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(54) Title: NON-FULLERENE ELECTRON ACCEPTORS

(57) Abstract: The invention provides electron acceptor compound of Formula (I) which may be used in organic compositions for optical or electronic devices.

NON-FULLERENE ELECTRON ACCEPTORS

FIELD OF INVENTION

The invention relates to non-fullerene electron acceptors which may be used in organic optical or electronic devices.

BACKGROUND

Solution processed organic photovoltaics (OPV) offer the attractive prospect of low-cost, light-weight and environmentally benign solar energy production. The development of low bandgap donor-acceptor polymers has led to high efficiency OPV devices in recent years, however many of these polymers suffer problems regarding stability and synthetic scalability.

In addition, most of these high performance devices employ fullerene acceptors. These fullerene-based acceptors have some significant limitations including (i) weak absorption in the abundant region of the incident solar spectrum, which limits their ability to harvest photocurrent, (ii) limited tunability in terms of spectral absorption, (iii) high synthetic costs, especially for the high performing C70 derivative, and (iv) morphological instability due to fullerene diffusion and aggregation in the thin film over time.

Non-fullerene acceptor compounds have been reported which offer improved performance in electrochemical devices over fullerene-based acceptors (see C. Nielsen *et al.*, Acc. Chem. Res. 2015, 48, 2803−2812, the contents of which are herein incorporated by reference in its entirety). Despite this, there remains a need for new acceptor compounds having greater extinction coefficients and hence absorptions. Compounds having higher extinction coefficients absorb more light and generate more photocurrent, enabling thinner film devices.

SUMMARY OF THE INVENTION

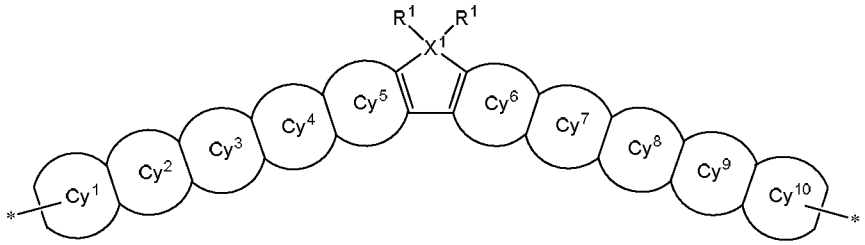
In a first aspect, the invention provides a compound of Formula (I)

$$T^1\text{-}(B^1)_a\text{-}(A)\text{-}(B^2)_b\text{-}T^2$$

Formula (I)

wherein

A is a divalent conjugated fused ring system having the structure:



wherein:

X_1 is C, Ge or Si;

R^1 is, at each occurrence, independently, H, or optionally substituted C_{1-30} aliphatic, aryl or heteroaryl;

Cy^{1-10} are, at each occurrence, independently, absent or a 5 or 6-membered ring having 0, 1 or 2 ring heteroatoms, or a fused polycyclic (for example bicyclic or tricyclic) ring optionally having one or more ring heteroatoms, provided that at least one of Cy^{1-5} and at least one of Cy^{6-10} is not absent, and wherein each of Cy^{1-10}, when present, is optionally substituted by one or more groups R^2;

R^2 is, at each occurrence, independently, halo, C_{1-30} aliphatic, aryl, heteroaryl, =O, =S, $=R^0$, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)OR^0$, $-C(=S)R^0$, $-C(=S)OR^0$, $-OC(=O)R^0$, $-OC(=S)R^0$, $-C(=O)SR^0$, $-SC(=O)R^0$, $-NH_2$, $-NR^0R^{00}$, $-NR^0C(O)R^0$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-CF_2-R^0$, $-SF_5$, silyl or hydrocarbyl with 1 to 40 C atoms and which optionally comprises one or more hetero atoms, wherein C_{1-30} aliphatic, aryl, heteroaryl, silyl or hydrocarbyl are optionally substituted, and wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C1-40 hydrocarbyl; or two R^2, with the intervening atoms form an optionally substituted fused aromatic or non-aromatic ring, having 0, 1 or 2 ring heteroatoms;

and wherein within A it is required that:

(i) X_1 is Ge; or

(ii) at least 2 adjacent Cy^{1-5} or Cy^{6-10} groups are both 6-membered rings, preferably 6-membered aromatic rings having 0, 1 or 2 ring heteroatoms (preferably phenyl, so that the 2 adjacent phenyl rings form a napthyl ring); or

