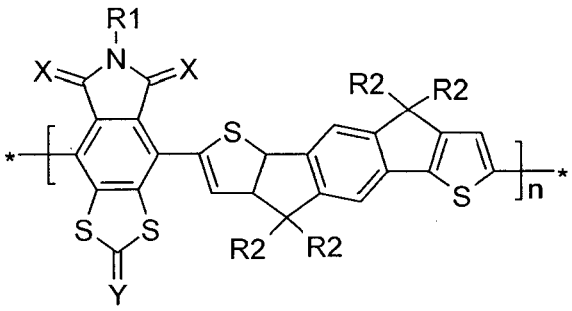

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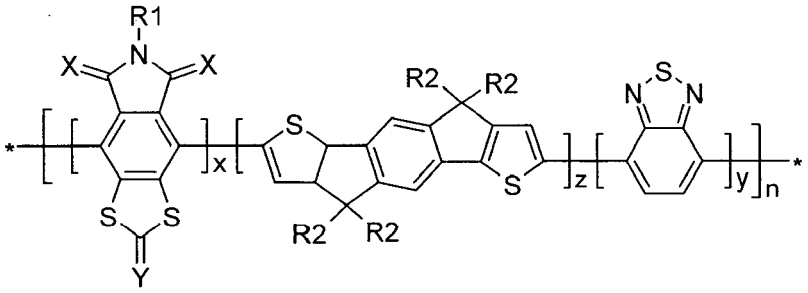

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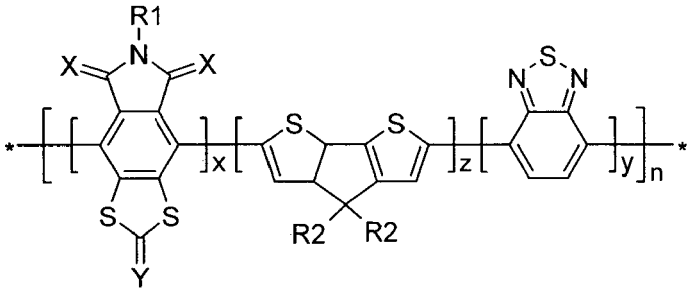

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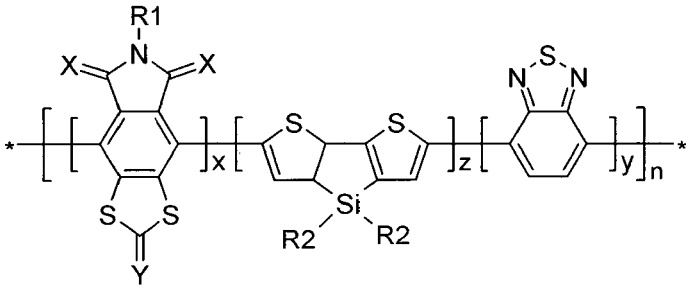

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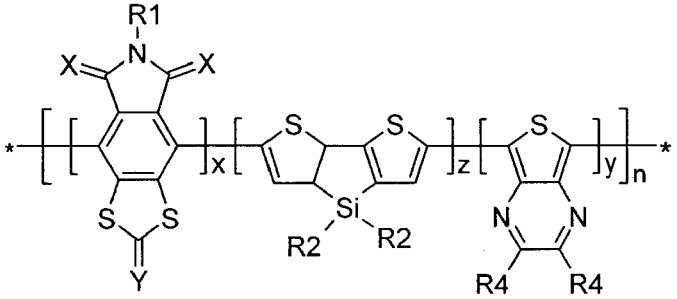

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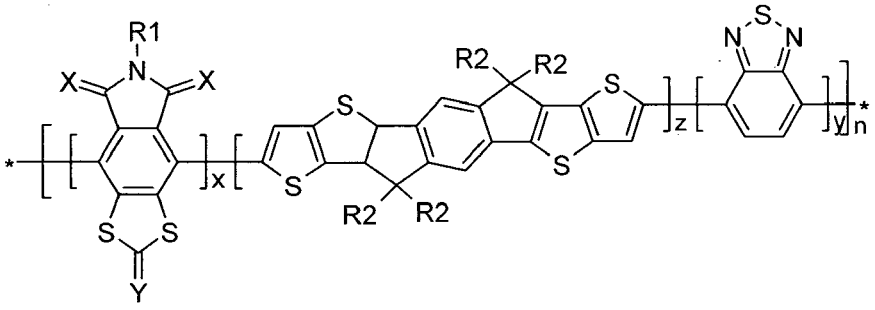

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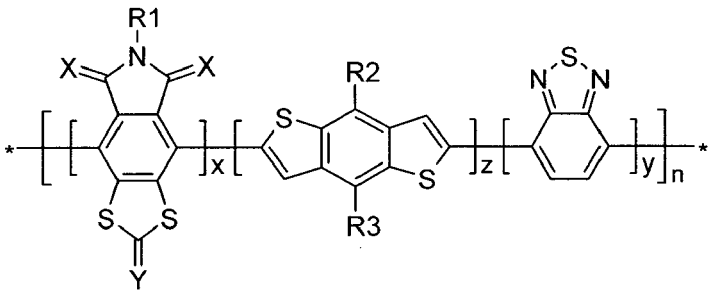

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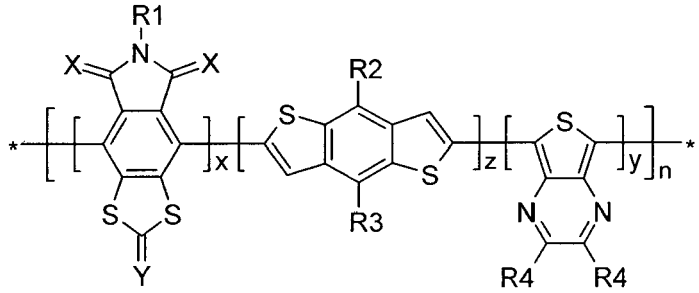

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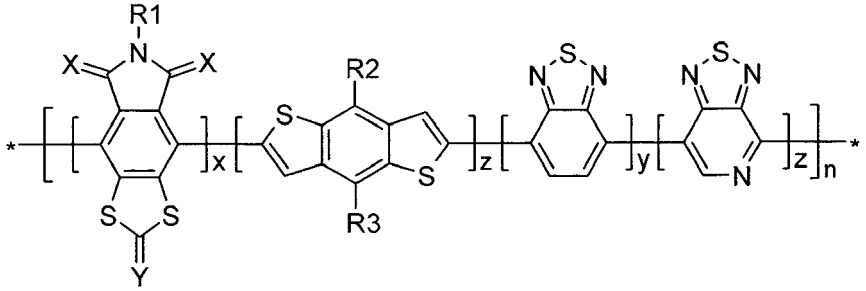

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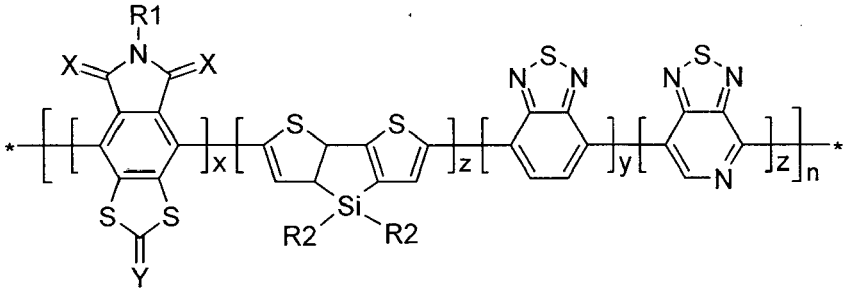
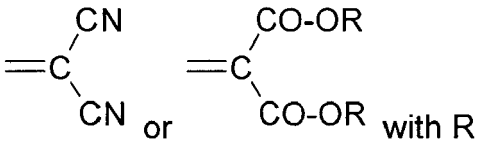


P32

wherein R^1, x, y and n are as defined above and below, $0<z<1$, $x+y+z=1$, X has on each occurrence identically or differently one of the meanings of X^1 as given above and below, Y is as defined above and below, t is 1, 2, 3 or 4, preferably 1 or 2, and R^2, R^3 and R^4 have independently of each other and on each occurrence identically or differently one of the meanings given for L.

[0140] In formulae P1-P32 X is preferably O or S, very preferably O.

[0141] In formulae P1-P32 Y is preferably O, S,



being as defined above.

[0142] Further preferred units, monomers, oligomers, polymers and small molecules of formulae I, II1, II2, III, III1-III5, IV, V1, V2, V1a-V1d, VI, R1-R11, P1-P32 and their subformulae are selected from the following embodiments, including any combination thereof:

- X^1 and X^2 denote O,
- X^1 and X^2 denote S,
- one of X^1 and X^2 denotes O and the other denotes S,
- Y is O,
- Y is S,
- Y is CU^1U^2,
- X^1, X^2 and Y are not at the same time O,
- if X^1 and X^2 are O then Y is S or CU^1U^2,
- in the units of formula I at least one of the groups attached to the 1- and 4-positions of the benzene ring is different from H,
- in the units of formula I both groups attached to the 1- and 4-positions of the benzene ring are different from H,
- R^1 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,
- R^1 is selected from $-C(=O)-R^n$, $-C(=O)-OR^n$, $-C(=O)-NHR^n$ and $-C(=O)-NR^nR^m$, 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,
- R^1 is cyclic alkyl with 4 to 20 ring atoms, wherein one or more CH_2 groups are optionally replaced by O, S, NR^0, C(=O), (C=S), $CY^1=CY^2$ or $CR^0=CR^{00}$, and which is unsubstituted or substituted by one or more groups L as defined in formula I,
- R^1 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 is straight-chain or branched alkyl with 1 to 25, preferably 1 to 18 C atoms which is optionally fluorinated,
- R is cyclic alkyl with 4 to 20 ring atoms, wherein one or more CH_2 groups are optionally replaced by O, S, NR^0, C(=O), (C=S), $CY^1=CY^2$ or $CR^0=CR^{00}$, and which is unsubstituted or substituted by one or more groups L as defined in formula I,
- R is aryl, heteroaryl, arylalkyl or heteroarylalkyl, each of which has 4 to 20 ring atoms, optionally contains fused rings, and is unsubstituted or substituted by one or more groups L as defined in formula I,
- U^1 and U^2 denote CN,
- U^1 and U^2 denote C(=O)R or C(=O)OR, wherein R has one of the meanings given above and below, and is preferably straight-chain or branched alkyl with 1 to 25, preferably 1 to 18 C atoms which is optionally fluorinated,
- L 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,
- L is selected from $-C(=O)-R^n$, $-C(=O)-OR^n$, $-C(=O)-NHR^n$ and $-C(=O)-NR^nR^m$, 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,
- L is halogen, preferably F or Cl,
- L is CN, F or Cl,
- R^7 and R^8 are different from H,
- R^7 and R^8 denote Br, $B(OZ^2)_2$ or $Sn(Z^4)_3$, wherein Z^2 and Z^4 are as defined in formula V1.

[0143] The polymers according to the present invention can be prepared for example by copolymerising one or more monomers of formula V1, V2, V3 or V1a-V1d with each other or with one or monomers of the following formulae in an aryl-aryl coupling reaction

$R^7\text{-}Ar^1\text{-}R^8$ MI

$R^7\text{-}Ar^2\text{-}R^8$ MII

R^7-Ar^3-R^8 MIII

R^7-Ar^4-R^8 MIV

wherein Ar^{1-4}, R^7 and R^8 have the meanings given in formula II2 and V1 or one of the preferred meanings given above and below.

[0144] The polymer 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.

[0145] For example, the polymer 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.

[0146] Preferably the polymer is prepared from monomers selected from formulae V1, V2, V3, V1a-d and MI-MIV as described above.

[0147] 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, V1a-d with each other and/or with one or more comonomers, preferably selected from formulae MI-MIV, in a polymerisation reaction, preferably in an aryl-aryl coupling reaction.

[0148] Preferred aryl-aryl coupling and polymerisation methods used in the processes described above and below are Yamamoto coupling, Kumada coupling, Negishi coupling, Suzuki coupling, Stille coupling, Sonogashira coupling, Heck coupling, C-H activation coupling, Ullmann coupling or Buchwald coupling. Especially preferred are Suzuki coupling, Negishi coupling, Stille coupling and Yamamoto coupling. Suzuki coupling is described for example in WO 00/53656 A1. Negishi coupling is described for example in J. Chem. Soc., Chem. Commun., 1977, 683-684. Yamamoto coupling is described in for example in T. Yamamoto et al., Prog. Polym. Sci., 1993, 17, 1153-1205, or WO 2004/022626 A1.Stille coupling is described for example in Z. Bao et al., J. Am. Chem. Soc., 1995, 117, 12426-12435. C-H activation is described for example for example in M. Leclerc et al, Angew. Chem. Int. Ed. 2012, 51, 2068 - 2071.For example, when using Yamamoto coupling, monomers having two reactive halide groups are preferably used. When using Suzuki coupling, monomers having two reactive boronic acid or boronic acid ester groups or two reactive halide groups are preferably used. When using Stille coupling, monomers having two reactive stannane groups or two reactive halide groups are preferably used. When using Negishi coupling, monomers having two reactive organozinc groups or two reactive halide groups are preferably used. When synthesizing a linear polymer by C-H activation polymerisation, preferably a monomer as described above is used wherein at least one reactive group is an activated hydrogen bond.

[0149] Preferred catalysts, especially for Suzuki, Negishi or Stille coupling, are selected from Pd(0) complexes or Pd(II) salts. Preferred Pd(0) complexes are those bearing at least one phosphine ligand such as $Pd(Ph_3P)_4$. Another preferred phosphine ligand is tris(*ortho*-tolyl)phosphine, i.e. $Pd(o\text{-}Tol_3P)_4$. Preferred Pd(II) salts include palladium acetate, i.e. $Pd(OAc)_2$ or trans-di(p-acetato)-bis[o-(di-o-tolylphosphino)benzyl]dipalladium(II). Alternatively the Pd(0) complex can be prepared in situ 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, tris(o-methoxyphenyl)phosphine, tri(tert-butyl)phosphine or 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl. Suzuki polymerisation is performed in the presence of a base, for example sodium carbonate, potassium carbonate, cesium carbonated, lithium hydroxide, potassium phosphate or an organic base such as tetraethylammonium carbonate or tetraethylammonium hydroxide. Yamamoto polymerisation employs a Ni(0) complex, for example bis(1,5-cyclooctadienyl) nickel(0).

[0150] Suzuki, Stille or C-H activation coupling polymerisation may be used to prepare homopolymers as well as statistical, alternating and block random copolymers. Statistical, random block copolymers or block copolymers can be prepared for example from the above monomers, wherein one of the reactive groups is halogen and the other reactive group is a C-H activated bond, boronic acid, boronic acid derivative group or and alkylstannane. The synthesis of statistical, alternating and block copolymers is described in detail for example in WO 03/048225 A2 or WO 2005/014688 A2.

[0151] As alternatives to halogen as described above, leaving groups of formula - $O\text{-}SO_2Z^1$ can be used wherein Z^1 is as defined above. Particular examples of such leaving groups are tosylate, mesylate and triflate.

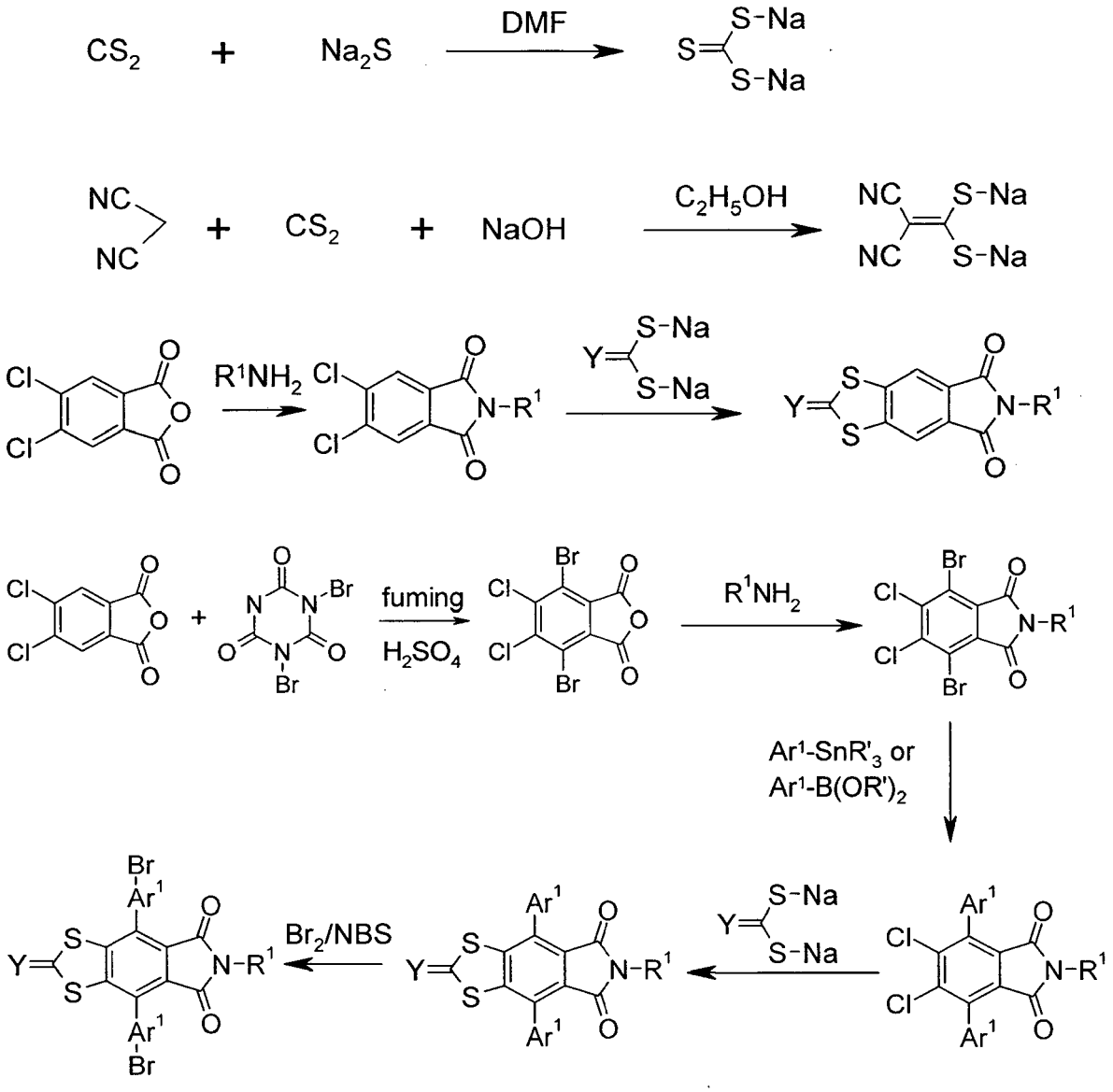
[0152] Preferred polymerisation conditions lead to alternating polymers which are particularly preferred for OTFT application, whereas statistical block copolymers are prepared preferably for OPV and OPD application. Preferred polycondensation are Suzuki coupling, Stille coupling, Sonogashira coupling, Heck coupling or Buchwald coupling, Negishi coupling or C-H activation coupling where the first set of reactive groups is composed of - Cl, -Br, -I, O-tosylate, O-triflate, O-mesylate and O-nonaflate and the second set of reactive groups is composed of -H, $-SiR_2F$, $-SiRF_2$, $-B(OR)_2$, -CR=CHR', -C≡CH, -ZnX, -MgX and $-Sn(R)_3$. If a Yamamoto coupling reaction is used to prepare the polymer, the

reactive monomer ends are both composed independently of -Cl, -Br, -I, O-tosylate, O-triflate, O-mesylate and O-nonaflate.

[0153] Suitable and preferred methods for preparing compounds according to the present invention are illustrated in the reaction schemes below, wherein R, R', R^1, R^2 and Ar^1 are as defined above. The compounds not shown, e.g. wherein in the units of formula I X is S, or Y is O, S or CU^1U^2, can be made in analogy thereto.

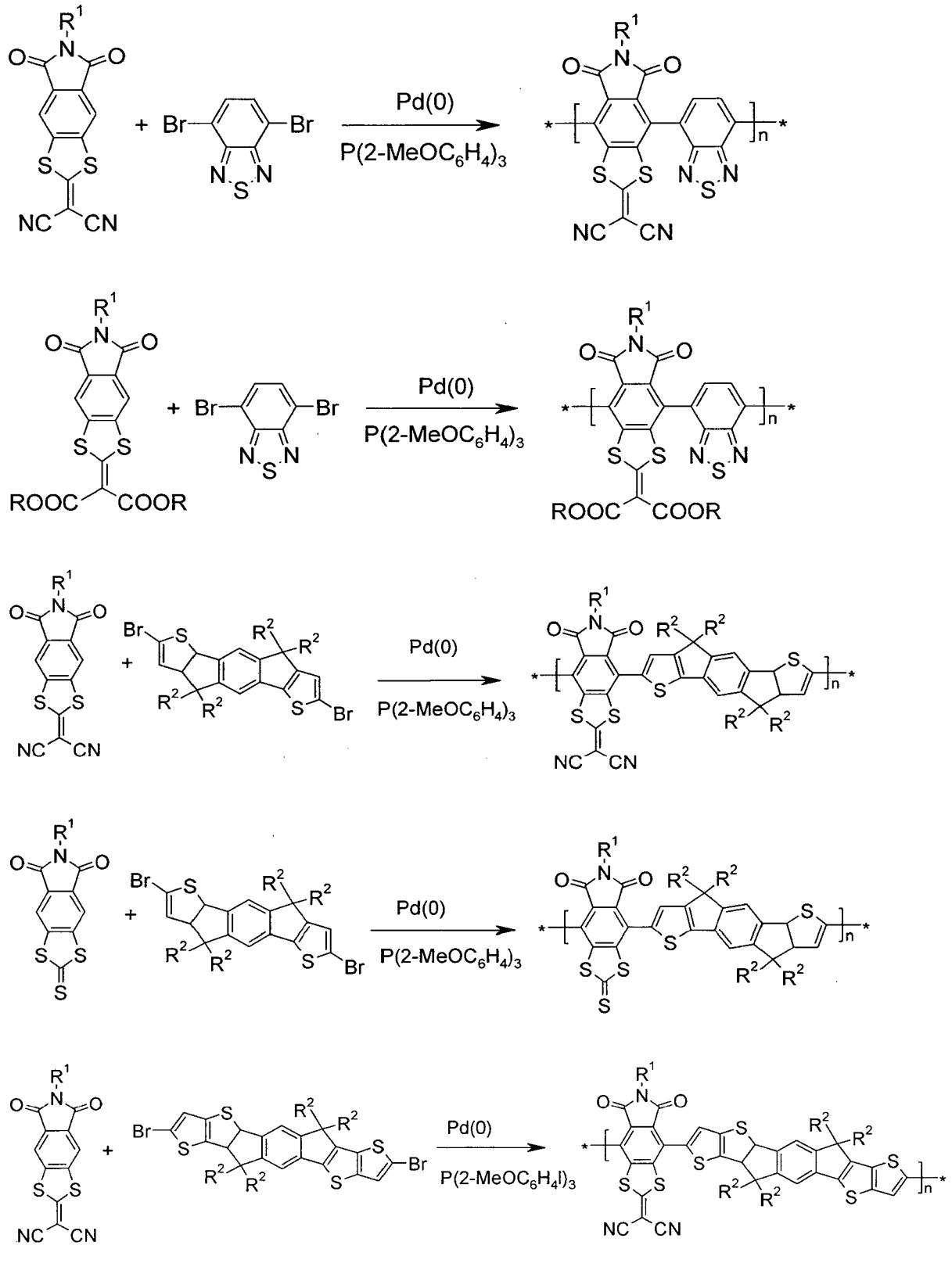
[0154] The DTPI units can be synthesized for example by reacting 3,6-diaryl-4,5-dichlorophthalimide with the corresponding dithiolate to form the [4,5-d] fused dithiol rings as exemplarily illustrated in Scheme 1. The 3,6-diaryl-4,5-dichlorophthalimides can be made from cross-couplings of 3,6-bromo-4,5-dichlorophthalimide with arylboronic acids, arylboronic esters or arylstannanes.

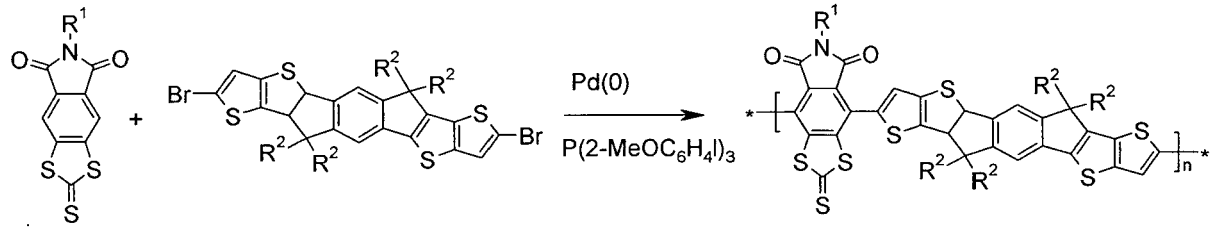
Scheme 1

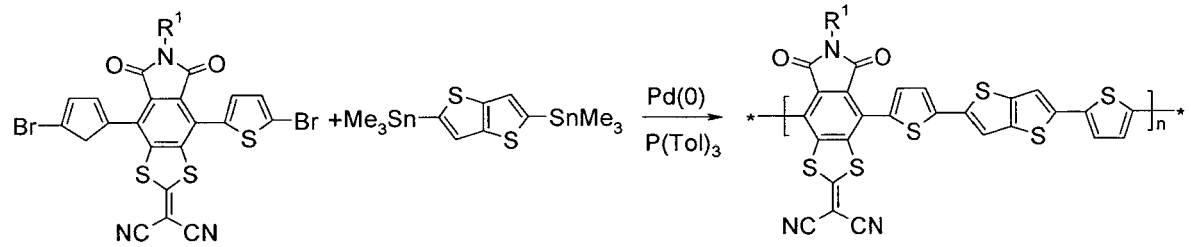


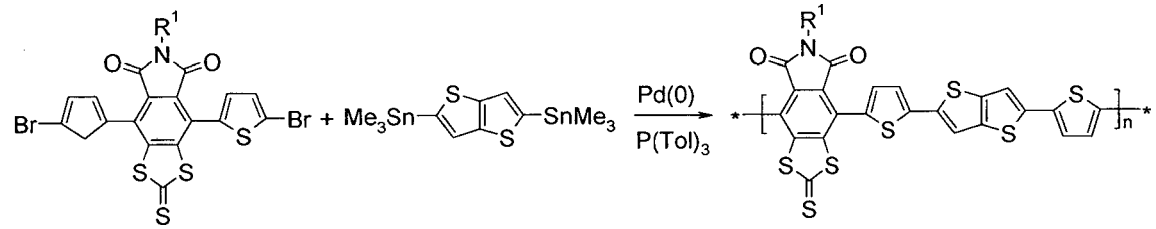
[0155] Conjugated polymers and co-polymers, including alternating co-polymers and statistical block co-polymers can be made by the methods described above. Particularly, conjugated polymer can be made by Pd catalysed direct arylation polymerisation with a dibromo counterpart (M. Wakioka, et al., Macromol., 2015, 48, 8382) or Pd catalysed polycondensations methods such as Yamamoto reaction (Yamamoto et al., Bull., Chem. Soc. Jpn., 1978, 51(7), 2091; Yamamo to et al., Macromolecules, 1992, 25(4), 1214), Suzuki-Miyaura reaction (Miyaura et al., Chem. Rev., 1995, 95, 2457) and Stille reaction (Bao et al., J. Am., Chem., Soc., 1995, 117(50), 12426) using the terminally brominated derivatives. Some preferred polymerization reactions are exemplarily illustrated represented in Scheme 2.

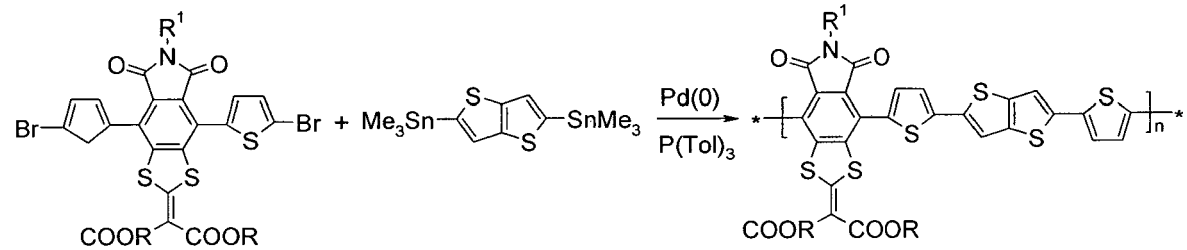
Scheme 2


Pd(0)
P(2-MeOC6H4)3
Pd(0)
P(2-MeOC6H4)3
Pd(0)
P(2-MeOC6H4)3
Pd(0)
P(2-MeOC6H4)3
Pd(0)
P(2-MeOC6H4I)3


Pd(0)
P(2-MeOC6H4I)3


Pd(0)
P(Tol)3


Pd(0)
P(Tol)3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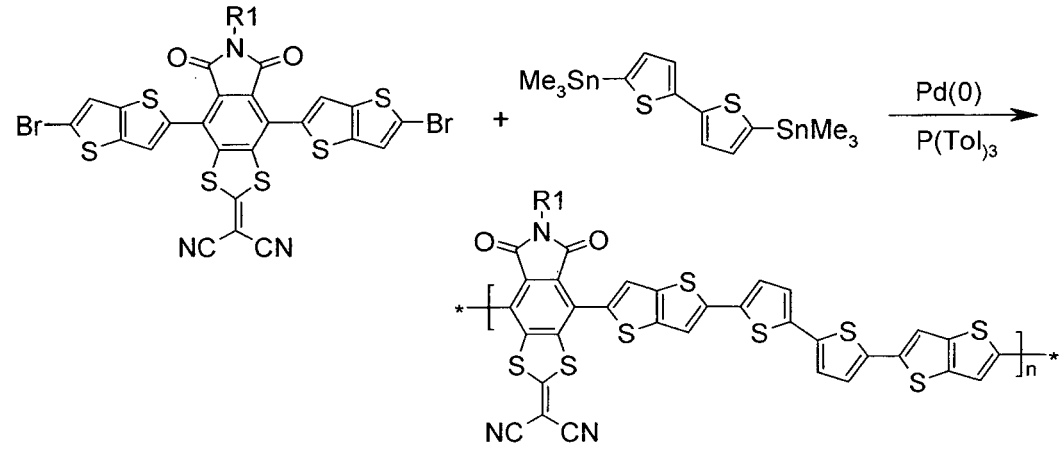
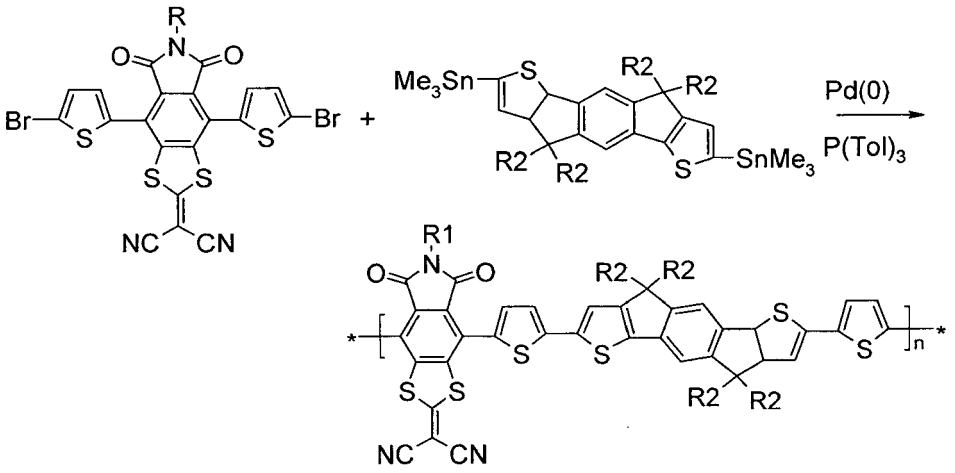
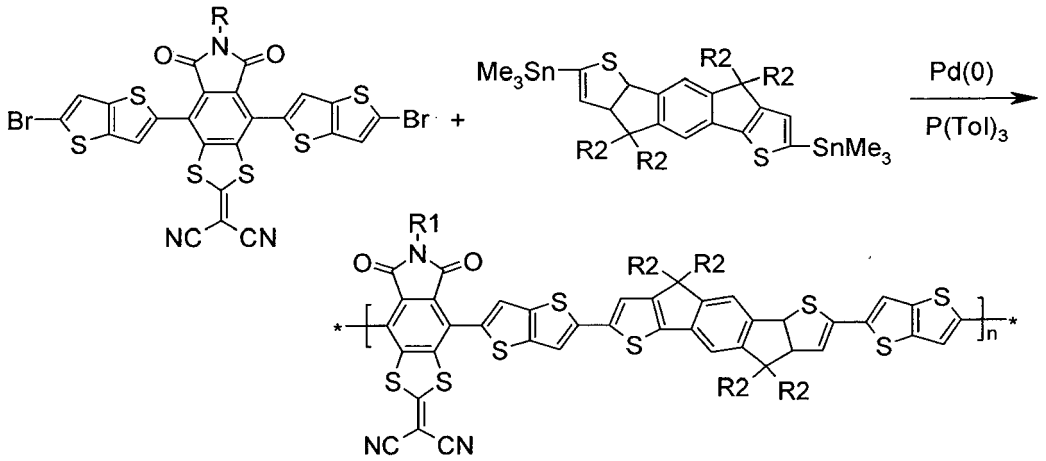
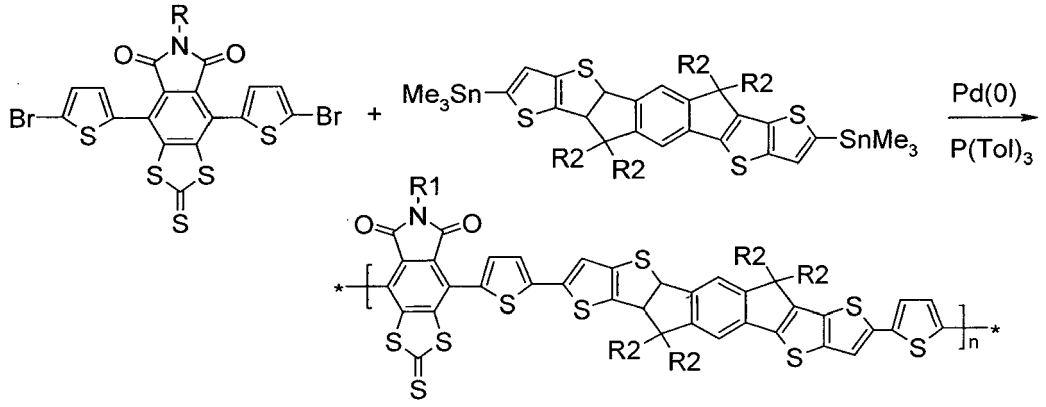
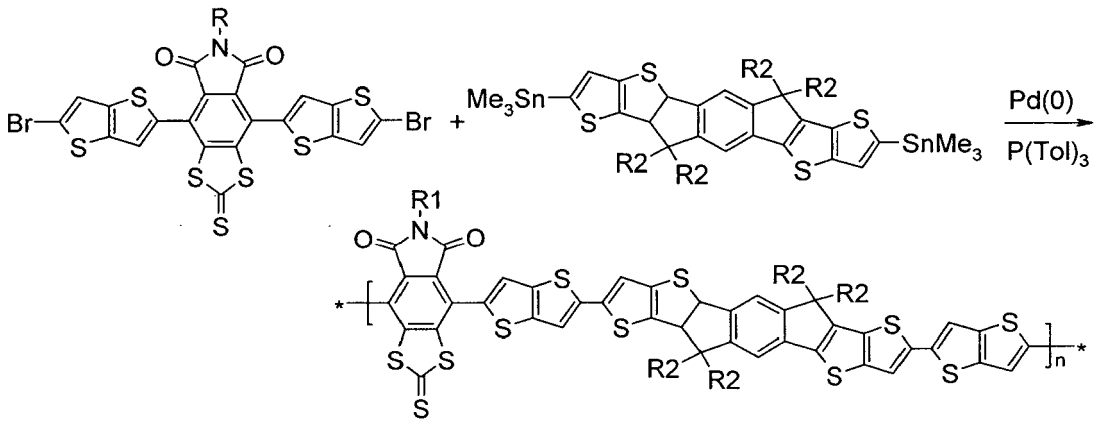
P(Tol)3


Pd(0)
P(Tol)3





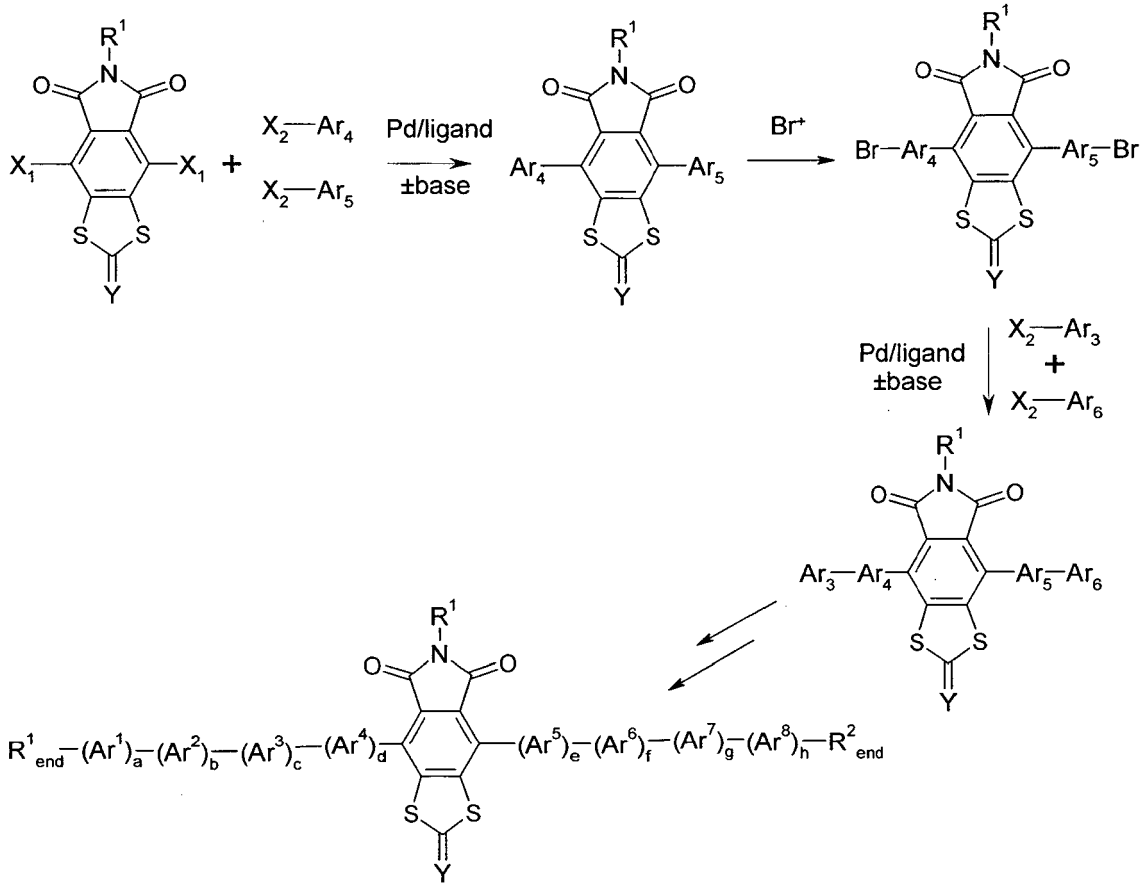




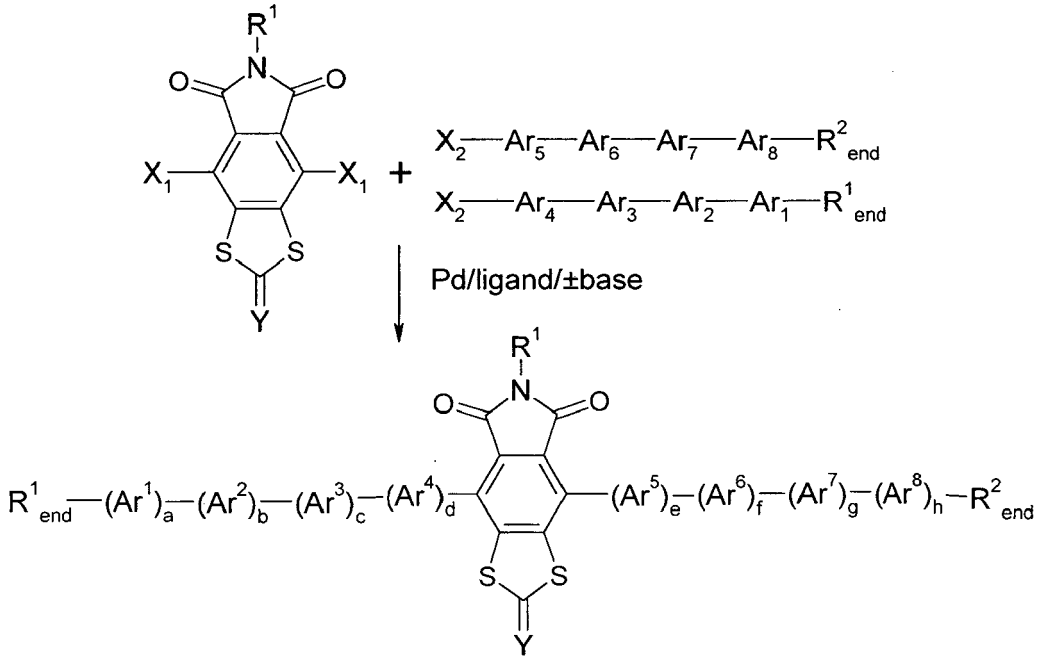
[0156] The novel polymers shown in Scheme 2 are a further subject of the invention.

