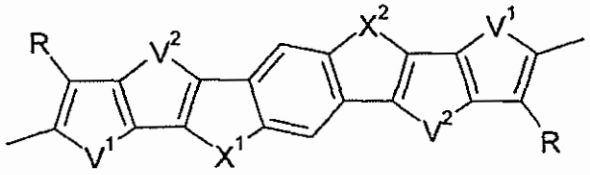
Patent Claims

1. Oligomer or polymer comprising divalent units of formula I



I

wherein

V^1 and V^2 are independently of each other O, S, Se or Te,

X^1 and X^2 are independently of each other CR^1R^2, $C=CR^1R^2$, SiR^1R^2 or GeR^1R^2,

R, R^1 and R^2 independently of each other, and on each occurrence identically or differently, denote H, F, Cl, Br, CN, straight-chain, branched or cyclic alkyl, with 1 to 30 C atoms, in which one or more non-adjacent C atoms are optionally replaced by -O-, -S-, -C(O)-, -C(O)-O-, -O-C(O)-, -O-C(O)-O-, -C(S)-, -C(S)-O-, -O-C(S)-, -O-C(S)-O-, -C(O)-S-, -S-C(O)-, -O-C(O)-S-, -S-C(O)-O-, -S-C(O)-S-, -S-C(S)-S-, -O-C(S)-S-, -S-C(S)-O-, -C(S)-S-, -S-C(S)-, $-NR^0-$, $-SiR^0R^{00}-$, $-CY^1=CY^2-$ 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, or R^1 and R^2, independently of each other, and on each occurrence identically or differently, denote aryl, heteroaryl, aryloxy or heteroaryloxy with 4 to 20 ring atoms which is optionally substituted, or R^1 and R^2 together form an alicyclic group with 1 to 20 C atoms, which is optionally fluorinated or alkylated,

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

R^0 and R^{00} are independently of each other H or optionally substituted C_{1-40} carbyl or hydrocarbyl.

2. Polymer according to claim 1, characterized in that it comprises one or more units of formula II

$$-[(Ar^1)_a-(U)_b-(Ar^2)_c-(Ar^3)_d]- \qquad II$$

wherein

U is a unit of formula I as defined in claim 1,

Ar^1, Ar^2, Ar^3 are, on each occurrence identically or differently, and independently of each other, aryl or heteroaryl that is different from U, preferably has 5 to 30 ring atoms and is optionally substituted, preferably by one or more groups R^S,

R^S is on each occurrence identically or differently F, Br, Cl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(O)NR^0R^{00}$, $-C(O)X^0$, $-C(O)R^0$, $-NH_2$, $-NR^0R^{00}$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-SF_5$, optionally substituted silyl, carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, or P-Sp-,

R^0 and R^{00} are independently of each other H or optionally substituted C_{1-40} carbyl or hydrocarbyl,

P is a polymerisable or crosslinkable group,

Sp is a spacer group or a single bond,

X^0 is halogen, preferably F, Cl or Br,

a, b, c are on each occurrence identically or differently 0, 1 or 2,

d is on each occurrence identically or differently 0 or an integer from 1 to 10,

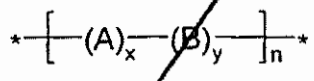
wherein the polymer comprises at least one repeating unit of formula II wherein b is at least 1.

3. Polymer according to claim 1 or 2, characterized in that it additionally comprises one or more repeating units selected of formula III

$$-[(Ar^1)_a-(A^1)_b-(Ar^2)_c-(Ar^3)_d]- \qquad III$$

wherein Ar^1, Ar^2, Ar^3, a, b, c and d are as defined in claim 3, and A^1 is an aryl or heteroaryl group that is different from U and Ar^{1-3}, has 5 to 30 ring atoms, is optionally substituted by one or more groups R^S as defined in claim 3, and is selected from aryl or heteroaryl groups having electron donor properties, wherein the polymer comprises at least one repeating unit of formula III wherein b is at least 1.

4. Polymer according to one or more of claims 1 to 3, characterized in that it is selected of formula IV:



IV

wherein

A is a unit of formula I as defined in claim 1,

B is a unit that is different from A and comprises one or more aryl or heteroaryl groups that are optionally substituted, and is preferably selected of formula III as defined in claim 3,

x is > 0 and ≤ 1,

y is ≥ 0 and < 1,

x + y is 1, and

n is an integer >1.

5. Polymer according to one or more of claims 1 to 4, characterized in that it is selected from the following formulae

-[(Ar^1-U-Ar^2)$_x$-(Ar^3)$_y$]$_n$- IVa

-[(Ar^1-U-Ar^2)$_x$-(Ar^3-Ar^3)$_y$]$_n$- IVb

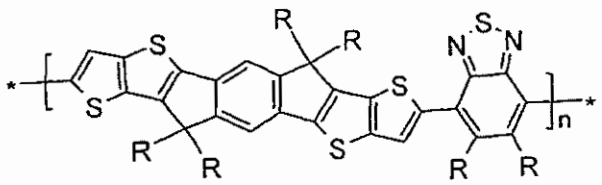
-[(Ar^1-U-Ar^2)$_x$-(Ar^3-Ar^3-Ar^3)$_y$]$_n$- IVc

-[(Ar^1)$_a$-(U)$_b$-(Ar^2)$_c$-(Ar^3)$_d$]$_n$- IVd

-([(Ar^1)$_a$-(U)$_b$-(Ar^2)$_c$-(Ar^3)$_d$]$_x$-[(Ar^1)$_a$-(A^1)$_b$-(Ar^2)$_c$-(Ar^3)$_d$]$_y$)$_n$- IVe

wherein U, Ar^1, Ar^2, Ar^3, a, b, c and d have in each occurrence identically or differently one of the meanings given in claim 4, A^1 has on each occurrence identically or differently one of the meanings given in claim 3, and x, y and n are as defined in claim 4, wherein these polymers can be alternating or random copolymers, and wherein in formula IVd and IVe in at least one of the repeating units [(Ar^1)$_a$-(U)$_b$-(Ar^2)$_c$-(Ar^3)$_d$] and in at least one of the repeating units [(Ar^1)$_a$-(A^1)$_b$-(Ar^2)$_c$-(Ar^3)$_d$] b is at least 1.

6. Polymer according to one or more of claims 1 to 5, characterized in that it is selected from the group consisting of the following formulae



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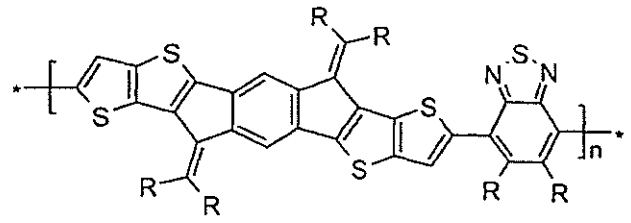

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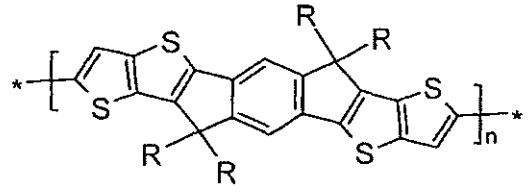

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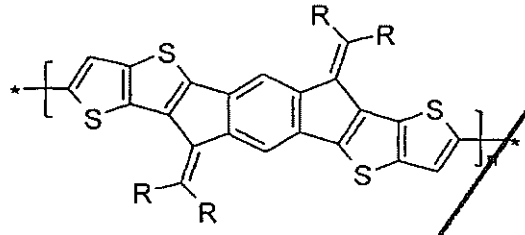

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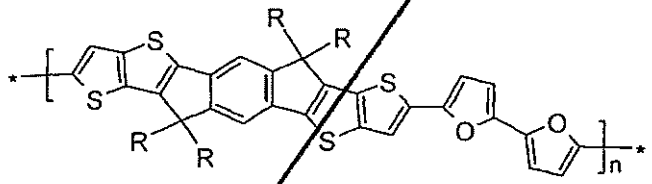

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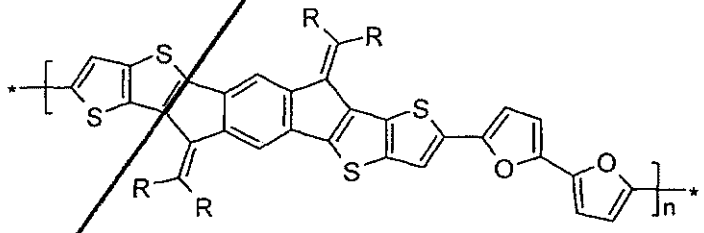

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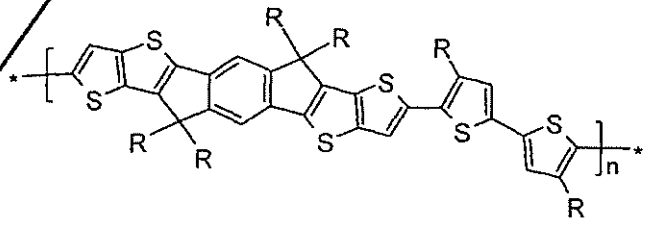

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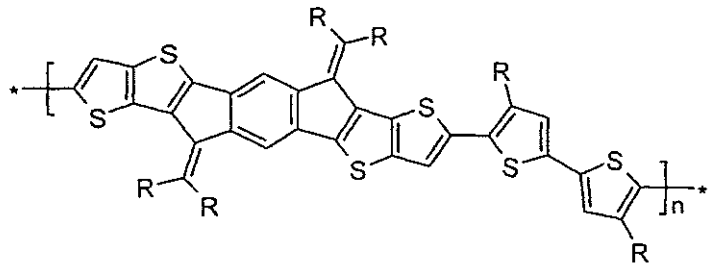

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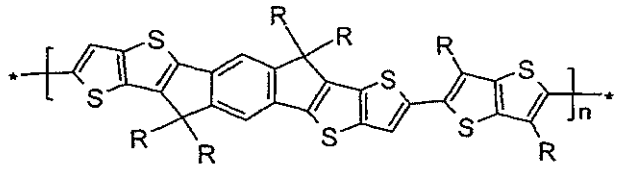

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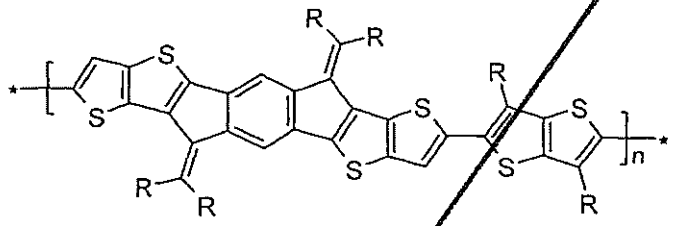

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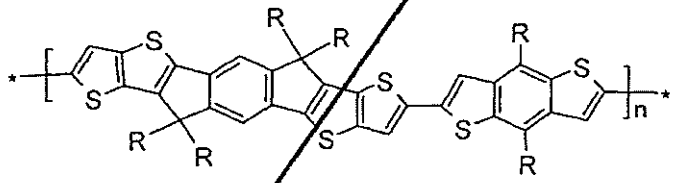

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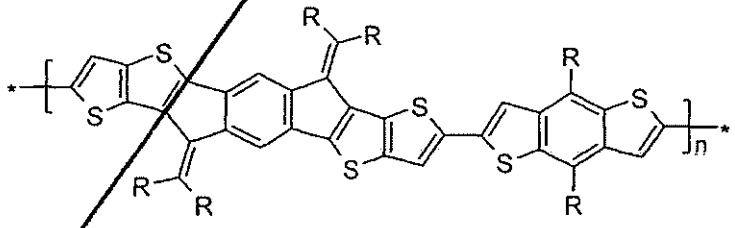

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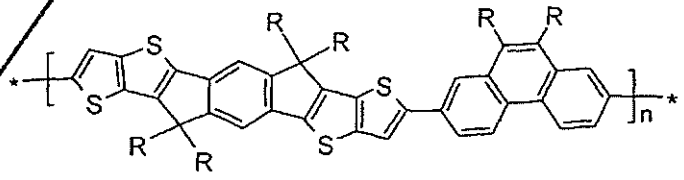

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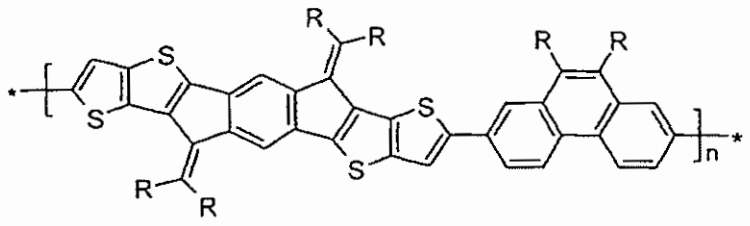


IV14

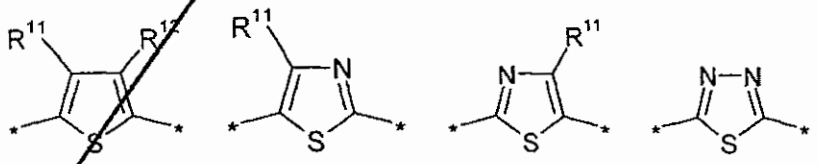
wherein R has on each occurrence identically or differently one of the meanings of R^1 as given in claim 1.