(iii) X_1 is Ge and at least 2 adjacent Cy^{1-5} or Cy^{6-10} groups are both 6-membered rings, preferably 6-membered aromatic rings having 0, 1 or 2 ring heteroatoms (preferably phenyl, so that the 2 adjacent phenyl rings form a napthyl ring);

each occurrence of B^1 and B^2 is, independently, $-CY^1=CY^2-$, —C≡C—, or a cyclic hydrocarbyl group with 5 to 30 ring atoms optionally including one or more heteroatoms, preferably aryl or heteroaryl, wherein each occurrence of B^1 and B^2 is, independently, unsubstituted or substituted by one or more groups R^3, wherein R^3 has the meaning of R^2;

Y^1 and Y^2 are, independently, H, F, Cl or CN;

a and b are, independently of each other, 0, 1 or 2;

T^1 and T^2 are, independently of each other, an electron deficient group conjugated to group B^1 or B^2, respectively, or wherein when a and/or b are 0, T^1 and T^2 are, independently of each other, an electron deficient group conjugated to group A, respectively; and

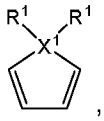
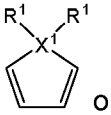
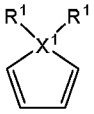
wherein A contains an optionally substituted aromatic ring having 0, 1, 2 or more ring heteroatoms directly bonded to groups B^1 and B^2, respectively, or wherein when a and/or b are 0, A contains an optionally substituted aromatic ring having 0, 1, 2 or more ring heteroatoms directly bonded to groups T^1 and T^2, respectively.

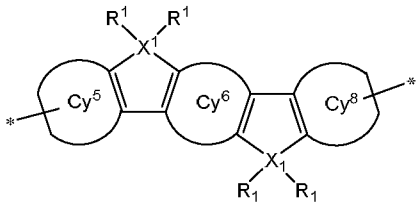
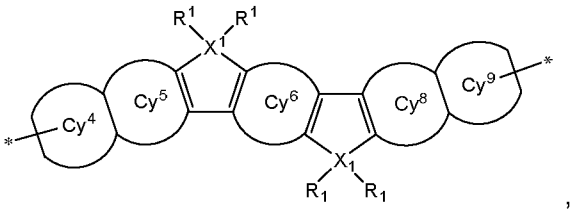
It will be appreciated that each occurrence of —— * represents the bond to B^1 and B^2, respectively. Where any one or more of $Cy^{1\text{-}10}$ is absent, the point of attachment to B^1 and B^2 is instead on the next adjacent one of $Cy^{1\text{-}10}$ that is not absent. For example, if Cy^1 is absent, but Cy^2 is present, the bond between A and B^1 will be between Cy^2 and B^1. Where a or b, respectively, is not 0, the one of $Cy^{1\text{-}10}$ which is bonded to B^1 or B^2, respectively, is an optionally substituted aromatic ring having 0, 1, 2 or more ring heteroatoms . When a and/or b is 0, the one of $Cy^{1\text{-}10}$ which is bonded to T^1 or T^2, respectively, is an optionally substituted aromatic ring having 0, 1, 2 or more ring heteroatoms directly bonded to groups T^1 and T^2, respectively.

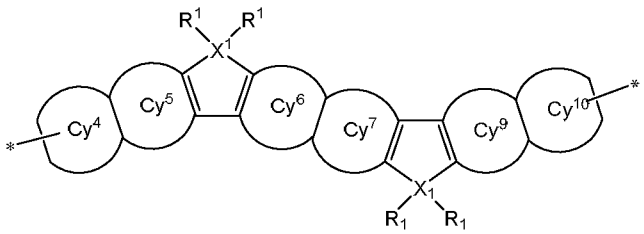
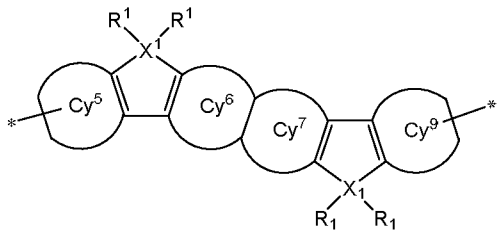
$Cy^{1\text{-}10}$ are preferably, at each occurrence, independently, absent or a 5 or 6-membered ring having 0, 1 or 2 ring heteroatoms, each optionally substituted by one or more groups R^2, provided that at least one of $Cy^{1\text{-}5}$ and at least one of $Cy^{6\text{-}10}$ is not absent.