[0157] The synthesis of oligomers and small molecules based on the DTPI core is exemplarily illustrated in Scheme 3. Alternatively these compounds can be obtained via a convergent synthesis strategy as shown in Scheme 4. Therein Y and R^1 are as defined in formula I, X_1 = Br and X_2 = SnR'_3 or $B(OR')_2$ or X_1 = SnR'_3 and X_2 = Br or X_1 = $B(OR')_2$ and X_2 = Br, $Ar_{1\text{-}8}$ correspond to $Ar^{1\text{-}8}$ as defined in formula VI, and Ar_5-Ar_6-Ar_7-Ar_8-R^2_{end} is identical to Ar_4-Ar_3-Ar_2-Ar_1-R^1_{end}, and R^1_{end} and R^2_{end} correspond to R^{1t} and R^{2t} in formula VI.

Scheme 3

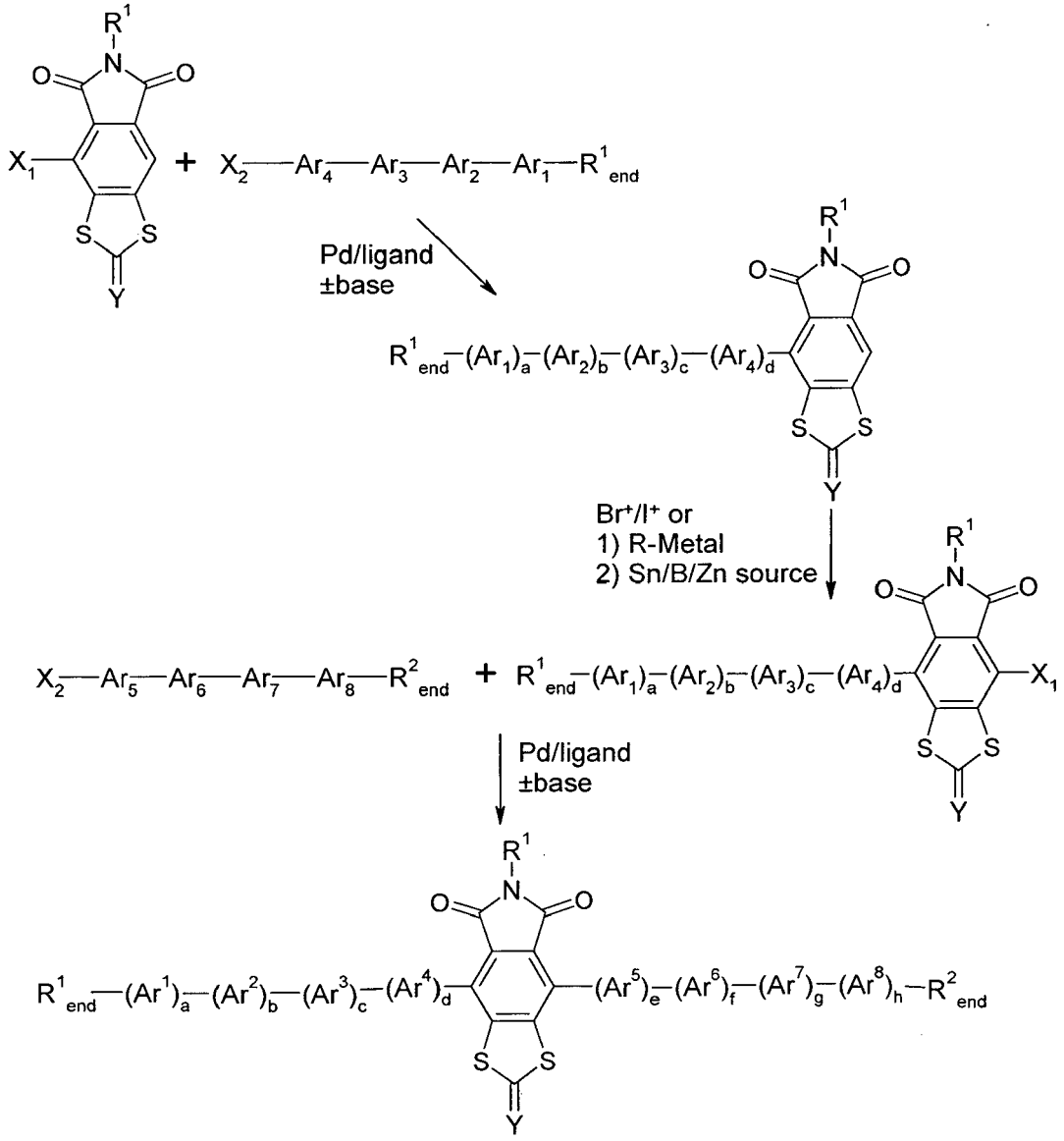


Scheme 4



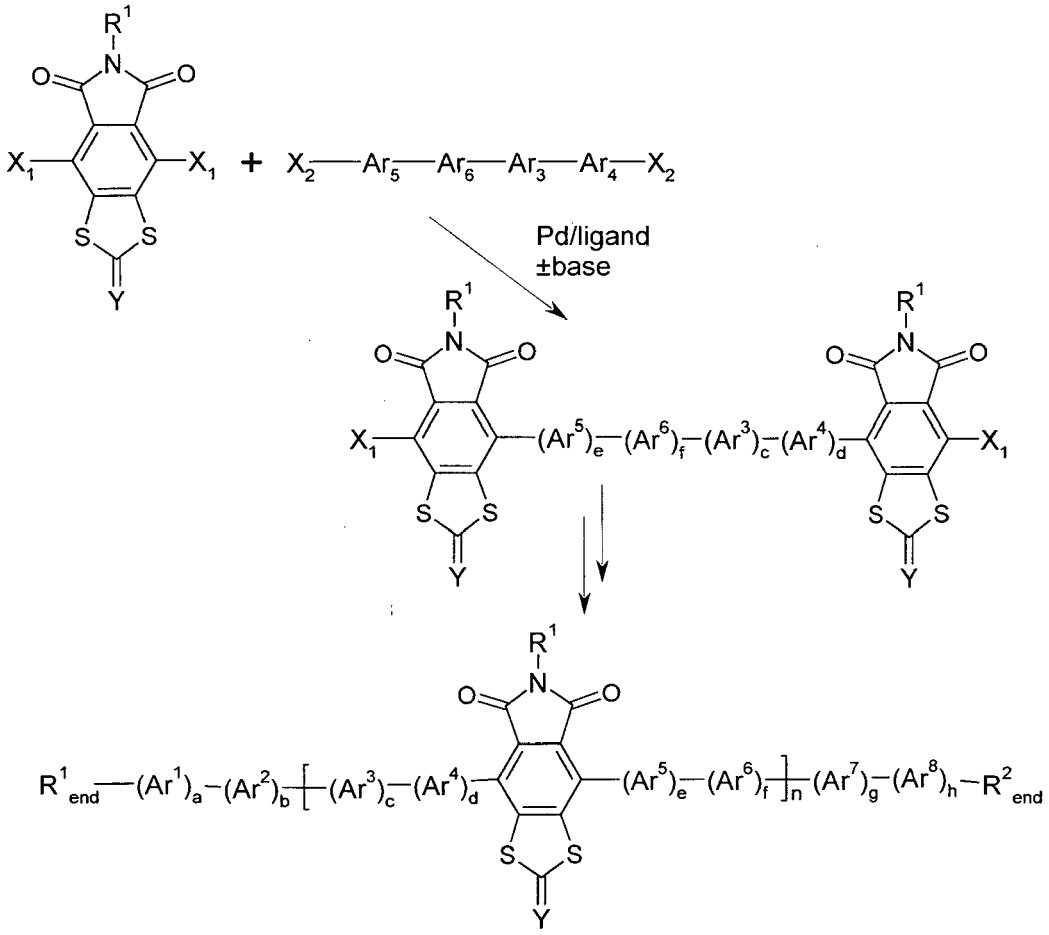
[0158] Alternatively asymmetric small molecules based on DTPI can be obtained via a convergent synthesis strategy as shown in Scheme 5, wherein the individual radicals are as defined in Scheme 3 and 4.

Scheme 5



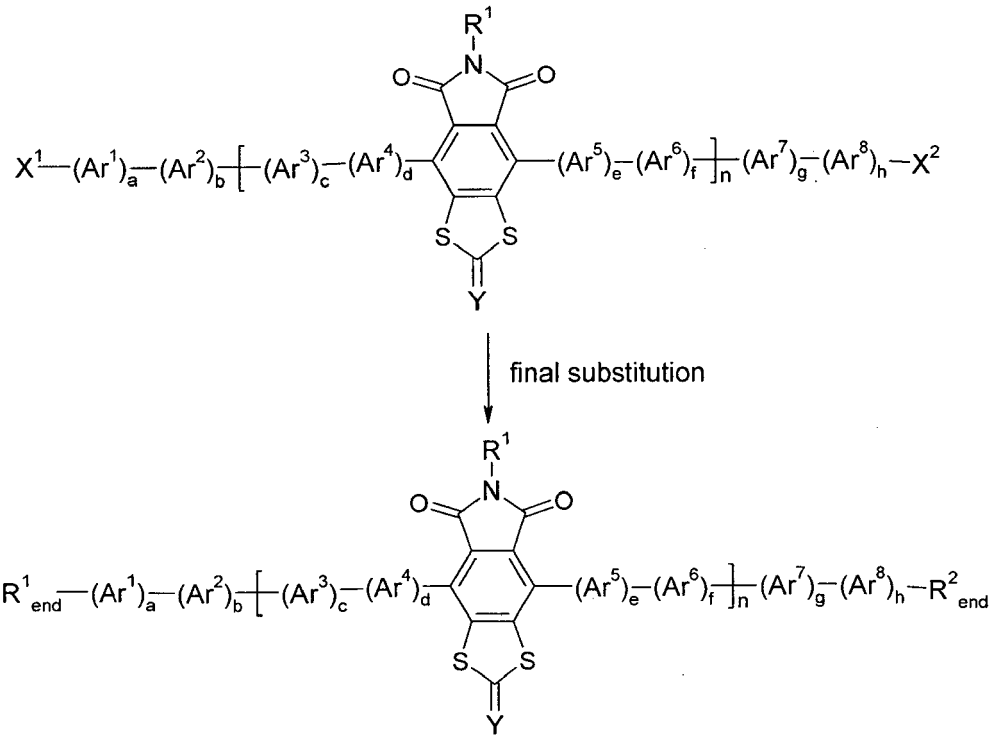
[0159] The synthesis of asymmetric compounds containing multiple DTPI units via a convergent synthesis strategy is shown in Scheme 6, wherein the individual radicals are as defined in Scheme 3, and $1<n\leq 3$.

Scheme 6



[0160] Further substitution can be added to the DTPI core at the $R^{1,2}{}_{end}$ substitution after the DTPI core compounds have been prepared as shown in Scheme 7, wherein the individual radicals are as defined in Scheme 6.

Scheme 7



[0161] The novel methods of preparing a compound, monomer or polymer as described above and below, and the novel monomers and intermediates used therein, are further aspects of the invention.

[0162] The polymer according to the present invention can also be used in mixtures or polymer blends, for example together with monomeric compounds or together with other polymers having charge-transport, semiconducting, electrically conducting, photoconducting and/or light-emitting semiconducting properties, or for example with polymers having hole blocking, electron blocking properties for use as interlayers, charge blocking layers, charge transporting layer in OLED devices, OPV devices or pervorskite based solar cells. Thus, another aspect of the invention relates to a polymer blend comprising one or more polymers according to the present invention and one or more further polymers having one or more of the above-mentioned properties. These blends can be prepared by conventional methods that are described in prior art and known to the skilled person. Typically the polymers are mixed with each other or dissolved in suitable solvents and the solutions combined.

[0163] Another aspect of the invention relates to a formulation comprising one or more polymers, polymer blends or mixtures as described above and below and one or more organic solvents.

[0164] Preferred solvents are aliphatic hydrocarbons, chlorinated hydrocarbons, aromatic hydrocarbons, ketones, ethers and mixtures thereof. Additional solvents which can be used include 1,2,4-trimethylbenzene, 1,2,3,4-tetramethyl benzene, pentylbenzene, mesitylene, cumene, cymene, cyclohexylbenzene, diethylbenzene, tetralin, decalin, 2,6-lutidine, 2-fluoro-m-xylene, 3-fluoro-o-xylene, 2-chlorobenzotrifluoride, N,N-dimethylformamide, 2-chloro-6-fluorotoluene, 2-fluoroanisole, anisole, 2,3-dimethylpyrazine, 4-fluoroanisole, 3-fluoroanisole, 3-trifluoro-methylanisole, 2-methylanisole, phenetol, 4-methylanisole, 3-methylanisole, 4-fluoro-3-methylanisole, 2-fluorobenzonitrile, 4-fluoroveratrol, 2,6-dimethylanisole, 3-fluorobenzo-nitrile, 2,5-dimethylanisole, 2,4-dimethylanisole, benzonitrile, 3,5-dimethyl-anisole, N,N-dimethylaniline, ethyl benzoate, 1-fluoro-3,5-dimethoxy-benzene, 1-methylnaphthalene, 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 or mixture of o-, m-, and p-isomers. Solvents with relatively low polarity are generally preferred. For inkjet printing solvents and solvent mixtures with high boiling temperatures are preferred. For spin coating alkylated benzenes like xylene and toluene are preferred.

[0165] Examples of especially preferred solvents include, without limitation, dichloromethane, trichloromethane, tetrachloromethane, chlorobenzene, o-dichlorobenzene, 1,2,4-trichlorobenzene, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, 1,8-diiodooctane, 1-chloronaphthalene, 1,8-octane-dithiol, anisole, 2,5-di-methylanisole, 2,4-dimethylanisole, toluene, o-xylene, m-xylene, p-xylene, mixture of o-, m-, and p-xylene isomers, 1,2,4-trimethylbenzene, mesitylene, cyclohexane, 1-methyhaphthatene, 2-methylnaphthalene, 1,2-dimethylnaphthalene, te-

traline, decaline, indane, 1-methyl-4-(1-methylethenyl)-cyclohexene (d-Limonene), 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptanes (β-pinene), methyl benzoate, ethyl benzoate, nitrobenzene, benzaldehyde, tetrahydrofuran, 1,4-dioxane, 1,3-dioxane, morpholine, acetone, methylethylketone, ethyl acetate, n-butyl acetate, N,N-dimethylformamide, dimethylacetamide, dimethylsulfoxide and/or mixtures thereof.

[0166] The concentration of the 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.

[0167] 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.

[0168] The polymer 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 polymer according to the present invention can be carried out for example by photolithography, electron beam lithography or laser patterning.

[0169] For use as thin layers in electronic or electrooptical devices the polymers, polymer blends or formulations of the present invention may be deposited by any suitable method. Liquid coating of devices is more desirable than vacuum deposition techniques. Solution deposition methods are especially preferred. The formulations of the present invention enable the use of a number of liquid coating techniques. Preferred deposition techniques include, without limitation, dip coating, spin coating, ink jet printing, nozzle printing, letter-press printing, screen printing, gravure printing, doctor blade coating, roller printing, reverse-roller printing, offset lithography printing, dry offset lithography printing, flexographic printing, web printing, spray coating, curtain coating, brush coating, slot dye coating or pad printing.

[0170] Ink jet printing is particularly preferred when high resolution layers and devices needs to be prepared.Selected formulations of the present invention may be applied to prefabricated device substrates by ink jet printing or microdispensing. Preferably industrial piezoelectric print heads such as but not limited to those supplied by Aprion, Hitachi-Koki, InkJet Technology, On Target Technology, Picojet, Spectra, Trident, Xaar may be used to apply the organic semiconductor layer to a substrate. Additionally semi-industrial heads such as those manufactured by Brother, Epson, Konica, Seiko Instruments Toshiba TEC or single nozzle microdispensers such as those produced by Microdrop and Microfab may be used.

[0171] In order to be applied by ink jet printing or microdispensing, the polymers should be first dissolved in a suitable solvent. Solvents must fulfil the requirements stated above and must not have any detrimental effect on the chosen print head. Additionally, solvents should have boiling points >100°C, preferably >140°C and more preferably >150°C in order to prevent operability problems caused by the solution drying out inside the print head. Apart from the solvents mentioned above, suitable solvents include substituted and non-substituted xylene derivatives, di-C_{1-2}-alkyl formamide, substituted and non-substituted anisoles and other phenol-ether derivatives, substituted heterocycles such as substituted pyridines, pyrazines, pyrimidines, pyrrolidinones, substituted and non-substituted *N,N*-di-C_{1-2}-alkylanilines and other fluorinated or chlorinated aromatics.

[0172] A preferred solvent for depositing a polymer according to the present invention by ink jet printing comprises a benzene derivative which has a benzene ring substituted by one or more substituents wherein the total number of carbon atoms among the one or more substituents is at least three. For example, the benzene derivative may be substituted with a propyl group or three methyl groups, in either case there being at least three carbon atoms in total. Such a solvent enables an ink jet fluid to be formed comprising the solvent with the compound or polymer, which reduces or prevents clogging of the jets and separation of the components during spraying. The solvent(s) may include those selected from the following list of examples: dodecylbenzene, 1-methyl-4-tert-butylbenzene, terpineol, limonene, isodurene, terpinolene, cymene, diethylbenzene. The solvent may be a solvent mixture, that is a combination of two or more solvents, each solvent preferably having a boiling point >100°C, more preferably >140°C. Such solvent(s) also enhance film formation in the layer deposited and reduce defects in the layer.

[0173] 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.

[0174] The polymers, polymer blends, mixtures and formulations according to the present invention can additionally comprise one or more further components or additives selected for example from surface-active compounds, lubricating agents, wetting agents, dispersing agents, hydrophobing agents, adhesive agents, flow improvers, defoaming agents, deaerators, diluents which may be reactive or non-reactive, auxiliaries, colourants, dyes or pigments, sensitizers, stabilizers, nanoparticles or inhibitors.

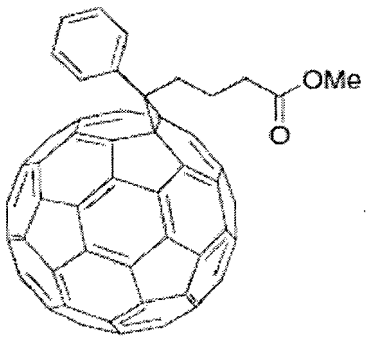
[0175] The polymers, polymer blends and mixtures according to the present invention are useful as charge transport, semiconducting, electrically conducting, photoconducting or light emitting material in optical, electrooptical, electronic, electroluminescent or photoluminescent components or devices. In these devices, a polymer, polymer blend or mixture of the present invention is typically applied as a thin layer or film.

[0176] Thus, the present invention also provides the use of the polymer, polymer blend, mixture or layer in an electronic device. The formulation may be used as a high mobility semiconducting material in various devices and apparatus. The formulation 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, mixture or polymer blend according to the invention. The layer or film may be less than about 30 microns. For various electronic device applications, the thickness may be less than about 1 micron thick. The layer may be deposited, for example on a part of an electronic device, by any of the aforementioned solution coating or printing techniques.

[0177] The invention additionally provides an electronic device comprising a polymer, polymer blend, mixture or organic semiconducting layer according to the present invention. Especially preferred devices are OTFTs, TFTs, ICs, logic circuits, capacitors, RFID tags, OLEDs, OLETs, OPEDs, OPVs, OPDs, solar cells, laser diodes, photoconductors, photodetectors, electrophotographic devices, electrophotographic recording devices, organic memory devices, sensor devices, charge injection layers, Schottky diodes, planarising layers, antistatic films, conducting substrates and conducting patterns.

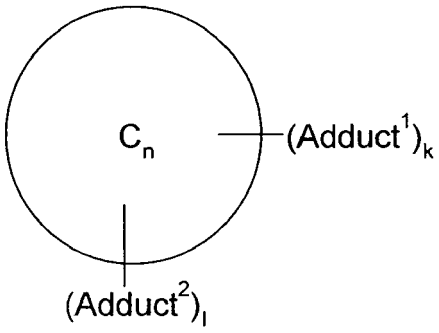
[0178] Especially preferred electronic device are OTFTs, OLEDs, OPV and OPD devices, in particular bulk heterojunction (BHJ) OPV devices. In an OTFT, for example, the active semiconductor channel between the drain and source may comprise the layer of the invention. As another example, in an OLED device, the charge (hole or electron) injection or transport layer may comprise the layer of the invention.

[0179] For use in OPV or OPD devices the polymer according to the present invention is preferably used in a formulation that comprises or contains, more preferably consists essentially of, very preferably exclusively of, one or more p-type (electron donor) semiconductor and one or more n-type (electron acceptor) semiconductor. The p-type semiconductor is constituted of a least one polymer according to the present invention. The n-type semiconductor can be an inorganic material such as zinc oxide (ZnO_x), zinc tin oxide (ZTO), titanium oxide (TiO_x), molybdenum oxide (MoO_x), nickel oxide (NiO_x), or cadmium selenide (CdSe), or an organic material such as graphene or a fullerene, a conjugated polymer or substituted fullerene, for example a (6,6)-phenyl-butyric acid methyl ester derivatized methano C_{60} fullerene, also known as "PCBM-C_{60}" or "C_{60}PCBM", as disclosed for example in Science 1995, 270, 1789 and having the structure shown below, or structural analogous compounds with e.g. a C_{70} fullerene group or an organic polymer (see for example Coakley, K. M. and McGehee, M. D. Chem. Mater. 2004, 16, 4533).



PCBM-C_{60}

[0180] Preferably the polymer according to the present invention is blended with an n-type semiconductor such as a fullerene or substituted fullerene of formula XII to form the active layer in an OPV or OPD device wherein,



XII

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

$Adduct^1$ is a primary adduct appended to the fullerene C_n with any connectivity,

$Adduct^2$ is a secondary adduct, or a combination of secondary adducts, appended to the fullerene C_n with any connectivity,

k is an integer ≥ 1,

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

[0181] In the formula XII and its subformulae, k preferably denotes 1, 2, 3 or, 4, very preferably 1 or 2.

[0182] The fullerene C_n in formula XII 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.

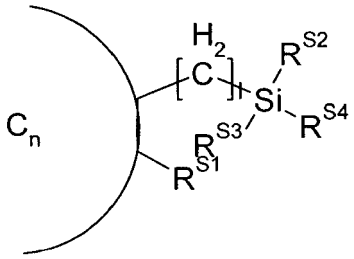
[0183] The fullerene C_n in formula XII and its subformulae is preferably selected from carbon based fullerenes, endohedral fullerenes, or mixtures thereof, very preferably from carbon based fullerenes.

[0184] Suitable and preferred carbon based fullerenes include, without limitation, $(C_{60\text{-}1h})$[5,6]fullerene, $(C_{70\text{-}D5h})$[5,6]fullerene, $(C_{76\text{-}D2^*})$[5,6]fullerene, $(C_{84\text{-}D2^*})$[5,6]fullerene, $(C_{84\text{-}D2d})$[5,6]fullerene, or a mixture of two or more of the aforementioned carbon based fullerenes.

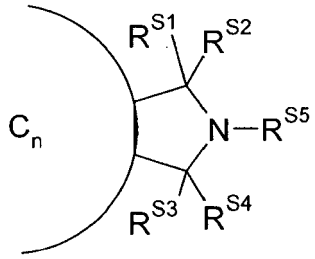
[0185] The endohedral fullerenes are preferably metallofullerenes. Suitable and preferred metallofullerenes include, without limitation, $La@C_{60}$, $La@C_{82}$, $Y@C_{82}$, $Sc_3N@C_{80}$, $Y_3N@C_{80}$, $Sc_3C_2@C_{80}$ or a mixture of two or more of the aforementioned metallofullerenes.

[0186] 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.

[0187] Primary and secondary adduct, named "Adduct" in formula XII and its subformulae, is preferably selected from the following formulae



S-1



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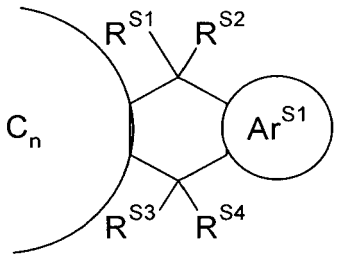

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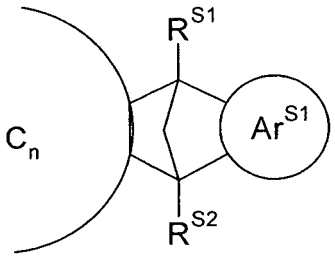

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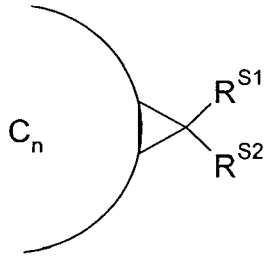

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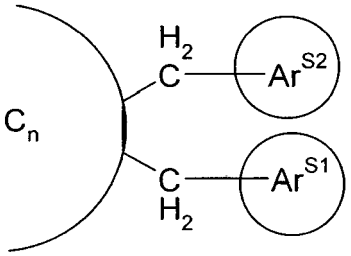

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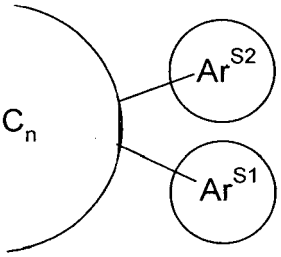

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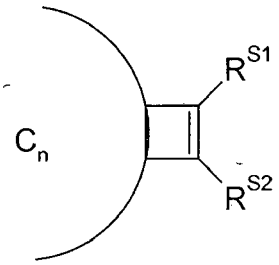

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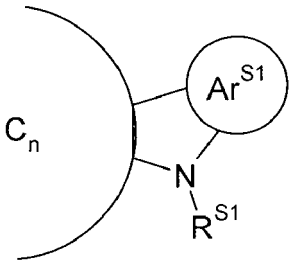

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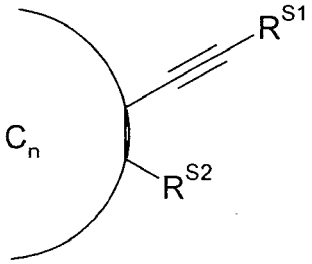

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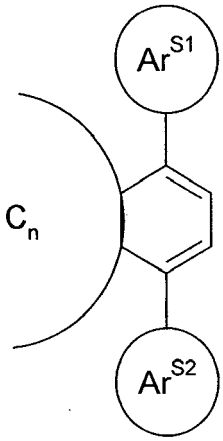

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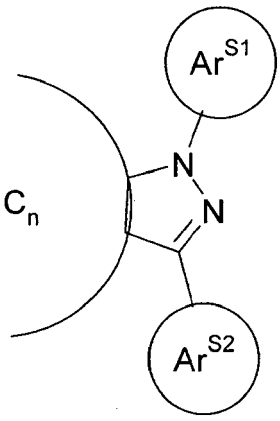

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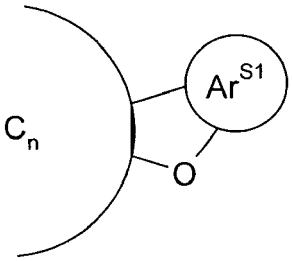

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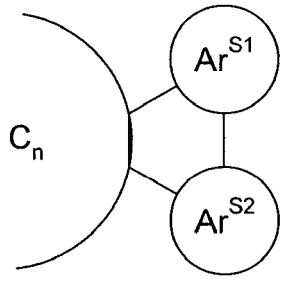
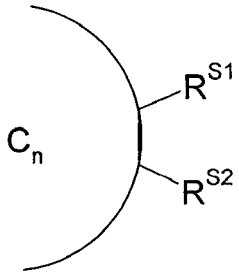


S-14



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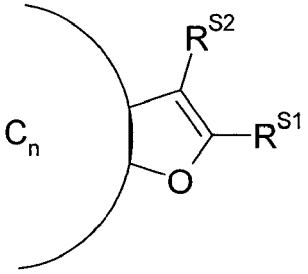

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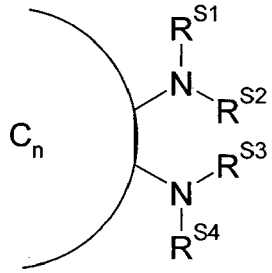
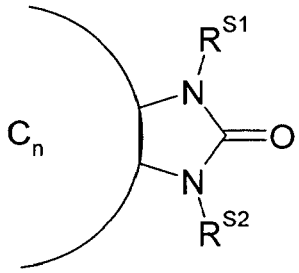
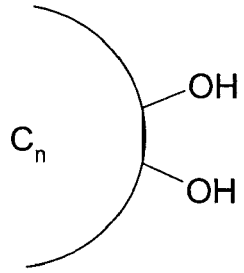


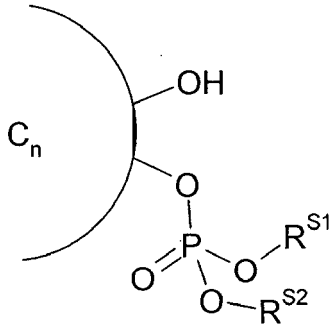
S-17



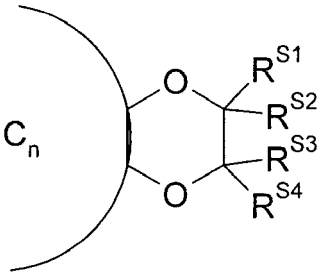
S-18



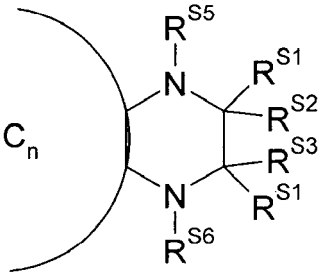
S-19



S-20



S-21



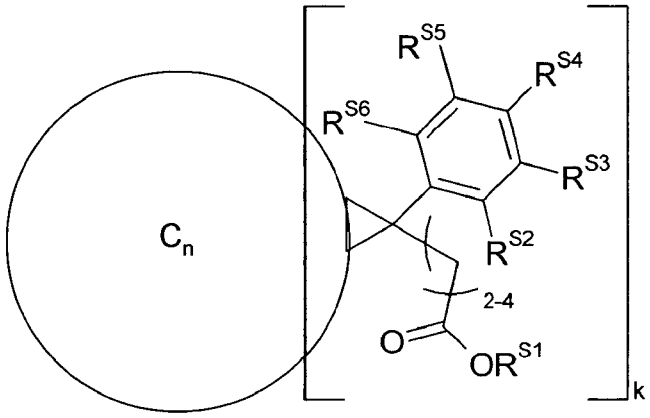
S-22

wherein C_n is as defined in formula XII,

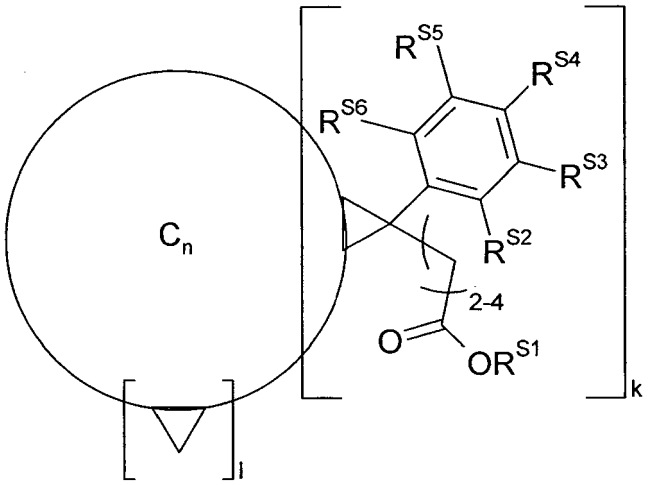
Ar^{S1}, Ar^{S2} denote, independently of each other, an arylene or heteroarylene group with 5 to 20, preferably 5 to 15, ring atoms, which is mono- or polycyclic, and which is optionally substituted by one or more identical or different substituents having one of the meanings of L as defined above and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

[0188] R^{S1}, R^{S2}, R^{S3}, R^{S4}, R^{S5} and R^{S6} independently of each other denote H, CN or have one of the meanings of L as defined above and below.

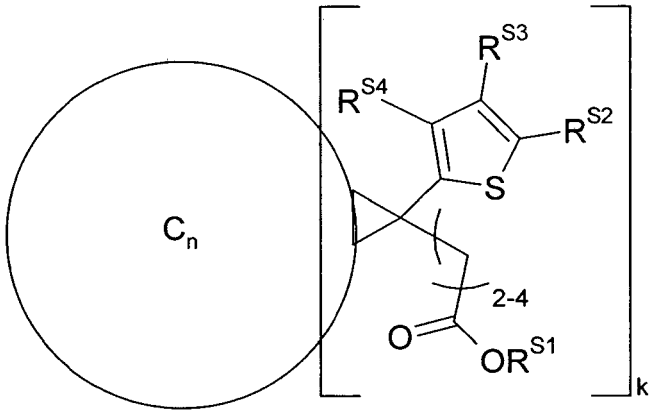
[0189] Preferred compounds of formula XII are selected from the following subformulae:



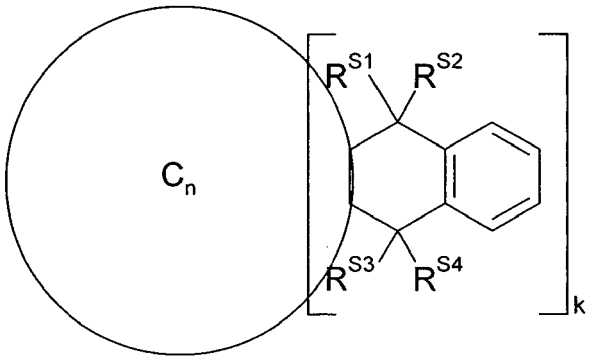
XIIa



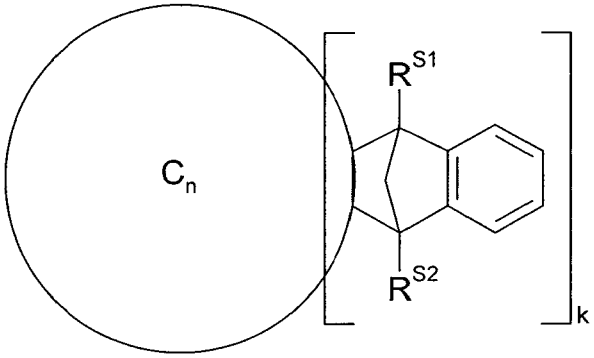
XIIb



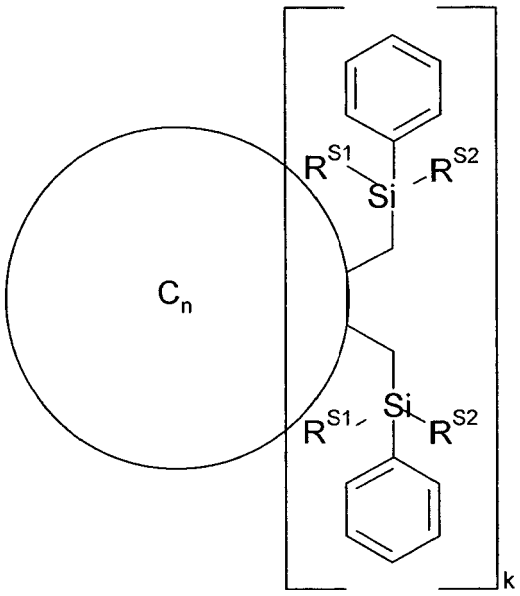
XIIc



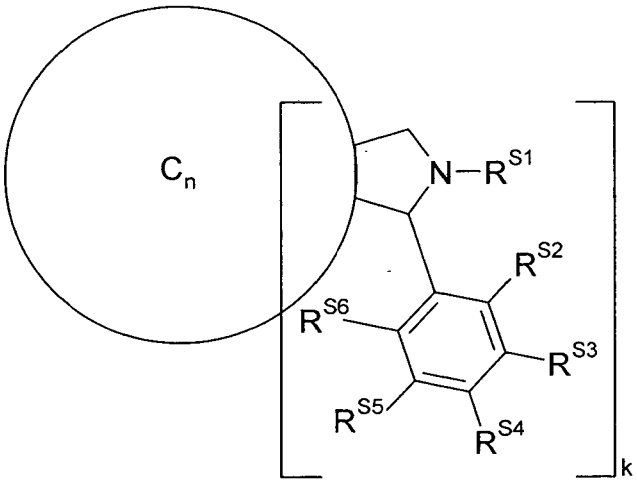
XIId



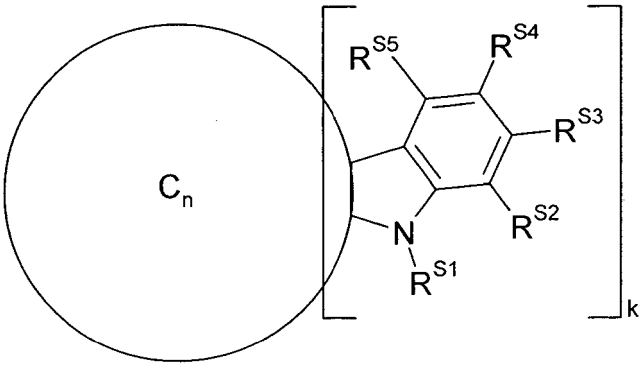
XIIe



XIIf



XIIg



XIIh

wherein C_n, k and l are as defined in formula XII, and
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 L as defined above and below.