7. Polymer according to one or more of claims 1 to 6, characterized in that it is selected of formula V

R^5-chain-R^6 V

wherein "chain" is a polymer chain selected of formulae IV, IVa-IVe and IV1-IV5 as defined in claim 6, 7 or 8, and R^5 and R^6 denote independently of each other F, Br, Cl, H, $-CH_2Cl$, -CHO, $-CH=CH_2$, -SiR'R"R"', -SnR'R"R"', -BR'R", -B(OR')(OR"), $-B(OH)_2$, -ZnCl, -MgCl, -MgBr or P-Sp-, wherein P and Sp are as defined in claim 4, R', R" and R"' have independently of each other one of the meanings of R^0 given claim 4, and two of R', R" and R"' may also form a ring together with the hetero atom to which they are attached.

8. Polymer according to one or more of claims 1 to 7, wherein one or more of Ar^1, Ar^2 and Ar^3 denote aryl or heteroaryl selected from the group consisting of the following formulae



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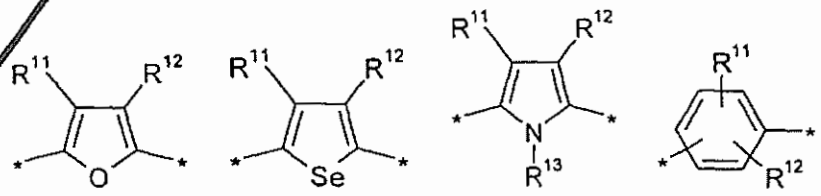
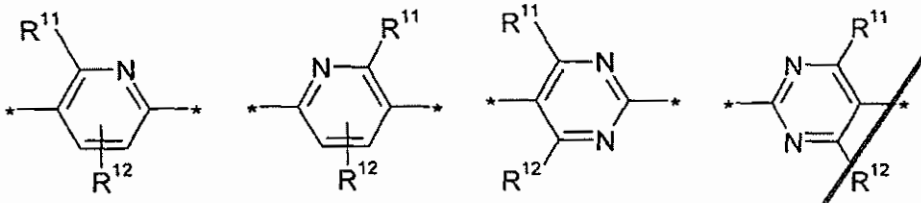
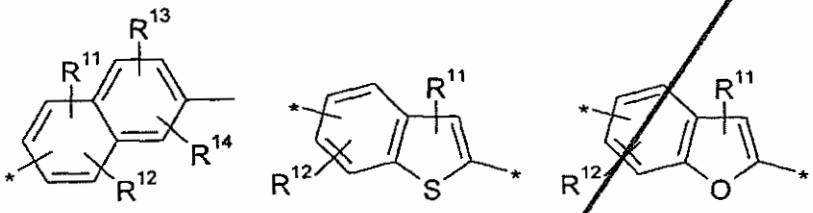


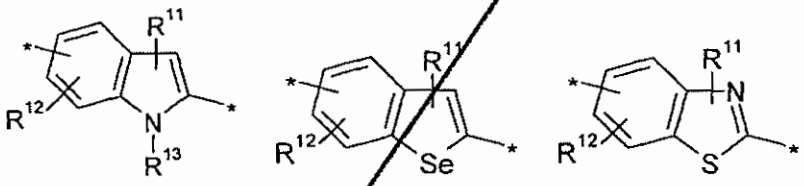
(D5) (D6) (D7) (D8)



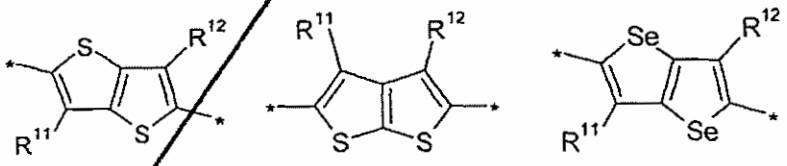
(D9) (D10) (D11) (D12)



(D13) (D14) (D15)



(D16) (D17) (D18)



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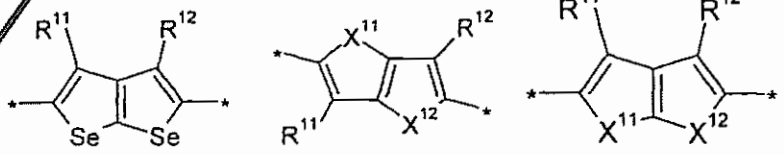

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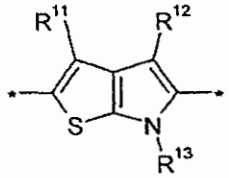

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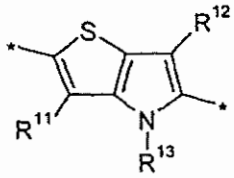

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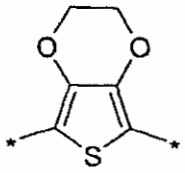

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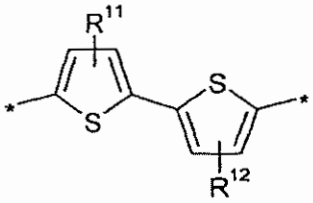

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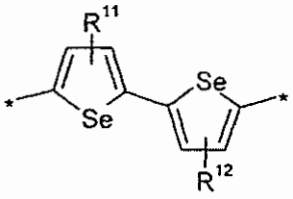

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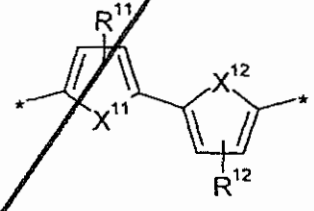

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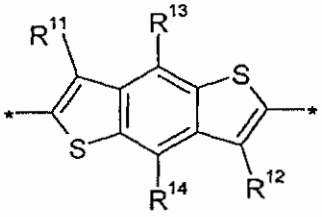

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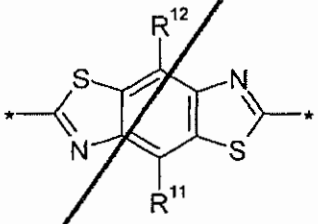

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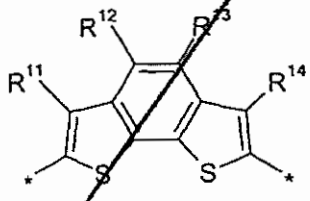

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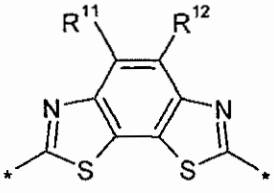

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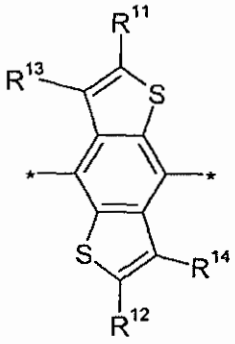

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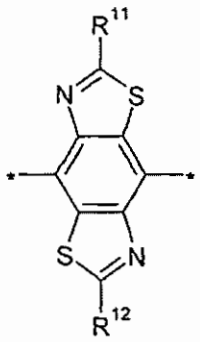

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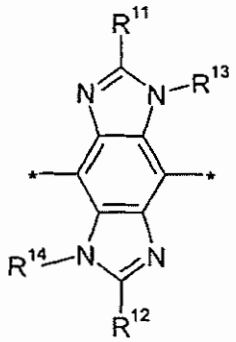

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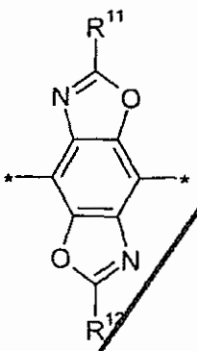

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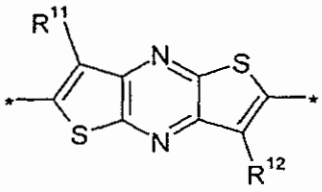

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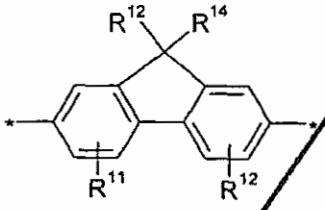

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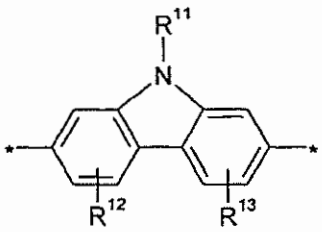

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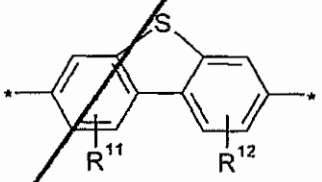

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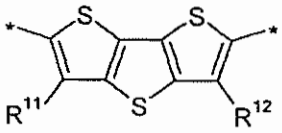

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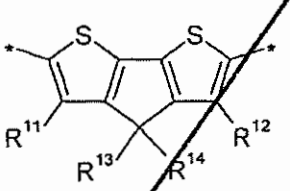

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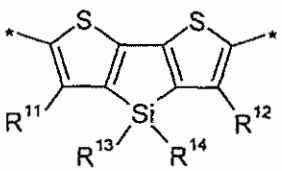

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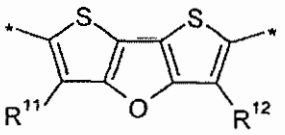

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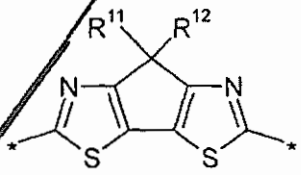

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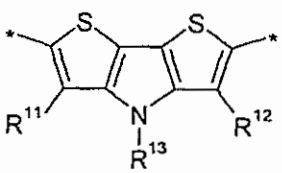

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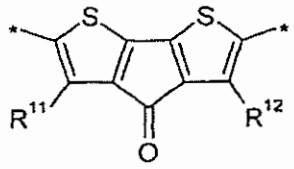

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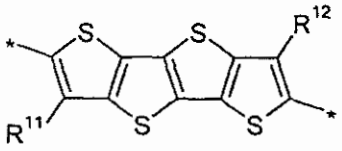