[0190] Also preferably the polymer according to the present invention is blended with other type of n-type semiconductor such as graphene, a metal oxide, like for example, ZnOx, TiOx, ZTO, MoOx, NiOx, quantum dots, like for example, CdSe or CdS, or a conjugated polymer, like for example a polynaphthalenediimide or polyperylenediimide as described, for example, in WO2013142841 A1 to form the active layer in an OPV or OPD device.

[0191] The device preferably further comprises a first transparent or semi-transparent electrode on a transparent or semi-transparent substrate on one side of the active layer, and a second metallic or semi-transparent electrode on the other side of the active layer.

[0192] Preferably, the active layer according to the present invention is further blended with additional organic and inorganic compounds to enhance the device properties. For example, metal particles such as Au or Ag nanoparticules or Au or Ag nanoprism for enhancements in light harvesting due to near-field effects (i.e. plasmonic effect) as described, for example in Adv. Mater. 2013, 25 (17), 2385-2396 and Adv. Ener. Mater. 2014, 4, 1400206, a molecular dopant such as 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane for enhancement in photoconductivity as described, for example in Adv. Mater. 2013, 25(48), 7038-7044, or a stabilising agent consisting of a UV absorption agent and/or anti-radical agent and/or antioxidant agent such as 2-hydroxybenzophenone, 2-hydroxyphenylbenzotriazole, oxalic acid anilides, hydroxyphenyl triazines, merocyanines, hindered phenol, N-aryl-thiomorpholine, N-aryl-thiomorpholine-1-oxide, N-aryl-thiomorpholine-1,1 -dioxide, N-aryl-thiazolidine, N-aryl-thiazolidine-1-oxide, N-aryl-thiazolidine-1,1-dioxide and 1,4-diazabicyclo[2.2.2]octane as described, for example, in WO2012095796 A1 and in WO2013021971 A1.

[0193] The device preferably may further comprise a UV to visible photo-conversion layer such as described, for example, in J. Mater. Chem. 2011, 21, 12331 or a NIR to visible or IR to NIR photo-conversion layer such as described, for example, in J. Appl. Phys. 2013, 113, 124509.

[0194] Further preferably the OPV or OPD device comprises, between the active layer and the first or second electrode, one or more additional buffer layers acting as hole transporting layer and/or electron blocking layer, which comprise a material such as metal oxides, like for example, ZTO, MoO_x, NiO_x, a doped conjugated polymer, like for example

PEDOT:PSS and polypyrrole-polystyrene sulfonate (PPy:PSS), a conjugated polymer, like for example polytriarylamine (PTAA), an organic compound, like for example substituted triaryl amine derivatives such as 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), graphene based materials, like for example, graphene oxide and graphene quantum dots or alternatively as hole blocking layer and/or electron transporting layer, which comprise a material such as metal oxide, like for example, ZnO_x, TiO_x, AZO (aluminium doped zinc oxide), 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)], a polymer, like for example poly(ethyleneimine) or crosslinked N-containing compound derivatives or an organic compound, like for example tris(8-quinolinolato)-aluminium(III) (Alq_3), phenanthroline derivative or C_{60} or C_{70} based fullerenes, like for example, as described in Adv. Energy Mater. 2012, 2, 82-86.

[0195] In a blend or mixture of a polymer according to the present invention with a fullerene or modified fullerene, the ratio polymer:fullerene is preferably from 5:1 to 1:5 by weight, more preferably from 2:1 to 1:3 by weight, most preferably 1:1 to 1:2 by weight. A polymeric binder may also be included, from 5 to 95% by weight. Examples of binder include polystyrene (PS), polypropylene (PP) and polymethylmethacrylate (PMMA).

[0196] To produce thin layers in BHJ OPV devices the polymers, polymer blends or mixtures of the present invention may be deposited by any suitable method. Liquid coating of devices is more desirable than vacuum deposition techniques. Solution deposition methods are especially preferred. The formulations of the present invention enable the use of a number of liquid coating techniques. Preferred deposition techniques include, without limitation, dip coating, spin coating, ink jet printing, nozzle printing, letter-press printing, screen printing, gravure printing, doctor blade coating, roller printing, reverse-roller printing, offset lithography printing, dry offset lithography printing, flexographic printing, web printing, spray coating, curtain coating, brush coating, slot dye coating or pad printing. For the fabrication of OPV devices and modules area printing method compatible with flexible substrates are preferred, for example slot dye coating, spray coating and the like.

[0197] Suitable solutions or formulations containing a blend or mixture of a polymer according to the present invention with a fullerene or modified fullerene like PCBM are preferably prepared. In the preparation of such a formulation, suitable solvents are preferably selected to ensure full dissolution of both component, p-type and n-type and take into account the boundary conditions (for example rheological properties) introduced by the chosen printing method.

[0198] Organic solvent are generally used for this purpose. Typical solvents can be aromatic solvents, halogenated solvents or chlorinated solvents, including chlorinated aromatic solvents. Examples include, but are not limited to dichloromethane, trichloromethane, tetrachloromethane, chlorobenzene, o-dichlorobenzene, 1,2,4-trichlorobenzene, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, 1,8-diiodooctane, 1-chloronaphthalene, 1,8-octanedithiol, anisole, 2,5-di-methylanisole, 2,4-dimethylanisole, toluene, o-xylene, m-xylene, p-xylene, mixture of xylene o-, m-, and p-isomers, 1,2,4-trimethylbenzene, mesitylene, cyclohexane, 1-methylnaphthalene, 2-methylnaphthalene, 1,2-dimethylnaphthalene, tetraline, decaline, indane, 1-methyl-4-(1-methylethenyl)-cyclohexene (d-Limonene), 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptanes (β -pinene), methyl benzoate, ethyl benzoate, nitrobenzene, benzaldehyde, tetrahydrofuran, 1,4-dioxane, 1,3-dioxane, morpholine, acetone, methylethylketone, ethyl acetate, n-butyl acetate, N,N-dimethylformamide, dimethylacetamide, dimethylsulfoxide and/or mixtures thereof.

[0199] 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).

[0200] A first preferred OPV device according to the invention comprises the following layers (in the sequence from bottom to top):

- optionally a substrate,
- a high work function electrode, preferably comprising a metal oxide, like for example ITO and FTO, serving as anode,
- an optional conducting polymer layer or hole transport layer, preferably comprising an organic polymer or polymer blend, for example PEDOT:PSS (poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate), substituted triaryl amine derivatives, for example,TBD (N,N'-dyphenyl-N-N'-bis(3-methylphenyl)-1,1'biphenyl-4,4'-diamine) or NBD (N,N'-dyphenyl-N-N'-bis(1-napthylphenyl)-1,1'biphenyl-4,4'-diamine),
- a layer, also referred to as "active layer", comprising of at least one p-type and at least one n-type organic semiconductor, which can exist for example as a p-type/n-type bilayer or as distinct p-type and n-type layers, or as blend or p-type and n-type semiconductor, forming a BHJ,
- optionally a layer having electron transport properties, for example comprising LiF, TiO_x, ZnO_x, PFN, a poly(ethyleneimine) or crosslinked nitrogen containing compound derivatives or a phenanthroline derivatives
- a low work function electrode, preferably comprising a metal like for example aluminum, serving as cathode,

wherein at least one of the electrodes, preferably the anode, is transparent to visible and/or NIR light, and wherein at least one p-type semiconductor is a polymer according to the present invention.

[0201] A second preferred OPV device according to the invention is an inverted OPV device and comprises the following layers (in the sequence from bottom to top):

- optionally a substrate,
- a high work function metal or metal oxide electrode, comprising for example ITO and FTO, serving as cathode, a layer having hole blocking properties, preferably comprising a metal oxide like TiO_x or ZnO_x, or comprising an organic compound such as polymer like poly(ethyleneimine) or crosslinked nitrogen containing compound derivatives or phenanthroline derivatives,
- an active layer comprising at least one p-type and at least one n-type organic semiconductor, situated between the electrodes, which can exist for example as a p-type/n-type bilayer or as distinct p-type and n-type layers, or as blend or p-type and n-type semiconductor, forming a BHJ,
- an optional conducting polymer layer or hole transport layer, preferably comprising an organic polymer or polymer blend, for example of PEDOT:PSS or substituted triaryl amine derivatives, for example, TBD or NBD,
- an electrode comprising a high work function metal like for example silver, serving as anode, wherein at least one of the electrodes, preferably the cathode, is transparent to visible and/or NIR light, and wherein at least one p-type semiconductor is a polymer according to the present invention.

[0202] 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/fullerene systems or polymer/polymer systems, as described above

[0203] When the active layer is deposited on the substrate, it forms a BHJ that phase separates at nanoscale level. For discussion on nanoscale phase separation see Dennler et al, Proceedings of the IEEE, 2005, 93 (8), 1429 or Hoppe et al, Adv. Func. Mater, 2004, 14(10), 1005. An optional annealing step may be then necessary to optimize blend morpohology and consequently OPV device performance.

[0204] 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, 1-chloronaphthalene, N,N-dimethylformamide, dimethylacetamide, dimethylsulfoxide and other additives have been used to obtain high-efficiency solar cells. Examples are disclosed in J. Peet, et al, Nat. Mater., 2007, 6, 497 or Frechet et al. J. Am. Chem. Soc., 2010, 132, 7595-7597.

[0205] The polymers, polymer blends, mixtures and layers of the present invention are also suitable for use in an OTFT as the semiconducting channel. Accordingly, the invention also provides an OTFT 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, polymer blend, mixture or organic semiconducting layer according to the present invention. Other features of the OTFT are well known to those skilled in the art.

[0206] OTFTs where an OSC material is arranged as a thin film between a gate dielectric and a drain and a source electrode, are generally known, and are described for example in US 5,892,244, US 5,998,804, US 6,723,394 and in the references cited in the background section. Due to the advantages, like low cost production using the solubility properties of the compounds according to the invention and thus the processibility of large surfaces, preferred applications of these FETs are such as integrated circuitry, TFT displays and security applications.

[0207] The gate, source and drain electrodes and the insulating and semiconducting layer in the OTFT 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.

[0208] An OTFT device according to the present invention preferably comprises:

- a source electrode,
- a drain electrode,
- a gate electrode,
- a semiconducting layer,
- one or more gate insulator layers,
- optionally a substrate.

wherein the semiconductor layer preferably comprises a polymer, polymer blend or mixture according to the present invention.

[0209] The OTFT device can be a top gate device or a bottom gate device. Suitable structures and manufacturing methods of an OTFT device are known to the skilled in the art and are described in the literature, for example in US 2007/0102696 A1.

[0210] The gate insulator layer preferably comprises a fluoropolymer, like e.g. the commercially available Cytop 809M®

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

[0211] In security applications, OTFTs and other devices with semiconducting materials according to the present invention, like transistors or diodes, can be used for RFID tags or security markings to authenticate and prevent counterfeiting of documents of value like banknotes, credit cards or ID cards, national ID documents, licenses or any product with monetry value, like stamps, tickets, shares, cheques etc.

[0212] Alternatively, the polymers, polymer blends and mixtures according to the 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 emissive layer where their recombination leads to the excitation and hence luminescence of the lumophor units contained in the emission layer.

[0213] The polymers, polymer blends and mixtures according to the invention can be employed in one or more of a buffer layer, electron or hole transport layer, electron or hole blocking layer and emissive layer, corresponding to their electrical and/or optical properties. Furthermore their use within the emissive layer is especially advantageous, if the compounds, materials and films according to the 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.

[0214] According to another use, the polymers, polymer blends and mixtures according to this 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.

[0215] A further aspect of the invention relates to both the oxidised and reduced form of a polymer according to this invention. Either loss or gain of electrons results in formation of a highly delocalised 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.

[0216] The doping process typically implies treatment of the semiconductor material with an oxidating or reducing agent in a redox reaction to form delocalised ionic centres 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-implantantion of the dopant into the semiconductor material.

[0217] When electrons are used as carriers, suitable dopants are for example halogens (e.g., I_2, Cl_2, Br2, ICl, ICl_3, IBr and IF), Lewis acids (e.g., PF_5, AsFs, SbF_5, BF_3, BCl_3, $SbCl_5$, BBr_3 and SO_3), protonic acids, organic acids, or amino acids (e.g., HF, HCl, HNO_3, H_2SO_4, $HClO_4$, FSO_3H and $ClSO_3H$), transition metal compounds (e.g., $FeCl_3$, FeOCl, $Fe(ClO_4)_3$, $Fe(4\text{-}CH_3C_6H_4SO_3)_3$, TiCl4, $ZrCl_4$, $HfCl_4$, NbF_5, $NbCl_5$, $TaCl_5$, MoF_5, $MoCl_5$, WFs, WCl_6, UF_6 and $LnCl_3$ (wherein Ln is a lanthanoid), anions (e.g., Cl^-, Br^-, I^-, I_3^-, HSO_4^-, SO_4^{2-}, NO_3^-, ClO_4^-, BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, $FeCl_4^-$, $Fe(CN)_6^{3-}$, and anions of various sulfonic acids, such as aryl-SO_3^-). When holes are used as carriers, examples of dopants are cations (e.g., H^+, Li^+, Na^+, K^+, Rb^+ and Cs^+), alkali metals (e.g., Li, Na, K, Rb, and Cs), alkaline-earth metals (e.g., Ca, Sr, and Ba), O_2, $XeOF_4$, (NO_2^+) (SbF_6^-), (NO_2^+) $(SbCl_6^-)$, (NO_2^+) (BF_4^-), $AgClO_4$, H_2IrCl_6, $La(NO_3)_3 \cdot 6H_{2O}$, FSO_2OOSO_2F, Eu, acetylcholine, R_4N^+, (R is an alkyl group), R_4P^+ (R is an alkyl group), R_6As^+ (R is an alkyl group), and R_3S^+ (R is an alkyl group).

[0218] The conducting form of a polymer of the present invention can be used as an organic "metal" in applications including, but not limited to, charge injection layers and ITO planarising 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.

[0219] The polymers, polymer blends and mixtures 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.

[0220] According to another use, the polymers 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 polymers according to the present invention can increase the electrical conductivity of the

alignment layer. When used in an LCD, this increased electrical conductivity can reduce adverse residual dc effects in the switchable LCD cell and suppress image sticking or, for example in ferroelectric LCDs, reduce the residual charge produced by the switching of the spontaneous polarisation charge of the ferroelectric LCs. When used in an OLED device comprising a light emitting material provided onto the alignment layer, this increased electrical conductivity can enhance the electroluminescence of the light emitting material. The polymers according to the present invention having mesogenic or liquid crystalline properties can form oriented anisotropic films as described above, which are especially useful as alignment layers to induce or enhance alignment in a liquid crystal medium provided onto said anisotropic film. The polymers according to the present invention may also be combined with photoisomerisable compounds and/or chromophores for use in or as photoalignment layers, as described in US 2003/0021913 A1.

[0221] According to another use the polymers, polymer blends and mixtures according to the present invention, especially their water-soluble derivatives (for example with polar or ionic side groups) or ionically doped forms, can be employed as chemical sensors or materials for detecting and discriminating DNA sequences. Such uses are described for example in L. Chen, D. W. McBranch, H. Wang, R. Helgeson, F. Wudl and D. G. Whitten, Proc. Natl. Acad. Sci. U.S.A., 1999, 96, 12287; D. Wang, X. Gong, P. S. Heeger, F. Rininsland, G. C. Bazan and A. J. Heeger, Proc. Natl. Acad. Sci. U.S.A., 2002, 99, 49; N. DiCesare, M. R. Pinot, K. S. Schanze and J. R. Lakowicz, Langmuir, 2002, 18, 7785; D. T. McQuade, A. E. Pullen, T. M. Swager, Chem. Rev., 2000, 100, 2537.

[0222] 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.

[0223] 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.

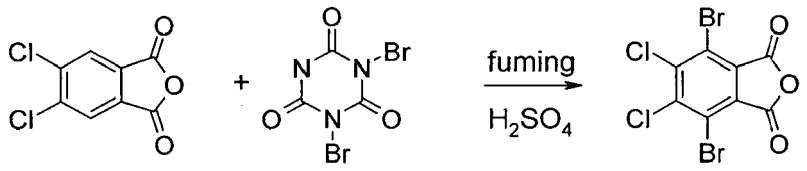
[0224] Above and below, unless stated otherwise percentages are percent by weight and temperatures are given in degrees Celsius. The values of the dielectric constant ε ("permittivity") refer to values taken at 20°C and 1,000 Hz.

[0225] The invention will now be described in more detail by reference to the following examples, which are illustrative only and do not limit the scope of the invention.

Example 1

3,6-Dibromo-4,5-dichlorophthalic anhydride (1.1)

[0226]



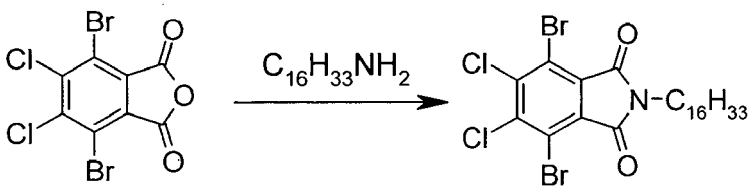
(1.1)

[0227] 4,5-Dichlorophthalic anhydride (11.43 g, 51.60 mmol) was added into stirred fuming sulfuric acid (100 cm^3) and the mixture was heated to 80 °C and stirred for 30 minutes to afford a clear solution. Dibromoisocyanuric acid (16.78 g, 56.74 mmol) was added in small portions under the heating and stirring conditions and the mixture was stirred at 80 °C for 20 hours after the addition to yield an orange suspension. The suspension was cooled to 23 °C then poured onto crushed ice (ca 1 kg). The solid was collected by filtration and washed with water three times then with methanol twice.

[0228] The solid was boiled in water (600 cm^3) then cooled, suction filtered, washed with water then air-dried. The boiling, filtering and washing process was repeated three times and the solid was finally washed with methanol and dried to yield 3,6-dibromo-4,5-dichlorophthalimide (1.1) (16.14 g, 83%) as a white solid ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.70, 135.70, 135.11, 119.97, 39.50. MS (EI) m/z 374.

3.6-Dibromo-4.5-dichloro-N-hexadecylphthalimide (1.2)

[0229]

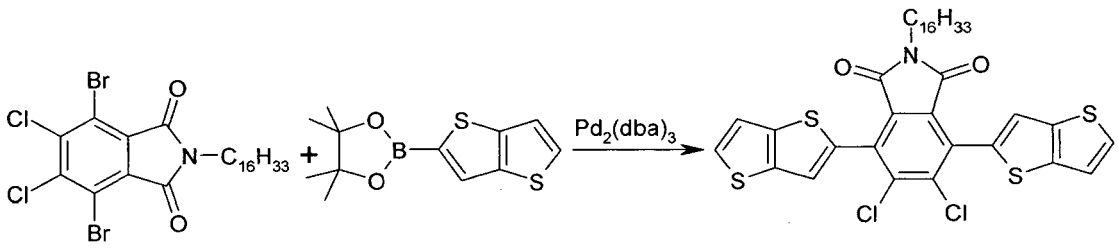


(1.1) (1.2)

[0230] A round bottom flask was charged with 4,7-dibromo-5,6-dichlorophthalic anhydride (1.1) (3.70 g, 9.87 mmol), hexadecylamine (2.62 g, 10.86 mmol) and propionic acid (40 cm^3). The mixture was stirred at 140 °C (external) for 3 hours and then cooled to 23 °C where a precipitate occurred. Ethanol (50 cm^3) was added and the solid collected by filtration, washed with ethanol then methanol to give 3,6-dibromo-4,5-dichloro-N-hexadecylphthalimide (1.2) (5.10 g, 86%) as a white crystalline solid. MS (EI) m/z 597. ^{1}H NMR (400 MHz, CDCb) δ 3.69 (t, *J* = 7.3 Hz, 2H), 1.66 (m, *J* = 7.2 Hz, 2H), 1.31 (s, 6H), 1.24 (s, 20H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CDCb) δ 163.79, 141.44, 129.95, 119.22, 39.11, 31.92, 29.68, 29.67, 29.64, 29.60, 29.54, 29.41, 29.35, 29.09, 28.20, 26.78, 22.68, 14.11.

4.5-Dichloro-3.6-bis(thieno[3,2-b]thiophen-2-yl)-N-hexadecylphthalimide (1.3)

[0231]

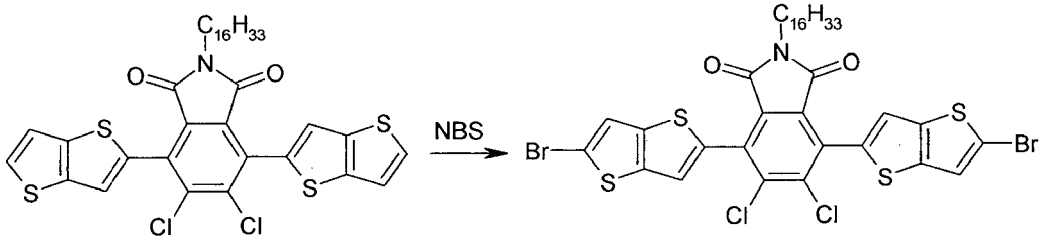


(1.2) (1.3)

[0232] A mixture of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thieno[3,2-b]thiophene (1.757 g, 6.600 mmol), 3,6-dibromo-4,5-dichloro-N-hexadecylphthalimide (1.2) (1.80 g, 3.00 mmol) and sodium carbonate 2 M aqueous solution (6.6 cm^3, 13.20 mmol) with toluene (40 cm^3) and THF (10.0 cm^3) was degassed by bubbling nitrogen for 20 minutes. The mixture of tris(dibenzylideneacetone)dipalladium(0) (55 mg, 0.060 mmol) and tri-o-tolylphosphine (73 mg, 0.24 mmol) was added in one portion and the mixture was degassed with nitrogen for an additional 10 minutes. The mixture was heated at reflux for 16 hours. The mixture was cooled to 23 °C and the solvents were removed by rotary evaporation *in vacuo*. The residue was triturated with methanol then suction filtered and the solid washed with methanol, water and methanol. The crude was purified by column chromatogaphy (1:1 v/v dichloromethane-petroleum ether (40-60)) to give 4,5-dichloro-3,6-bis(thieno[3,2-b]thiophen-2-yl)-N-hexadecylphthalimide (1.3) (1.01 g, 47%) as a bright yellow microcrystalline solid. ^{1}HNMR (400 MHz, DCM-d_2) δ 7.50 (d, *J* = 5.3 Hz, 2H), 7.36 (dd, *J* = 5.3, 0.7 Hz, 2H), 7.32 (d, *J* = 0.7 Hz, 2H), 3.51 (q, *J* = 8.0 Hz, 2H), 1.53 (s, 2H), 1.34 - 1.13 (m, 26H), 0.86 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 165.32, 141.22, 141.05, 139.11, 134.70, 133.31, 130.00, 128.59, 122.01, 119.82, 38.84, 32.27, 30.03, 30.00, 29.96, 29.89, 29.77, 29.70, 29.43, 28.52, 27.15, 23.04, 14.24.

3,6-Bis(5-bromothieno[3.2-b]thiophen-2-yl)-4.5-dichloro-N-hexadecylphthalimide (1.4)

[0233]

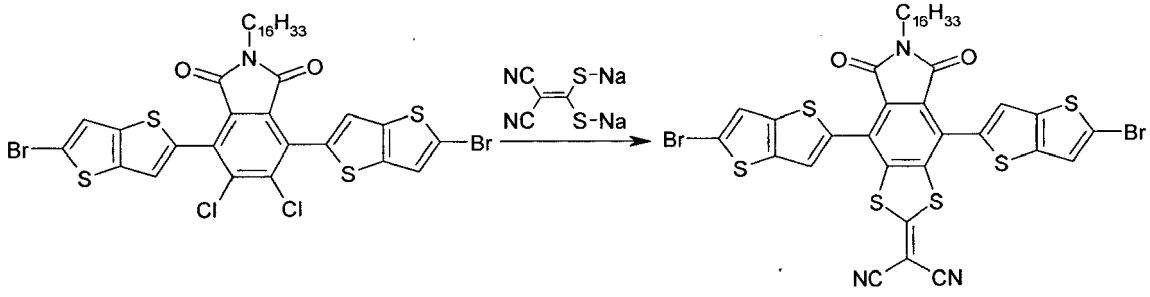


(1.3) (1.4)

[0234] To a solution of 4,5-dichloro-3,6-bis(thieno[3,2-b]thiophen-2-yl)-N-hexadecylphthalimide (1.3) (4.75 g, 6.63 mmol) in anhydrous tetrahydrofuran (130 cm^3) was added N-bromosuccinimide (3.57 g, 19.88 mmol) in one portion. The solution was heated at reflux for 4 hours. Further N-bromosuccinimide (1.2 g) was added and the mixture heated at reflux for a further 2 hours. The mixture was concentrated to dryness *in vacuo* and the residue was triturated in ethanol (100 cm^3). The solid was collected by filtration, washed with ethanol 2 times and acetone 3 times followed by recrystallisation from cyclohexane to give 3,6-bis(5-bromothieno[3,2-b]thiophen-2-yl)-4,5-dichloro-N-hexadecylphthalimide (1.4) (4.81g, 83%) as a green-yellow solid. ^1H NMR (400 MHz, CD_2Cl_2) δ 7.38 (s, 2H), 7.23 (s, 2H), 3.50 (t, J = 7.3 Hz, 2H), 1.52 (m, 2H), 1.34 - 1.14 (m, 26H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 165.27, 141.08, 140.09, 139.30, 134.21, 132.97, 130.06, 122.66, 121.73, 114.98, 38.93, 32.33, 30.09, 30.06, 30.02, 29.94, 29.82, 29.76, 29.47, 28.57, 27.20, 23.10, 14.30.

3,6-Bis(5-bromothieno[3,2-b]thiophen-2-yl)-N-hexadecyl(2-dicyanomethylene-1,3-dithiolo[4.5-d])phthalimide (1)

[0235]



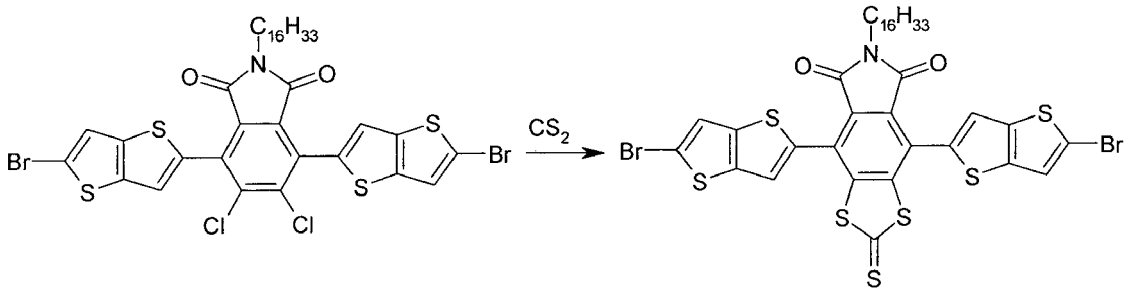
(1.4) (1)

[0236] To a solution of 3,6-bis(5-bromothieno[3,2-b]thiophen-2-yl)-4,5-dichloro-N-hexadecylphthalimide (1.4) (2.62 g, 3.00 mmol) in anhydrous N,N-dimethylformamide (80 cm^3) at 50 °C was added di(sodiummercapto)methylenemalononitrile (0.838 g, 4.50 mmol) in one portion. The solution was stirred at 50 °C for 8 hours and the solvent was removed *in vacuo*. The residue was triturated with methanol and the solid was collected by suction filtration. The solid was purified by column chromatography (3:1 dichloromethane-cyclohexane) followed by recrystallization from chloroform-octane to give 3,6-bis(5-bromothieno[3,2-b]thiophen-2-yl)-N-hexadecyl(2-dicyanomethylene-1,3-dithiolo[4,5-d])phthalimide (1) (1.95g, 68%) as a yellow solid. ^1H NMR (400 MHz, CDCb) δ 7.41 (s, 2H), 7.36 (s, 2H), 3.59 (t, J = 7.3 Hz, 2H), 1.59 (m, 2H), 1.36 - 1.15 (m, 26H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, CDCb) δ 175.85, 164.77, 144.38, 140.41, 139.33, 132.67, 129.41, 127.79, 122.08, 121.89, 116.74, 111.92, 67.74, 38.81, 31.91, 29.68, 29.66, 29.63, 29.58, 29.50, 29.40, 29.34, 29.04, 28.24, 26.84, 22.68, 14.12.

Example 2

3,6-Bis(5-bromothieno[3,2-b]thiophen-2 -yl)-N-hexadecyl(2-thioxo-1,3-dithiolo[4,5-d])phthalimide (2)

[0237]

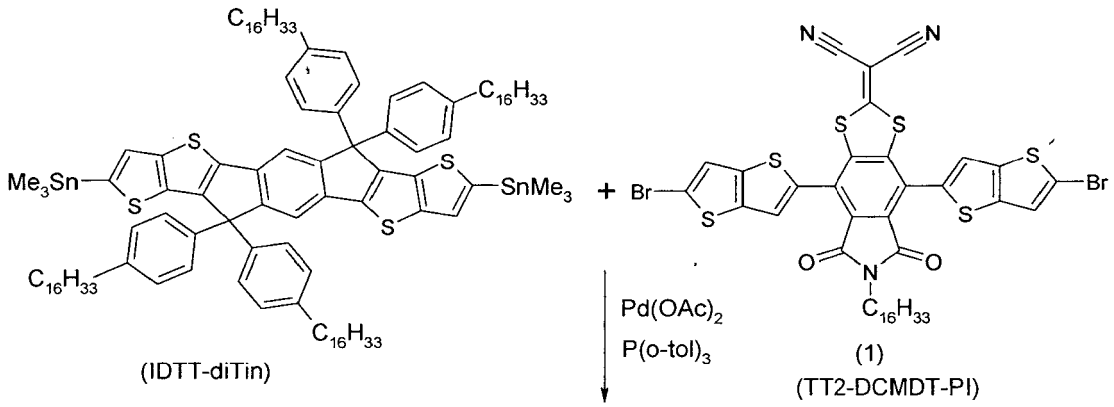


(1.4) (2)

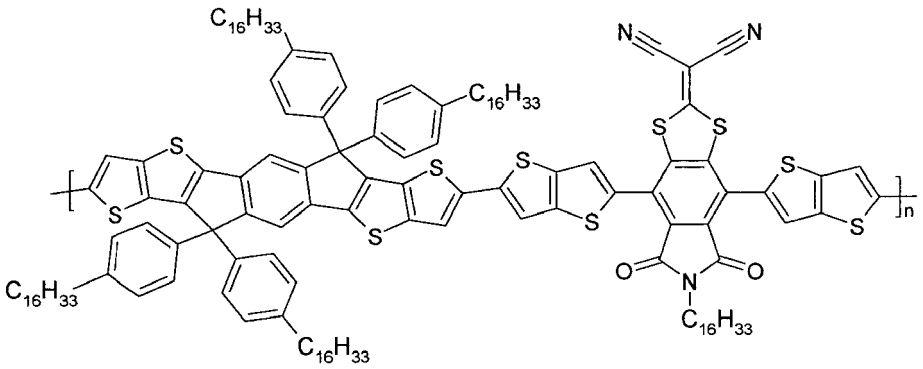
[0238] To a suspension of anhydrous sodium sulfide (0.351 g, 4.50 mmol) in anhydrous N,N-dimethylformamide (50 cm^3) was added carbon disulfide (0.5 cm^3, 8.27 mmol) in one portion. The mixture was stirred at 23°C for 2 hours and 3,6-bis(5-bromothieno[3,2-b]thiophen-2-yl)-4,5-dichloro-N-hexadecylphthalimide (1.4) (2.62 g, 3.00 mmol) was added. The mixture was stirred at 50 °C for 2 hours and at 100 °C for 1 hour. Methanol (50 cm^3) was added under stirring and the mixture was allowed to cool to 23 °C. The solid was collected by suction filtration, washed with methanol, recrystallised from chloroform-ethanol then passed through a silica plug (chloroform). The solid was finally recrystallised from chloroform-cyclohexane to give 3,6-bis(5-bromothieno[3,2-b]thiophen-2-yl)-N-hexadecyl(2-thioxo-1,3-dithiolo[4,5-d])phthalimide (1.92 g, 70%) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 2H), 7.33 (s, 2H), 3.58 (t, J = 7.4 Hz, 2H), 1.60 (m, 2H), 1.23 (m, 26 H), 0.87 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CDC13) δ 208.54, 165.42, 149.46, 140.09, 139.12, 133.62, 128.50, 126.00, 122.08, 121.57, 116.00, 38.65, 31.92, 29.68, 29.67, 29.64, 29.59, 29.52, 29.42, 29.35, 29.07, 28.28, 26.90, 26.87, 22.69, 14.13.

Example 3 - Polymer 1 (P1)

[0239]



(IDTT-diTin) (1) (TT2-DCMDT-PI)

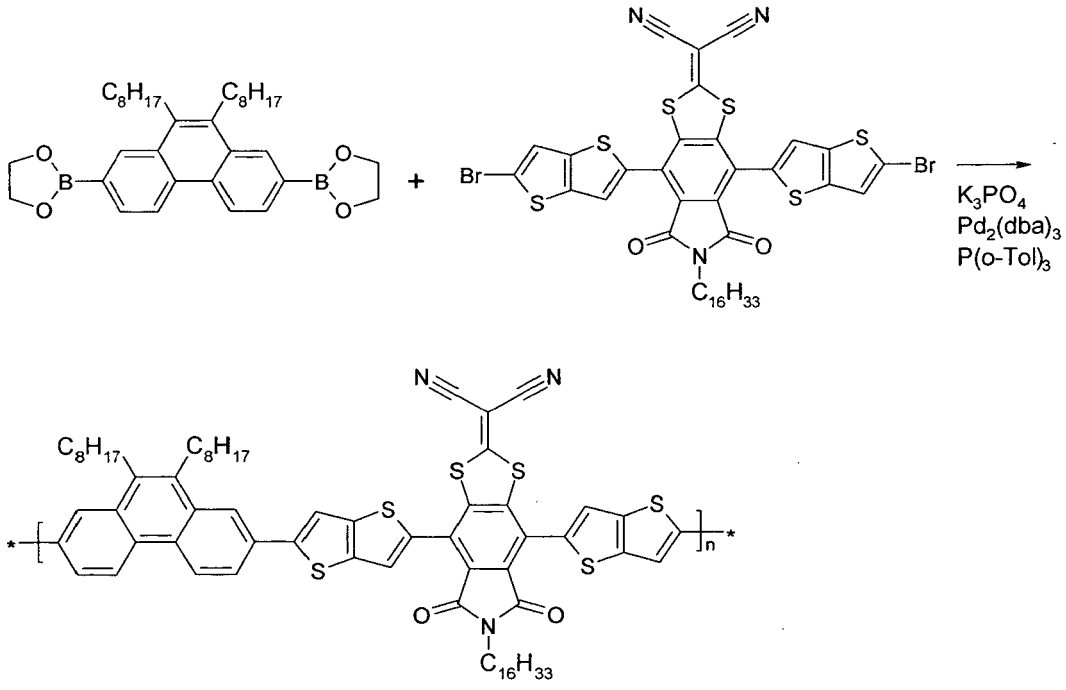


(P1)

[0240] A flask was charged with 3,6-bis(5-bromothieno[3,2-b]thiophen-2-yl)-N-hexadecyl(2-dicyanomethylene-1,3-dithiolo[4,5-d])phthalimide (1) (TT2-DCMDT-PI)(236.0 mg, 0.250 mmol), 2,8-bis(trimethylstannyl)-[6,6,12,12-tetrakis(4-hexadecylphenyl)-6, 12-dihydrodithieno[2, 3-d:2', 3'-d']-s-indaceno[1, 2-b:5, 6-b']dithiophene (IDTT-diTin) (476.6 mg, 0.250 mmol), anhydrous toluene (5.0 cm^3) and anhydrous N,N-dimethylformamide (1.0 cm^3). The mixture was degassed by bubbling nitrogen for 30 minutes and tris(dibenzylideneacetone)dipalladium(0) (7.0 mg, 0.010 mmol) and tri-o-tolylphosphine (12.2 mg, 0.040 mmol) were added. The mixture was degassed for an additional 15 minutes, then vigorously stirred at 120°C under nitrogen for 5 minutes, Iodobenzene (0.20 cm^3, 1.8 mmol) and toluene (5 cm^3) were added and the mixture was stirred for another 60 minutes at 120°C. The solution was precipitated into stirred acetone (100 cm^3) and the mixture was stirred at 20 °C for 30 minutes. The solid was collected by suction filtration, washed with acetone, then Soxhlet extracted with acetone, petroleum ether (40-60), petroleum ether (80-100) sequentially and finally dissolved in chloroform. The chloroform solution was concentrated and precipitated into acetone. The solid was collected by suction filtration to give polymer 1 (0.52 g, 88%) as a deep red solid. GPC (chlorobenzene, 50 °C): Mn = 94,000 Kg/mol, Mw = 352,000 kg/mol, PDI = 3.73.

Example 4 - Polymer 2 (P2)

[0241]



(P2)

[0242] A 25 cm^3 round-bottom flask was charged 9,10-dioctyl-2,7-phenanthrylene-bis(1,3,2-dioxaborolane) (122.3 mg, 0.225 mmol), 3,6-bis(5-bromothieno[3,2-b]thiophen-2-yl)-N-hexadecyl(2-dicyanomethylene-1,3-dithiolo[4,5-d])phthalimide (1) (TT2-DCMDT-PI)(212.9 mg, 0.225 mmol) and potassium phosphate monohydrate (208 mg, 0.902 mmol). To this mixture were added 1,4-dioxane (2 cm^3) and water (HPLC grade, 2 cm^3). The thick yellow suspension was degassed by bubbling nitrogen gas for 40 minutes. In the meantime, a stock solution of catalyst prepared from tris(dibenzylideneacetone)dipalladium(0) (2.6 mg, 0.003 mmol) and tri-o-tolylphosphine (5.5 mg, 0.018 mmol) in 1,4-dioxane (0.4 cm^3) was degassed and then added through a syringe. The mixture was further degassed for 10 minutes. The flask was lowered into a preheated oil bath and vigorously stirred for 20 hours at 120°C to yield a red suspension. The suspension was cooled briefly then precipitated into methanol (50 cm^3). The red solid was collected by suction filtration, washed with methanol, water, acetone sequentially and finally air-dried (0.26g, 97%). The polymer P2 solid was very insoluble in most organic solvents. The soluble fraction from chlorobenzene gave molecular weights of Mn = 28,600 kg/mol and Mw = 32,500 kg/mol. PDI = 1.14.

Use Example A

Field-effect transistor fabrication and measurements: General procedure

[0243] Top-gate thin-film organic field-effect transistors (OFETs) were fabricated on glass substrates with vacuum evaporated Au source-drain electrodes. A 7 mg/cm^3 solution of the organic semiconductor in dichlorobenzene was spin-coated on top (an optional annealing of the film is 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 vacuum evaporated Au 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):

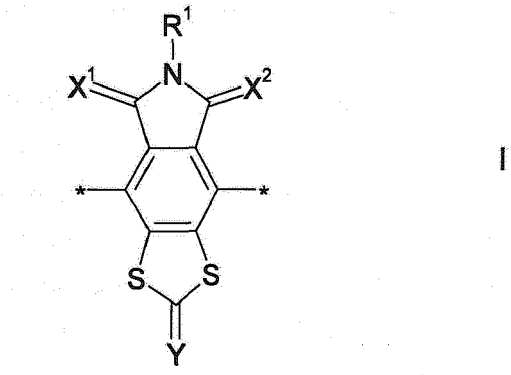
$$\left(\frac{dI_d^{sat}}{dV_g}\right)_{V_d} = \frac{WC_i}{L}\mu^{sat}(V_g - V_0) \qquad (1)$$

where W is 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} is the charge carrier mobility in the saturation regime. Turn-on voltage (V_0) was determined as the onset of source-drain current.

[0244] The μ_{sat} for polymer 1 was shown to be 5 x 10^{-4} cm^2A/s with I_{on}/I_{off} of 10^4

Claims

1. A compound comprising one or more divalent heteroarylene units of formula I

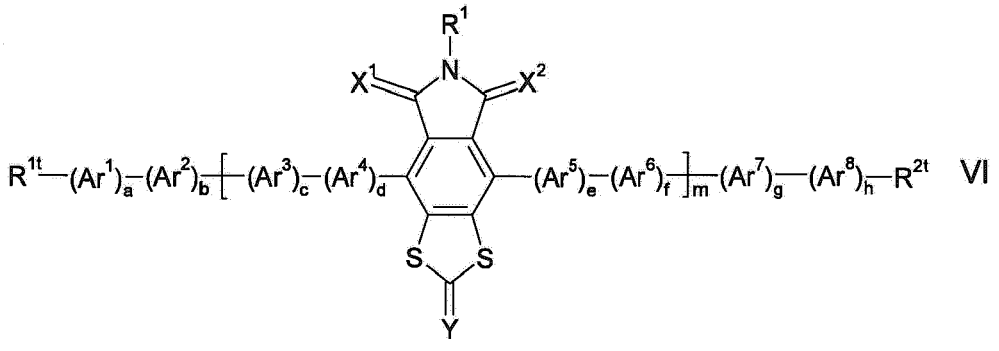


I

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

X^1, X^2 O or S,
Y O, S or CU^1U^2,
U1, U^2 an electron withdrawing group, preferably selected from CN, C(=O)R or C(=O)OR, or U^1 and U^2 together form a carbocyclic, heterocyclic, aromatic or heteroaromatic ring having 4 to 15 ring atoms that is optionally substituted by one or more groups L,
R^1 H or straight-chain, branched or cyclic alkyl with 1 to 30 C atoms, in which one or more CH_2 groups are optionally replaced by -O-, -S-, -C(=O)-, -C(=S)-, -C(=O)-O-, -O-C(=O)-, $-NR^0-$, $-SiR^0R^{00}-$, $-CF_2-$, $-CR^0=CR^{00}-$, $-CY^1=CY^2-$ or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, and in which one or more H atoms are optionally replaced by F, Cl, Br, I or CN, and in which one or more CH_2 or CH_3 groups are optionally replaced by a cationic or anionic group, or aryl, heteroaryl, arylalkyl, heteroarylalkyl, aryloxy or heteroaryloxy, wherein each of the aforementioned cyclic groups has 5 to 20 ring atoms, is mono- or polycyclic, does optionally contain fused rings, and is unsubstituted or substituted by one or more identical or different groups L,
R straight-chain, branched or cyclic alkyl with 1 to 30 C atoms, in which one or more CH_2 groups are optionally replaced by-O-, -S-, -C(=O)-, -C(=S)-, -C(=O)-O-, -O-C(=O)-, $-NR^0-$,$-SiR^0R^{00}-$, $-CF_2-$, $-CR^0=CR^{00}-$, $-CY^1=CY^2-$ or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, and in which one or more H atoms are optionally replaced by F, Cl, Br, I or CN, and in which one or more CH_2 or CH_3 groups are optionally replaced by a cationic or anionic group, or aryl, heteroaryl, arylalkyl or heteroarylalkyl, 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,
L F, Cl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, R^0, OR^0, SR^0,$-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)-OR^0$, $-O-C(=O)-R^0$, $-NH_2$, $-NHR^0$, $-NR^0R^{00}$, $-C(=O)NHR^0$, $-C(=O)NR^0R^{00}$, $-SO_3R^0$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-SF_5$, or optionally substituted silyl, or carbyl or hydrocarbyl with 1 to 20 C atoms that is optionally substituted and optionally comprises one or more hetero atoms,
Y^1, Y^2 H, F, Cl or CN,
X^0 halogen,
R^0, R^{00} H or straight-chain or branched alkyl with 1 to 20 C atoms that is optionally fluorinated,

with the proviso that, if X^1, X^2 and Y are O, then the unit of formula I is bonded via the 1- or 4-position of the benzene ring to at least one group that is different from H,
wherein the compound is a conjugated polymer comprising one or more units selected of formula I, and further comprising one or more arylene or heteroarylene units that have from 5 to 20 ring atoms, are mono- or polycyclic, do optionally contain fused rings, are unsubstituted or substituted by one or more identical or different groups L, and are either selected of formula I or are structurally different from formula I, and wherein all the aforementioned units are directly connected to each other,
or the compound is selected of formula VI

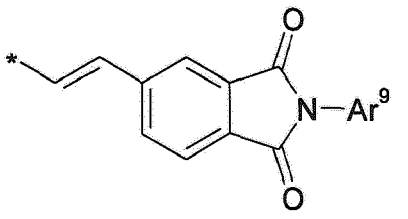


VI

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

Ar^{1-8} arylene or heteroarylene that has 5 to 20 ring atoms, is mono- or polycyclic, does optionally contain fused rings, is unsubstituted or substituted by one or more identical or different groups L, and is different from formula I,
Y^1, Y^2 H, F, Cl or CN,
$R^{1t,2t}$ H, F, Cl, Br, -CN, $-CF_3$, R*, $-CF_2-R^*$, -O-R*, -S-R*, $-SO_2-R^*$,$-SO_3-R^*$, -C(=O)-R*, -C(=S)-R*, $-C(=O)-CF_2-R^*$, -C(=O)-OR*, -C(=S)-OR*, -O-C(=O)-R*, -O-C(=S)-R*, -C(=O)-SR*, -S-C(=O)-R*, -C(=O)NR*R**, -NR*-

C(=O)-R*, -NHR*,-NR*R**,-CR*=CR*R**, -C≡C-R*, -C≡C-SiR*R**R***, -SiR*R**R***,-CH=C(CN)-C(=O)-OR*, -CH=C(CO-OR*)$_2$, CH=C(CO-NR*R**)$_2$, CH=C(CN)(Ar^9),



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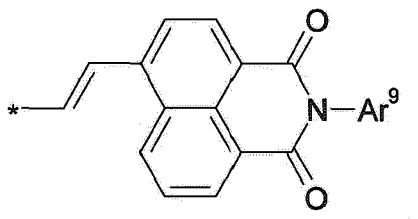

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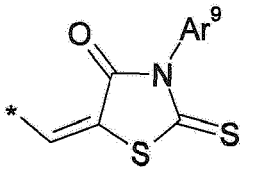

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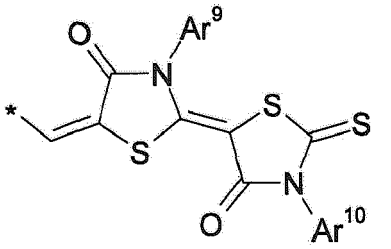

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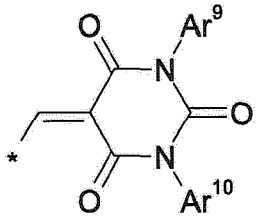

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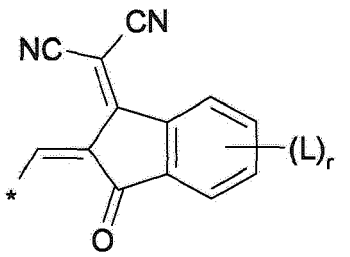

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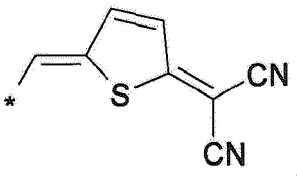


,

Ar^{9,10} aryl or heteroaryl, each having from 4 to 30 ring atoms, optionally containing fused rings and being unsubstituted or substituted with one or more groups L,
R*, R**, R*** alkyl with 1 to 20 C atoms which is straight-chain, branched or cyclic, and is unsubstituted, or substituted with one or more F or Cl atoms or CN groups, or perfluorinated, and in which one or more C atoms are optionally replaced by -O-, -S-, -C(=O)-, -C(=S)-, -SiR^{0}R^{00}-, -NR^{0}R^{00}-, -CHR^0=CR^{00}- or -C≡C- such that O- and/or S-atoms are not directly linked to each other,
R^0, R^{00} H or straight-chain or branched alkyl with 1 to 20 C atoms that is optionally fluorinated,
a-h 0 or 1, with at least one of a-h being 1,
m 1,2 or 3,
L one of the meanings given above,
r 0, 1, 2, 3 or 4.

2. The compound according to claim 1, wherein R^1 and R denote alkyl, alkoxy or thiaalkyl, all of which are straight-chain or branched, have 1 to 25 C atoms, and are optionally fluorinated.

3. The compound according to claim 1 or 2, which is a conjugated polymer comprising one or more repeating units of formula II1 or II2, and optionally one or more repeating units of formula II3:

$$-(Ar^1)_a-U-(Ar^2)_b-(Ar^3)_c-(Ar^4)_d- \qquad II1$$

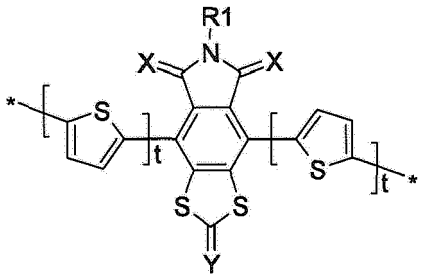
$$-(Ar^1)_a-(Ar^2)_b-U-(Ar^3)_c-(Ar^4)_d- \qquad II2$$

$$-(Ar^1)_a-(Ar^2)_b-(Ar^3)_c-(Ar^4)_d- \qquad II3$$

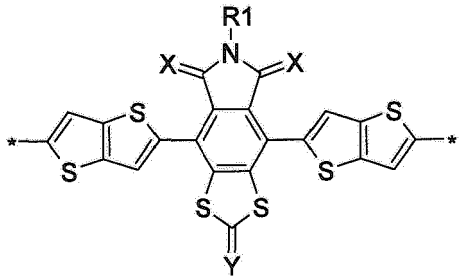
wherein the individual radicals, independently of each other and on each occurrence identically or differently, have the following meanings

U a unit of formula I as defined in claim 1 or 2,
Ar^{1-4} one of the meanings given in claim 1,
a, b, c, d 0 or 1, wherein in formula II3 a+b+c+d≥1.

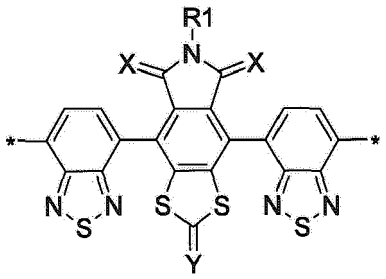
4. The compound according to any of claims 1 to 3, which comprises one or more repeating units selected from the following formulae.



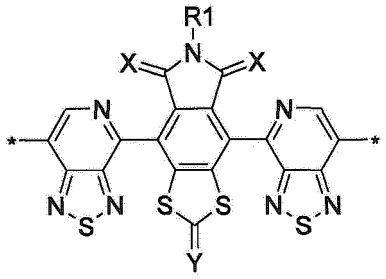
R1



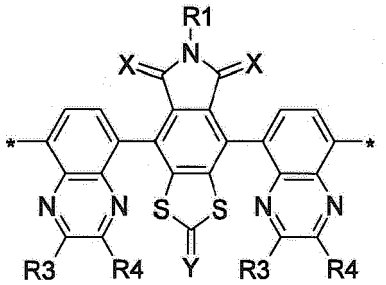
R2



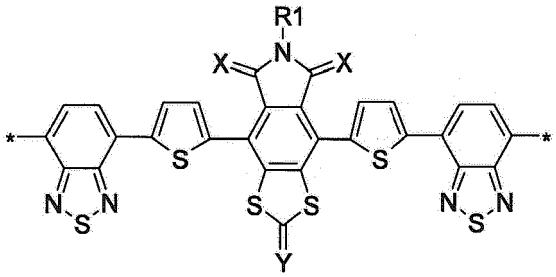
R3



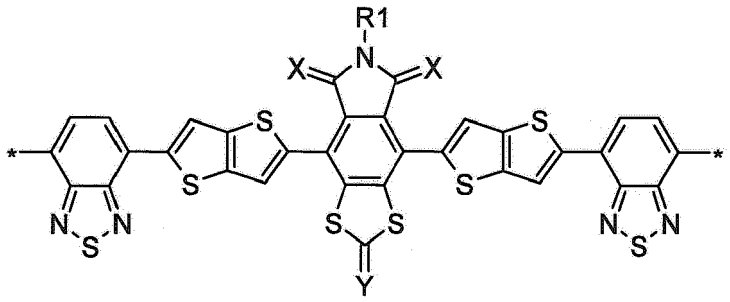
R4



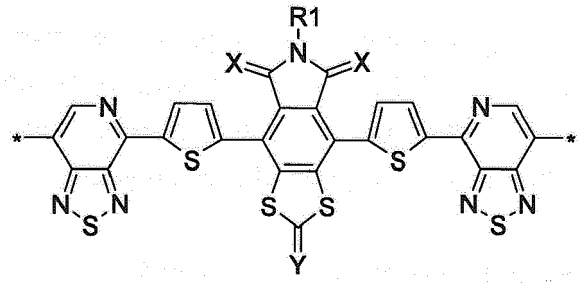
R5



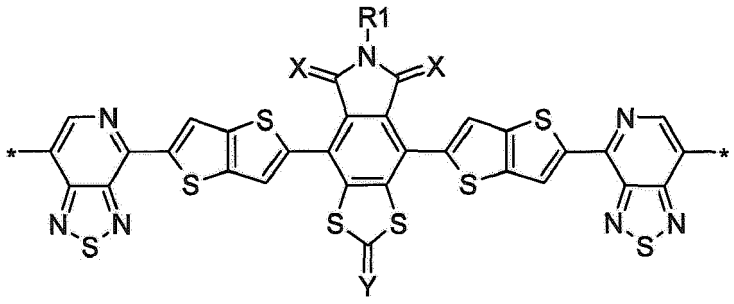
R6



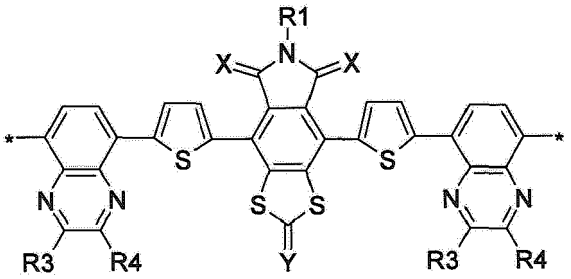
R7



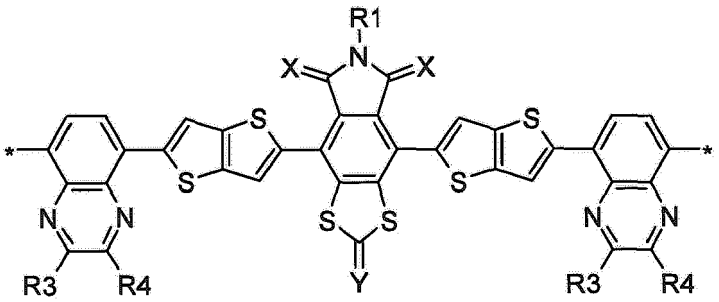
R8



R9



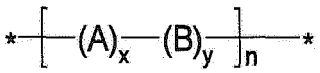
R10



R11

wherein R^1 is as defined in claim 1 or 2, X has on each occurrence identically or differently one of the meanings of X^1 as given in claim 1, Y is as defined in claim 1, t is 1, 2, 3 or 4, and R^2, R^3 and R^4 have independently of each other and on each occurrence identically or differently one of the meanings given of L given in claim 1.

5. The compound according to any of claims 1 to 4, which is a conjugated polymer of formula III:

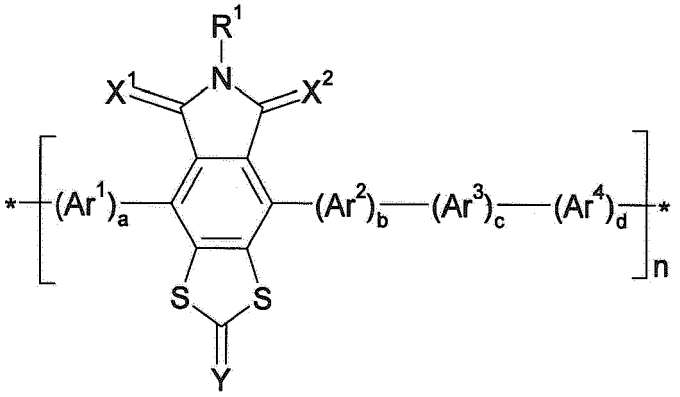


III

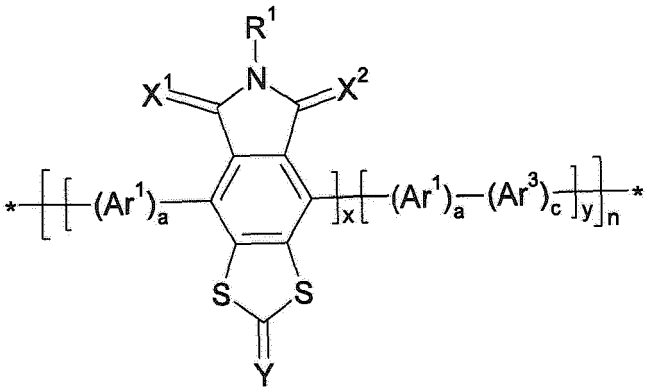
wherein

A is a unit of formula I, II1, II2 or R1-R11 as defined in any of claims 1 to 4,
B is a unit of formula I, II1, II2, II3 or R1-R11 as defined in any of claims 1 to 4 which is different from A,
x is > 0 and ≤ 1,
y is ≥ 0 and < 1,
x+y is 1, and
n is an integer ≥5.

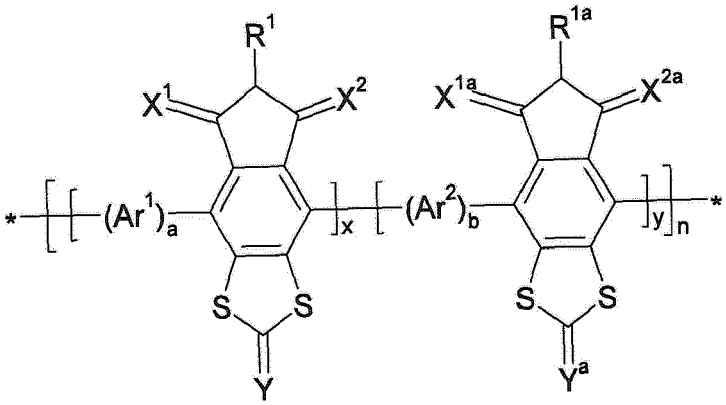
6. The compound according to any of claims 1 to 5, which is a conjugated polymer selected from the following formulae



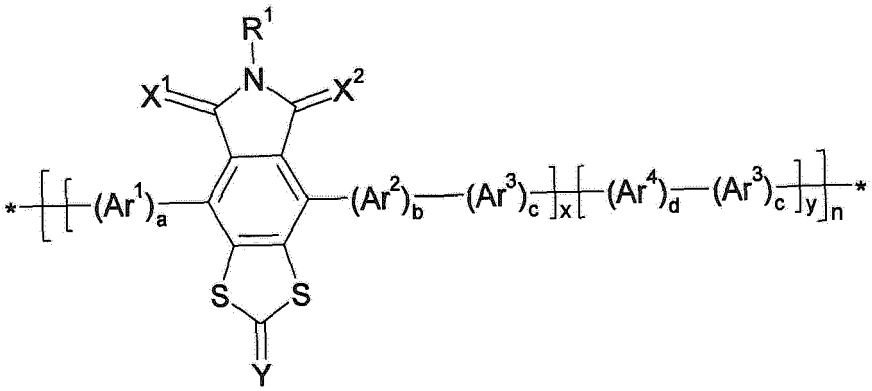
III1



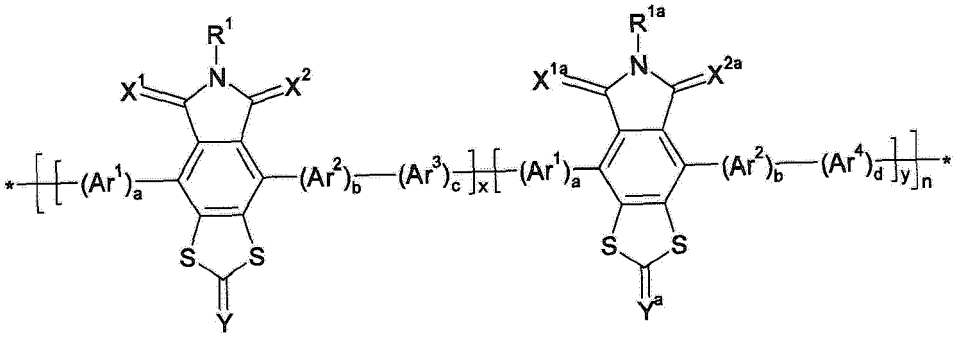
III2



III3



III4



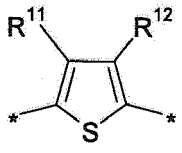
III5

wherein

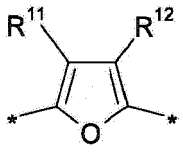
X^1, X^2, Y and R^1 have the meanings given in claim 1,
X^{1a} has one of the meanings given for X^1,

X^{2a} has one of the meanings given for X^1,
Y^a has one of the meanings given for Y,
R^{1a} has one of the meanings given for R^1,
Ar^2, Ar^3, Ar^4, a, b, c and d have the meanings given in claim 3,
x, y and n have the meanings given in claim 5, and
in formula III3 and III5 at least one of X^1, X^2, Y and R^1 is different from its corresponding radical X^{1a}, X^{2a}, Y^a and R^{1a}, respectively.

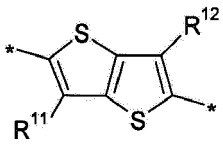
7. The compound according to any of claims 1 to 6, wherein one or more of Ar^1, Ar^2, Ar^3 and Ar^4 denote arylene or heteroarylene selected from the group consisting of the following formulae



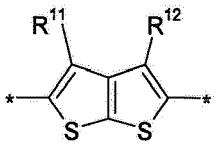
(D1)



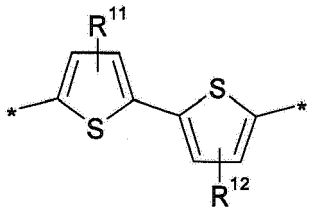
(D7)



(D10)



(D11)



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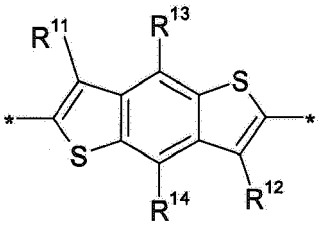
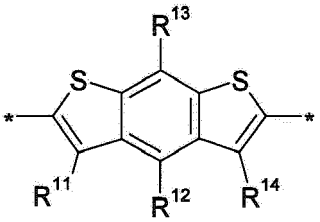
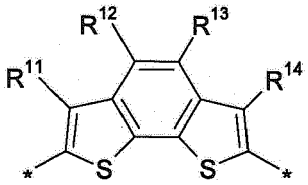


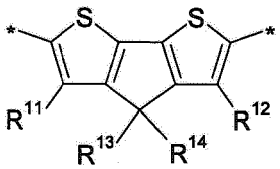
(D22)



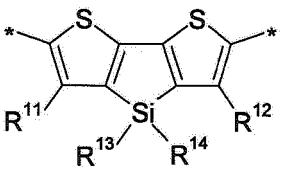
(D29)



(D30)



(D35)



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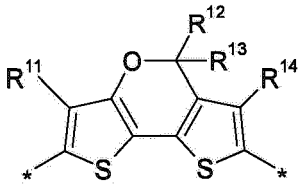

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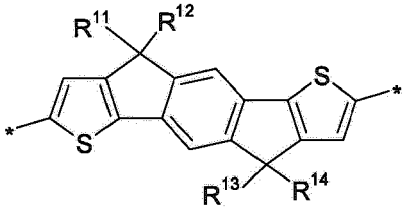

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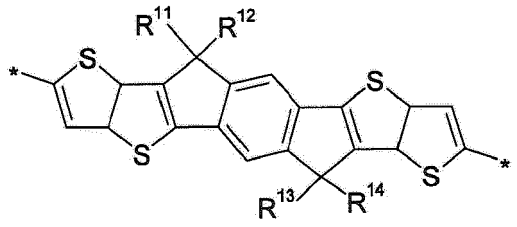
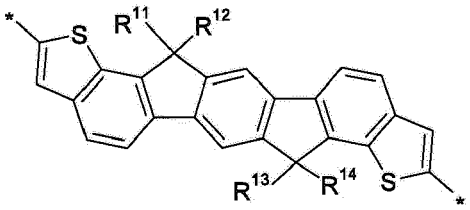
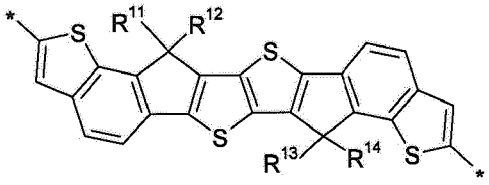


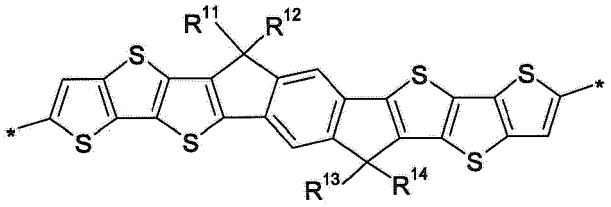
(D84)



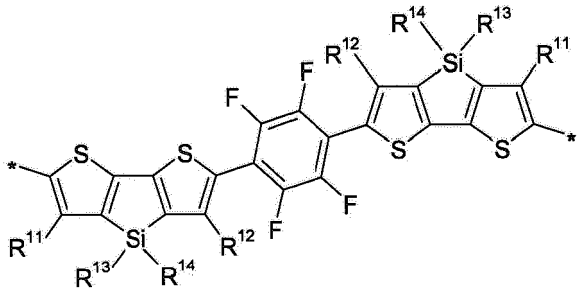
(D87)



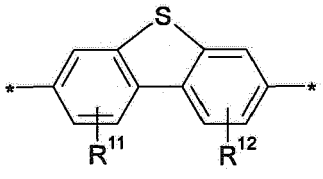
(D88)



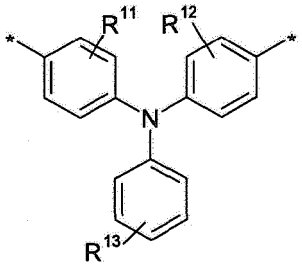
(D89)



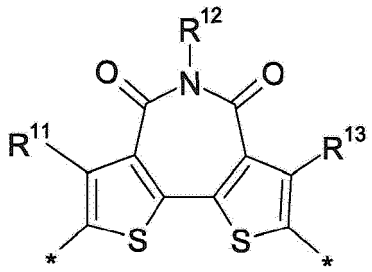
(D93)



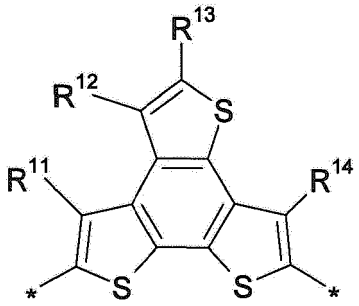
(D106)



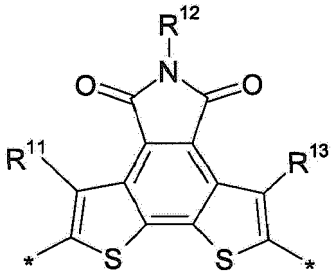
(D111)



(D140



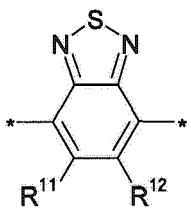
(D141)



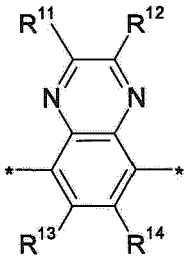
(D146)

wherein R^{11}, R^{12}, R^{13}, R^{14} independently of each other denote H or have one of the meanings of L as defined in claim 1.

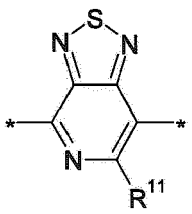
8. The compound according to any of claims 1 to 7, wherein one or more of Ar^1, Ar^2, Ar^3 and Ar^4 denote arylene or heteroarylene selected from the group consisting of the following formulae



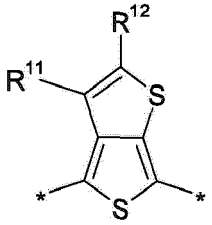
(A1)



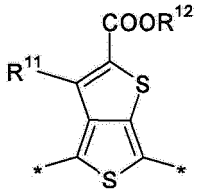
(A6)



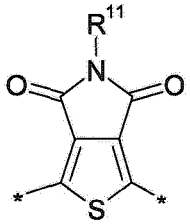
(A7)



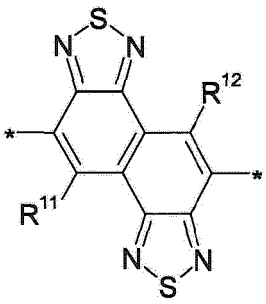
(A15)



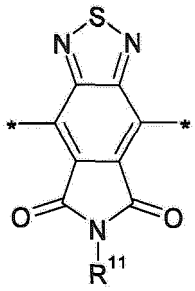
(A16)



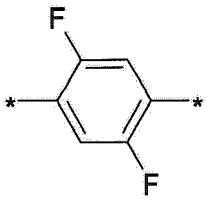
(A20)



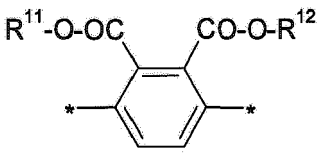
(A74)



(A88)



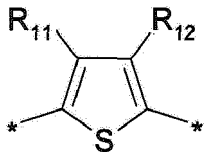
(A92)



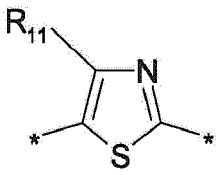
(A98)

wherein R^{11}, R^{12}, R^{13}, R^{14} independently of each other denote H or have one of the meanings of L as defined in claim 1.

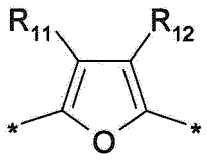
9. The compound according to any of claims 1 to 8, wherein one or more of Ar^1, Ar^2, Ar^3 and Ar^4 denote arylene or heteroarylene selected from the group consisting of the following formulae



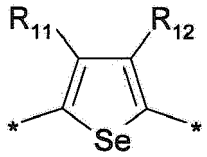
Sp1



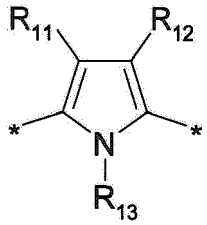
Sp2



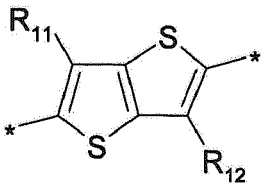
Sp3



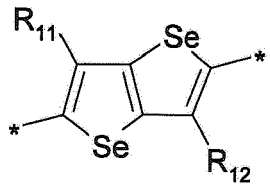
Sp4



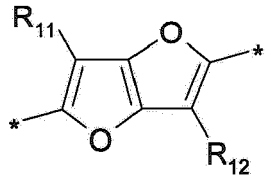
Sp5



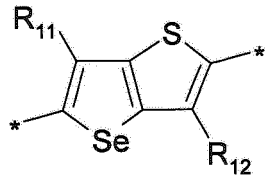
Sp6



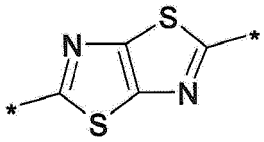
Sp7



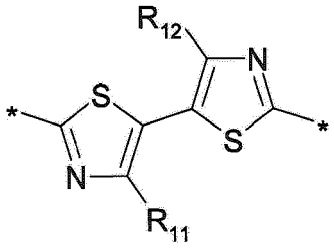
Sp8



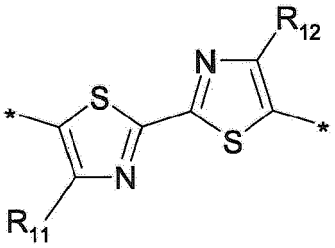
Sp9



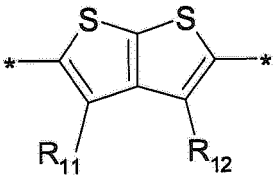
Sp10



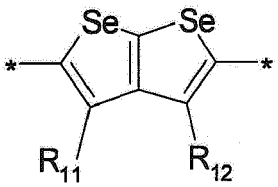
Sp11



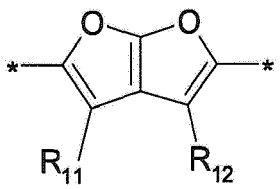
Sp12



Sp13



Sp14



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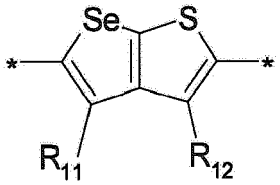
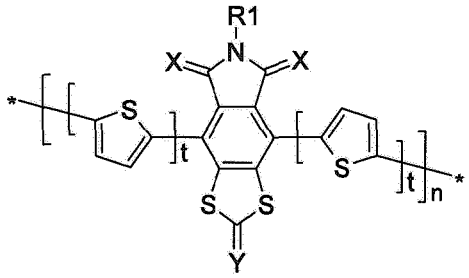


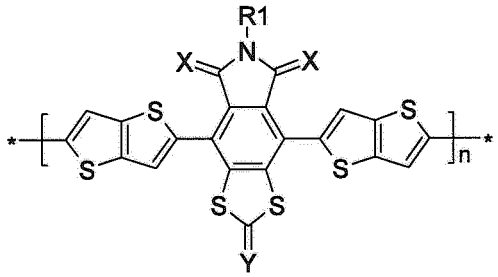
Sp16

wherein R^{11} and R^{12} independently of each other denote H or have one of the meanings of L as defined in claim 1.