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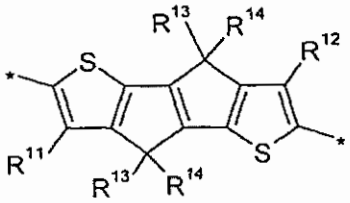

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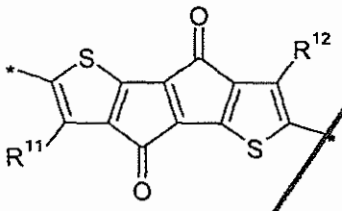

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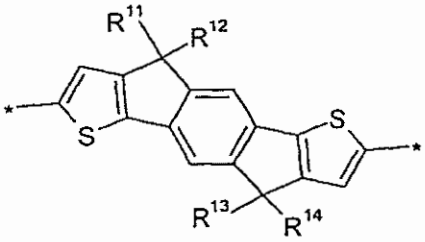

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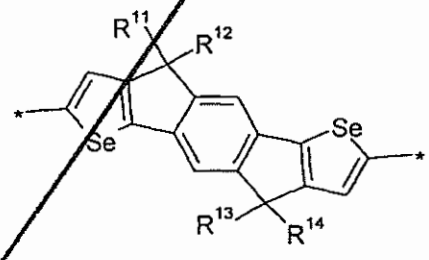

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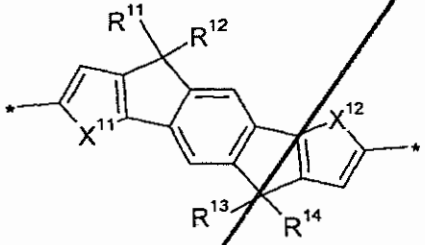

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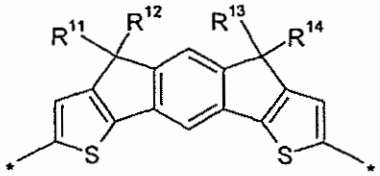

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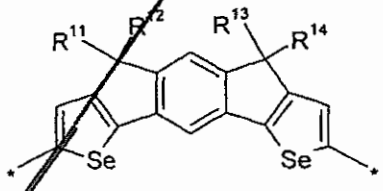

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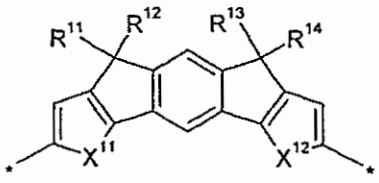

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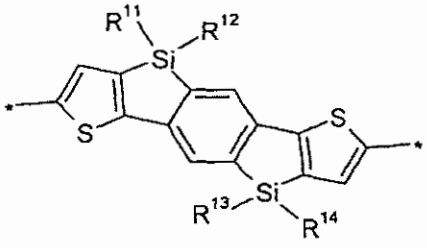

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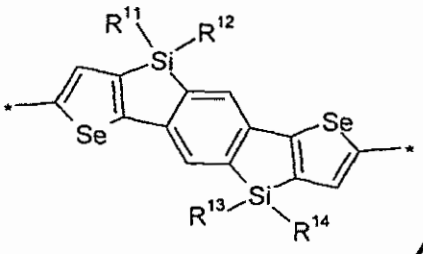

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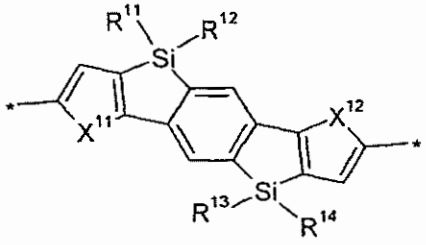

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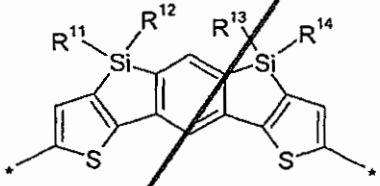

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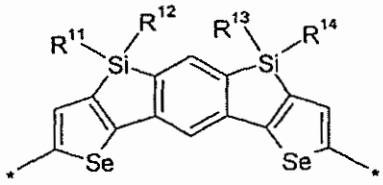

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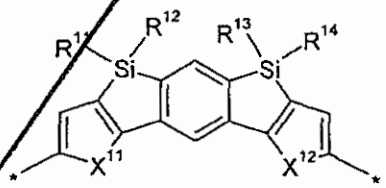

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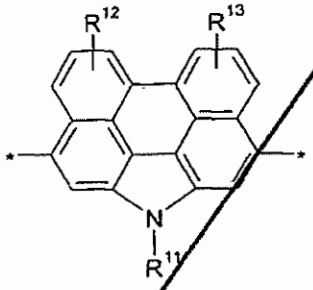

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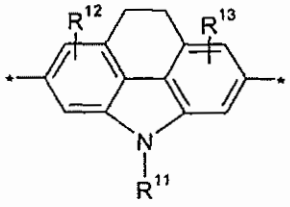

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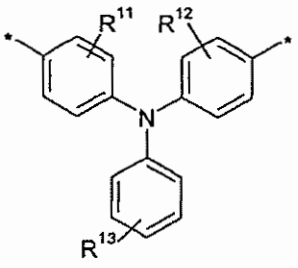

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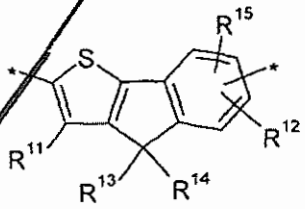

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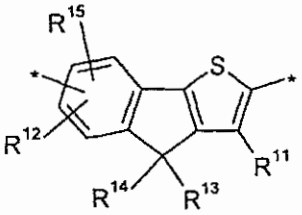

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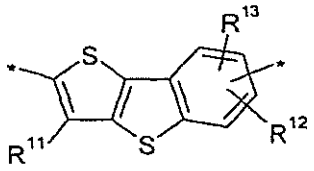

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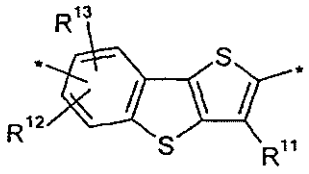

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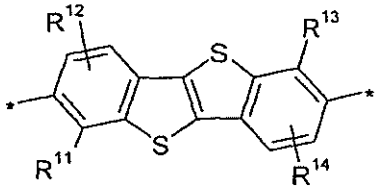

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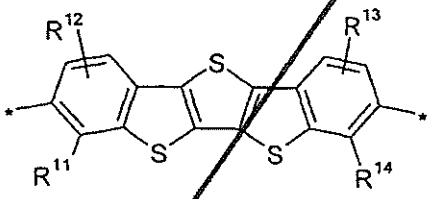

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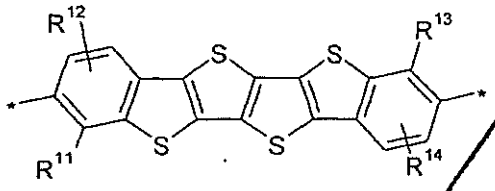

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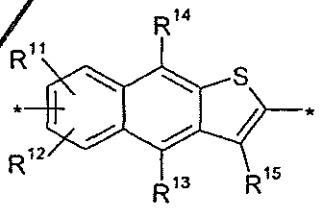

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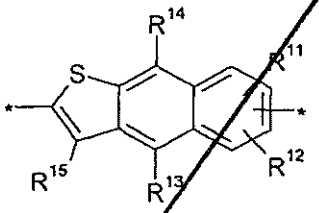

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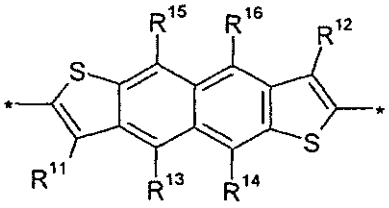

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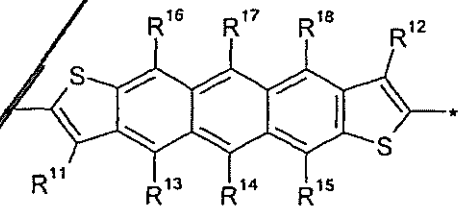

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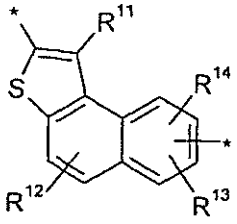

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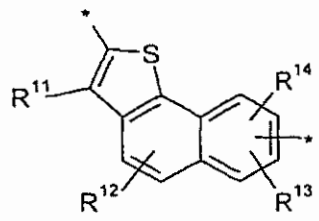

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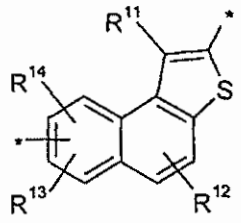

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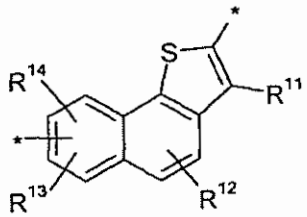

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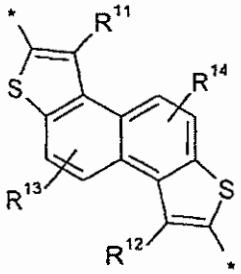

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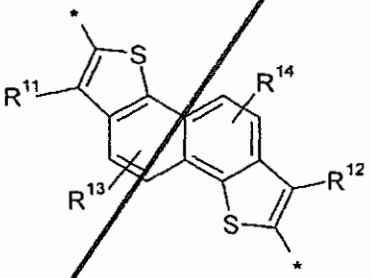

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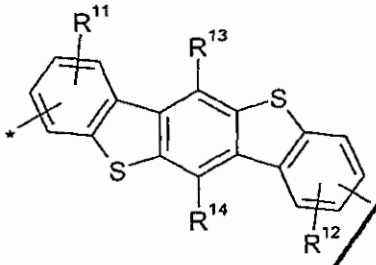

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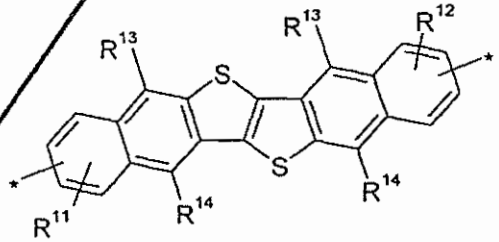
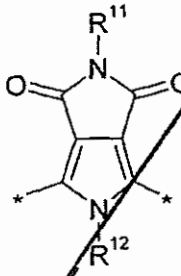


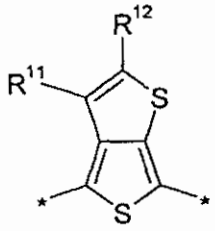
(D87)



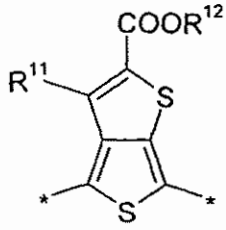
(D88)

wherein one of X^{11} and X^{12} is S and the other is Se, and 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 R^1 as defined in claim 1.