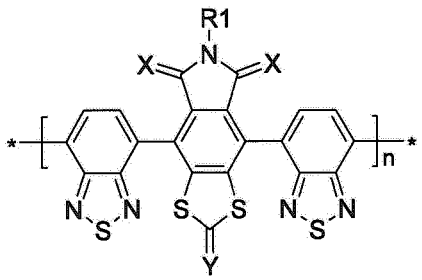
10. The compound according to any of claims 1 to 9 which is a conjugated polymer selected from the following formulae



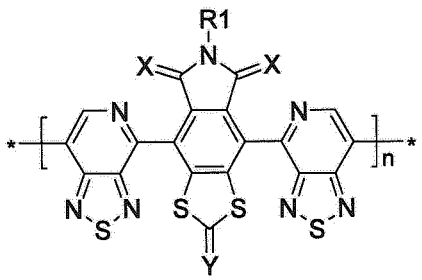
P1



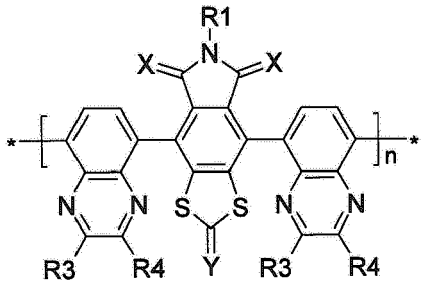
P2



P3



P4



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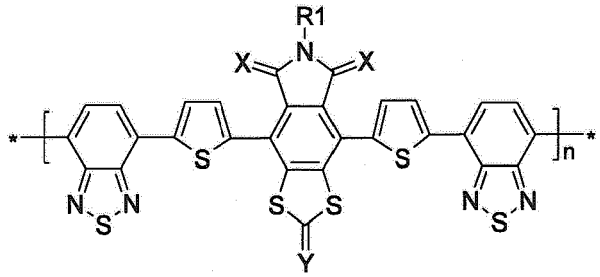

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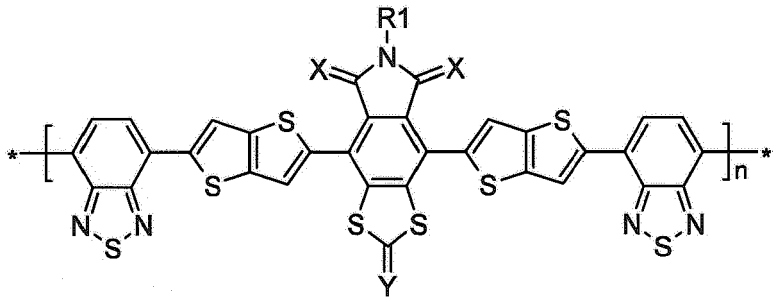

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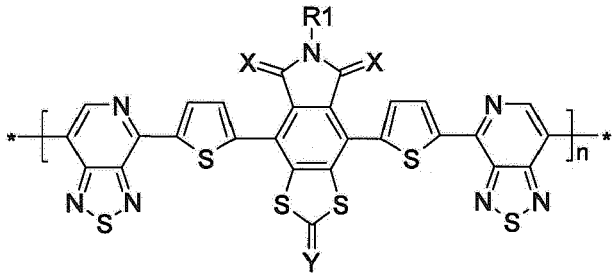

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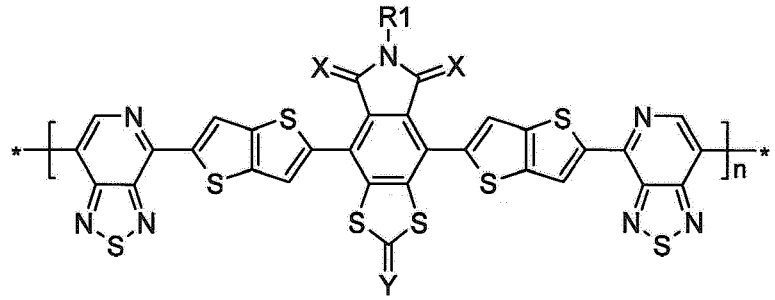

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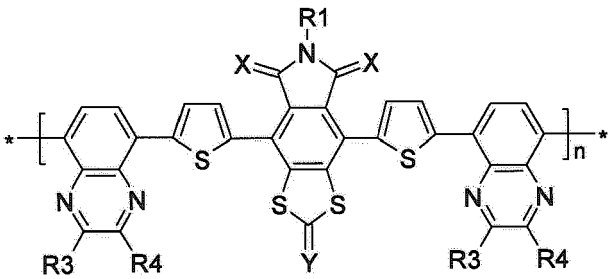

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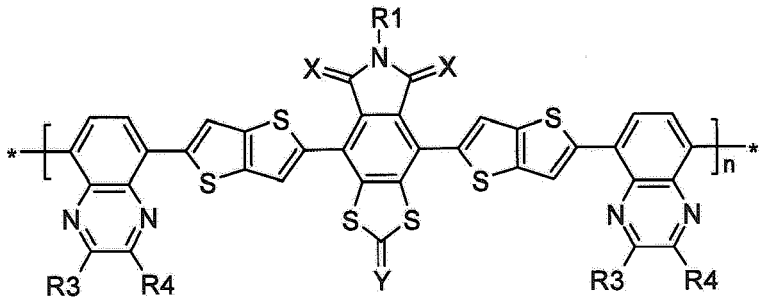

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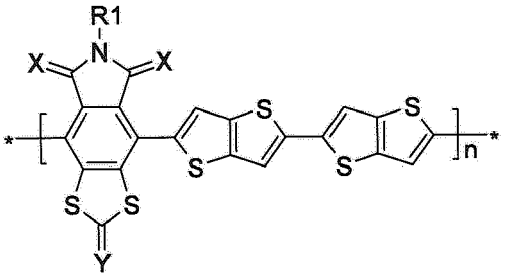

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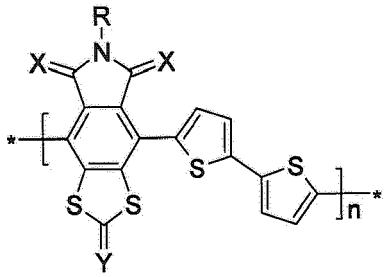

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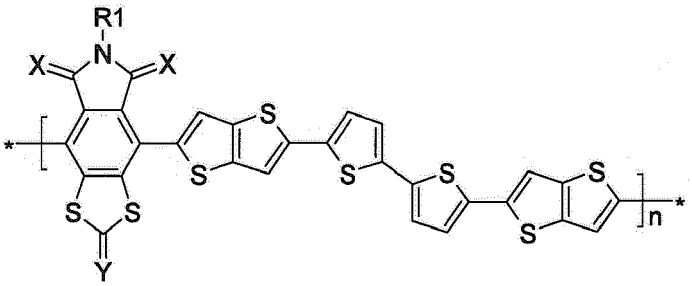

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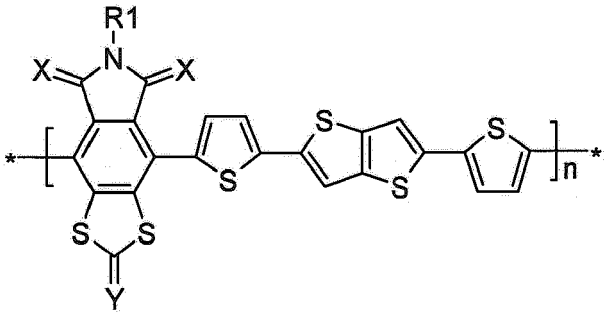

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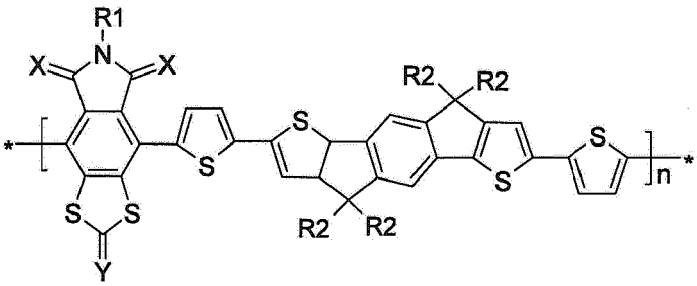

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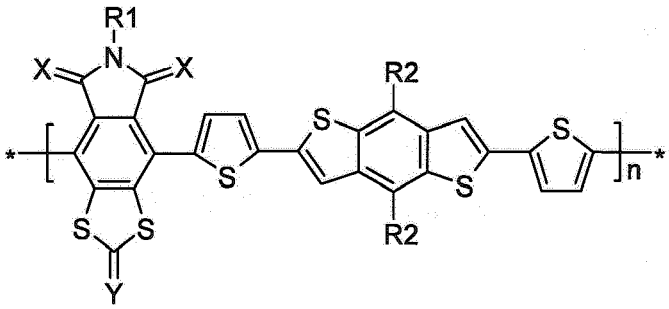

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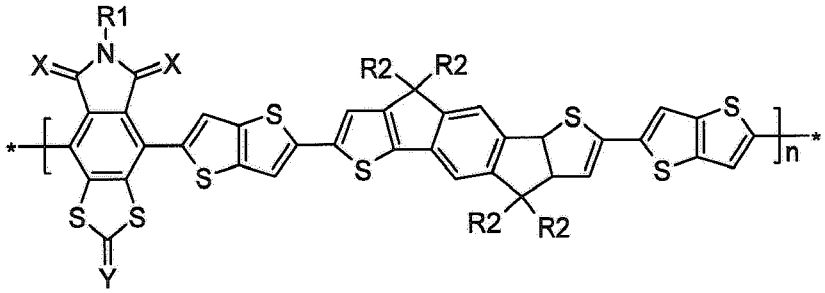

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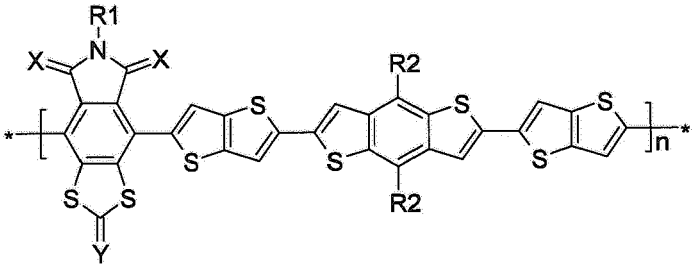

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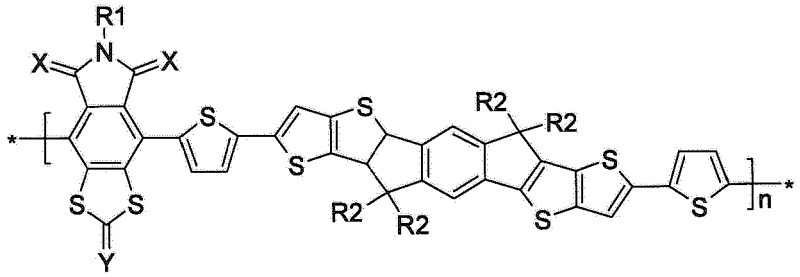

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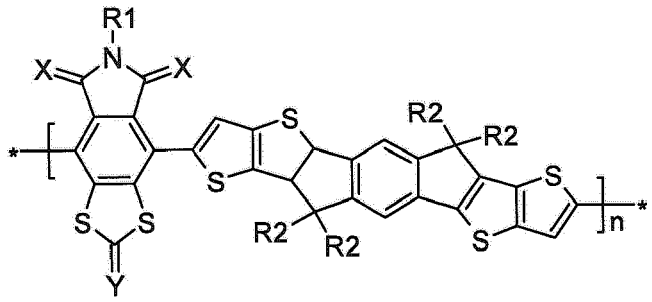

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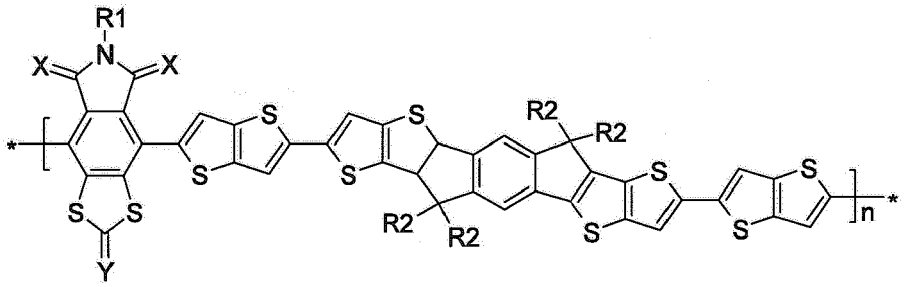

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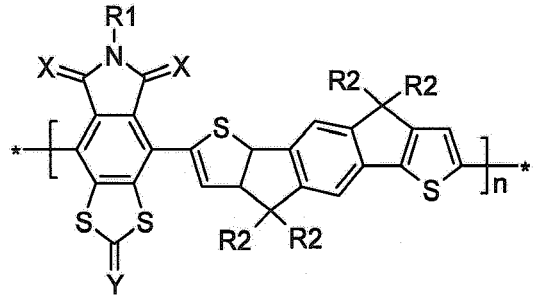

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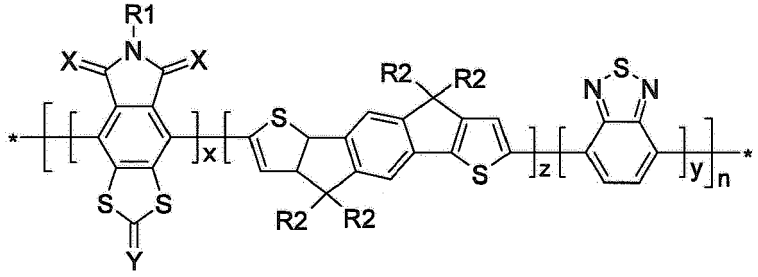

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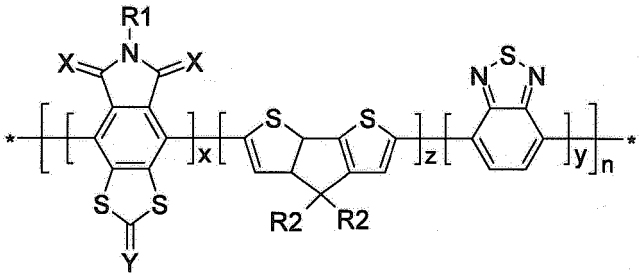

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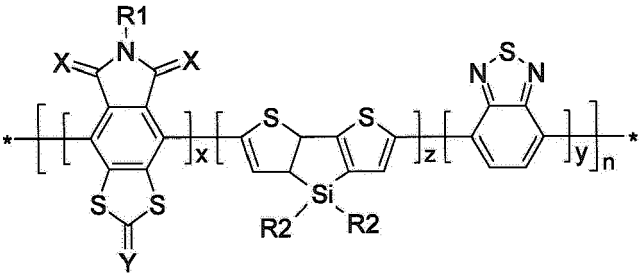

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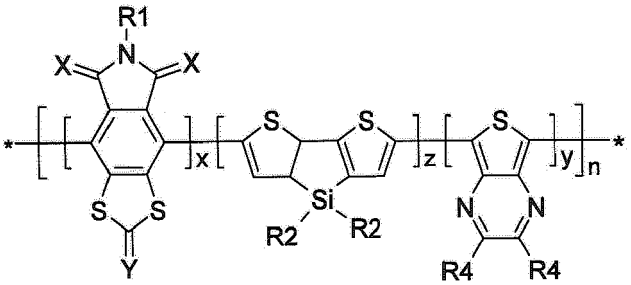

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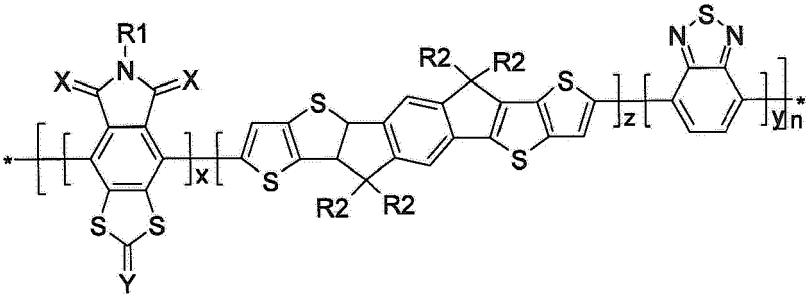

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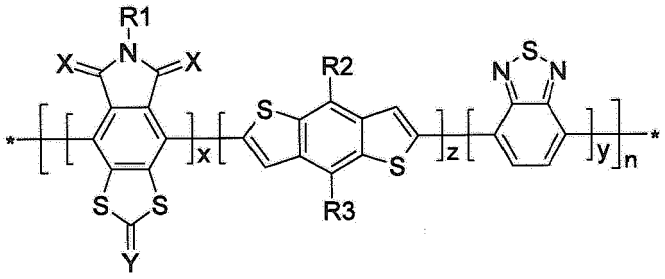

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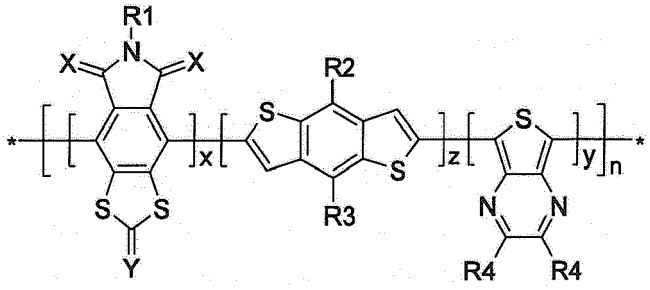

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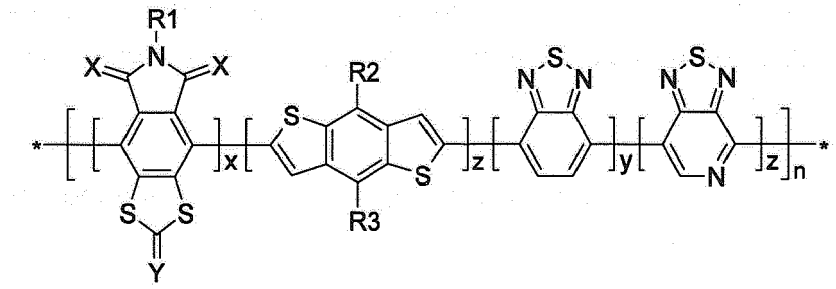

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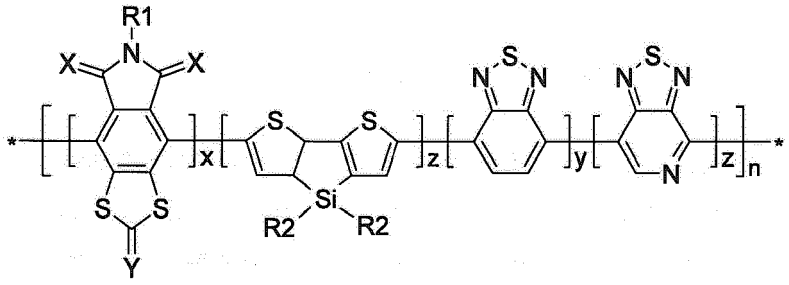


P32

wherein R^1 is as defined in claim 1 or 2, X has on each occurrence identically or differently one of the meanings of X^1 given in claim 1, Y is as defined in claim 1, t is 1, 2, 3 or 4, n is as defined in claim 5, and R^2, R^3 and R^4 have independently of each other and on each occurrence identically or differently one of the meanings given for L.

11. The compound according to any of claims 1 to 10, which is a conjugated polymer of formula IV

$$R^5\text{-chain-}R^6 \qquad \text{IV}$$

wherein "chain" denotes a polymer chain selected from formulae III, III1-III8 and P1-P32 as defined in claims 5, 6 and 10, and R^5 and R^6 have independently of each other one of the meanings of R^1 or L as defined in claim 1 or 2, or denote, independently of each other, H, F, Br, Cl, I, $-CH_2Cl$, -CHO, $-CR'=CR''_2$, -SiR'R"R'", -SiR'X'X", -SiR'R"X', -SnR'R"R'", -BR'R", -B(OR')(OR"), $-B(OH)_2$, $-O-SO_2-R'$, -C≡CH, $-C\equiv C-SiR'_3$, -ZnX' or an endcap group, X' and X" denote halogen, R', R" and R'" have independently of each other one of the meanings of R^0 given in claim 1, 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.

12. The compound according to claim 1 or 2, which is a monomer of formula V1 or V2

$$R^7\text{-}(Ar^1)_a\text{-}U\text{-}(Ar^2)_b\text{-}(Ar^3)_c\text{-}(Ar^4)_d\text{-}R^8 \qquad \text{V1}$$

$$R^7\text{-}(Ar^1)_a\text{-}(Ar^2)_b\text{-}U\text{-}(Ar^3)_c\text{-}(Ar^4)_d\text{-}R^8 \qquad \text{V2}$$

wherein U, Ar^{1-4}, a, b, c and d have the meanings given in claim 3, 7, 8 or 9, and R^7 and R^8 are independently of each other selected from the group consisting of H, Cl, Br, I, O-tosylate, O-triflate, O-mesylate, O-nonaflate, $-SiMe_3$, $-SiMe_2F$, $-SiMeF_2$, $-O-SO_2Z^1$ $-B(OZ^2)_2$, $-CZ^3=C(Z^3)_2$, $-C\equiv CH$, $-C\equiv CSi(Z^1)_3$, $-ZnX^0$, $Mg-X^0$ and $-Sn(Z^4)_3$, wherein X^0 is halogen, Z^{1-4} are selected from the group consisting of 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^7 and R^8 is different from H.

13. The compound of claim 12, which is selected from the following formulae

R^7-Ar^1-U-Ar^2-R^8 V1a

R^7-U-R^8 V1b

R^7-Ar^1-U-R^8 V1c

R^7-U-Ar^2-R^8 V1d

wherein U, Ar^1, Ar^2, R^7 and R^8 are as defined in claim 12.

14. The compound of claim 12, which is selected of formula V3

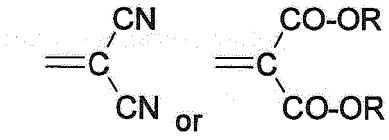
R^7-U*-R^8 V3

wherein U* is a unit selected from formula R1-R11 as defined in claim , and R^7 and R^8 are as defined in claim 12.

15. The compound according to any of claims 1 to 14, wherein

a) one or more of Ar^1, Ar^2, Ar^3 and Ar^4 denote arylene or heteroarylene selected from the group consisting of the formulae D1, D7, D10, D11, D19, D22, D29, D30, D35, D36, D44, D55, D84, D87, D88, D89, D93, D106, D111, D140, D141 and D146 as defined in claim 7, and/or
b) one or more of Ar^1, Ar^2, Ar^3 and Ar^4 denote arylene or heteroarylene selected from the group consisting of the formulae A1, A6, A7, A15, A16, A20, A74, A88, A92 and A98 as defined in claim 8,
and
c) one or more of Ar^1, Ar^2, Ar^3 and Ar^4 denote arylene or heteroarylene selected from the group consisting of the formulae Sp1, Sp6 and Sp13 as defined in claim 9.

16. The compound according to claim 4 or 10, wherein Y is O, S,



with R being as defined in claim 1 or 2.

17. The compound of formula VI according to claim 1, wherein Ar^{1-10} are selected from the following groups

a) the group consisting of the formulae D1, D7, D10, D11, D19, D22, D29, D30, D35, D36, D44, D55, D84, D87, D88, D89, D93, D106, D111, D140 and D141 as defined in claim 7,
b) the group consisting of the formulae A1, A6, A7, A15, A16, A20, A74, A88, A92 and A98 as defined in claim 8,
c) the group consisting of the formulae formulae Sp1, Sp6 and Sp10 as defined in claim 9.

18. The compound of formula VI according to claim 1 or 17, which is selected of formula VI1

R^{1t}-U*-R^{2t} VI1

wherein U* is a unit selected from formulae R1-R11 as defined in claim 4, and R^{1t} and R^{2t} have the meanings given

in claim 1.

19. A mixture comprising one or more compounds according to any of claims 1 to 18 and one or more additional compounds having one or more of semiconducting, charge transport, hole or electron transport, hole or electron blocking, electrically conducting, photoconducting or light emitting properties.

20. A mixture comprising one or more compounds according to any of claims 1 to 18 and one or more n-type organic semiconductors.

21. The mixture of claim 20, wherein the n-type organic semiconductors are selected from fullerenes or substituted fullerenes.

22. A formulation comprising one or more compounds or mixtures according to any of claims 1 to 21, and further comprising one or more solvents selected from organic solvents.

23. An optical, electrooptical, electronic, electroluminescent or photoluminescent device, or a component thereof, or an assembly comprising it, which comprises one or more compounds or mixtures according to any of claims 1 to 21.

24. Use of a compound or mixture according to any of claims 1 to 21 as semiconducting, charge transport, electrically conducting, photoconducting or light emitting material, or in an optical, electrooptical, electronic, electroluminescent or photoluminescent device, or in a component of such a device or in an assembly comprising such a device or component.

25. A semiconducting, charge transport, electrically conducting, photoconducting or light emitting material comprising a compound or mixture according to any of claims 1 to 21.

26. An optical, electrooptical, electronic, electroluminescent or photoluminescent device, or a component thereof, or an assembly comprising it, which comprises a semiconducting, charge transport, electrically conducting, photoconducting or light emitting material according to claim 25.

27. The optical, electrooptical, electronic, electroluminescent or photoluminescent device of claim 26, which is selected from organic thin film transistors (OTFT), 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, laser diodes, Schottky diodes, photoconductors and photodetectors.

28. The component of claim 26, which is selected from charge injection layers, charge transport layers, interlayers, planarising layers, antistatic films, polymer electrolyte membranes (PEM), conducting substrates and conducting patterns.

29. The assembly of claim 26, which is selected from integrated circuits (IC), radio frequency identification (RFID) tags or security markings or security devices containg them, flat panel displays or backlights thereof, electrophotographic devices, electrophotographic recording devices, organic memory devices, sensor devices, biosensors and biochips.

30. A bulk heterojunction which comprises a mixture according to any of claims 19 to 21.

31. A bulk heterojunction (BHJ) OPV device or inverted BHJ OPV device, comprising the bulk heterojunction of claim 30.

32. A process of preparing a conjugated polymer according to any of claims 1 to 11, by coupling one or more monomers selected from claims 12, 13, 14 and 15 with each other and/or with one or more monomers of formulae MI-MIV in an aryl-aryl coupling reaction

R^7-Ar^1-R^8 MI

R^7-Ar^2-R^8 MII

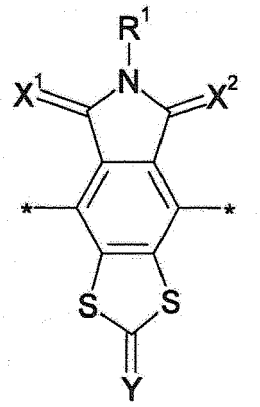
R^7-Ar^3-R^8 MIII

R^7-Ar^4-R^8 MIV

wherein Ar^{1-4}, R^7 and R^8 have the meanings given in claim 12.

Patentansprüche

1. Verbindung, umfassend ein oder mehrere divalente Heteroaryleneinheiten von Formel I

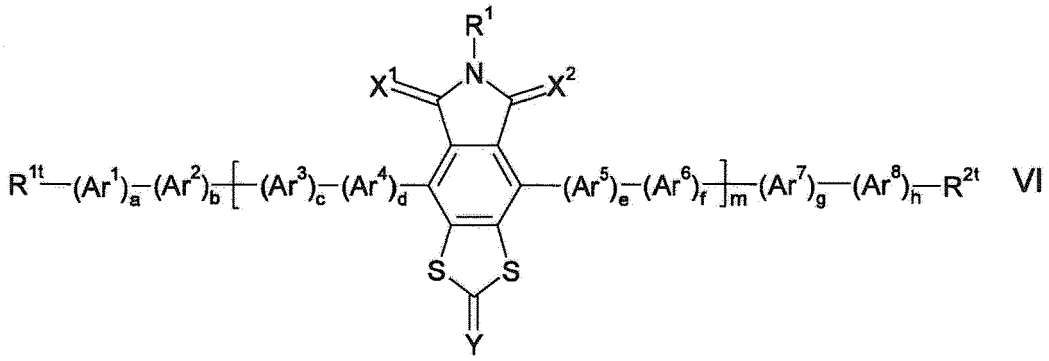


I

wobei die individuellen Radikale unabhängig voneinander und bei jedem Auftreten, identisch oder verschieden, die folgenden Bedeutungen aufweisen

X^1 X^2 O oder S
Y O, S oder CU^1U^2,
U^1, U^2 eine elektronenabziehende Gruppe, bevorzugt ausgewählt aus CN, C(=O)R oder C(=O)OR, oder U^1 und U^2 gemeinsam einen karbozyklischen, heterozyklischen, aromatischen oder heteroaromatischen Ring bilden, 4 bis 15 Ringatome aufweisend, der optional durch eine oder mehrere Gruppen L ersetzt ist,
R^1 H oder geradkettiges, verzweigtes oder zyklisches Alkyl mit 1 bis 30 C-Atomen, in denen eine oder mehrere CH_2-Gruppen optional durch -O-, -S-, -C(=O)-, -C(=S)-, -C(=O)-O-, -O-C(=O)-, $-NR^0$-, SiR^0R^{00}-, $-CF_2$-, $-CR^0=CR^{00}$-, $-CY^1=CY^2$- oder -C≡C- so ersetzt sind, dass O und/oder S-Atome nicht direkt miteinander verbunden sind, und in denen ein oder mehrere H-Atome optional durch F, Cl, Br, I oder CN ersetzt sind und in denen ein oder mehrere CH_2 oder CH_3-Gruppen optional durch eine kationische oder anionische Gruppe, oder Aryl, Heteroaryl, Arylalkyl, Heteroarylalkyl, Aryloxy oder Heteroaryloxy ersetzt sind, wobei jede der zuvor erwähnten zyklischen Gruppen 5 bis 20 Ringatome aufweist, mono- oder polyzyklisch ist, optional fusionierte Ringe enthält und nichtsubstituiert oder durch eine oder mehrere identische oder verschiedene Gruppen L substituiert ist,
R geradkettiges, verzweigtes oder zyklisches Alkyl mit 1 bis 30 C-Atomen, in denen eine oder mehrere CH_2-Gruppen optional durch O-, -S-, -C(=O)-, -C(=S)-, -C(=O)-O-, -O-C(=O)-, $-NR^0$-, SiR^0R^{00}-, $-CF_2$-, $-CR^0=CR^{00}$-, $-CY^1=CY^2$- oder -C≡C- so ersetzt sind, dass O und/oder S-Atome nicht direkt miteinander verbunden sind, und in denen ein oder mehrere H-Atome optional durch F, Cl, Br, I oder CN ersetzt sind und in denen ein oder mehrere CH_2 oder CH_3-Gruppen optional durch eine kationische oder anionische Gruppe, oder Aryl, Heteroaryl, Arylalkyl oder Heteroarylalkyl ersetzt sind, wobei jede der zuvor erwähnten zyklischen Gruppen 5 bis 20 Ringatome aufweist, mono- oder polyzyklisch ist, optional fusionierte Ringe enthält und nichtsubstituiert oder durch eine oder mehrere identische oder verschiedene Gruppen L substituiert ist,
L F, Cl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, R^0, OR^0, SR^0, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)-OR^0$, $-O-C(=O)-R^0$, $-NH_2$, $-NHR^0$, $-NR^0R^{00}$, $-C(=O)NHR^0$, $-C(=O)NR^0R^{00}$, $-SO_3R^0$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-SF_5$ oder optional substituiertes Silyl oder Carbyl oder Hydrocarbyl mit 1 bis 20 C-Atomen, das optional substituiert ist und optional ein oder mehrere Heteroatome umfasst,
Y^1, Y^2 H, F, Cl oder CN,
X^0 Halogen,
R^0R^{00} H oder geradkettiges oder verzweigtes Alkyl mit 1 bis 20 C-Atomen, das optional fluoriert ist,
mit der Bedingung, dass, falls X^1, X^2 und Y O sind, die Einheit von Formel I dann über die 1- oder 4-Position des Benzolrings an mindestens eine Gruppe gebunden ist, die sich von H unterscheidet,
wobei die Verbindung ein konjugiertes Polymer ist, das eine oder mehrere Einheiten aus Formel I ausgewählt

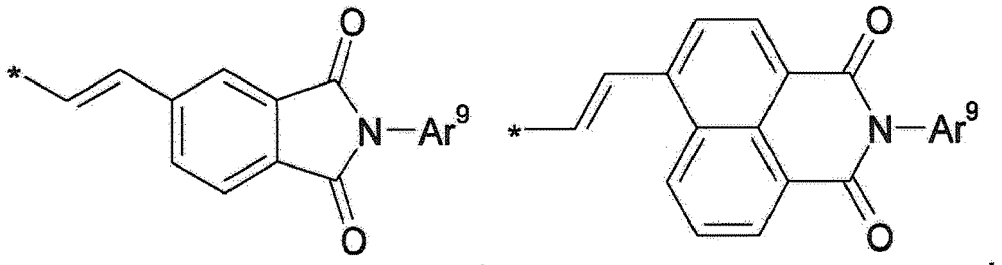
umfasst und weiter eine oder mehrere Arylen- oder Heteroaryleneinheiten umfasst, die 5 bis 20 Ringatome aufweisen, mono- oder polyzyklisch sind, optional fusionierte Ringe enthalten, nichtsubstituiert sind oder durch eine oder mehrere identische oder verschiedene Gruppen L substituiert sind und entweder aus Formel I ausgewählt sind oder sich strukturell von Formel I unterscheiden und wobei alle der zuvor erwähnten Einheiten direkt miteinander verbunden sind,
oder die Verbindung aus Formel VI ausgewählt ist

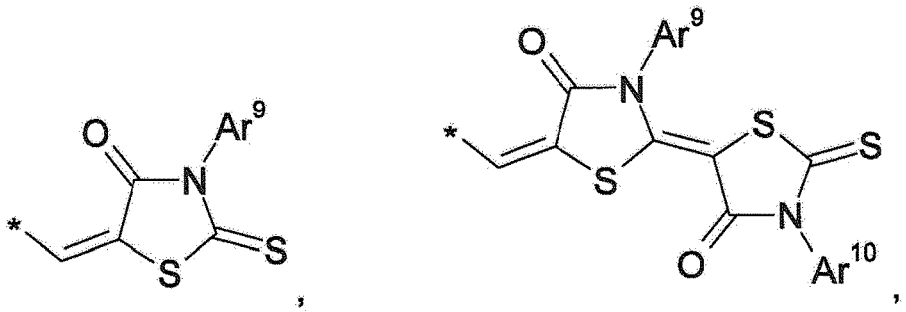


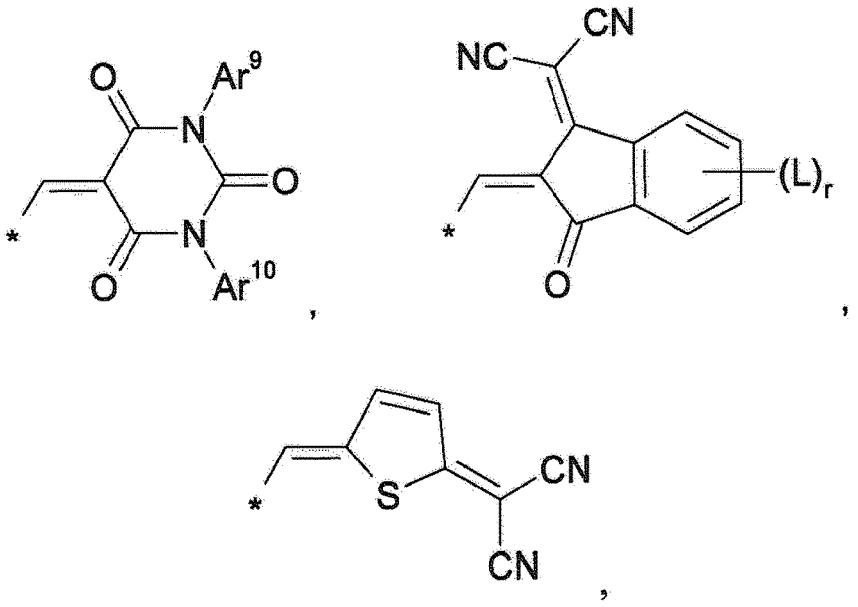
VI

wobei die individuellen Radikale unabhängig voneinander und bei jedem Auftreten, identisch oder verschieden, die folgenden Bedeutungen aufweisen,

AR^{1-8} Arylen oder Heteroarylen, das 5 bis 20 Ringatome aufweist, mono- oder polyzyklisch ist, optional fusionierte Ringe enthält, nichtsubstituiert ist oder durch eine oder mehrere identische oder verschiedene Gruppen L substituiert ist und sich von Formel I unterscheidet,
Y^1, Y^2 H, F, Cl oder CN,
$R^{1t, 2t}$ H, F, Cl, Br, -CN, $-CF_3$, R*, $-CF_2$-R*, -O-R*, -S-R*, $-SO_2$-R*, $-SO_3$-R*, -C(=O)-R*, -C(=S)-R*, $-C(=O)-CF_2$-R*, -C(=O)-O R*, -C(=S)-OR*, -O-C(=O)-R*, -O-C(=S)-R*, -C(=O)-SR*, -S-C(=O)-R*, -C(=O)NR*R**, -NR*-C(=O)-R*, -NHR*, -NR*R**, -CR*=CR*R**, -C≡C-R*, -C≡C-SiR*R**R***, -SiR*R**R***, -CH=C(CN)-C(=O)-OR*, $-CH=C(CO-OR^*)_2$, $CH=C(CO-NR^*R^{**})_2$, $CH=C(CN)(Ar^9)$,







$AR^{9,10}$ Aryl oder Heteroaryl, wobei jedes 4 bis 30 Ringatome aufweist, optional fusionierte Ringe enthält und nichtsubstituiert ist oder durch eine oder mehrere Gruppen L substituiert ist,
R*, R**, R*** Alkyl mit 1 bis 20 C-Atomen, das geradkettig, verzweigt oder zyklisch ist und nichtsubstituiert ist oder durch eine oder mehrere F- oder Cl-Atome oder CN-Gruppen substituiert ist, oder perfluoriert ist und in dem ein oder mehrere C-Atome optional durch -O-, -S-, -C(=O)-, -C(=S)-, $-SiR^0R^{00}-$, $-NR^0R^{00}-$, $-CHR^0=CR^{00}-$ oder -C≡C- ersetzt sind, sodass O- und/oder S-Atome nicht direkt miteinander verbunden sind,
R^0, R^{00}H oder geradkettiges oder verzweigtes Alkyl mit 1 bis 20 C-Atomen, das optional fluoriert ist,
a-h 0 oder 1, wobei mindestens eines von a-h 1 ist,
m 1, 2 oder 3,
L eine der zuvor gegebenen Bedeutungen,
r 0, 1, 2, 3 oder 4.

2. Verbindung nach Anspruch 1, wobei R^1 und R Alkyl, Alkoxy oder Thiaalkyl bezeichnen, von denen alle geradkettig oder verzweigt sind, 1 bis 25 C-Atome aufweisen und optional fluoriert sind.

3. Verbindung nach Anspruch 1 oder 2, die ein konjugiertes Polymer ist, das eine oder mehrere sich wiederholende Einheiten von Formel II1 oder II2 umfasst und optional eine oder mehrere sich wiederholende Einheiten von Formel II3:

$$-(Ar^1)_a-U-(Ar^2)_b-(Ar^3)_c-(Ar^4)_d- \qquad \text{II1}$$

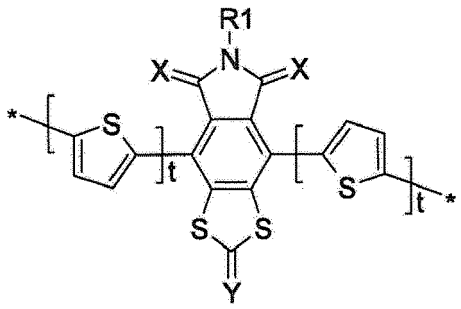
$$-(Ar^1)_a-(Ar^2)_b-U-(Ar^3)_c-(Ar^4)_d- \qquad \text{II2}$$

$$-(Ar^1)_a-(Ar^2)_b-(Ar^3)_c-(Ar^4)_d- \qquad \text{II3}$$

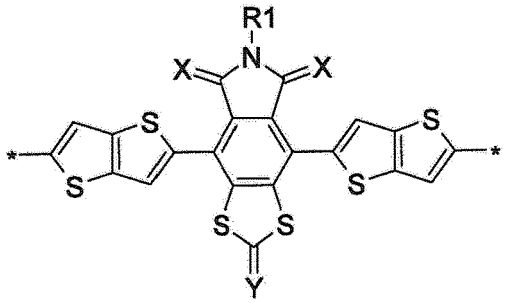
wobei die individuellen Radikale unabhängig voneinander und bei jedem Auftreten, identisch oder verschieden, die folgenden Bedeutungen aufweisen

U eine Einheit von Formel I, wie in Anspruch 1 oder 2 definiert,
Ar^{1-4} eine der in Anspruch 1 gegebenen Bedeutungen,
a, b, c, d 0 oder 1, wobei in Formel II3 a+b+c+d≥1 ist.

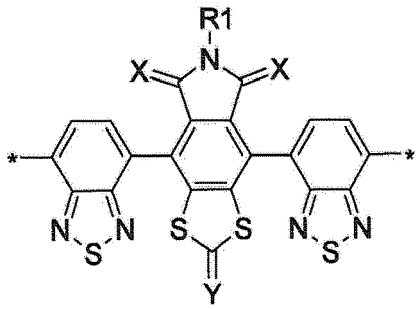
4. Verbindung nach einem der Ansprüche 1 bis 3, die eine oder mehrere sich wiederholende Einheiten aufweist, die aus den folgenden Formeln ausgewählt sind.



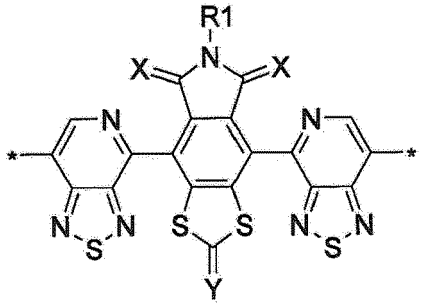
R1



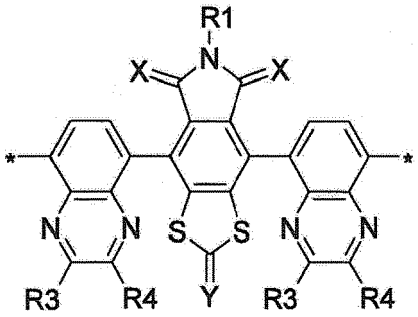
R2



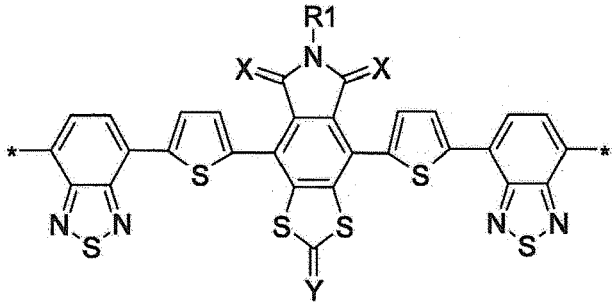
R3



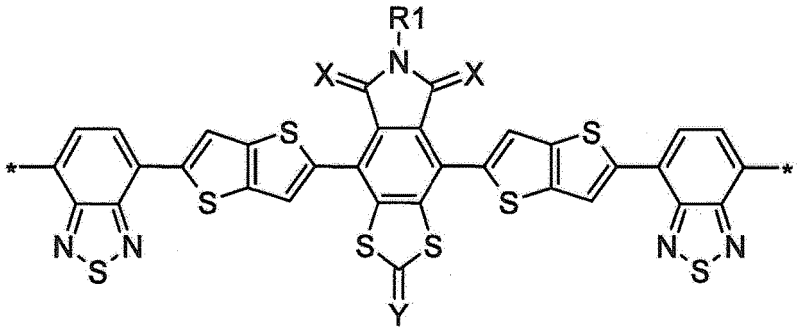
R4



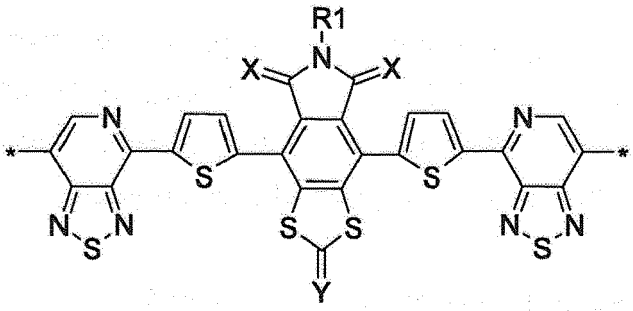
R5



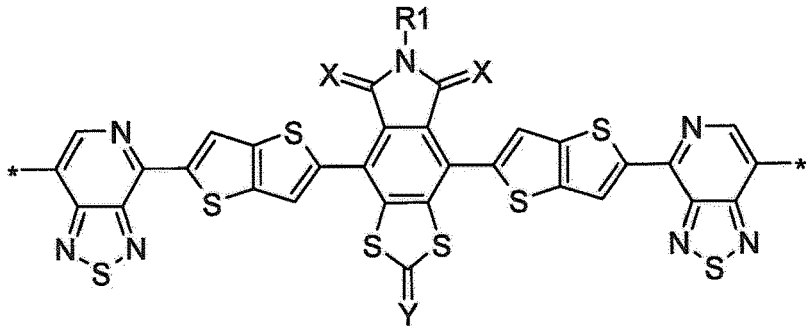
R6



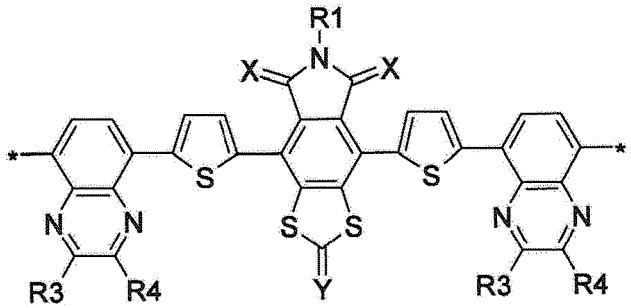
R7



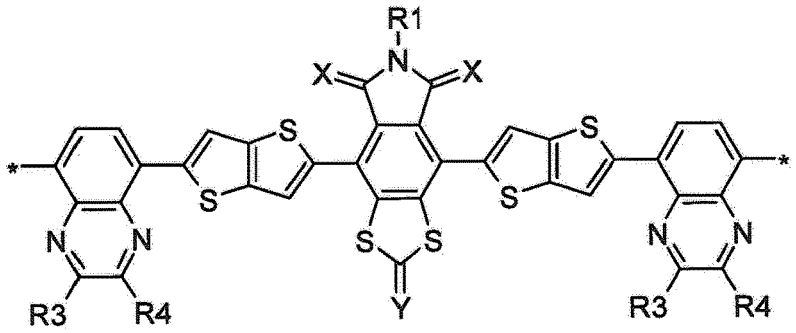
R8



R9



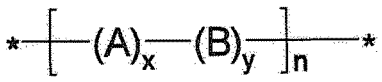
R10



R11

wobei R^1 wie in Anspruch 1 oder 2 definiert ist, X bei jedem Auftreten, identisch oder verschieden, eine der Bedeutungen von X^1 wie in Anspruch 1 gegeben aufweist, Y wie in Anspruch 1 definiert ist, t 1, 2, 3 oder 4 ist und R^2, R^3 und R^4 unabhängig voneinander und bei jedem Auftreten, identisch oder verschieden, eine der von L in Anspruch 1 gegebenen Bedeutungen aufweisen.

5. Verbindung nach einem der Ansprüche 1 bis 4, die ein konjugiertes Polymer von Formel III ist:

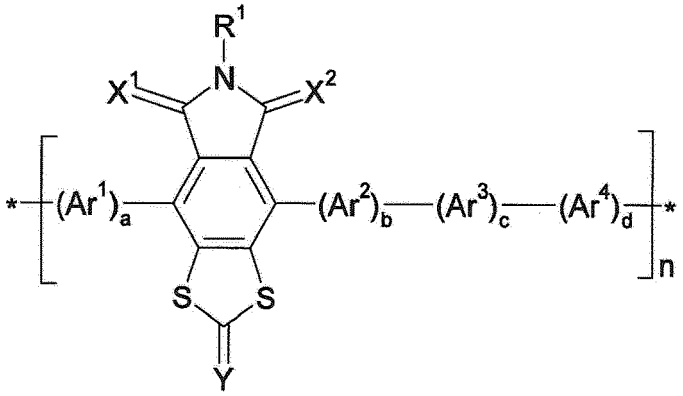


III

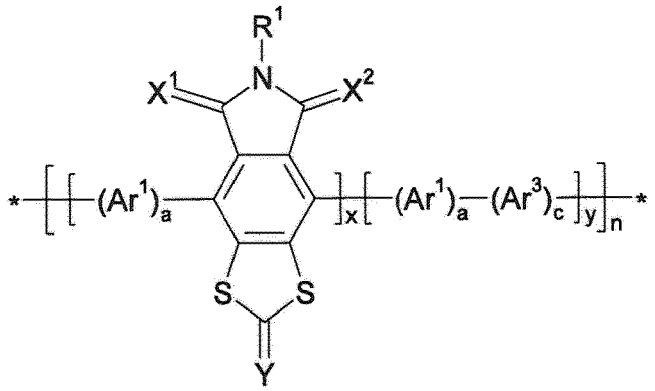
wobei

A eine Einheit von Formel I, II1, II2 oder R1-R11 wie in einem der Ansprüche 1 bis 4 definiert ist,
B eine Einheit von Formel I, II1, II2, II3 oder R1-R11 wie in einem der Ansprüche 1 bis 4 definiert ist, die sich von A unterscheidet,
x >0 und ≤1 ist,
y ≥0 und <1 ist,
x+y 1 ist und
n eine Ganzzahl ≥5 ist.

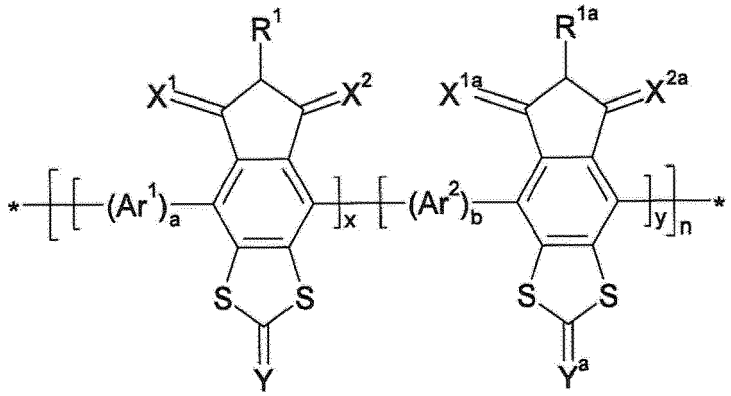
6. Verbindung nach einem der Ansprüche 1 bis 5, die ein konjugiertes Polymer ist, das aus den folgenden Formeln ausgewählt ist



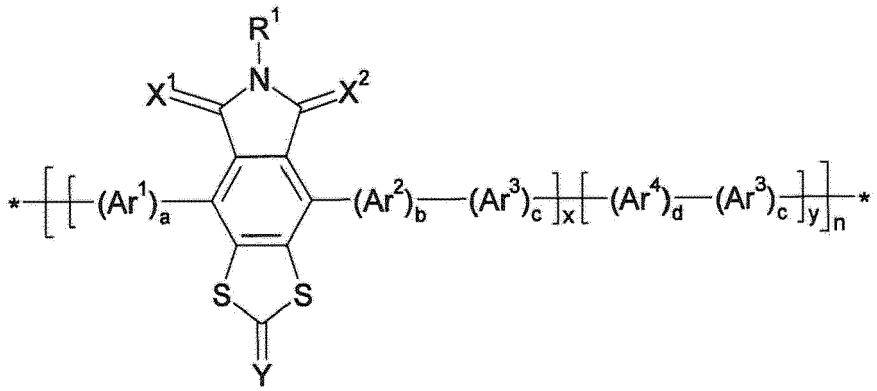
III1



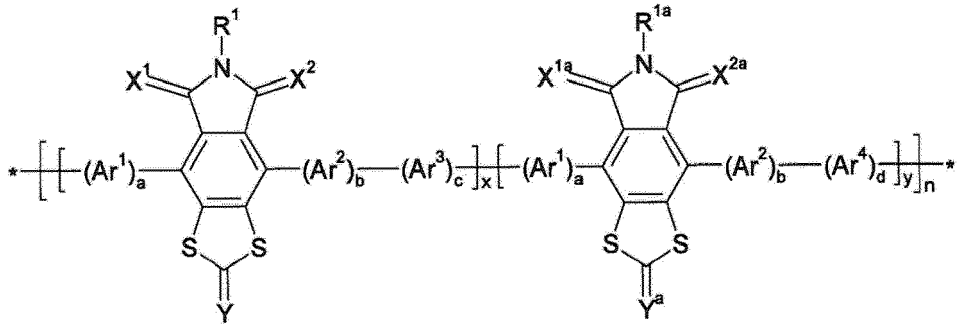
III2



III3



III4



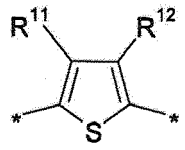
III5

wobei

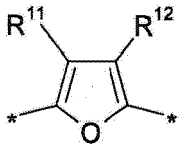
X^1, X^2, Y und R^1 die in Anspruch 1 gegebenen Bedeutungen aufweisen,
X^{1a} eine der für X^1 gegebenen Bedeutungen aufweist,

X^{2a} eine der für X^1 gegebenen Bedeutungen aufweist,
Y^a eine der für Y gegebenen Bedeutungen aufweist,
R^{1a} eine der für R^1 gegebenen Bedeutungen aufweist,
Ar^2, Ar^3, Ar^4, a, b, c und d die in Anspruch 3 gegebenen Bedeutungen aufweisen,
x, y und n die in Anspruch 5 gegebenen Bedeutungen aufweisen und
in Formel III3 und III5 mindestens eines von X^1, X^2, Y und R^1 sich von seinem entsprechenden Radikal X^{1a}, X^{2a}, Y^a beziehungsweise R^{1a} unterscheidet.

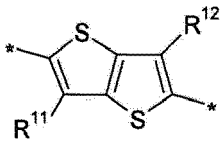
7. Verbindung nach einem der Ansprüche 1 bis 6, wobei eines oder mehrere von AR^1, Ar^2, Ar^3 und Ar^4 Arylen oder Heteroarylen bezeichnen, ausgewählt aus der Gruppe, bestehend aus den folgenden Formeln



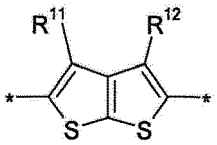
(D1)



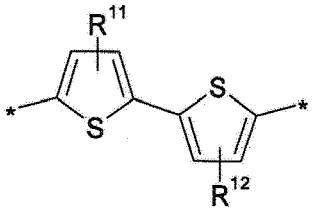
(D7)



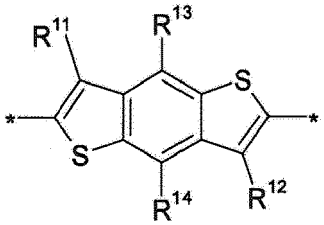
(D10)



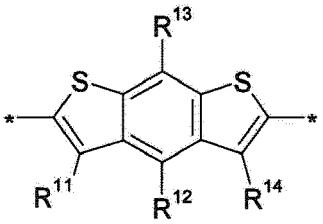
(D11)



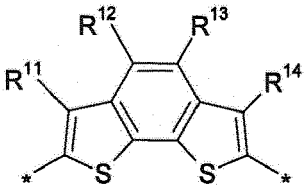
(D19)



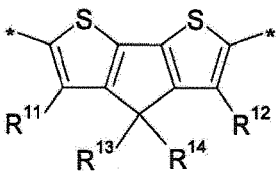
(D22)



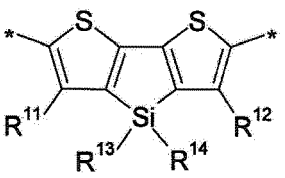
(D29)



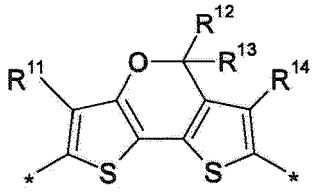
(D30)



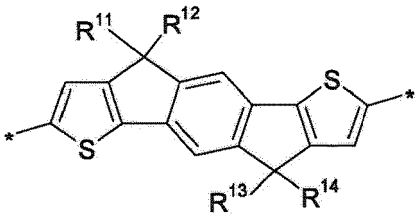
(D35)



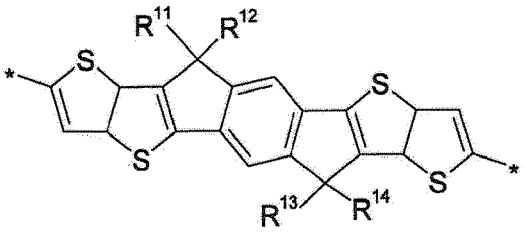
(D36)



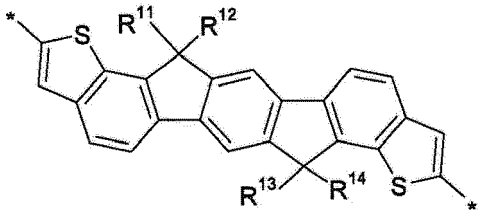
(D44)



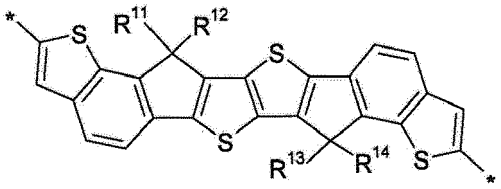
(D55)



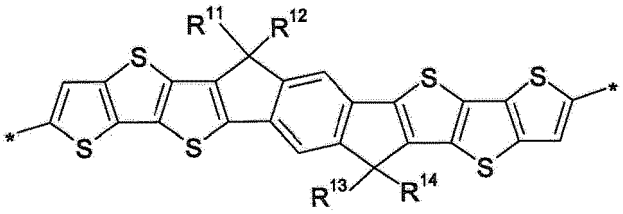
(D84)



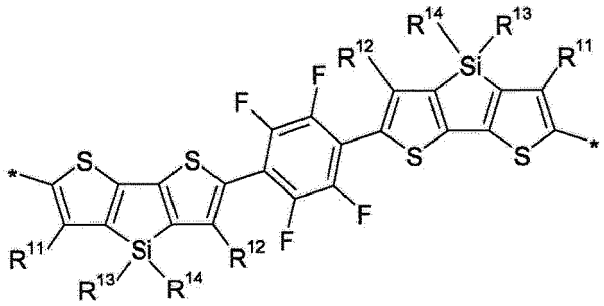
(D87)



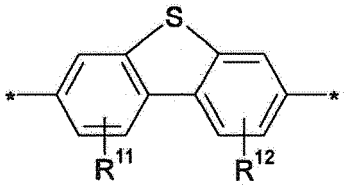
(D88)



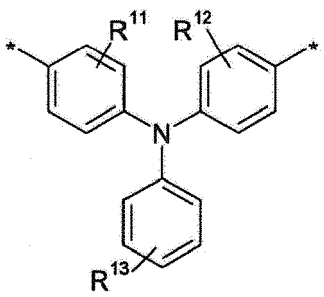
(D89)



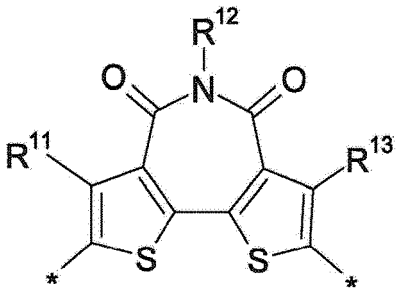
(D93)



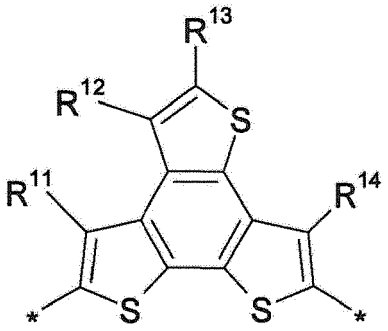
(D106)



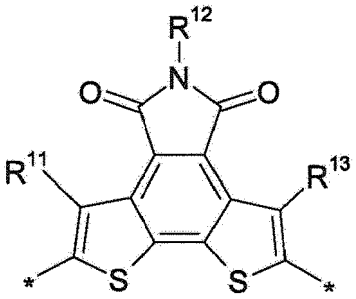
(D111)



(D140



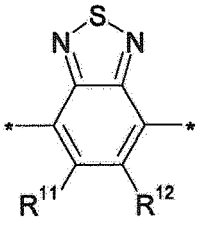
(D141)



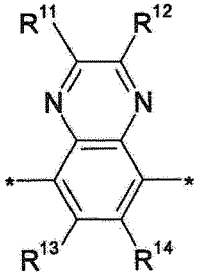
(D146)

wobei R^{11}, R^{12}, R^{13}, R^{14} unabhängig voneinander H bezeichnen oder eine der wie in Anspruch 1 definierten Bedeutungen von L aufweisen.

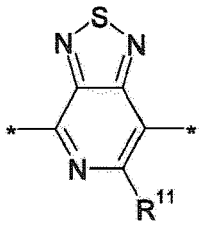
8. Verbindung nach einem der Ansprüche 1 bis 7, wobei eines oder mehrere von Ar^1, Ar^2, Ar^3 und Ar^4 Arylen oder Heteroarylen bezeichnen, ausgewählt aus der Gruppe, bestehend aus den folgenden Formeln



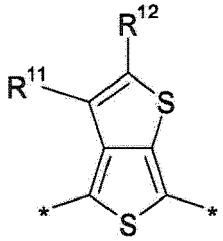
(A1)



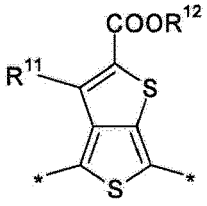
(A6)



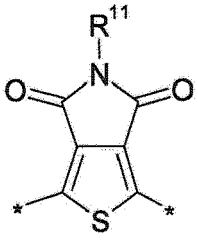
(A7)



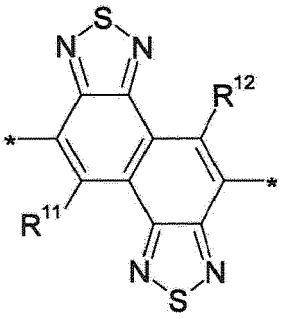
(A15)



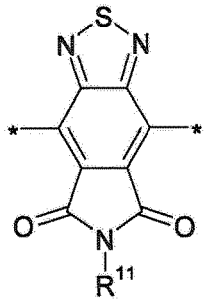
(A16)



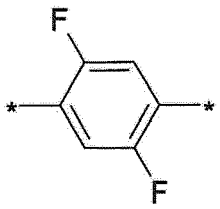
(A20)



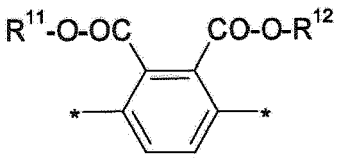
(A74)



(A88)



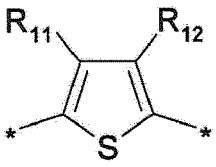
(A92)



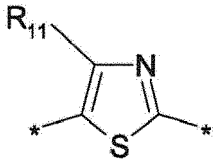
(A98)

wobei R^{11}, R^{12}, R^{13}, R^{14} unabhängig voneinander H bezeichnen oder eine der wie in Anspruch 1 definierten Bedeutungen von L aufweisen.

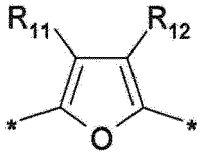
9. Verbindung nach einem der Ansprüche 1 bis 8, wobei eines oder mehrere von Ar^1, Ar^2, Ar^3 und Ar^4 Arylen oder Heteroarylen bezeichnen, ausgewählt aus der Gruppe, bestehend aus den folgenden Formeln



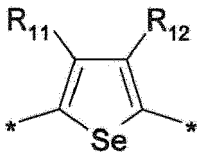
Sp1



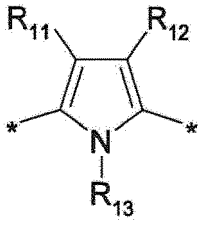
Sp2



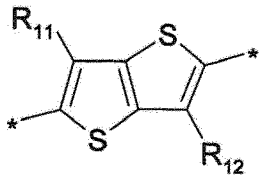
Sp3



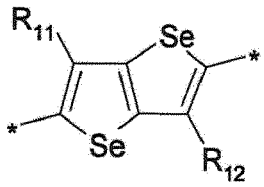
Sp4



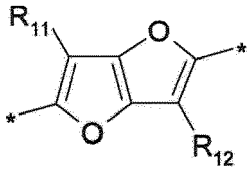
Sp5



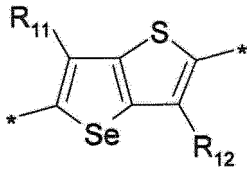
Sp6



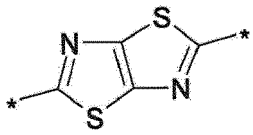
Sp7



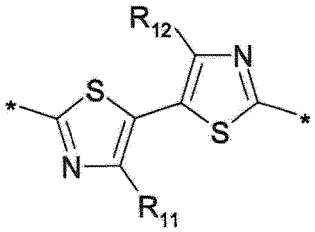
Sp8



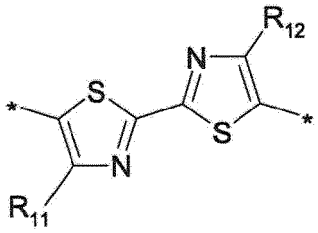
Sp9



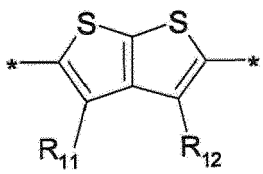
Sp10



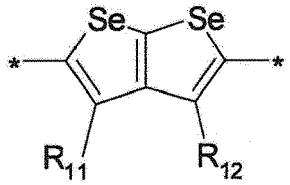
Sp11



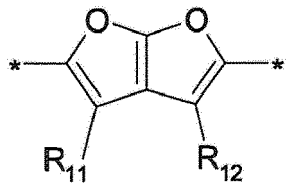
Sp12



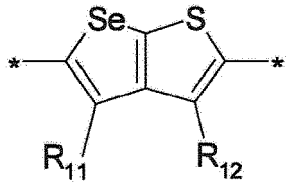
Sp13



Sp14



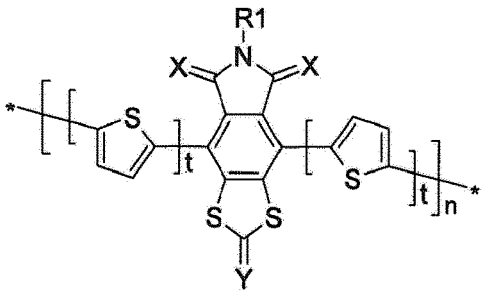
Sp15



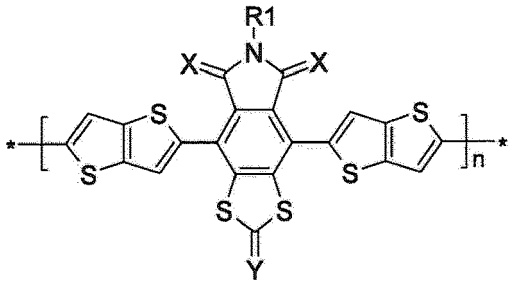
Sp16

wobei R^{11} und R^{12} unabhängig voneinander H bezeichnen oder eine der wie in Anspruch 1 definierten Bedeutungen von L aufweisen.

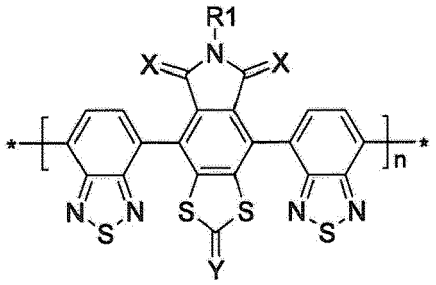
10. Verbindung nach einem der Ansprüche 1 bis 9, die ein konjugiertes Polymer ist, ausgewählt aus den folgenden Formeln