9. Polymer according to one or more of claims 1 to 8, wherein one or more of the units Ar^3 and A^1 denote aryl or heteroaryl selected from the group consisting of the following formulae



(A1)



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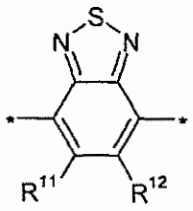

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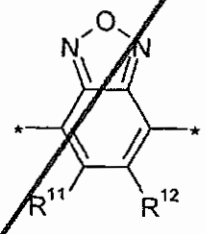

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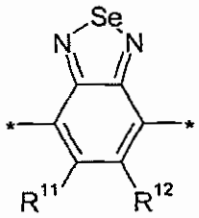

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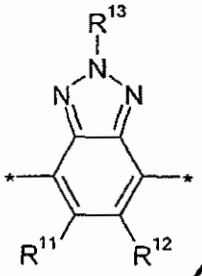

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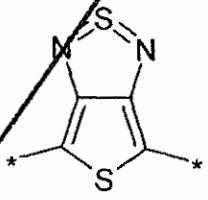

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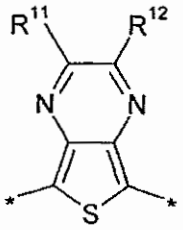

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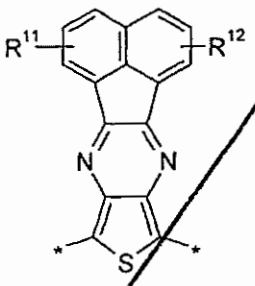

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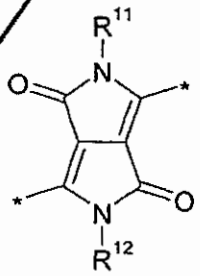

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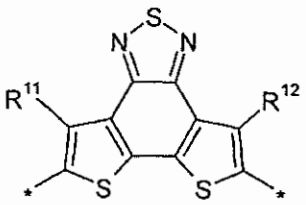

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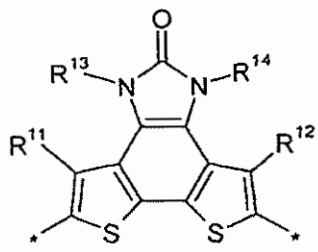

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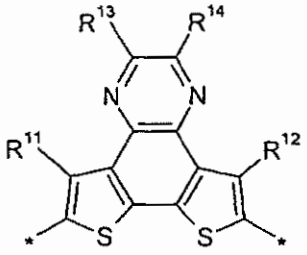

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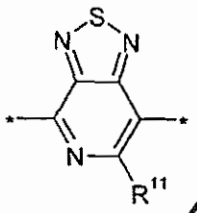

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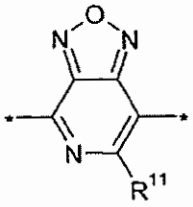

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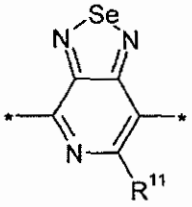

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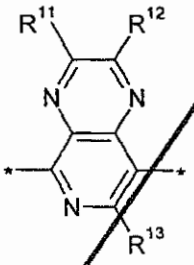

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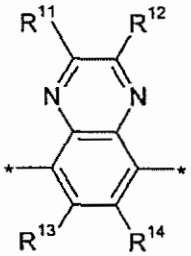

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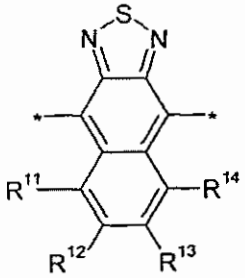

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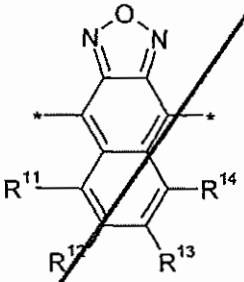

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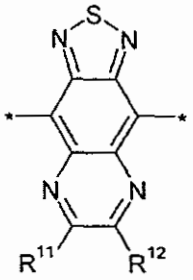

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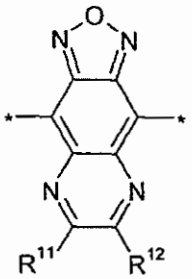

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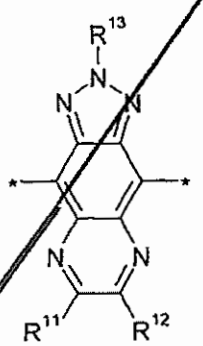

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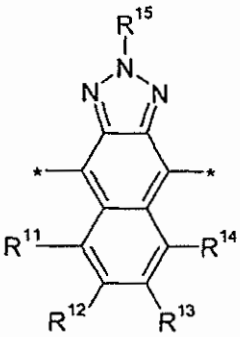

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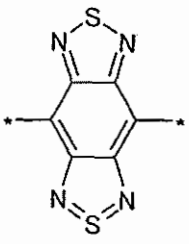

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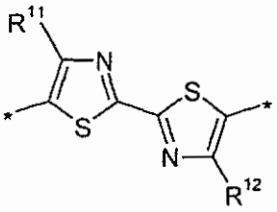

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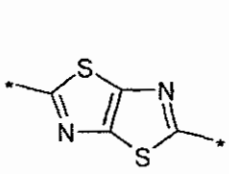

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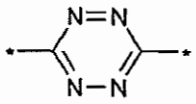

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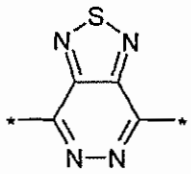

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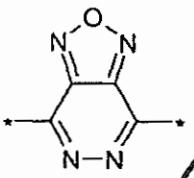

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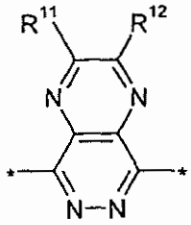

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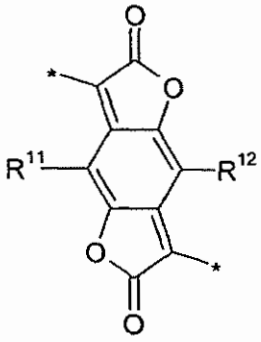

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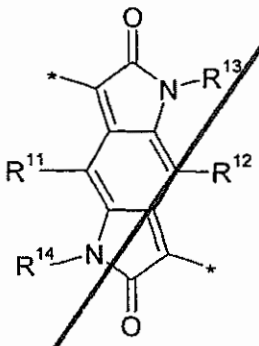

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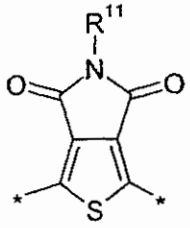

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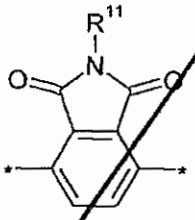

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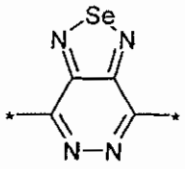

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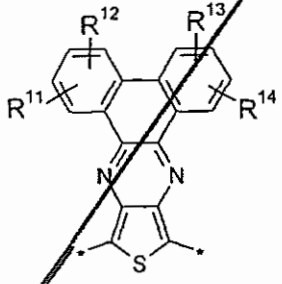

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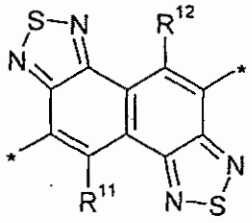

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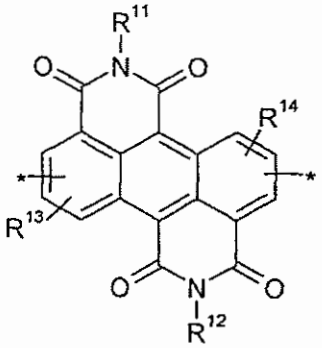

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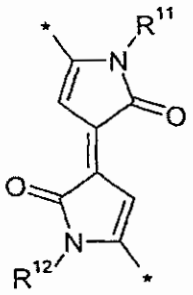
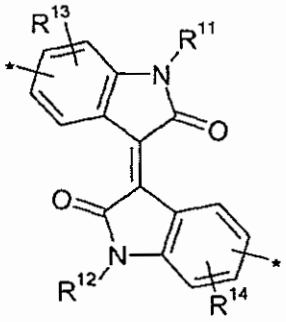
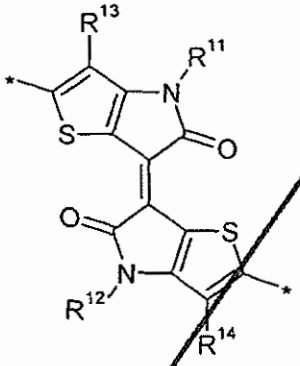


(A40)



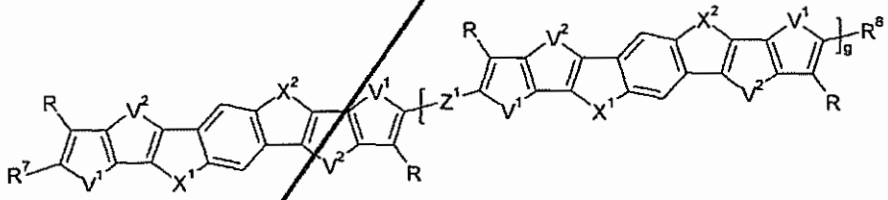
(A41)



(A42)

wherein one of X^{11} and X^{12} is S and the other is Se, and R^{11}, R^{12}, R^{13}, R^{14} and R^{15} independently of each other denote H or have one of the meanings of R^1 as defined in claim 1.

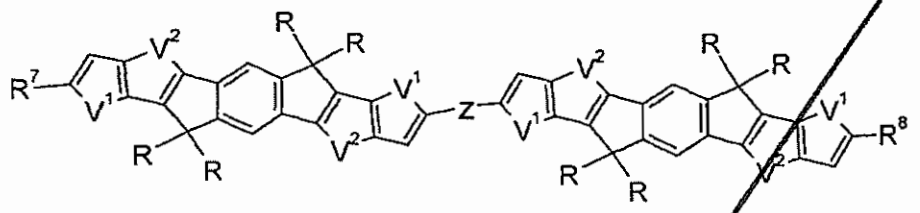
10. Oligomer according to claim 1, characterized in that it is selected of formula VII



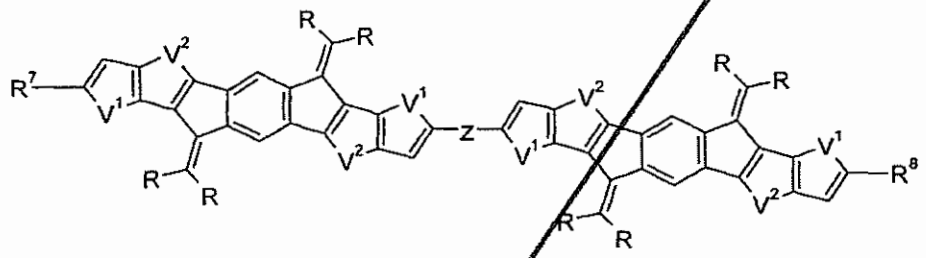
VII

wherein R, V^1, V^2, X^1 and X^2 are as defined in claim 1, Z^1 denotes a single bond, $(CY^1=CY^2)_h$, $(C\equiv C)_h$, wherein h = 1 or 2, or Ar^5, wherein Y^1, Y^2 are as defined in claim 1 and Ar^5 has one of the meanings of Ar^1 or Ar^3 as defined in claim 2, 8 or 9, R^7 and R^8 independently of each other denote H, F, Br, Cl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(O)NR^0R^{00}$, $-C(O)X^0$, $-C(O)R^0$, $-C(O)OR^0$, $-O-C(O)R^0$, $-NH_2$, $-NR^0R^{00}$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-SF_5$, P-Sp-, or optionally substituted silyl, carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, and wherein one or more C atoms are optionally replaced by a hetero atom, and R^0, R^{00} and X^0 are as defined in claim 2, and g is 1, 2 or 3.

11. Oligomer according to claim 10, which is selected from the following formulae



VIIa



VIIb

wherein V^1, V^2, R, R^7 and R^8 are as defined in claim 10, and Z has one of the meanings of Z^1 in claim 10.