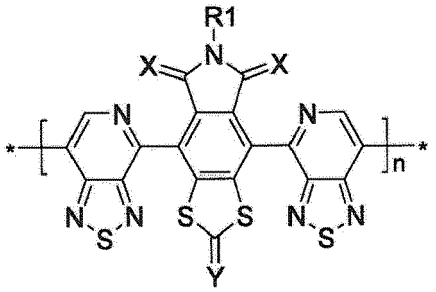
P1



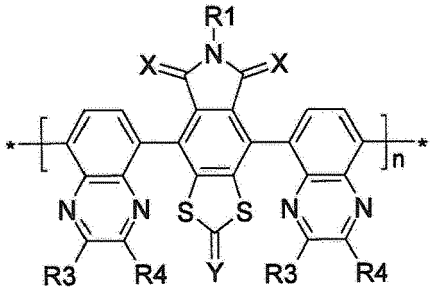
P2



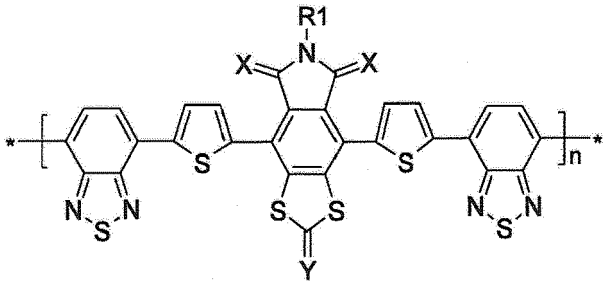
P3



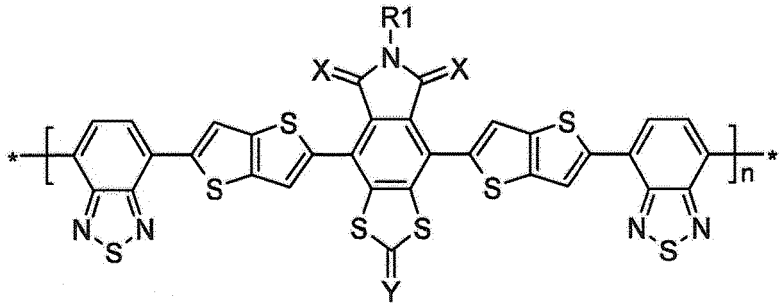
P4



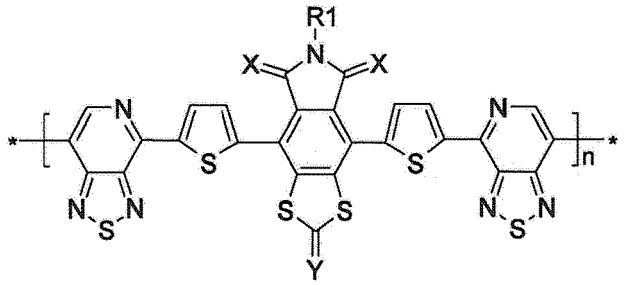
P5



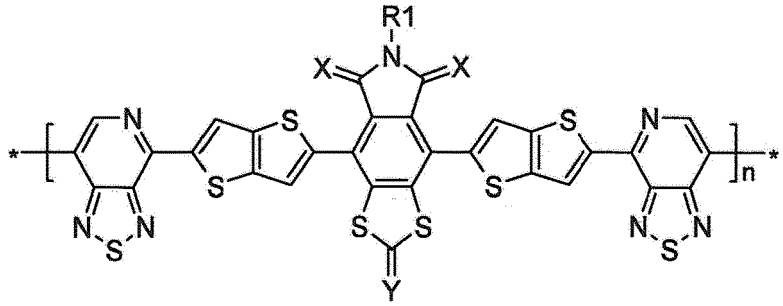
P6



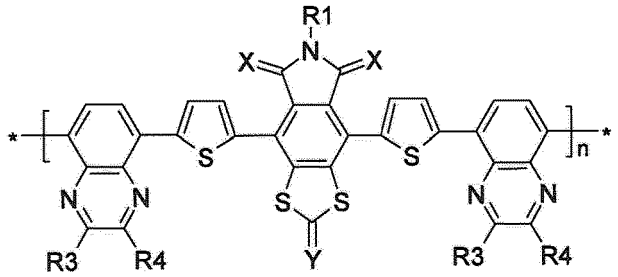
P7



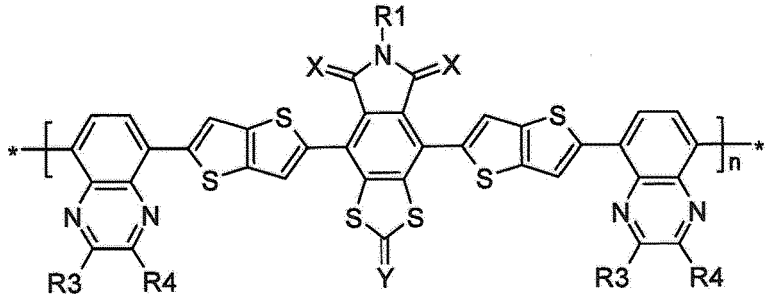
P8



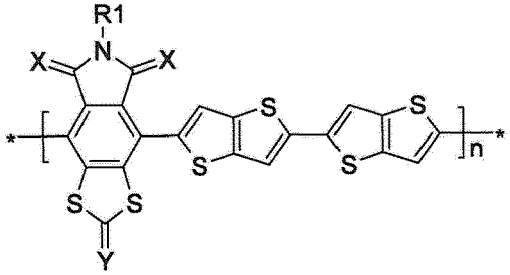
P9



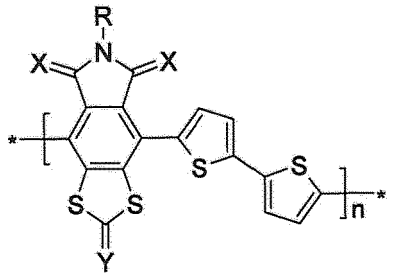
P10



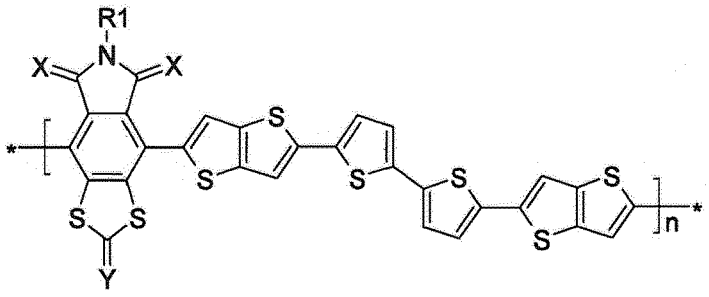
P11



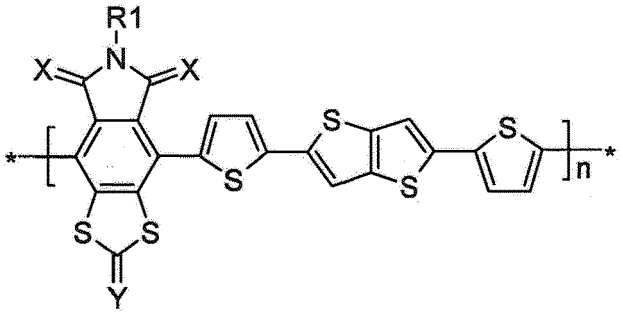
P12



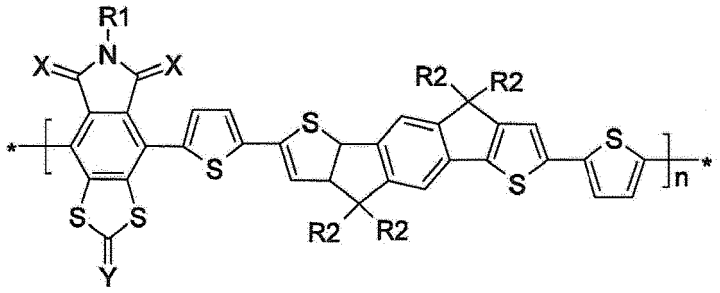
P13



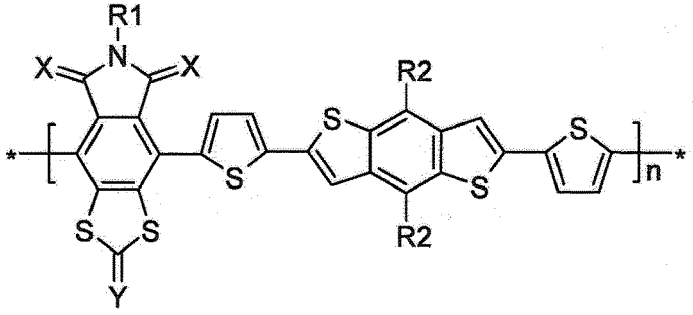
P14



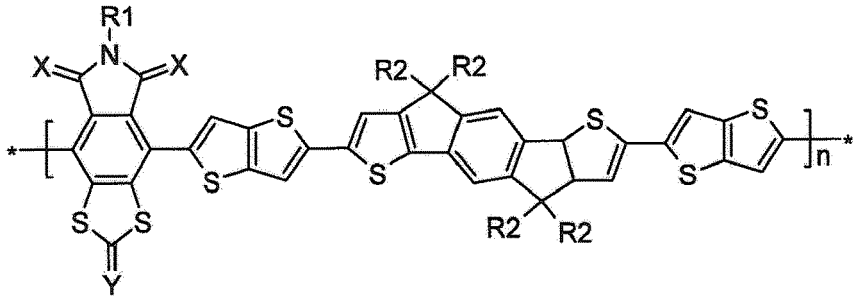
P15



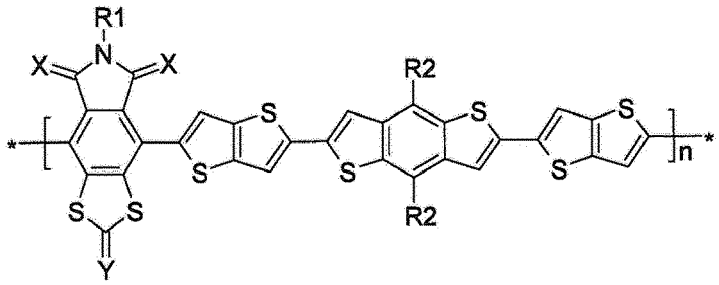
P16



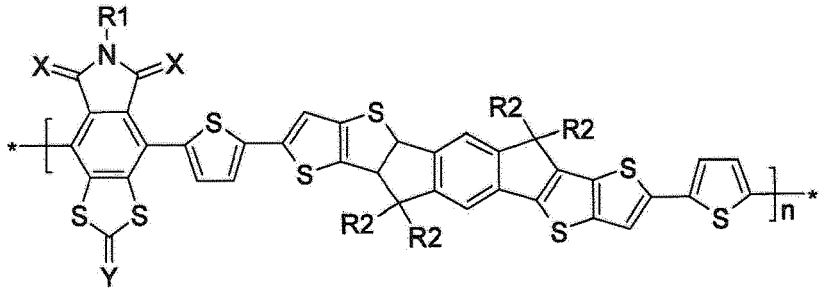
P17



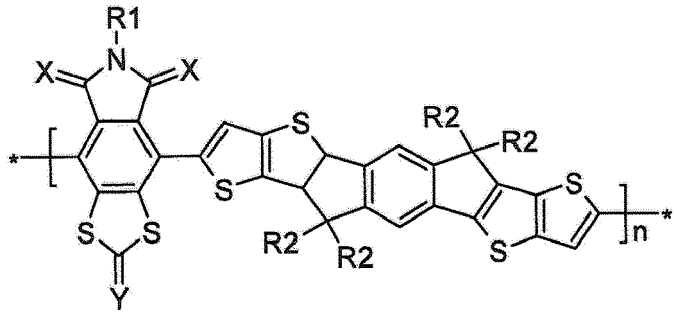
P18



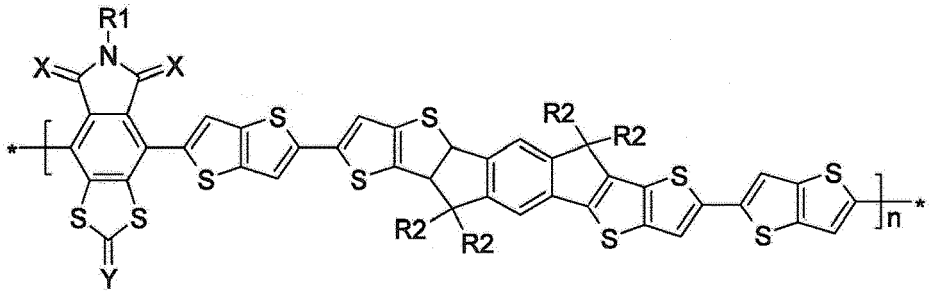
P19



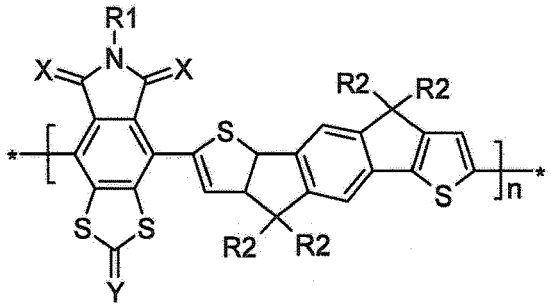
P20



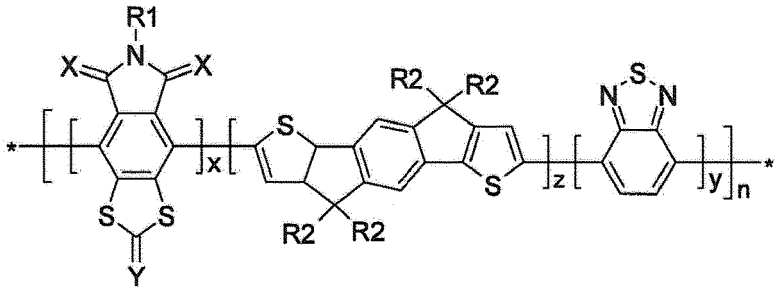
P21



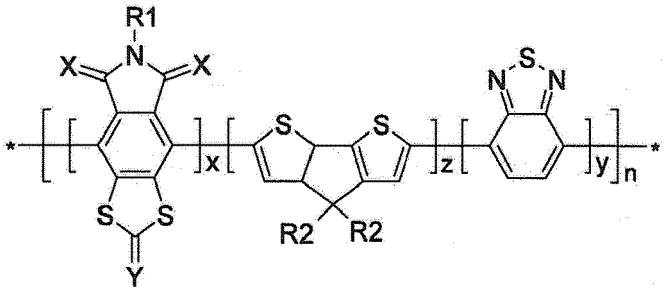
P22



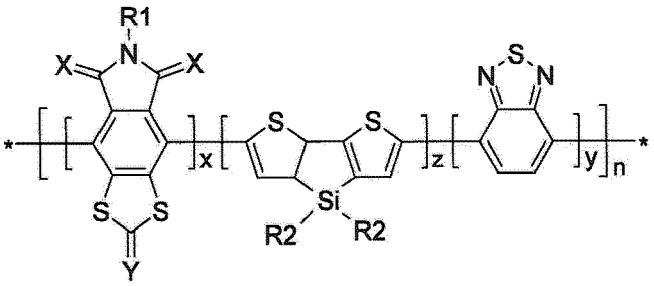
P23



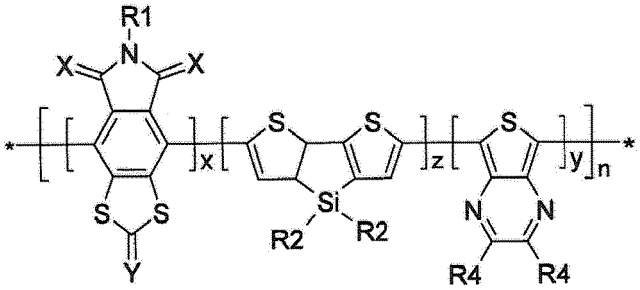
P24



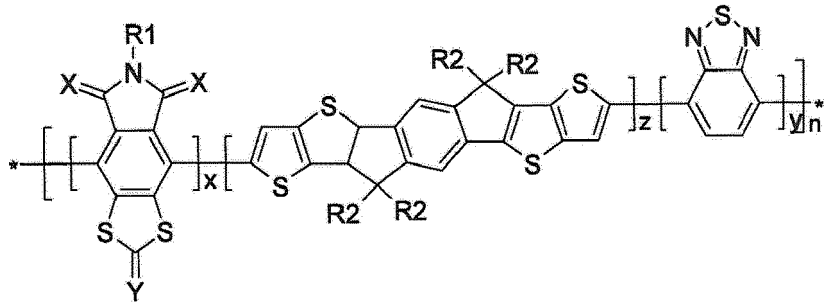
P25



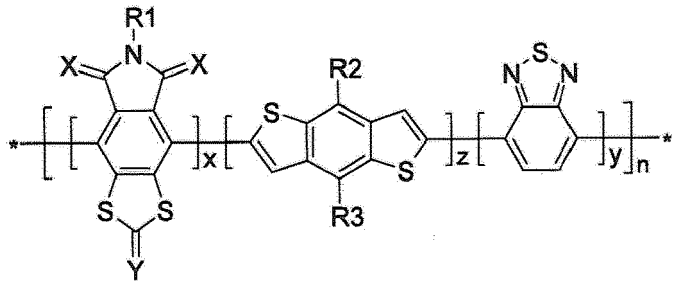
P26



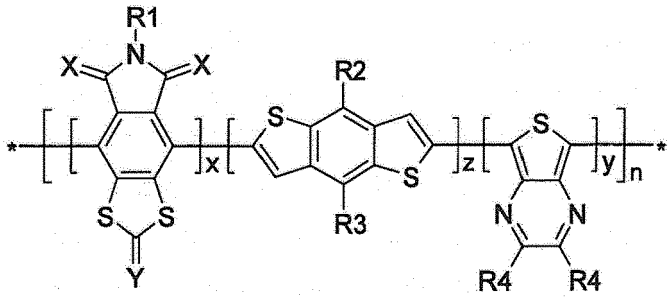
P27



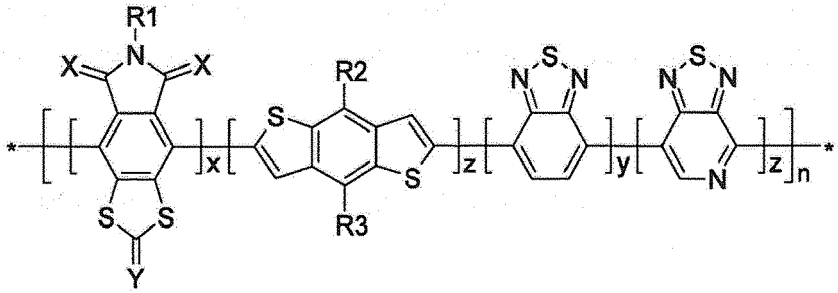
P28



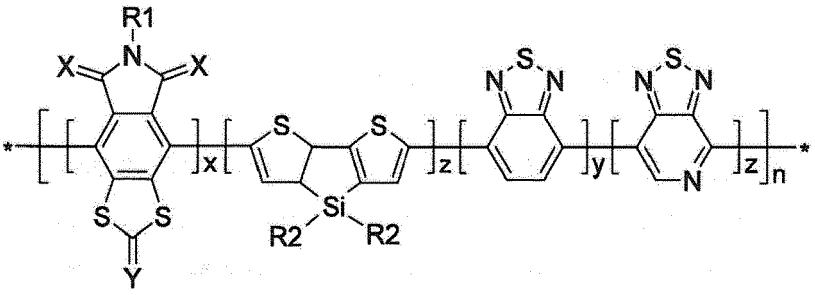
P29



P30



P31



P32

wobei R^1 wie in Anspruch 1 oder 2 definiert ist, X bei jedem Auftreten, identisch oder verschieden, eine der Bedeutungen von X^1 aufweist, die in Anspruch 1 gegeben sind, Y wie in Anspruch 1 definiert ist, t1, 2, 3 oder 4 ist, n wie

in Anspruch 5 definiert ist und R^2, R^3 und R^4 unabhängig voneinander und bei jedem Auftreten, identisch oder verschieden, eine der Bedeutungen aufweisen, die für L gegeben ist.

11. Verbindung nach einem der Ansprüche 1 bis 10, die ein konjugiertes Polymer von Formel IV ist

$$R^5\text{-Kette-}R^6 \qquad \text{IV}$$

wobei "Kette" eine Polymerkette bezeichnet, die aus Formel III, III1-III8 und P1-P32 wie in den Ansprüchen 5, 6 und 10 definiert, ausgewählt ist und R^5 und R^6 unabhängig voneinander die Bedeutungen von R^1 oder L wie in Anspruch 1 oder 2 definiert aufweisen oder unabhängig voneinander, H, F, Br, Cl, I, $-CH_2Cl$, -CHO, $-CR'=CR"_2$, -SiR'R"R"', -SiR'X'X", -SiR'R"X', -SnR'R"R"', -BR'R", $-B(OR')(OR")$, $-B(OH)_2$, $-O-SO_2-R'$, $-C\equiv CH$, $-C\equiv C-SiR'_3$, -ZnX' oder eine Endkappengruppe bezeichnen, X' und X" Halogen bezeichnen, R', R" und R"' unabhängig voneinander eine der in Anspruch 1 gegebenen Bedeutungen von R^0 aufweisen und zwei von R', R" und R"' auch eine Cyclosilyl-, Cyclostannyl-, Cycloboran- oder Cycloboronatgruppe mit 2 bis 20 C-Atomen gemeinsam mit dem jeweiligen Heteroatom, an das sie angehängt sind, bilden können.

12. Verbindung nach Anspruch 1 oder 2, die ein Monomer von Formel V1 oder V2 ist

$$\mathbf{R^7\text{-}(Ar^1)_a\text{-}U\text{-}(Ar^2)_b\text{-}(Ar^3)_c\text{-}(Ar^4)_d\text{-}R^8} \qquad \mathbf{V1}$$

$$\mathbf{R^7\text{-}(Ar^1)_a\text{-}(Ar^2)_b\text{-}U\text{-}(Ar^3)_c\text{-}(Ar^4)_d\text{-}R^8} \qquad \mathbf{V2}$$

wobei U, AR^{1-4}, a, b, c und d die in Anspruch 3, 7, 8 oder 9 gegebenen Bedeutungen aufweisen und R^7 und R^8 unabhängig voneinander aus der Gruppe ausgewählt sind, bestehend aus H, Cl, Br, I, O-Tosylat, O-Triflat, O-Mesylat, O-Nonaflat, $-SiMe_3$, $-SiMe_2F$, $-SiMeF_2$, $-O-SO_2Z^1$, $-B(OZ^2)_2$, $-CZ^3=C(Z^3)_2$, $-C\equiv CH$, $-C\equiv CSi(Z^1)_3$, $-ZnX^0$, $Mg-X^0$ und $-Sn(Z^4)_3$, wobei X^0 Halogen ist, Z^{1-4} aus der Gruppe ausgewählt sind, bestehend aus C_{1-10} Alkyl und C_{6-12} Aryl, jeweils optional substituiert, und zwei Gruppen Z^2 auch eine Cycloboronatgruppe bilden können, die 2 bis 20 C-Atome gemeinsam mit den B- und O-Atomen aufweist und wobei mindestens eines von R^7 und R^8 von H verschieden ist.

13. Verbindung nach Anspruch 12, die aus den folgenden Formeln ausgewählt ist

$$\mathbf{R^7\text{-}Ar^1\text{-}U\text{-}Ar^2\text{-}R^8} \qquad \mathbf{V1a}$$

$$\mathbf{R^7\text{-}U\text{-}R^8} \qquad \mathbf{V1b}$$

$$\mathbf{R^7\text{-}Ar^1\text{-}U\text{-}R^8} \qquad \mathbf{V1c}$$

$$\mathbf{R^7\text{-}U\text{-}Ar^2\text{-}R^8} \qquad \mathbf{V1d}$$

wobei U, Ar^1, Ar^2, R^7 und R^8 wie in Anspruch 12 definiert sind.

14. Verbindung nach Anspruch 12, die aus Formel V3 ausgewählt ist

$$\mathbf{R^7\text{-}U^*\text{-}R^8} \qquad \mathbf{V3}$$

wobei U* eine Einheit, ausgewählt aus Formel R1-R11, wie im Anspruch definiert ist und R^7 und R^8 wie in Anspruch 12 definiert sind.

15. Verbindung nach einem der Ansprüche 1 bis 14, wobei

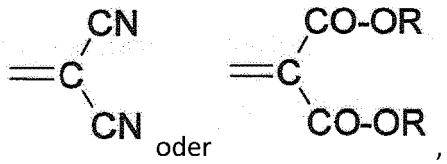
a) eines oder mehrere von Ar^1, Ar^2, Ar^3 und Ar^4 Arylen oder Heteroarylen bezeichnen, ausgewählt aus der Gruppe, bestehend aus den Formeln D1, D7, D10, D11, D19, D22, D29, D30, D35, D36, D44, D55, D84, D87, D88, D89, D93, D106, D111, D140, D141 und D146 wie in Anspruch 7 definiert, und/oder

b) eines oder mehrere von Ar^1, Ar^2, Ar^3 und Ar^4 Arylen oder Heteroarylen bezeichnen, ausgewählt aus der Gruppe, bestehend aus den Formeln A1, A6, A7, A15, A16, A20, A74, A88, A92 und A98 wie in Anspruch 8 definiert,

und

c) eines oder mehrere von Ar^1, Ar^2, Ar^3 und Ar^4 Arylen oder Heteroarylen bezeichnen, ausgewählt aus der Gruppe, bestehend aus den Formeln Sp1, Sp6 und Sp13 wie in Anspruch 9 definiert.

16. Verbindung nach Anspruch 4 oder 10, wobei Y O, S ist,



wobei R wie in Anspruch 1 oder 2 definiert ist.

17. Verbindung von Formel VI nach Anspruch 1, wobei Ar^{1-10} aus den folgenden Gruppen ausgewählt sind,

a) der Gruppe, bestehend aus den Formeln D1, D7, D10, D11, D19, D22, D29, D30, D35, D36, D44, D55, D84, D87, D88, D89, D93, D106, D111, D140 und D141 wie in Anspruch 7 definiert,
b) der Gruppe, bestehend aus den Formeln A1, A6, A7, A15, A16, A20, A74, A88, A92 und A98 wie in Anspruch 8 definiert,
c) der Gruppe, bestehend aus den Formeln Formeln Sp1, Sp6 und Sp10 wie in Anspruch 9 definiert.

18. Verbindung von Formel VI nach Anspruch 1 oder 17, die aus Formel VI1 ausgewählt ist

$$R^{1t}\text{-}U^*\text{-}R^{2t} \qquad \text{VI1}$$

wobei U* eine Einheit ist, ausgewählt aus Formeln R1-R11, wie in Anspruch 4 definiert, und R^{1t} und R^{2t} die in Anspruch 1 gegebenen Bedeutungen aufweisen.

19. Gemisch, das eine oder mehrere Verbindungen nach einem der Ansprüche 1 bis 18 und eine oder mehrere zusätzliche Verbindungen, die eine oder mehrere von halbleitenden, Ladungstransport-, Loch- oder Elektronentransport-, Loch- oder Elektronenblockierungs-, elektrisch leitenden, lichtleitenden oder lichtemittierenden Eigenschaften aufweisen, umfassen.

20. Gemisch, umfassend eine oder mehrere Verbindungen nach einem der Ansprüche 1 bis 18 und einen oder mehrere organische n-Halbleiter.

21. Gemisch nach Anspruch 20, wobei die organischen n-Halbleiter aus Fullerenen oder substituierten Fullerenen ausgewählt sind.

22. Formulierung, umfassend eine oder mehrere Verbindungen oder Gemische nach einem der Ansprüche 1 bis 21 und weiter umfassend ein oder mehrere Lösemittel, ausgewählt aus organischen Lösemitteln.

23. Optische, elektrooptische, elektronische, elektrolumineszierende oder photolumineszierende Vorrichtung oder eine Komponente davon, oder eine Anordnung die sie umfasst, die ein oder mehrere Verbindungen oder Gemische nach einem der Ansprüche 1 bis 21 umfasst.

24. Verwendung einer Verbindung oder eines Gemisches nach einem der Ansprüche 1 bis 21 als halbleitendes, ladungstransportierendes, elektrisch leitendes, lichtleitendes oder lichtemittierendes Material, oder in einer optischen, elektrooptischen, elektronischen, elektrolumineszierenden oder photolumineszierenden Vorrichtung oder in einer Komponente, wie einer Vorrichtung oder in einer Anordnung, die solch eine Vorrichtung oder Komponente umfasst.

25. Halbleitendes, ladungstransportierendes, elektrisch leitendes, photoleitendes oder lichtemittierendes Material, das eine Verbindung oder ein Gemisch nach einem der Ansprüche 1 bis 21 umfasst.

26. Optische, elektrooptische, elektronische, elektrolumineszierende oder photolumineszierende Vorrichtung oder eine Komponente davon, oder eine Anordnung, die sie umfasst, die ein halbleitendes, ladungstransportierendes, elektrisch leitendes, photoleitendes oder lichtemittierendes Material nach Anspruch 25 umfasst.

27. Optische, elektrooptische, elektronische, elektrolumineszierende oder photolumineszierende Vorrichtung nach Anspruch 26, die aus organischen Dünnfilmtransistoren (OTFT), organischen Dünnfilmtransistoren (OTFT), organischen lichtemittierenden Dioden (OLED), organischen lichtemittierenden Transistoren (OLET), organischen Photovoltaikvorrichtungen (OPV), organischen Photodetektoren (OPD), organischen Solarzellen, farbstoffempfindlichen Solarzellen (DSSC), Perowskit-basierten Solarzellen, Laserdioden, Schottky-Dioden, Photoleitern und Photodetektoren ausgewählt ist.

28. Komponente nach Anspruch 26, die aus Ladungsinjektionsschichten, Ladungstransportschichten, Zwischenschichten, Planarisierungsschichten, antistatischen Filmen, Polymerelektrolytmembranen (PEM), leitenden Substraten und leitenden Strukturen ausgewählt ist.

29. Anordnung nach Anspruch 26, die aus integrierten Schaltungen (IC), Funkfrequenzkennungs- (RFID) -etiketten oder Sicherheitsmarkierungen oder Sicherheitsvorrichtungen, die diese enthalten, Flachbildschirmanzeigen oder Hintergrundbeleuchtungen davon, elektrophotografischen Vorrichtungen, elektrophotografischen Aufzeichnungsvorrichtungen, organischen Speichervorrichtungen, Sensorvorrichtungen, Biosensoren und Biochips ausgewählt ist.

30. Massenheteroübergang, der ein Gemisch nach einem der Ansprüche 19 bis 21 umfasst.

31. Massenheteroübergang (BHJ) OPV-Vorrichtung oder umgekehrte BHJ-OPV-Vorrichtung, die den Massenheteroübergang nach Anspruch 30 umfasst.

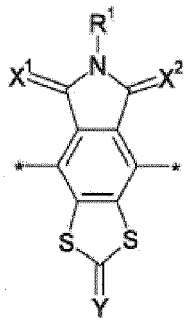
32. Prozess zum Zubereiten eines konjugierten Polymers nach einem der Ansprüche 1 bis 11, indem ein oder mehrere Monomere, die aus Ansprüchen 12, 13, 14 und 15 ausgewählt sind, miteinander und/oder mit einem oder mehreren Monomeren der Formeln MI-MIV in einer Aryl-Aryl-Kopplungsreaktion gekoppelt sind

R^7-Ar^1-R^8	**MI**
R^7-Ar^2-R^8	**MII**
R^7-Ar^3-R^8	**MIII**
R^7-Ar^4-R^8	**MIV**

wobei AR^{1-4}, R^7 und R^8 die in Anspruch 12 gegebenen Bedeutungen aufweisen.

Revendications

1. Composé comprenant une ou plusieurs unités hétéroarylène divalent de formule I



I

dans lequel les radicaux individuels, indépendamment les uns des autres et à chaque occurrence de manière identique ou différente, présentent les significations suivantes

X^1, X^2 O ou S,
Y O, S ou CU^1U^2,
U^1, U^2 un groupe attracteur d'électrons, de préférence choisi parmi CN, C(=O)R ou C(=O)OR, ou U^1 et U^2

forment ensemble un noyau carbocyclique, hétérocyclique, aromatique ou hétéroaromatique présentant de 4 à 15 atomes de noyau qui est optionnellement substitué par un ou plusieurs groupes L,

R^1 H ou alkyle à chaîne linéaire, ramifié ou cyclique comportant de 1 à 30 atomes de C, dans lequel un ou plusieurs groupes CH_2 sont optionnellement remplacés par -O-, -S-, -C(=O)-, -C(=S)-, -C(=O)-O-, -O-C(=O)-, $-NR^0$-, $-SiR^0R^{00}$-, $-CF_2$-, $CR^0=CR^{00}$-, - $CY^1=CY^2$- ou -C≡C- d'une manière telle que des atomes de O et/ou de S ne sont pas liés directement les uns aux autres, et dans lequel un ou plusieurs atomes de H sont optionnellement remplacés par F, Cl, Br, I ou CN, et dans lequel un ou plusieurs groupes CH_2 ou CH_3 sont optionnellement remplacés par un groupe cationique ou anionique, ou un aryle, hétéroaryle, arylalkyle, hétéroarylalkyle, aryloxy ou hétéroaryloxy, dans lequel chacun des groupes cycliques mentionnés ci-dessus présente de 5 à 20 atomes de noyau, est mono- ou polycyclique, contient optionnellement des noyaux fusionnés, et est non substitué ou substitué par un ou plusieurs groupes L identiques ou différents,

R akyle à chaîne linéaire, ramifié ou cyclique comportant de 1 à 30 atomes de C, dans lequel un ou plusieurs groupes CH_2 sont optionnellement remplacés par -O-, -S-, - C(=O)-, -C(=S)-, -C(=O)-O-, -O-C(=O)-, $-NR^0$-, $-SiR^0R^{00}$-, $-CF_2$-, $-CR^0=CR^{00}$-, $-CY^1=CY^2$- ou -C≡C-d'une manière telle que des atomes de O et/ou de S ne sont pas liés directement les uns aux autres, et dans lequel un ou plusieurs atomes de H sont optionnellement remplacés par F, Cl, Br, I ou CN, et dans lequel un ou plusieurs groupes CH_2 ou CH_3 sont optionnellement remplacés par un groupe cationique ou anionique, ou un aryle, hétéroaryle, arylalkyle ou hétéroarylalkyle, dans lequel chacun des groupes cycliques mentionnés ci-dessus présente de 5 à 20 atomes de noyau, est mono- ou polycyclique, contient optionnellement des noyaux fusionnés, et est non substitué ou substitué par un ou plusieurs groupes L identiques ou différents,

L F, Cl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, R^0, OR^0, SR^0, $-C(=O)X^0$, $-C(=O)R^0$, - $C(=O)-OR^0$, $-O-C(=O)-R^0$, $-NH_2$, $-NHR^0$, $-NR^0R^{00}$, $-C(=O)NHR^0$, $-C(=O)NR^0R^{00}$, $-SO_3R^0$, $-SO_2R^0$, - OH, $-NO_2$, $-CF_3$, $-SF_5$, ou un silyle optionnellement substitué, ou un carbyle ou un hydrocarbyle comportant de 1 à 20 atomes de C qui est optionnellement substitué et comprend optionnellement un ou plusieurs hétéroatomes,

Y^1, Y^2 H, F, Cl ou CN,

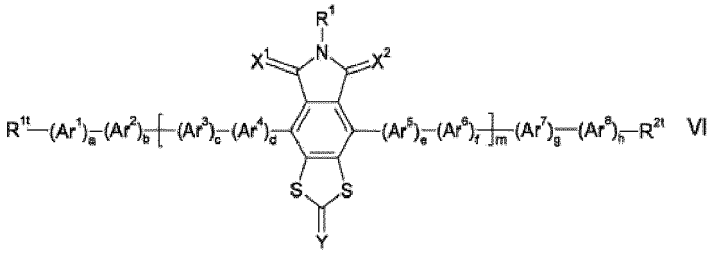
X^0 halogène,

R^0, R^{00}H ou un alkyle à chaîne linéaire ou ramifié comportant de 1 à 20 atomes de C qui est optionnellement fluoré,

à condition que, si X^1, X^2 et Y sont O, alors l'unité de formule I est liée via la position 1 ou 4 du noyau benzène à au moins un groupe qui est différent de H,

dans lequel le composé est un polymère conjugué comprenant une ou plusieurs unités choisies de formule I, et comprenant en outre une ou plusieurs unités arylène ou hétéroarylène qui présentent de 5 à 20 atomes de noyau, sont mono- ou polycycliques, contiennent optionnellement des noyaux fusionnés, sont non substituées ou substituées par un ou plusieurs groupes L identiques ou différents, et soit sont choisies parmi la formule I soit sont structurellement différentes de la formule I, et dans lequel toutes les unités mentionnées ci-dessus sont directement reliées les unes aux autres,

ou le composé est choisi parmi la formule VI



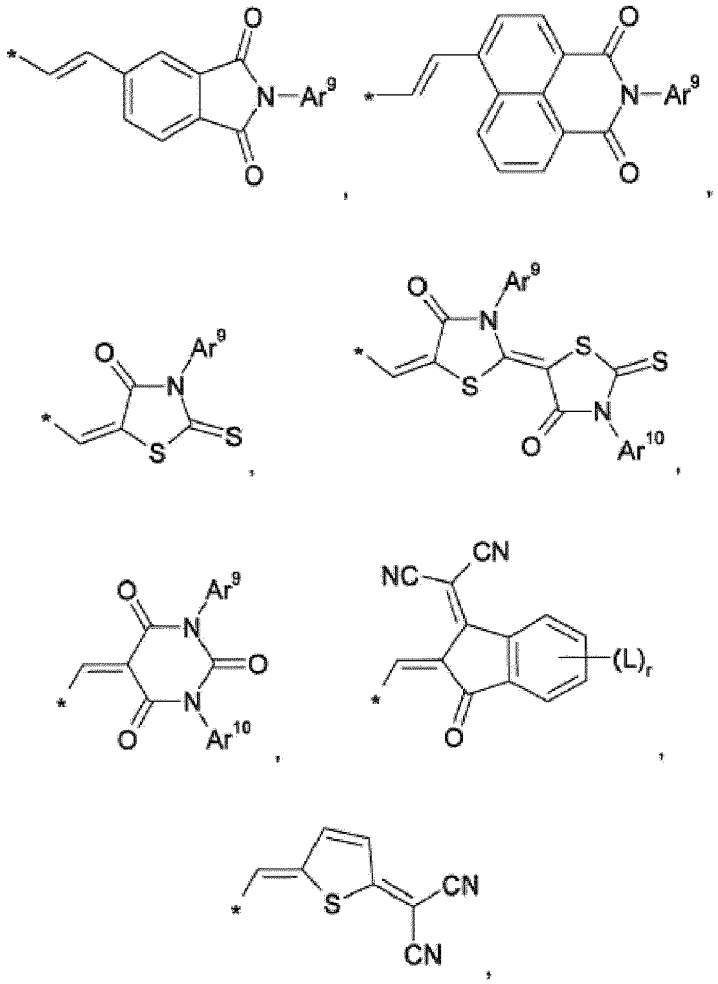
dans lequel les radicaux individuels, indépendamment les uns des autres et à chaque occurrence de manière identique ou différente, présentent les significations suivantes

Ar^{1-8} arylène ou hétéroarylène qui présente de 5 à 20 atomes de noyau, est mono-ou polycyclique, contient optionnellement des noyaux fusionnés, est non substitué ou substitué par un ou plusieurs groupes L identiques ou différents, et est différent de la formule I,

Y^1, Y^2 H, F, Cl ou CN,

$R^{1t, 2t}$ H, F, Cl, Br, -CN, $-CF_3$, R*, $-CF_2$-R*, -O-R*, -S-R*, $-SO_2$-R*, $-SO_3$-R*, -C(=O)-R*, - C(=S)-R*, $-C(=O)-CF_2$-R*, -C(=O)-OR*, -C(=S)-OR*, -O-C(=O)-R*, -O-C(=S)-R*, -C(=O)-SR*, - S-C(=O)-R*, -C(=O)NR*R**, -NR*-C(=O)-R*, -NHR*, -NR*R**, -CR*=CR*R**, -C≡C-R*, - C≡C-SiR*R**R***, -SiR*R**R***,

-CH=C(CN)-C(=O)-OR*, -CH=C(CO-OR*)$_2$, CH=C(CO-NR*R**)$_2$, CH=C(CN)(Ar^9),



Ar^{9,10} aryle ou hétéroaryle, présentant chacun de 4 à 30 atomes de noyau, contenant optionnellement des noyaux fusionnés et étant non substitués ou substitués par un ou plusieurs groupes L,
R*, R**, R*** alkyle comportant de 1 à 20 atomes de C qui est à chaîne linéaire, ramifié ou cyclique, et est non substitué, ou substitué par un ou plusieurs atomes de F ou de Cl ou groupes CN, ou perfluoré, et dans lequel un ou plusieurs atomes de C sont optionnellement remplacés par -O-, -S-, -C(=O)-, -C(=S)-, -SiR^{0}R^{00}-, -NR^{0}R^{00}-, - CHR^0=CR^{00}- ou -C≡C- de telle manière que des atomes de O et/ou de S ne sont pas directement liés les uns aux autres,
R^0, R^{00}H ou alkyle à chaîne linéaire ou ramifié comportant de 1 à 20 atomes de C qui est optionnellement fluoré,
a-h 0 ou 1, avec au moins l'un de a-h valant 1,
m 1, 2 ou 3,
L l'une des significations données ci-dessus,
r 0, 1, 2, 3 ou 4.

2. Composé selon la revendication 1, dans lequel R^1 et R désignent un alkyle, un alcoxy ou un thiaalkyle, tous étant à chaîne linéaire ou ramifiés, présentant de 1 à 25 atomes de C, et étant optionnellement fluorés.

3. Composé selon la revendication 1 ou 2, qui est un polymère conjugué comprenant une ou plusieurs unités répétitives de formule II1 ou II2, et optionnellement une ou plusieurs unités répétitives de formule II3 :

-(Ar^1)$_a$-U-(Ar^2)$_b$-(Ar^3)$_c$-(Ar^4)$_d$- **II1**

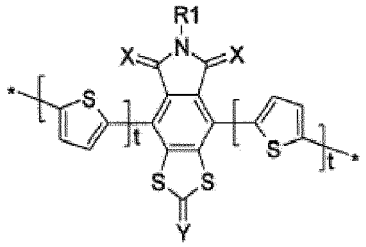
-(Ar^1)$_a$-(Ar^2)$_b$,-U-(Ar^3)$_c$-(Ar^4)$_d$- **II2**

$-(Ar^1)_a-(Ar^2)_b-(Ar^3)_c-(Ar^4)_d-$ II3

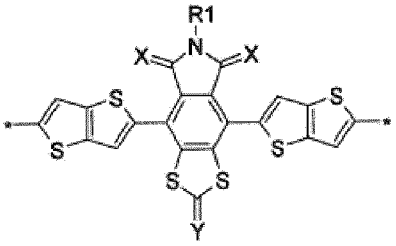
dans lequel les radicaux individuels, indépendamment les uns des autres et à chaque occurrence de manière identique ou différente, présentent les significations suivantes

U une unité de formule I selon la revendication 1 ou 2,
Ar^{1-4} l'une des significations données dans la revendication 1,
a, b, c, d 0 ou 1, dans lequel dans la formule II3 a + b + c + d ≥ 1.

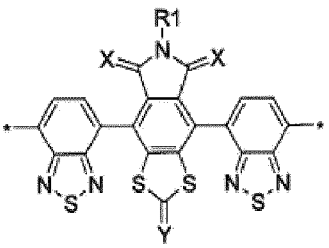
4. Composé selon l'une quelconque des revendications 1 à 3, qui comprend une ou plusieurs unités répétitives choisies parmi les formules suivantes.



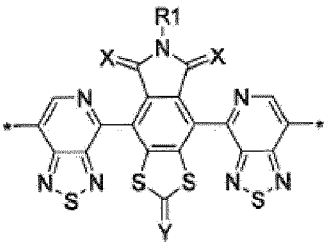
R1



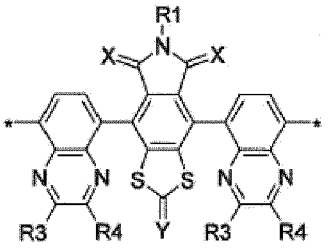
R2



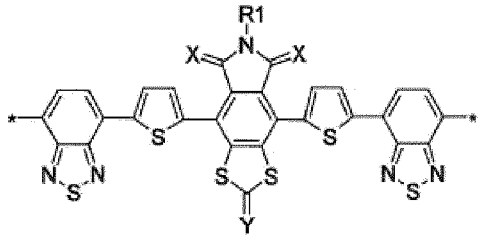
R3



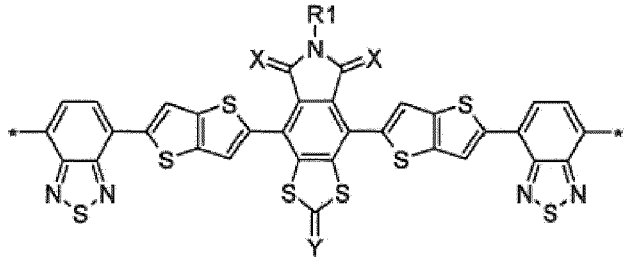
R4



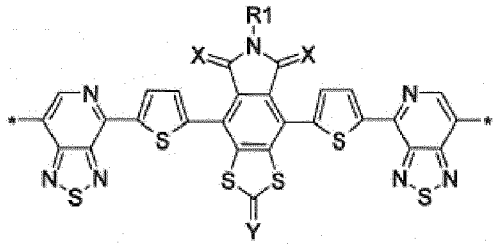
R5



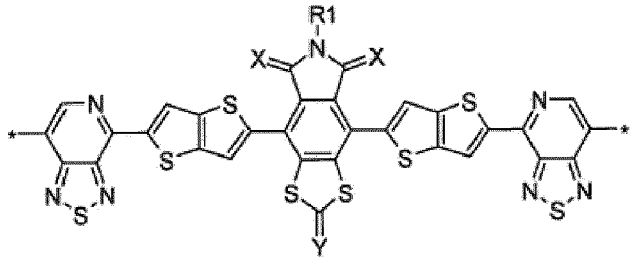
R6



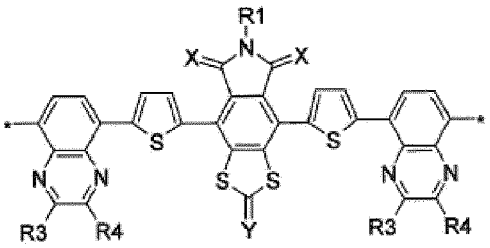
R7



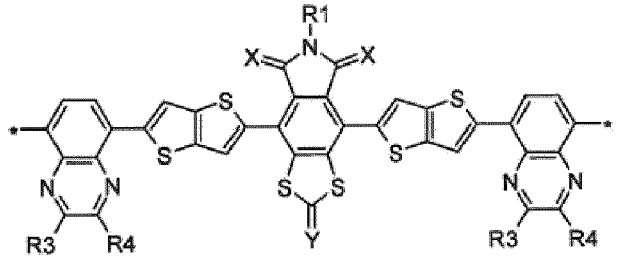
R8



R9



R10

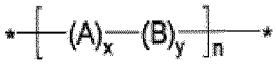


R11

dans lequel R^1 est selon la revendication 1 ou 2, X présente à chaque occurrence de manière identique ou différente

l'une des significations de X^1 telles que données dans la revendication 1, Y est selon la revendication 1, t e 2, 3 ou 4, et R^2, R^3 et R^4 présentent indépendamment les uns des autres et à chaque occurrence de manière identique ou différente l'une des significations données de L données dans la revendication 1.

5. Composé selon l'une quelconque des revendications 1 à 4, qui est un polymère conjugué de formule III :

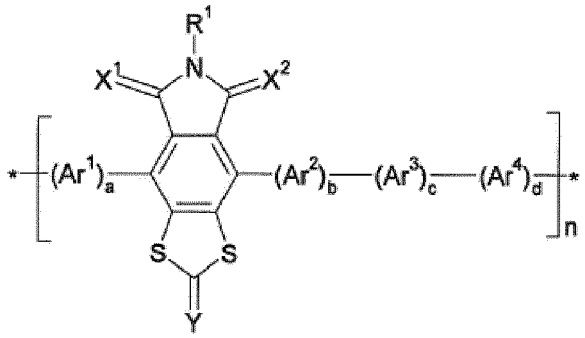


III

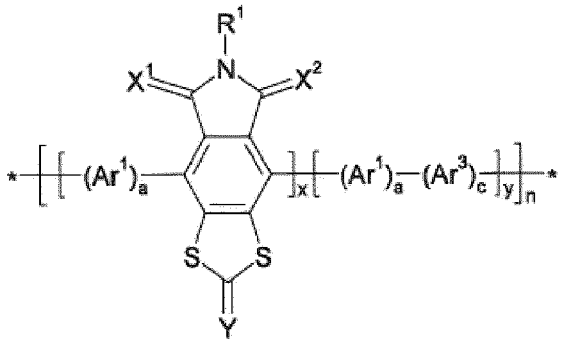
dans lequel

A est une unité de formule I, II1, II2 ou R1-R11 selon l'une quelconque des revendications 1 à 4,
B est une unité de formule I, II1, II2, II3 ou R1-R11 selon l'une quelconque des revendications 1 à 4 qui est différent de A,
x est > 0 et ≤ 1,
y est ≥ 0 et < 1,
x + y vaut 1, et
n est un nombre entier ≥ 5.

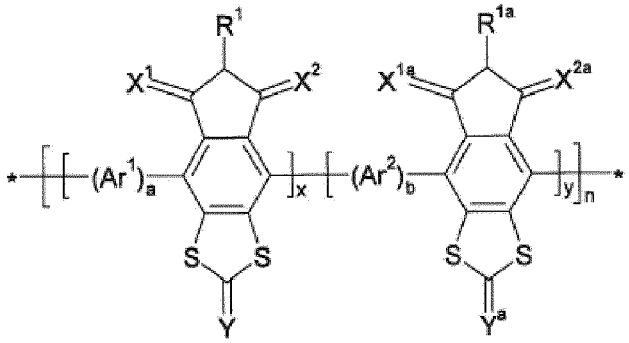
6. Composé selon l'une quelconque des revendications 1 à 5, qui est un polymère conjugué choisi parmi les formules suivantes



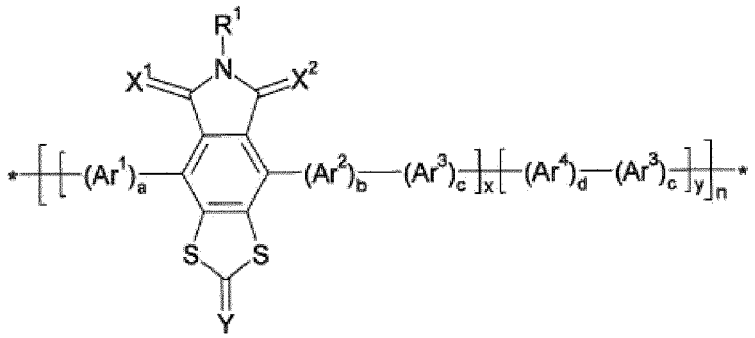
III1



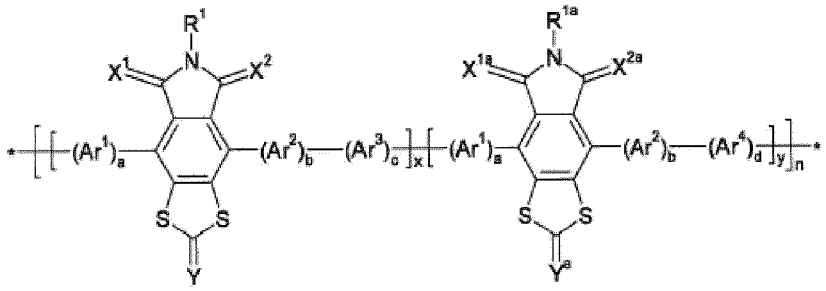
III2



III3



III4

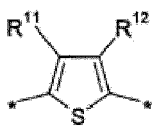


III5

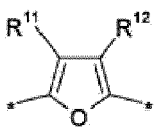
dans lequel

X^1, X^2, Y et R^1 présentent les significations données dans la revendication 1,
X^{1a} présente l'une des significations données pour X^1,
X^{2a} présente l'une des significations données pour X^1,
Y^a présente l'une des significations données pour Y,
R^{1a} présente l'une des significations données pour R^1,
Ar^2, Ar^3, Ar^4, a, b, c et d présentent les significations données dans la revendication 3,
x, y et n présentent les significations données dans la revendication 5, et
dans la formule III3 et III5 au moins l'un de X^1, X^2, Y et R^1 est différent de son radical correspondant X^{1a}, X^{2a}, Y^a et R^{1a}, respectivement.

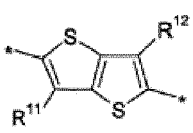
7. Composé selon l'une quelconque des revendications 1 à 6, dans lequel un ou plusieurs de Ar^1, Ar^2, Ar^3 et Ar^4 désignent un arylène ou un hétéroarylène choisi dans le groupe constitué des formules suivantes



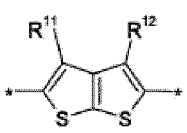
(D1)



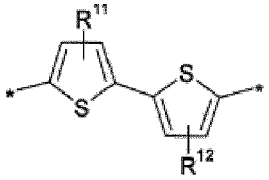
(D7)



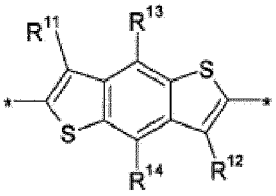
(D10)



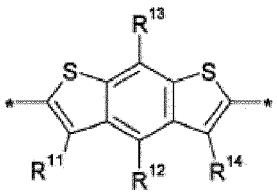
(D11)



(D19)



(D22)



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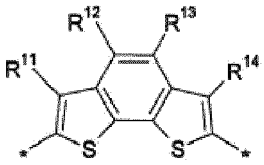
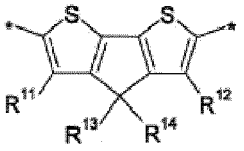
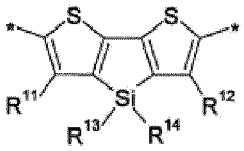


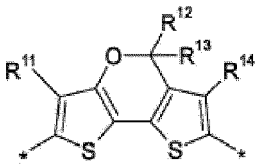
(D30)



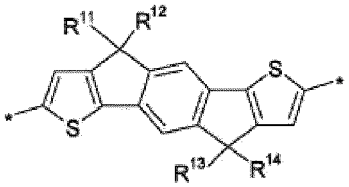
(D35)



(D36)



(D44)



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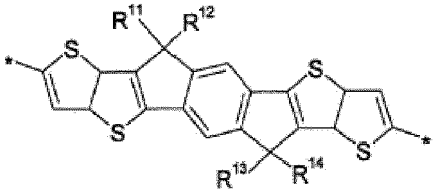
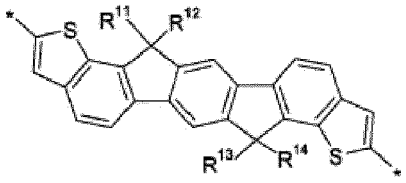


(D84)



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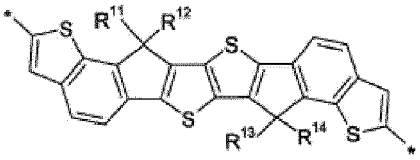

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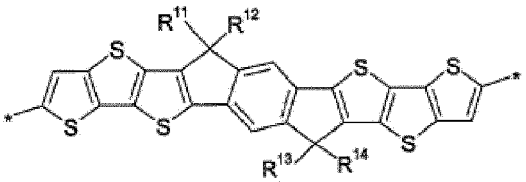

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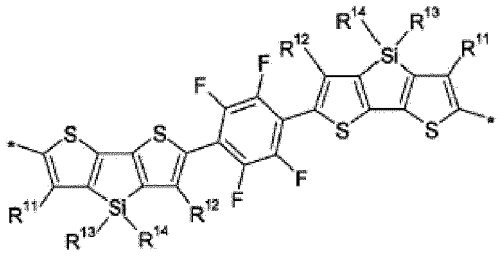

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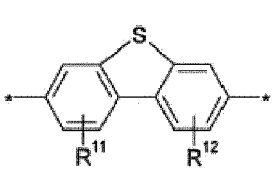
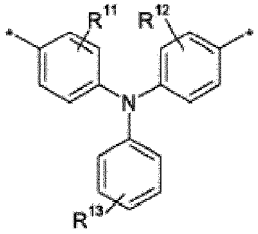
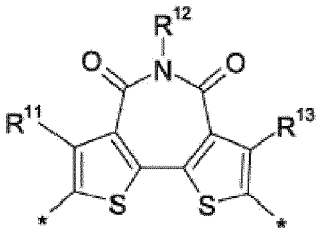


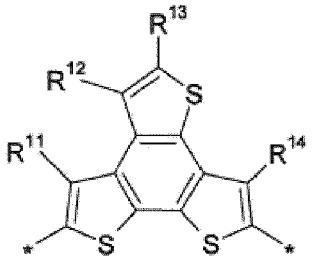
(D106)



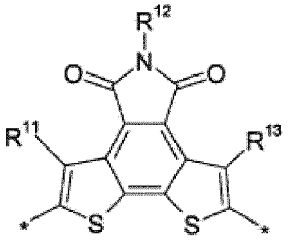
(D111)



(D140



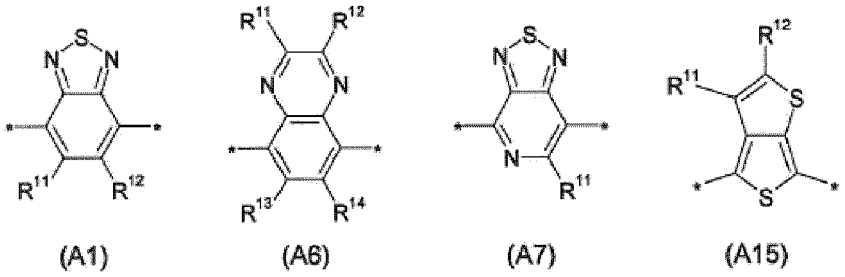
(D141)



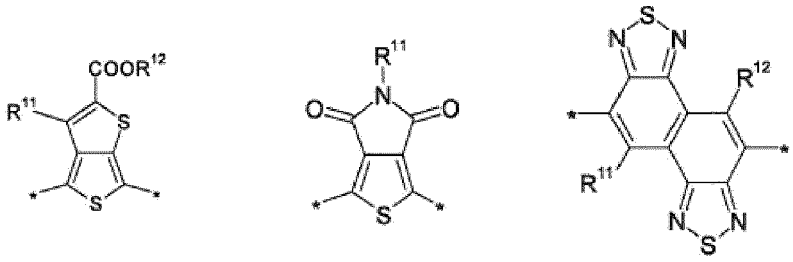
(D146)

dans lequel R^{11}, R^{12}, R^{13}, R^{14} indépendamment les uns des autres désignent H ou présentent l'une des significations de L selon la revendication 1.

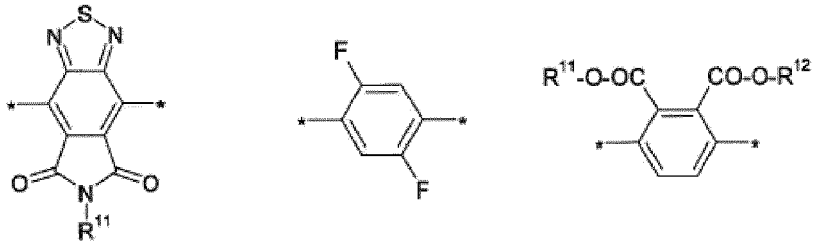
8. Composé selon l'une quelconque des revendications 1 à 7, dans lequel un ou plusieurs de Ar^1, Ar^2, Ar^3 et Ar^4 désignent un arylène ou un hétéroarylène choisi dans le groupe constitué des formules suivantes



(A1) (A6) (A7) (A15)



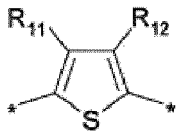
(A16) (A20) (A74)



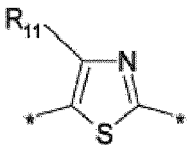
(A88) (A92) (A98)

dans lequel R^{11}, R^{12}, R^{13}, R^{14} indépendamment les uns des autres désignent H ou présentent l'une des significations de L selon la revendication 1.

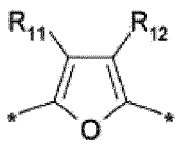
9. Composé selon l'une quelconque des revendications 1 à 8, dans lequel un ou plusieurs de Ar^1, Ar^2, Ar^3 et Ar^4 désignent un arylène ou un hétéroarylène choisi dans le groupe constitué des formules suivantes



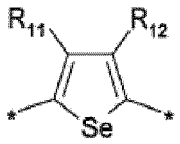
Sp1



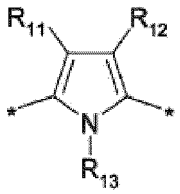
Sp2



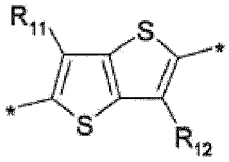
Sp3



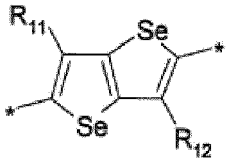
Sp4



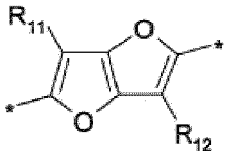
Sp5



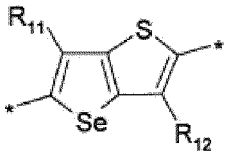
Sp6



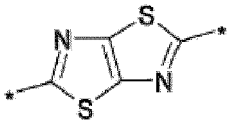
Sp7



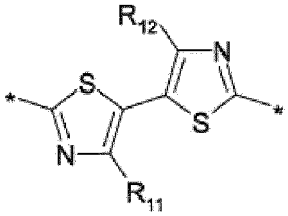
Sp8



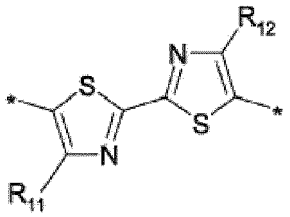
Sp9



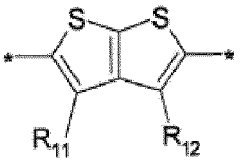
Sp10



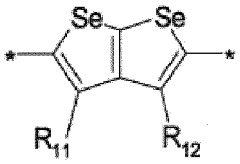
Sp11



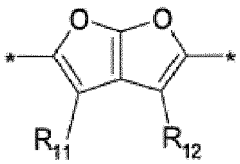
Sp12



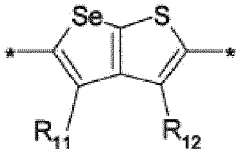
Sp13



Sp14



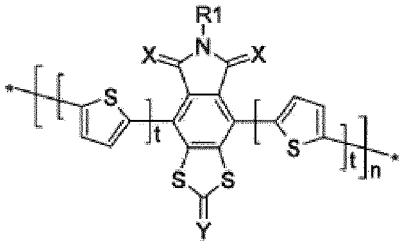
Sp15



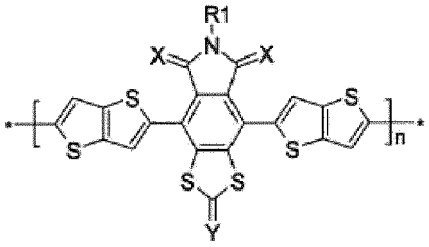
Sp16

dans lequel R^{11} et R^{12} indépendamment l'un de l'autre désignent H ou présentent l'une des significations de L selon la revendication 1.

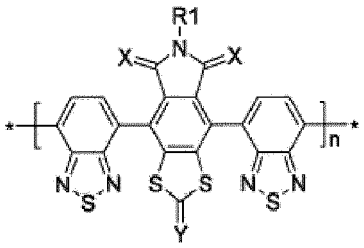
10. Composé selon l'une quelconque des revendications 1 à 9 qui est un polymère conjugué choisi parmi les formules suivantes



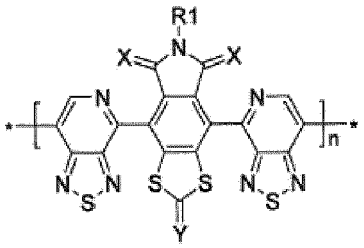
P1



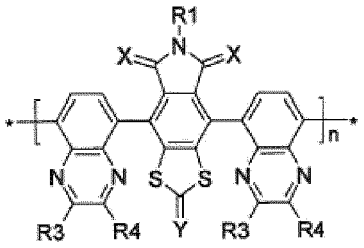
P2



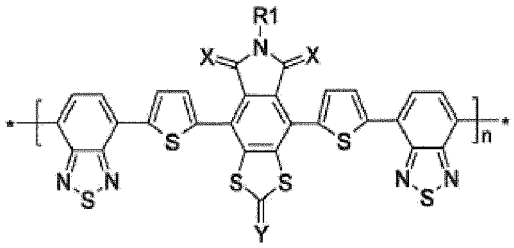
P3



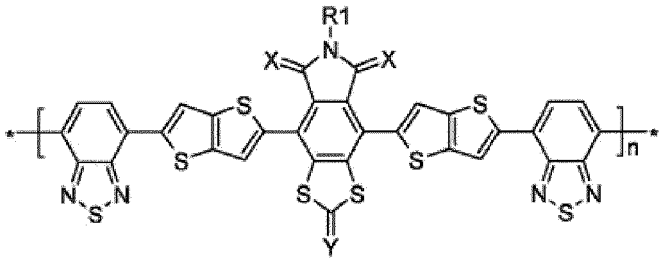
P4



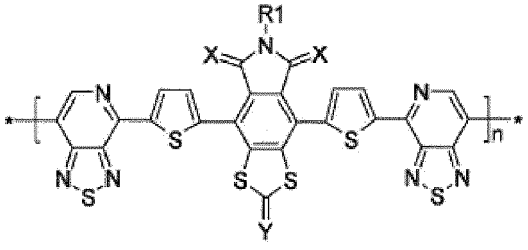
P5



P6



P7



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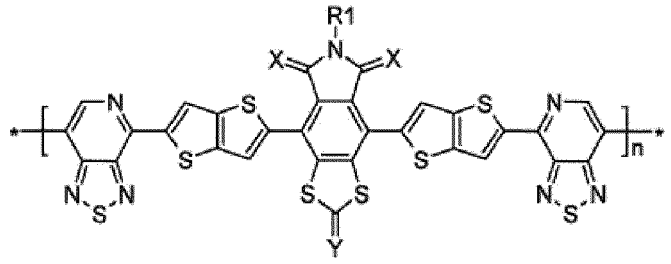

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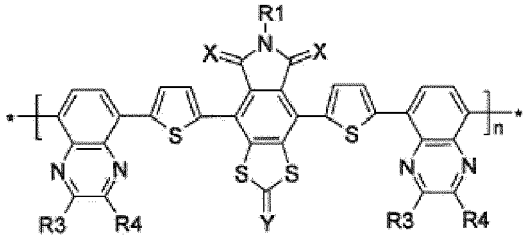

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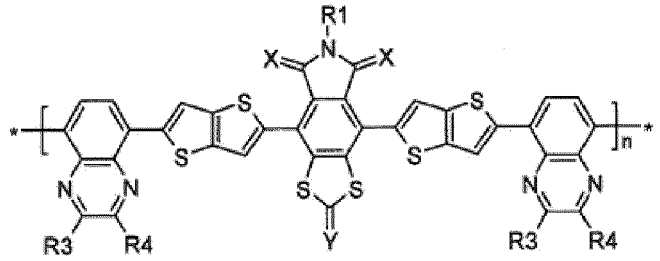

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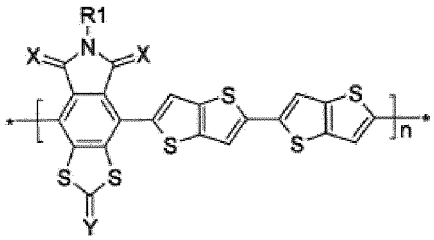

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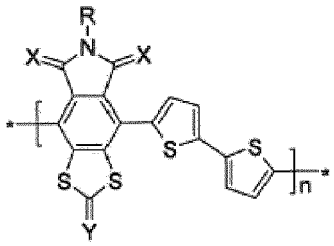

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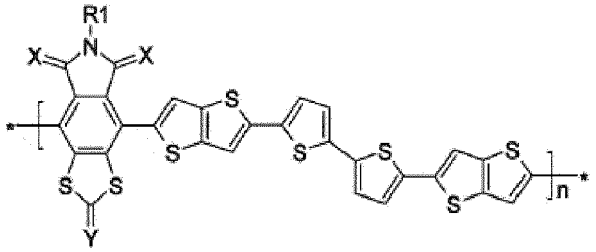

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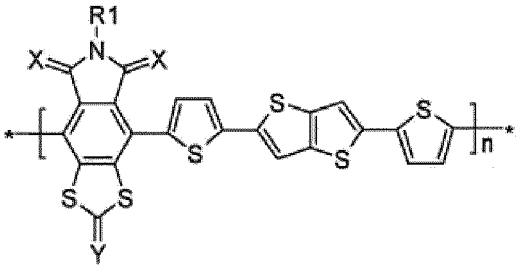

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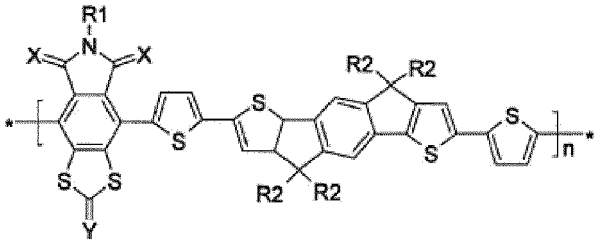

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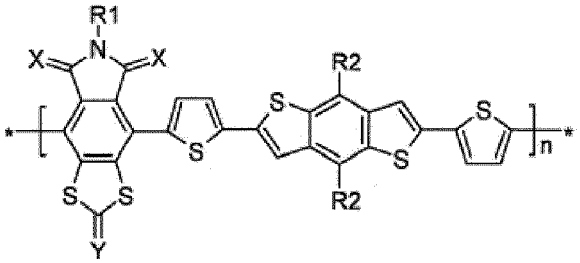

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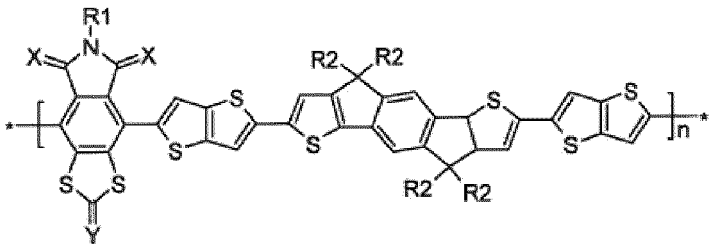

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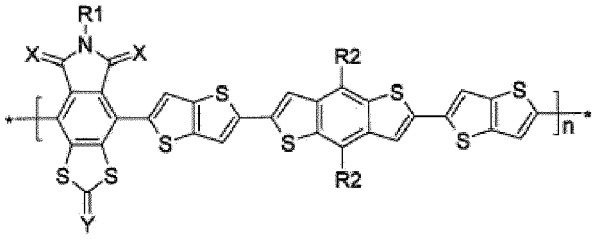

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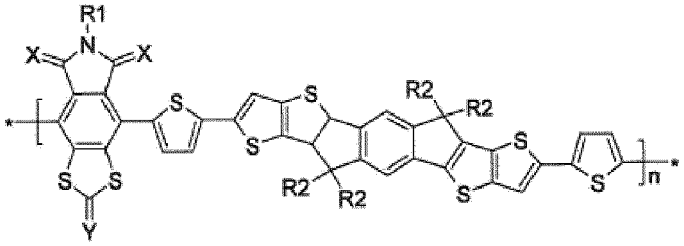

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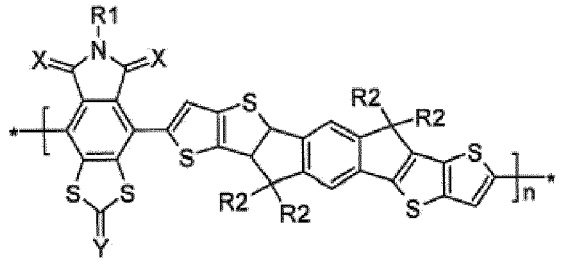

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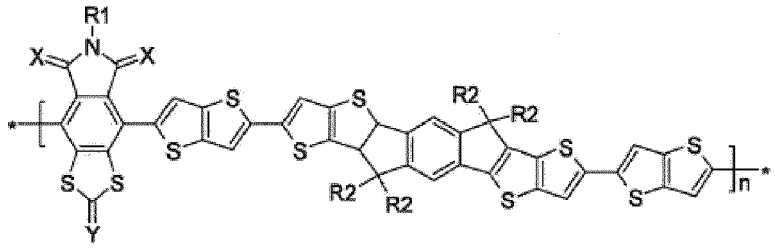

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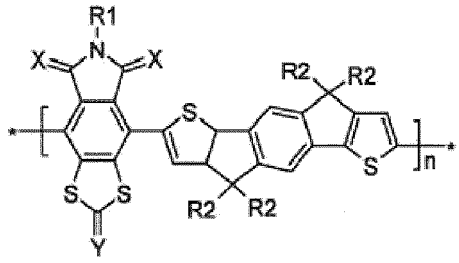

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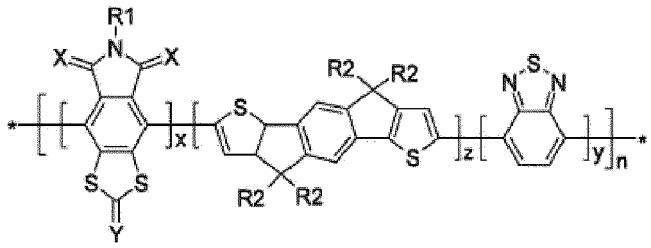

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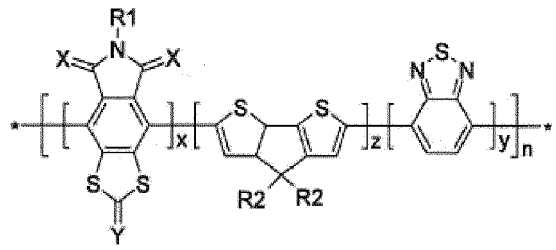

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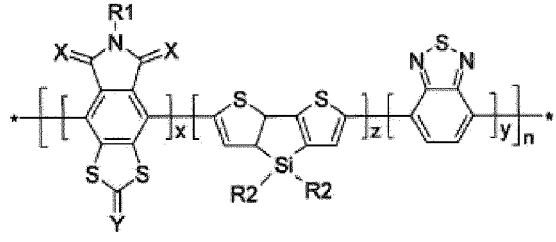

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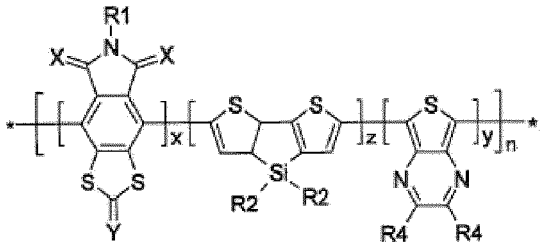

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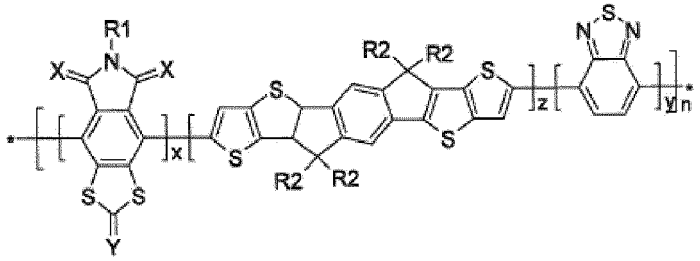

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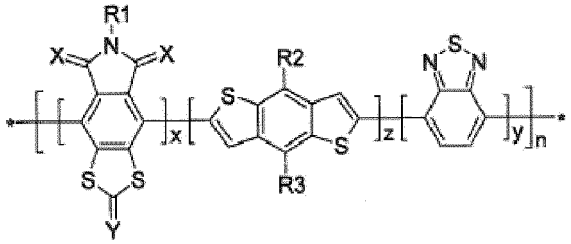

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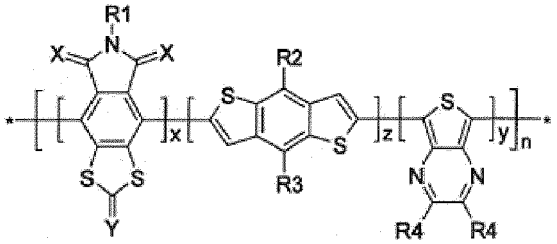

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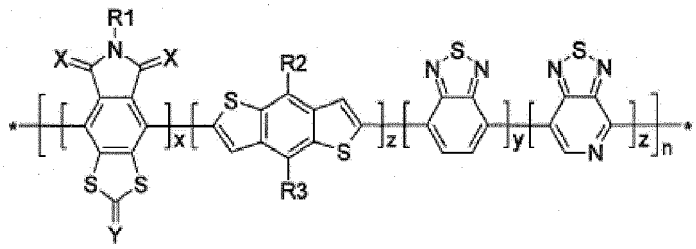

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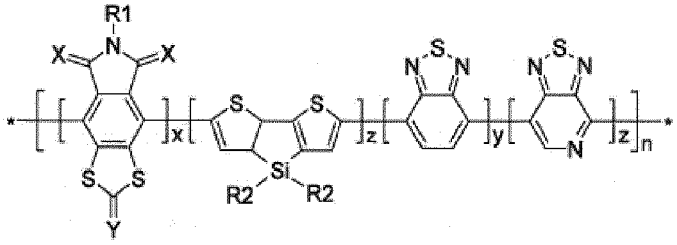


P32

dans lequel R^1 est selon la revendication 1 ou 2, X présente à chaque occurrence de manière identique ou différente l'une des significations de X^1 données dans la revendication 1, Y est selon la revendication 1, t vaut 1, 2, 3 ou 4, n est selon la revendication 5, et R^2, R^3 et R^4 présentent indépendamment les uns des autres et à chaque occurrence

de manière identique ou différente l'une des significations données pour L.

11. Composé selon l'une quelconque des revendications 1 à 10, qui est un polymère conjugué de formule IV

R^5-chaîne-R^6 IV

dans lequel « chaîne » désigne une chaîne polymère choisie parmi les formules III, III1-III8 et P1-P32 selon les revendications 5, 6 et 10, et R^5 et R^6 présentent indépendamment les uns des autres l'une des significations de R^1 ou L selon la revendication 1 ou 2, ou désignent, indépendamment les uns des autres, H, F, Br, Cl, I, - CH_2Cl, -CHO, -CR'=CR"$_2$, -SiR'R"R"', -SiR'X'X", -SiR'R"X', -SnR'R"R"', -BR'R", -B(OR')(OR"), - $B(OH)_2$, -O-SO_2-R', -C≡CH, -C≡C-SiR'$_3$, -ZnX' ou un groupe de coiffage terminal, X' et X" désignent un halogène, R', R" et R'" présentent indépendamment les uns des autres l'une des significations de R^0 données dans la revendication 1, et deux de R', R" et R'" peuvent également former un groupe cyclosilyle, cyclostannyle, cycloborane ou cycloboronate comportant de 2 à 20 atomes de C conjointement avec l'hétéroatome respectif auquel ils sont fixés.

12. Composé selon la revendication 1 ou 2, qui est un monomère de formule V1 ou V2

$$\mathbf{R^7\text{-}(Ar^1)_a\text{-}U\text{-}(Ar^2)_b\text{-}(Ar^3)_c\text{-}(Ar^4)_d\text{-}R^8} \qquad \mathbf{V1}$$

$$\mathbf{R^7\text{-}(Ar^1)_a\text{-}(Ar^2)_b\text{-}U\text{-}(Ar^3)_c\text{-}(Ar^4)_d\text{-}R^8} \qquad \mathbf{V2}$$

dans lequel U, $Ar^{1\text{-}4}$, a, b, c et d présentent les significations données dans la revendication 3, 7, 8 ou 9, et R^7et R^8 sont indépendamment l'un de l'autre choisis dans le groupe constitué de H, Cl, Br, I, O-tosylate, O-triflate, O-mésylate, O-nonaflate, -$SiMe_3$, - $SiMe_2F$, -$SiMeF_2$, -O-SO_2Z^1, -$B(OZ^2)_2$, -CZ^3=$C(Z^3)_2$, -C≡CH, -C≡C$Si(Z^1)_3$, -ZnX^0, Mg-X^0 et - $Sn(Z^4)_3$, dans lequel X^0 est un halogène, $Z^{1\text{-}4}$ sont choisis dans le groupe constitué d'un alkyle en $C_{1\text{-}10}$ et d'un aryle en $C_{6\text{-}12}$, chacun étant optionnellement substitué, et deux groupes Z^2 peuvent également former un groupe cycloboronate présentant de 2 à 20 atomes de C conjointement avec les atomes de B et de O, et dans lequel au moins l'un de R^7et R^8 est différent de H.

13. Composé selon la revendication 12, qui est choisi parmi les formules suivantes

$$\mathbf{R^7\text{-}Ar^1\text{-}U\text{-}Ar^2\text{-}R^8} \qquad \mathbf{V1a}$$

$$\mathbf{R^7\text{-}U\text{-}R^8} \qquad \mathbf{V1b}$$

$$\mathbf{R^7\text{-}Ar^1\text{-}U\text{-}R^8} \qquad \mathbf{V1c}$$

$$\mathbf{R^7\text{-}U\text{-}Ar^2\text{-}R^8} \qquad \mathbf{V1d}$$

dans lequel U, Ar^1, Ar^2, R^7 et R^8 sont selon la revendication 12.

14. Composé selon la revendication 12, qui est choisi parmi la formule V3

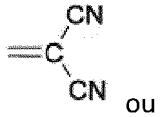
$$\mathbf{R^7\text{-}U^*\text{-}R^8} \qquad \mathbf{V3}$$

dans lequel U* est une unité choisie parmi une formule R1-R11 selon la revendication, et R^7 et R^8 sont selon la revendication 12.

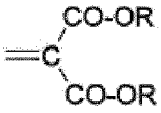
15. Composé selon l'une quelconque des revendications 1 à 14, dans lequel

a) un ou plusieurs de Ar^1, Ar^2, Ar^3 et Ar^4 désignent un arylène ou un hétéroarylène choisi dans le groupe constitué des formules D1, D7, D10, D11, D19, D22, D29, D30, D35, D36, D44, D55, D84, D87, D88, D89, D93, D106, D111, D140, D141 et D146 selon la revendication 7, et/ou
b) un ou plusieurs de Ar^1, Ar^2, Ar^3 et Ar^4 désignent un arylène ou un hétéroarylène choisi dans le groupe constitué des formules A1, A6, A7, A15, A16, A20, A74, A88, A92 et A98 selon la revendication 8,
et
c) un ou plusieurs de Ar^1, Ar^2, Ar^3 et Ar^4 désignent un arylène ou un hétéroarylène choisi dans le groupe constitué des formules Sp1, Sp6 et Sp13 selon la revendication 9.

16. Composé selon la revendication 4 ou 10, dans lequel Y est O, S,



ou



avec R étant selon la revendication 1 ou 2.

17. Composé de formule VI selon la revendication 1, dans lequel Ar^{1-10} sont choisis parmi les groupes suivants

a) le groupe constitué des formules D1, D7, D10, D11, D19, D22, D29, D30, D35, D36, D44, D55, D84, D87, D88, D89, D93, D106, D111, D140 et D141 selon la revendication 7,
b) le groupe constitué des formules A1, A6, A7, A15, A16, A20, A74, A88, A92 et A98 selon la revendication 8,
c) le groupe constitué des formules formules Sp1, Sp6 et Sp10 selon la revendication 9.

18. Composé de formule VI selon la revendication 1 ou 17, qui est choisi parmi la formule VI1

$$R^{1t}\text{-}U^{*}\text{-}R^{2t} \qquad \text{VI1}$$

dans lequel U* est une unité choisie parmi les formules R1-R11 selon la revendication 4, et R^{1t} et R^{2t} présentent les significations données dans la revendication 1.

19. Mélange comprenant un ou plusieurs composés selon l'une quelconque des revendications 1 à 18 et un ou plusieurs composés additionnels présentant une ou plusieurs de propriétés semi-conductrices, de transport de charge, de transport de trous ou d'électrons, de blocage de trous ou d'électrons, de conduction électrique, de photoconduction ou d'émission de lumière.

20. Mélange comprenant un ou plusieurs composés selon l'une quelconque des revendications 1 à 18 et un ou plusieurs semi-conducteurs organiques de type n.

21. Mélange selon la revendication 20, dans lequel les semi-conducteurs organiques de type n sont choisis parmi des fullerènes ou des fullerènes substitués.

22. Formulation comprenant un ou plusieurs composés ou mélanges selon l'une quelconque des revendications 1 à 21, et comprenant en outre un ou plusieurs solvants choisis parmi des solvants organiques.

23. Dispositif optique, électro-optique, électronique, électroluminescent ou photoluminescent, ou un composant de celui-ci, ou un ensemble le comprenant, qui comprend un ou plusieurs composés ou mélanges selon l'une quelconque des revendications 1 à 21.

24. Utilisation d'un composé ou d'un mélange selon l'une quelconque des revendications 1 à 21 en tant que matériau semi-conducteur, de transport de charge, de conduction électrique, de photoconduction ou d'émission de lumière, ou dans un dispositif optique, électro-optique, électronique, électroluminescent ou photoluminescent, ou dans un composant d'un tel dispositif ou dans un ensemble comprenant un tel dispositif ou composant.

25. Matériau semi-conducteur, de transport de charge, de conduction électrique, de photoconduction ou d'émission de lumière comprenant un composé ou un mélange selon l'une quelconque des revendications 1 à 21.

26. Dispositif optique, électro-optique, électronique, électroluminescent ou photoluminescent, ou un composant de celui-ci, ou un ensemble le comprenant, qui comprend un matériau semi-conducteur, de transport de charge, de conduction électrique, de photoconduction ou d'émission de lumière selon la revendication 25.

27. Dispositif optique, électro-optique, électronique, électroluminescent ou photoluminescent selon la revendication 26, qui est choisi parmi des transistors à films minces organiques (OTFT), des transistors à films minces organiques (OTFT), des diodes électroluminescentes organiques (OLED), des transistors électroluminescents organiques (OLET), des dispositifs photovoltaïques organiques (OPV), des photodétecteurs organiques (OPD), des cellules solaires organiques, des cellules solaires à colorant (DSSC), des cellules solaires à base de pérovskite, des diodes laser, des diodes Schottky, des photoconducteurs et des photodétecteurs.

28. Composant selon la revendication 26, qui est choisi parmi des couches d'injection de charge, des couches de transport de charge, des couches intermédiaires, des couches de planarisation, des films antistatiques, des membranes d'électrolyte polymère (PEM), des substrats conducteurs et des motifs conducteurs.

29. Ensemble selon la revendication 26, qui est choisi parmi des circuits intégrés (IC), des étiquettes d'identification par radiofréquence (RFID) ou des marquages de sécurité ou des dispositifs de sécurité les contenant, des écrans plats ou des rétroéclairages de ceux-ci, des dispositifs électrophotographiques, des dispositifs d'enregistrement électrophotographique, des dispositifs de mémoire organique, des dispositifs capteurs, des biocapteurs et des biopuces.

30. Hétérojonction en masse qui comprend un mélange selon l'une quelconque des revendications 19 à 21.

31. Dispositif OPV à hétérojonction en masse (BHJ) ou dispositif OPV à BHJ inversé, comprenant l'hétérojonction en masse selon la revendication 30.

32. Procédé de préparation d'un polymère conjugué selon l'une quelconque des revendications 1 à 11, par couplage d'un ou plusieurs monomères choisis parmi les revendications 12, 13, 14 et 15 les uns aux autres et/ou à un ou plusieurs monomères de formules MI-MIV dans une réaction de couplage aryle-aryle

R^7-Ar^1-R^8 **MI**

R^7-Ar^2-R^8 **MII**

R^7-Ar^3-R^8 **MIII**

R^7-Ar^4-R^8 **MIV**

dans lequel Ar^{1-4}, R^7 et R^8 présentent les significations données dans la revendication 12.

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