12. Oligomer or polymer according to one or more of claims 1 to 11, characterized in that R^1 and R^2 independently of each other denote straight-chain, branched or cyclic alkyl with 1 to 20 C atoms which is unsubsituted or substituted by one or more F atoms, or R^1 and R^2 independently of each other denote aryl or heteroaryl, each of which is optionally fluorinated, alkylated or alkoxylated and has 4 to 30 ring atoms, or one of R^1 and R^2 denotes H and the other is selected from the aforementioned alkyl, aryl or heteroaryl groups, or R^1 and R^2 together form a cyclic alkyl group with 1 to 20 C atoms, which is unsubstituted or substituted by one or more F atoms or by one or more C_1-C_{10} alkyl groups.

13. Mixture or blend comprising one or more oligomers or polymers according to one or more of claims 1 to 12, and one or more compounds or polymers having semiconducting, charge transport, hole/electron transport, hole/electron blocking, electrically conducting, photoconducting or light emitting properties.

14. Mixture or blend according to claim 13, characterized in that it comprises one or more oligomers or polymers according to one or more of claims 1 to 12 and one or more n-type organic semiconductor compounds.

15. Mixture or blend according to claim 14, characterized in that the n-type organic semiconductor compound is a fullerene or substituted fullerene.

16. Formulation comprising one or more oligomers, polymers, mixtures or blends according to one or more of claims 1 to 15, and one or more solvents, preferably selected from organic solvents.

17. Use of a oligomer, polymer, mixture, blend or formulation according to one or more of claims 1 to 16 as charge transport, semiconducting, electrically conducting, photoconducting or light emitting material in optical, electrooptical, electronic, electroluminescent or photoluminescent components or devices.

18 Optical, electrooptical or electronic component or device comprising one or more oligomers, polymers, mixtures, blends or formulations according to one or more of claims 1 to 17.

19. Component or device according to claim 18, which is selected from the group consisting of organic field effect transistors (OFET), thin film transistors (TFT), integrated circuits (IC), logic circuits, capacitors, radio frequency identification (RFID) tags, devices or components, organic light emitting diodes (OLED), organic light emitting transistors (OLET), flat panel displays, backlights of displays, organic photovoltaic devices (OPV), organic solar cells (O-SC), photodiodes, laser diodes, photoconductors, photodetectors, electrophotographic devices, electrophotographic recording devices, organic memory devices, sensor devices, charge injection layers, charge transport layers or interlayers in polymer light emitting diodes (PLEDs), Schottky diodes, planarising layers, antistatic films, polymer electrolyte membranes (PEM), conducting substrates, conducting

patterns, electrode materials in batteries, alignment layers, biosensors, biochips, security markings, security devices, and components or devices for detecting and discriminating DNA sequences.

20. Component or device according to claim 18 or 19, which is an OFET, bulk heterojunction (BHJ) OPV device or inverted BHJ OPV device.

21. Monomer of formula VI

R^9-Ar^1-U-Ar^2-R^{10} VI

wherein U, Ar^1, Ar^2 are as defined in claim 3 or 10, and R^9 and R^{10} independently of each other denote F, Br, Cl, $-CH_2Cl$, -CHO, $-CH=CH_2$, -SiR'R"R'", -SnR'R"R'", -BR'R", -B(OR')(OR"), $-B(OH)_2$, -ZnCl, -MgCl, or -MgBr, wherein R', R" and R'" have independently of each other one of the meanings of R^0 as defined above, and two of R', R" and R'" may also form a ring together with the hetero atom to which they are attached.

22. Process of preparing a polymer according to one or more of claims 1 to 9, by coupling one or more monomers according to claim 21, wherein R^9 and R^{10} are selected from halogen, stannyl and boronate groups, with each other and/or with one or more monomers selected from the following formulae

R^9-Ar^3-R^{10} C1

R^9-A^1-R^{10} C2

wherein Ar^3 is as defined in claim 2, 8 or 9, A^1 is as defined in claim 3 or 9, R^9 and R^{10} are selected from halogen, stannyl and boronate groups as defined in claim 21, in an aryl-aryl coupling reaction.

Patent Claims

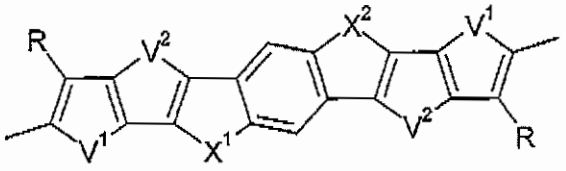
1. Conjugated polymer selected from formulae IVd and IVe

$$*\text{-}[(Ar^1)_a\text{-}(U)_b\text{-}(Ar^2)_c\text{-}(Ar^3)_d]_n\text{-}* \qquad \text{IVd}$$

$$*\text{-}([(Ar^1)_a\text{-}(U)_b\text{-}(Ar^2)_c\text{-}(Ar^3)_d]_x\text{-}[(Ar^1)_a\text{-}(A^1)_b\text{-}(Ar^2)_c\text{-}(Ar^3)_d]_y)_n\text{-}* \qquad \text{IVe}$$

wherein

U is a unit of formula I,



I

wherein

V^1 and V^2 are S,

X^1 and X^2 are independently of each other CR^1R^2 or $C{=}CR^1R^2$,

R, R^1 and R^2 independently of each other, and on each occurrence identically or differently, denote H, F, Cl, Br, CN, straight-chain, branched or cyclic alkyl, with 1 to 30 C atoms, in which one or more non-adjacent C atoms are optionally replaced by -O-, -S-, -C(O)-, -C(O)-O-, -O-C(O)-, -O-C(O)-O-, -C(S)-, -C(S)-O-, -O-C(S)-, -O-C(S)-O-, -C(O)-S-, -S-C(O)-, -O-C(O)-S-, -S-C(O)-O-, -S-C(O)-S-, -S-C(S)-S-, -O-C(S)-S-, -S-C(S)-O-, -C(S)-S-, -S-C(S)-, $-NR^0$-, $-SiR^0R^{00}$-, $-CY^1{=}CY^2$- 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, or R^1 and R^2, independently of each other, and on each occurrence

identically or differently, denote aryl, heteroaryl, aryloxy or heteroaryloxy with 4 to 20 ring atoms which is optionally substituted, or R^1 and R^2 together form an alicyclic group with 1 to 20 C atoms, which is optionally fluorinated or alkylated,

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

R^0 and R^{00} are independently of each other H or optionally substituted C_{1-40} carbyl or hydrocarbyl,

Ar^1, Ar^2, Ar^3 are, on each occurrence identically or differently, and independently of each other, aryl or heteroaryl that is different from U, preferably has 5 to 30 ring atoms and is optionally substituted, preferably by one or more groups R^S,

R^S is on each occurrence identically or differently F, Br, Cl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(O)NR^0R^{00}$, $-C(O)X^0$, $-C(O)R^0$, $-NH_2$, $-NR^0R^{00}$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-SF_5$, optionally substituted silyl, carbyl or hydrocarbyl with 1 to 40 C atoms that is optionally substituted and optionally comprises one or more hetero atoms, or P-Sp-,

R^0 and R^{00} are independently of each other H or optionally substituted C_{1-40} carbyl or hydrocarbyl,

P is a polymerisable or crosslinkable group,

Sp is a spacer group or a single bond,

X^0 is halogen, preferably F, Cl or Br,

a, b, c are on each occurrence identically or differently 0, 1 or 2,

d is on each occurrence identically or differently 0 or an integer from 1 to 10,

A^1 is an aryl or heteroaryl group that is different from U and Ar^{1-3}, has 5 to 30 ring atoms, is optionally substituted by one or more groups R^S as defined in claim 3, and is selected from aryl or heteroaryl groups having electron acceptor properties,

x is > 0 and ≤ 1,

y is ≥ 0 and < 1,

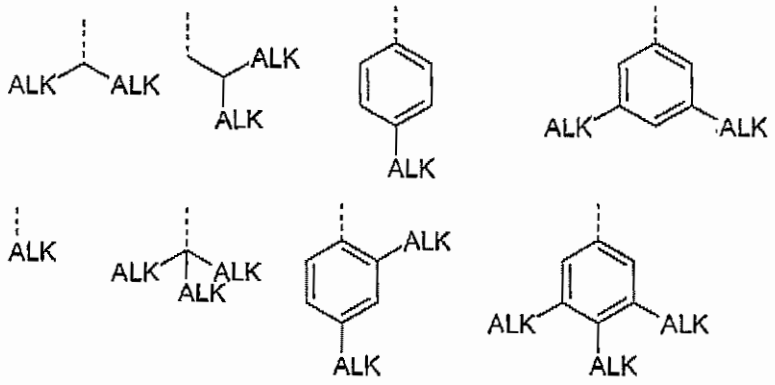
x + y is 1, and

n is an integer >1.

wherein the polymer can be an alternating or random copolymer, and wherein in formula IVd and IVe in at least one of the repeating units $[(Ar^1)_a\text{-}(U)_b\text{-}(Ar^2)_c\text{-}(Ar^3)_d]$ and in at least one of the repeating units $[(Ar^1)_a\text{-}(A^1)_b\text{-}(Ar^2)_c\text{-}(Ar^3)_d]$ b is at least 1.

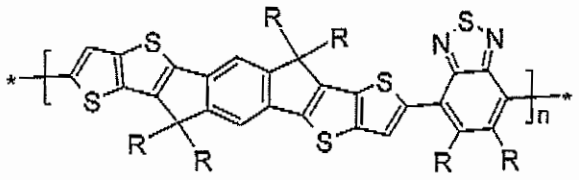
2. Polymer according to claim 1, wherein R^1 and R^2 are independently of each other selected from primary, secondary or tertiary alkyl or alkoxy with 1 to 30 C atoms, wherein one or more H atoms are optionally replaced by F, or aryl, aryloxy, heteroaryl or heteroaryloxy that is optionally alkylated or alkoxylated and has 4 to 30 ring atoms.

3. Polymer according to claim 1 or 2, wherein R^1 and R^2 are independently of each other selected from the group consisting of the following formulae

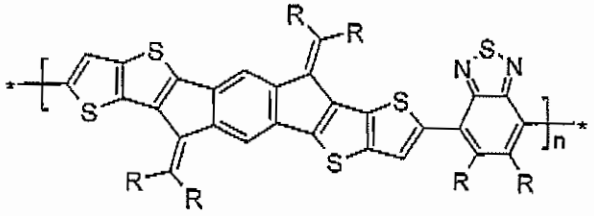


wherein "ALK" denotes optionally fluorinated, preferably linear, alkyl or alkoxy with 1 to 20, preferably 1 to 12 C-atoms, in case of tertiary groups very preferably 1 to 9 C atoms, and the dashed line denotes the link to the ring to which these groups are attached.

4. Polymer according to one or more of claims 1 to 3, characterized in that it is selected from the group consisting of the following formulae



IV1



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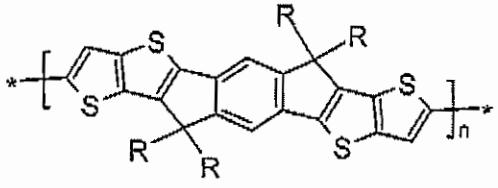
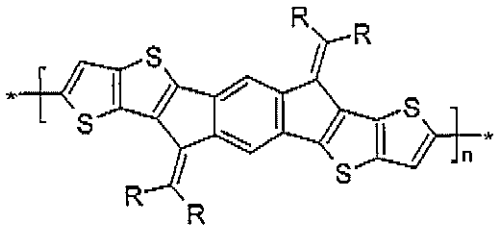


IV3



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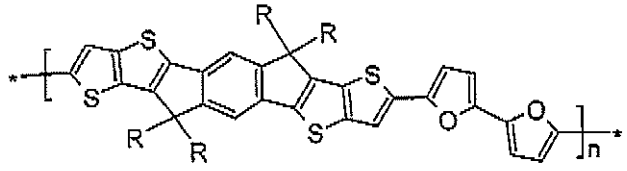
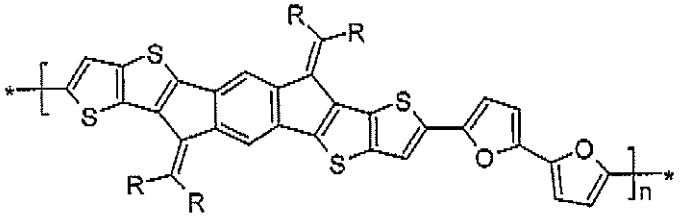
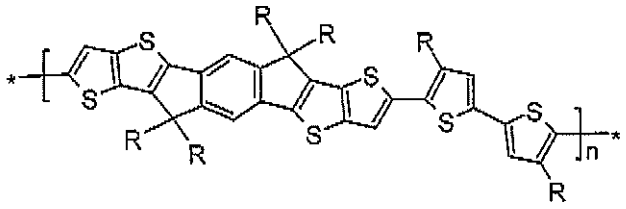


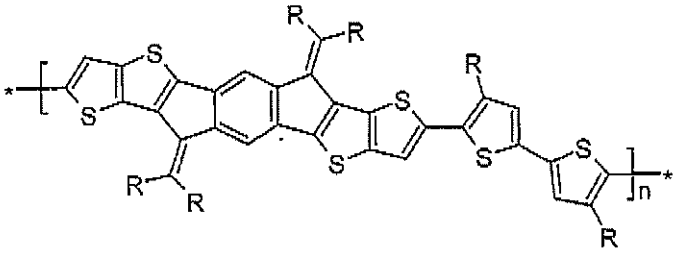
IV5



IV6



IV7



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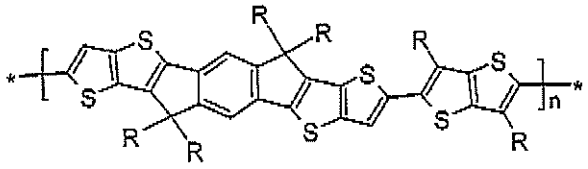

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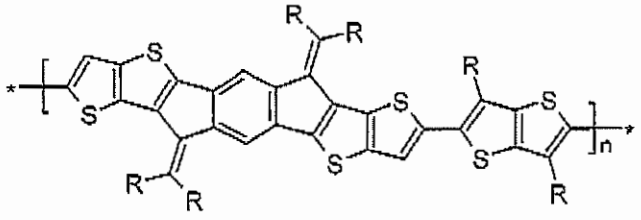

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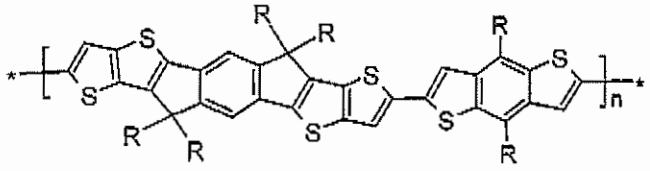

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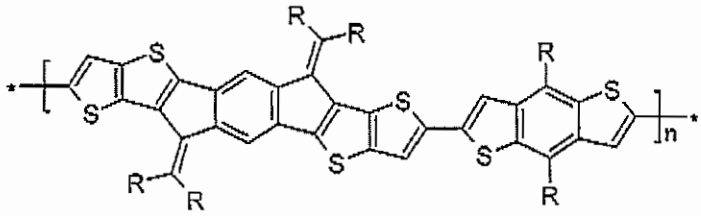

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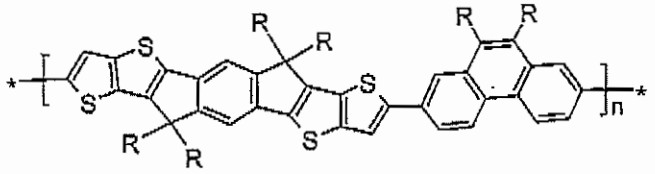

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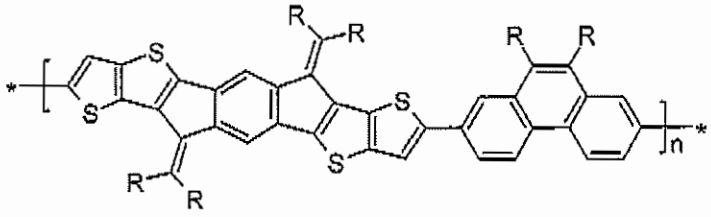


IV14

wherein R has on each occurrence identically or differently one of the meanings of R^1 as given in claim 1, 2 or 3.

5. Polymer according to one or more of claims 1 to 4, characterized in that R denotes H.

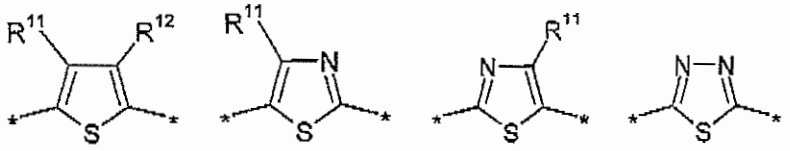
6. Polymer according to one or more of claims 1 to 5, characterized in that R denotes straight-chain, branched or cyclic alkyl with 1 to 30 C atoms which is unsubsituted or substituted by one or more F atoms.

7. Polymer according to one or more of claims 1 to 6, characterized in that it is selected of formula V

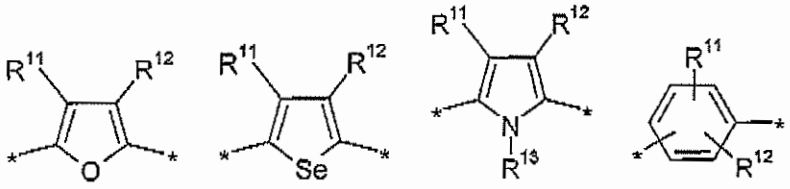
R^5-chain-R^6 V

wherein "chain" is a polymer chain selected of formulae IVe or IV1-IV5 as defined in claim 1 or 4, and R^5 and R^6 denote independently of each other F, Br, Cl, H, $-CH_2Cl$, $-CHO$, $-CH=CH_2$, $-SiR'R''R'''$, $-SnR'R''R'''$, $-BR'R''$, $-B(OR')(OR'')$, $-B(OH)_2$, -ZnCl, -MgCl, -MgBr or P-Sp-, wherein P and Sp are as defined in claim 1, R', R'' and R''' have independently of each other one of the meanings of R^0 given claim 1, and two of R', R'' and R''' may also form a ring together with the hetero atom to which they are attached.

8. Polymer according to one or more of claims 1 to 7, wherein one or more of Ar^1, Ar^2 and Ar^3 denote aryl or heteroaryl selected from the group consisting of the following formulae



(D1) (D2) (D3) (D4)



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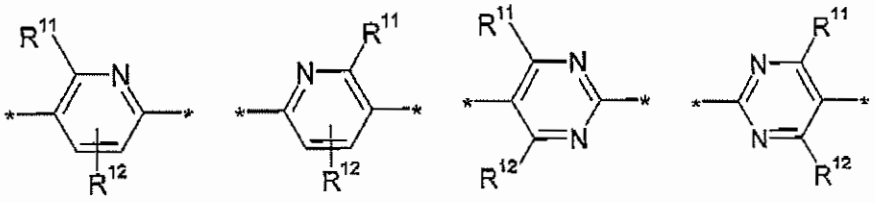

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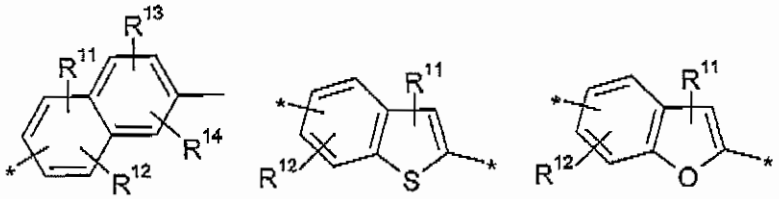

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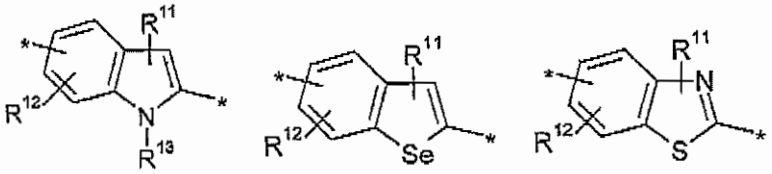

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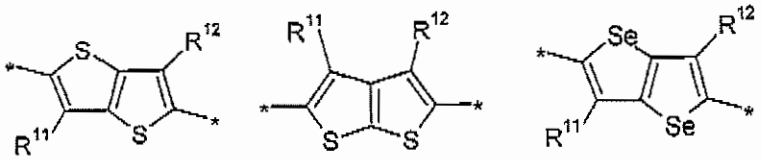

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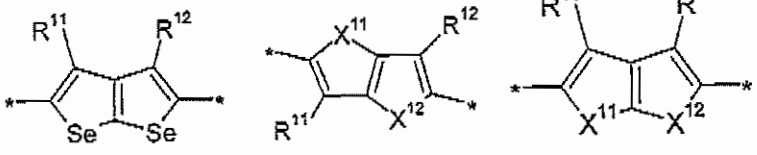

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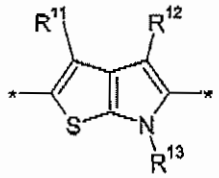

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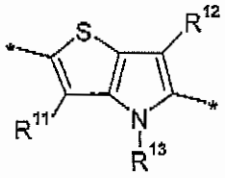

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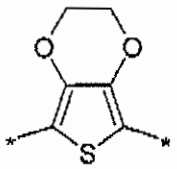

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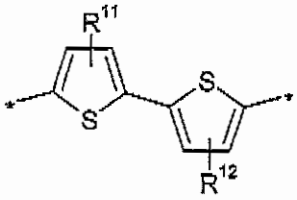

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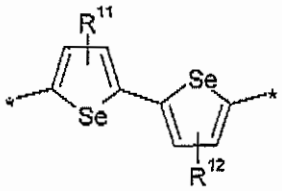

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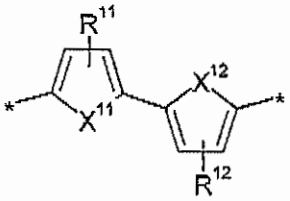

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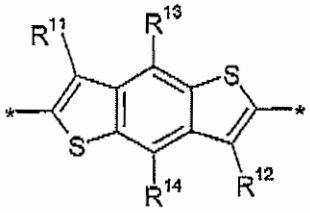

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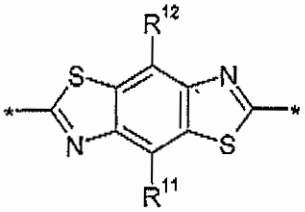

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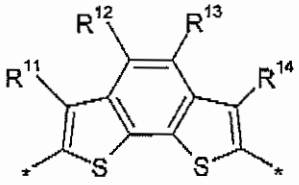

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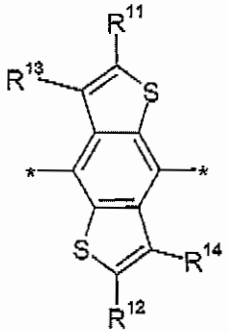

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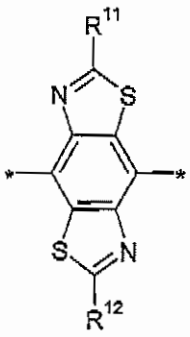

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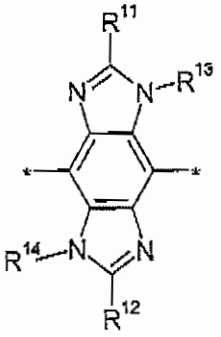

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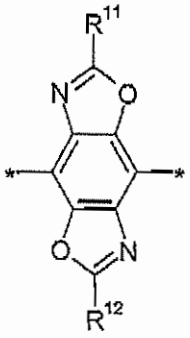

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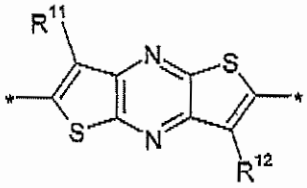

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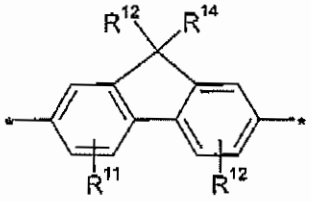

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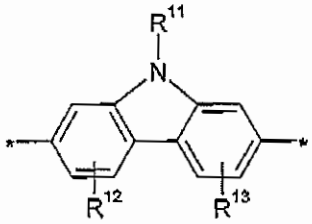

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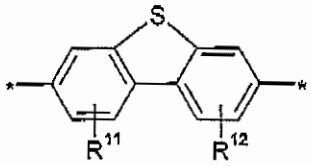

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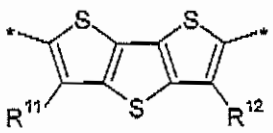

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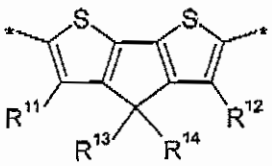

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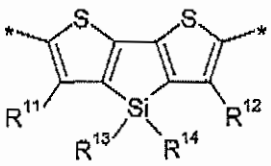

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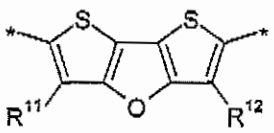

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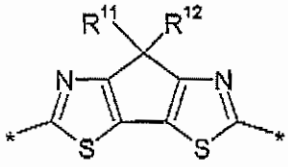

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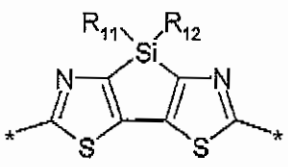

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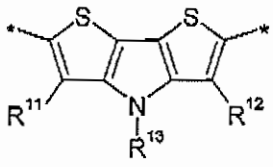

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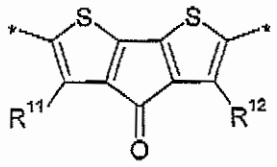

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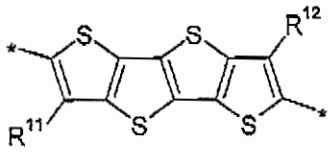

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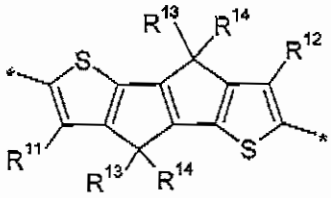

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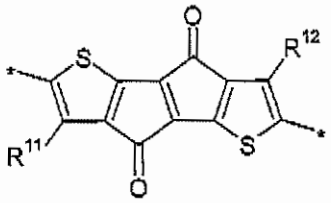

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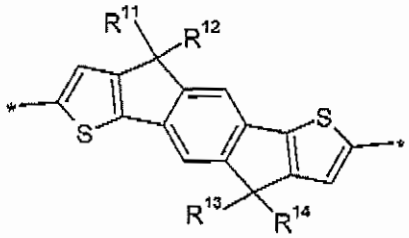

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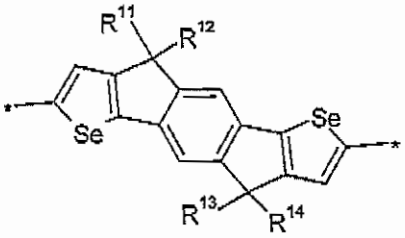

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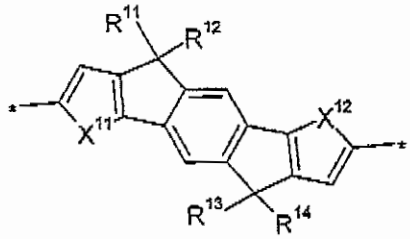

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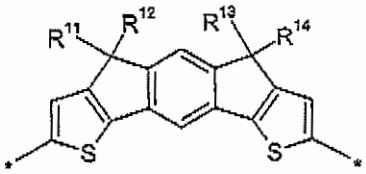

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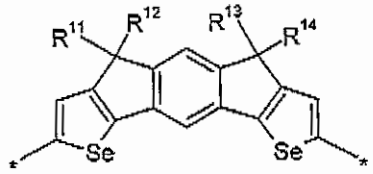

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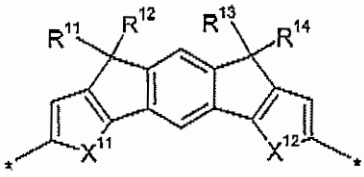

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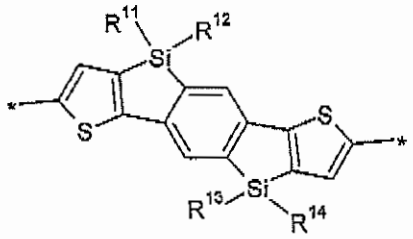

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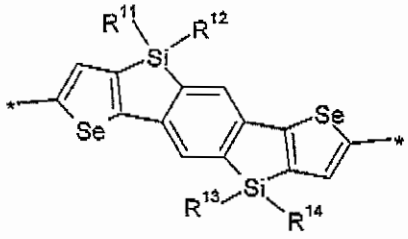

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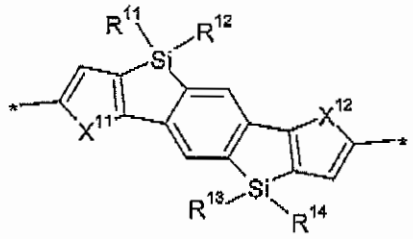

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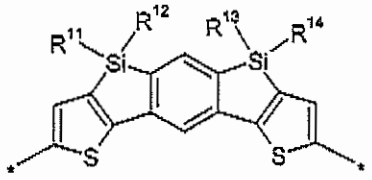

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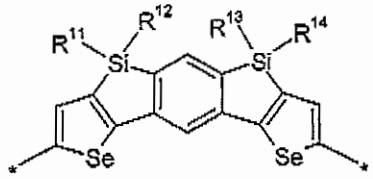

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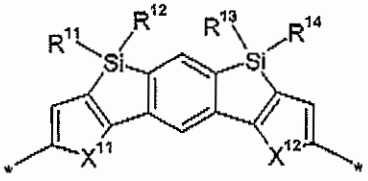

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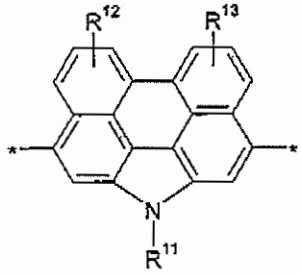

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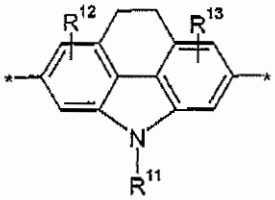

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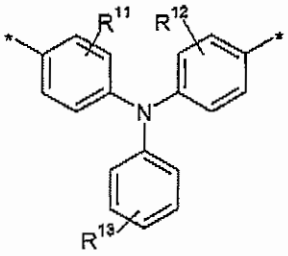

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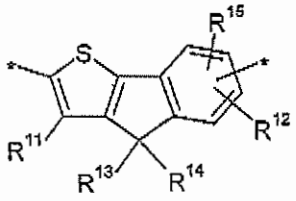

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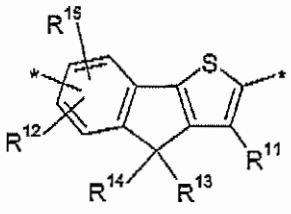

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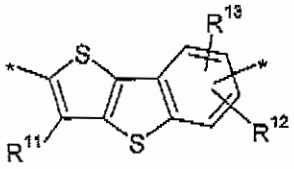

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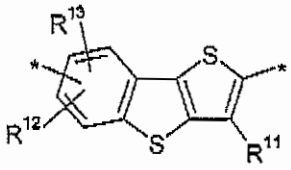

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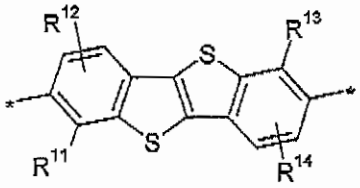

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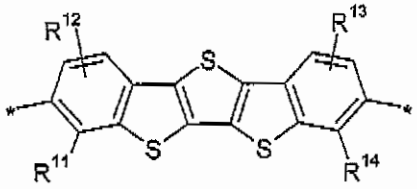

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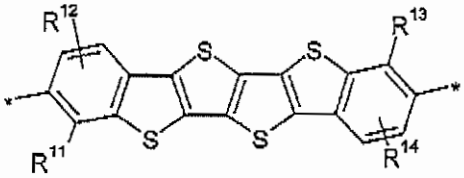

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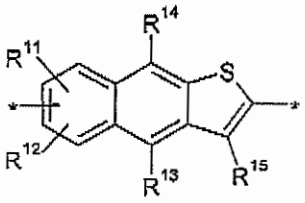

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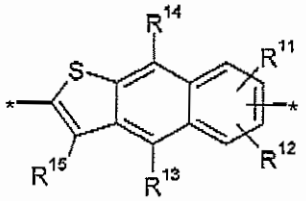

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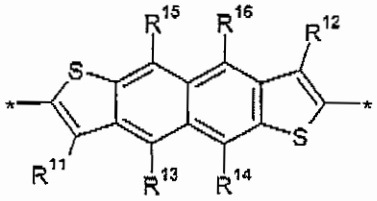

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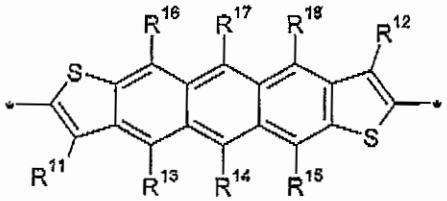

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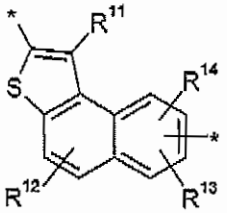

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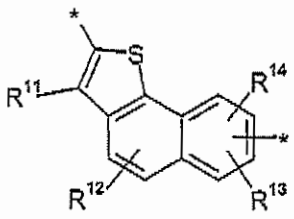

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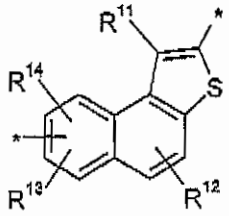

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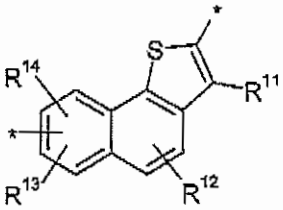

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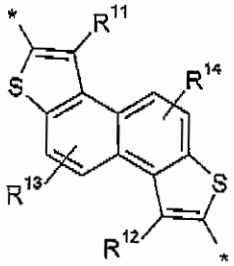

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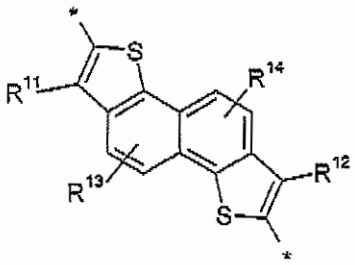

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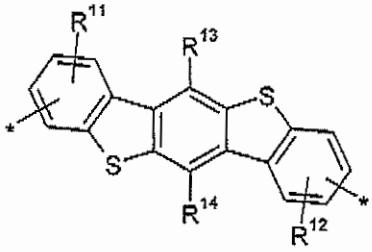

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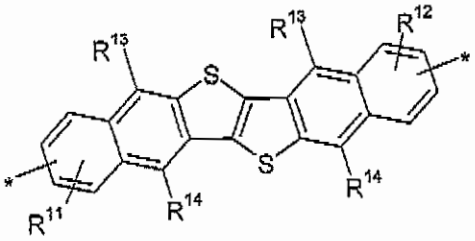

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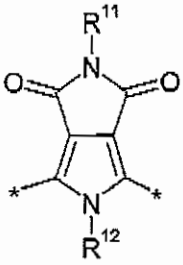
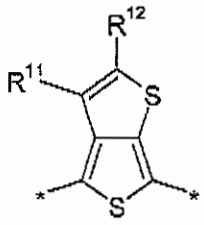


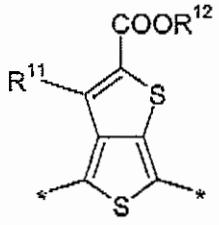
(D88)

wherein one of X^{11} and X^{12} is S and the other is Se, and 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 R^1 as defined in claim 1.

9. Polymer according to one or more of claims 1 to 8, wherein one or more of the units Ar^3 and A^1 denote aryl or heteroaryl selected from the group consisting of the following formulae



(A1)



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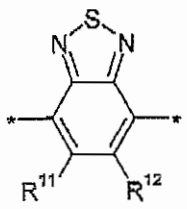

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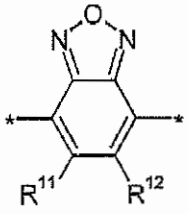

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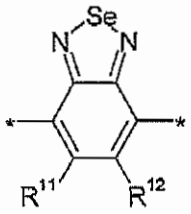

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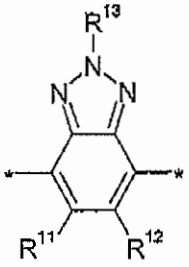

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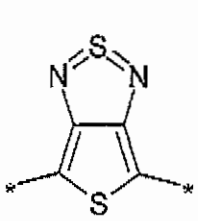

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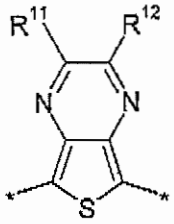

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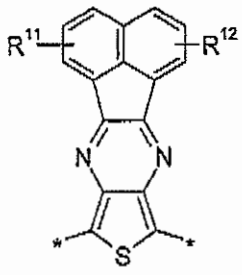

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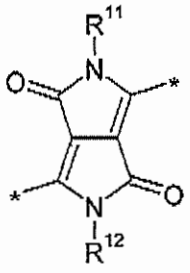

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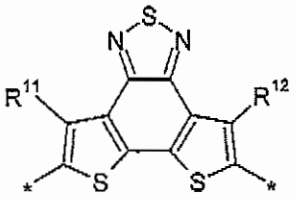

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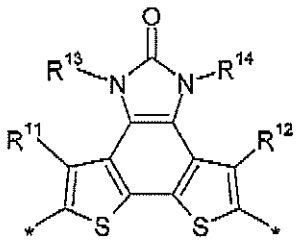

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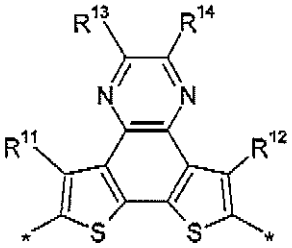

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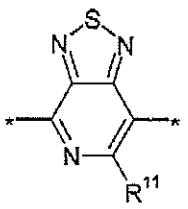

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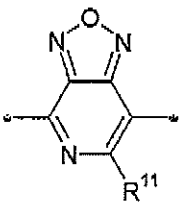

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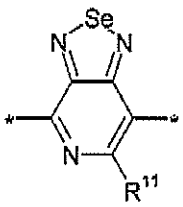

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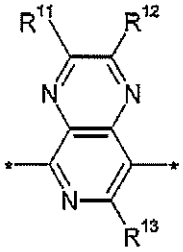

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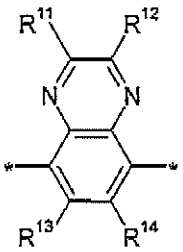

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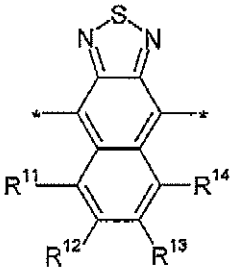

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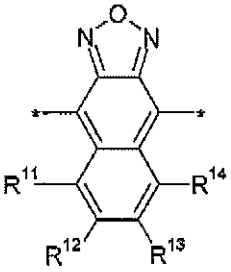

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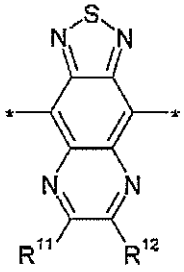

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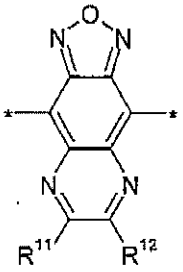

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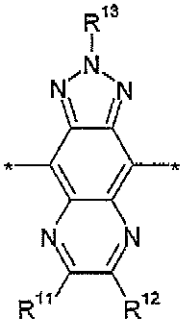

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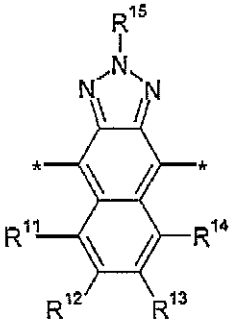

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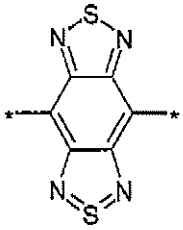

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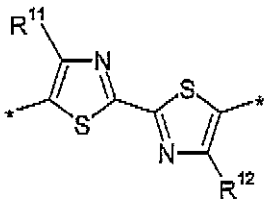

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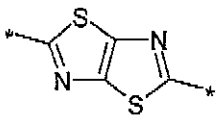

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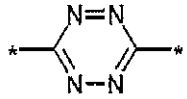

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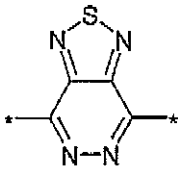

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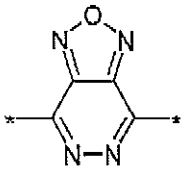

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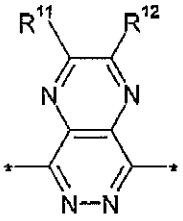

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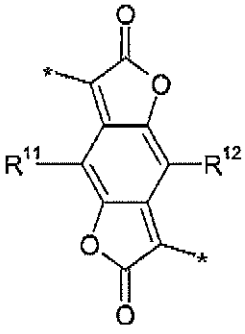

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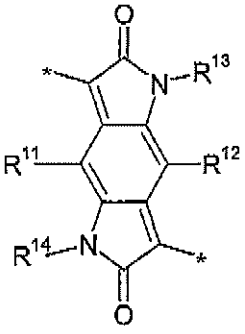

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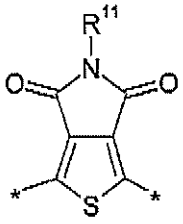

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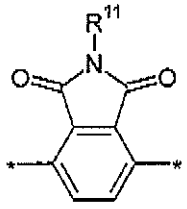

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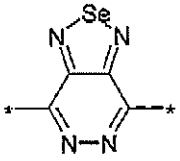

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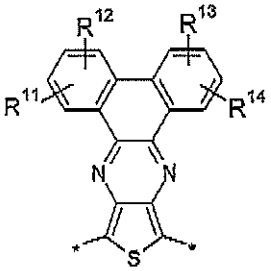
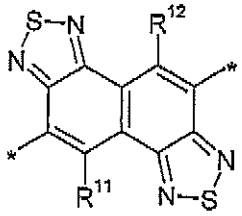
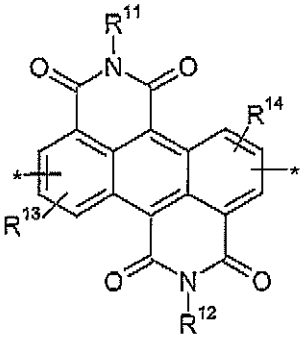


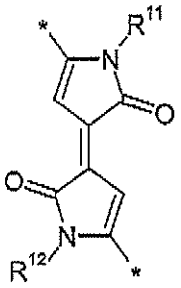
(A37)



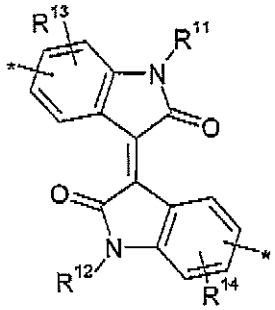
(A38)



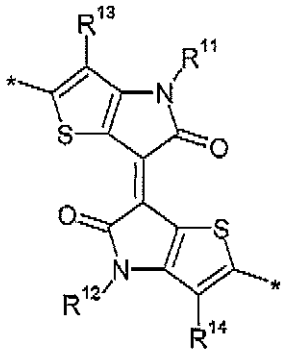
(A39)



(A40)



(A41)



(A42)

wherein one of X^{11} and X^{12} is S and the other is Se, and R^{11}, R^{12}, R^{13}, R^{14} and R^{15} independently of each other denote H or have one of the meanings of R^1 as defined in claim 1.

10. Mixture or blend comprising one or more polymers according to one or more of claims 1 to 9, and one or more compounds or polymers having semiconducting, charge transport, hole/electron transport, hole/electron blocking, electrically conducting, photoconducting or light emitting properties.

11. Mixture or blend according to claim 12, characterized in that it comprises one or more polymers according to one or more of claims 1 to 9 and one or more n-type organic semiconductor compounds.

12. Mixture or blend according to claim 11, characterized in that the n-type organic semiconductor compound is a fullerene or substituted fullerene.

13. Formulation comprising one or more polymers, mixtures or blends according to one or more of claims 1 to 12, and one or more solvents, preferably selected from organic solvents.

14. Use of a polymer, mixture, blend or formulation according to one or more of claims 1 to 13 as charge transport, semiconducting, electrically conducting, photoconducting or light emitting material in optical, electrooptical, electronic, electroluminescent or

photoluminescent components or devices.

15. Optical, electrooptical or electronic component or device comprising one or more polymers, mixtures, blends or formulations according to one or more of claims 1 to 13.

16. Component or device according to claim 15, which is selected from the group consisting of organic field effect transistors (OFET), thin film transistors (TFT), integrated circuits (IC), logic circuits, capacitors, radio frequency identification (RFID) tags, devices or components, organic light emitting diodes (OLED), organic light emitting transistors (OLET), flat panel displays, backlights of displays, organic photovoltaic devices (OPV), organic solar cells (O-SC), photodiodes, laser diodes, photoconductors, photodetectors, electrophotographic devices, electrophotographic recording devices, organic memory devices, sensor devices, charge injection layers, charge transport layers or interlayers in polymer light emitting diodes (PLEDs), Schottky diodes, planarising layers, antistatic films, polymer electrolyte membranes (PEM), conducting substrates, conducting patterns, electrode materials in batteries, alignment layers, biosensors, biochips, security markings, security devices, and components or devices for detecting and discriminating DNA sequences.

17. Component or device according to claim 15 or 16, which is an OFET, bulk heterojunction (BHJ) OPV device or inverted BHJ OPV device.