Preferably the one of $Cy^{1\text{-}5}$ and at the one of $Cy^{6\text{-}10}$ that are directly bonded to groups B^1 and B^2, or wherein when a and/or b are 0, the one of $Cy^{1\text{-}5}$ and at the one of $Cy^{6\text{-}10}$ that are directly bonded to groups T^1 and T^2, are each independently a 5 or 6-membered aromatic ring having 0, 1 or 2 ring heteroatoms (preferably phenyl or thiophenyl), each optionally substituted by one or more groups R^2.

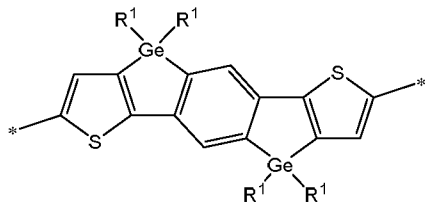
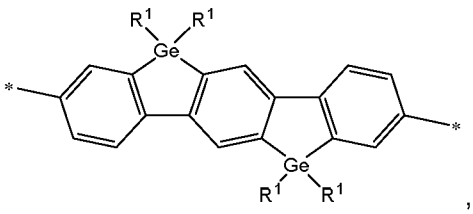
Preferably at least three of $Cy^{1\text{-}10}$ are, independently, a 5 or 6-membered aromatic ring having 0, 1 or 2 ring heteroatoms (preferably phenyl or thiophenyl), each optionally substituted by one or more groups R^2.

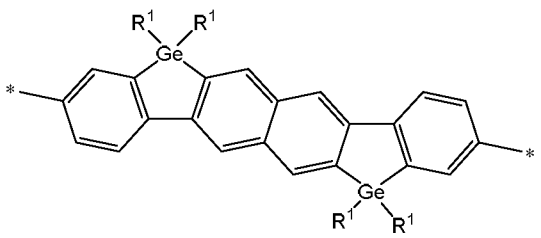
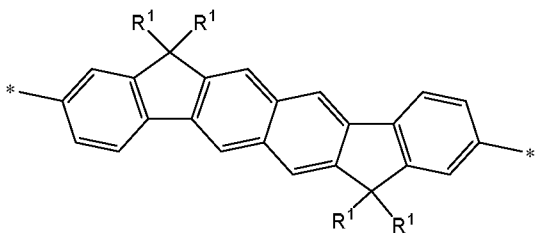
Any one or more of Cy^{1-10} may have the structure  , wherein X_1 is C, Ge or Si. Each of Cy^{1-10} is preferably, independently, absent,  or a 5 or 6-membered aromatic ring having 0, 1 or 2 ring heteroatoms (preferably phenyl or thiophenyl) , each optionally substituted by one or more groups R^2. Preferably one of Cy^{1-10} is  , and the remainder of Cy^{1-10} are absent or a 5 or 6-membered aromatic ring having 0, 1 or 2 ring heteroatoms, each optionally substituted by one or more groups R^2, preferably at least three of Cy^{1-10} are a 5 or 6-membered aromatic ring having 0, 1 or 2 ring heteroatoms, each optionally substituted by one or more groups R^2. For example, in a compound of Formula (I) as defined herein, A may preferably be selected from:

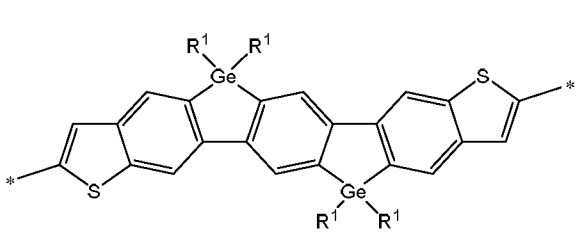
 ,  ,

 or 

wherein Cy^{4-10} are as defined above. Preferably, Cy^{4-10} are at each occurrence, independently a 5 or 6-membered aromatic ring having 0, 1 or 2 ring heteroatoms (preferably phenyl or thiophenyl) , each optionally substituted by one or more groups R^2. Preferably A may be selected from:

 ,  ,

 ,  ,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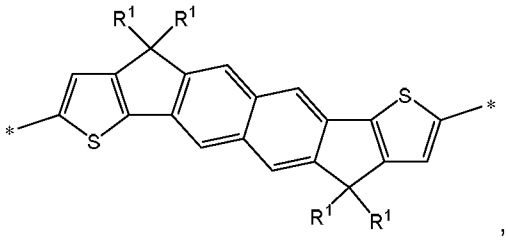
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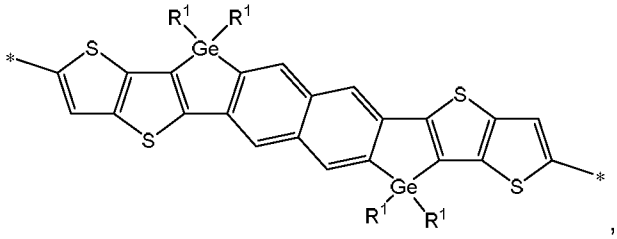
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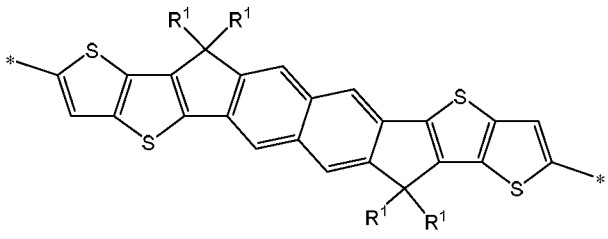
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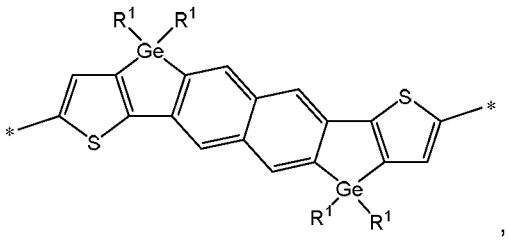
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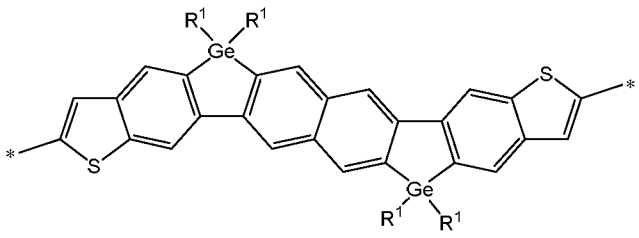
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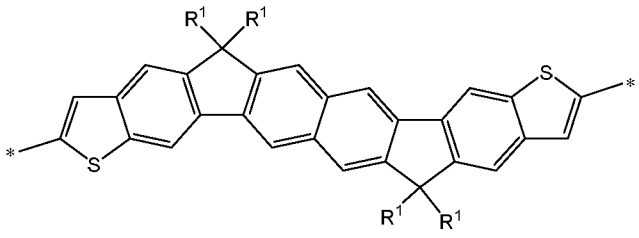
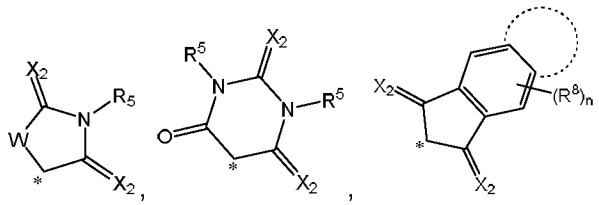

, optionally substituted by one or more groups R^2.

In any of the structures described above, R^1 may, at each occurrence, independently, be C_{1-30} aliphatic or aryl optionally substituted with C_{1-10} aliphatic, preferably C_{6-10} aliphatic (for example, linear or branched C_8 aliphatic) or aryl (for example, phenyl) substituted with C_{1-6} aliphatic.

In any of the structures described above, R^2 may, at each occurrence, independently, be H, optionally substituted C_{1-30} aliphatic, aryl or heteroaryl, preferably C_{1-30} aliphatic or aryl substituted with C_{1-10} aliphatic, preferably C_{6-8} aliphatic (for example, linear or branched C_8 aliphatic) or aryl (for example, phenyl) substituted with C_{1-6} aliphatic.

Within any of the structures described above for a compound of Formula (I), T^1 and T^2 may be, independently of each other, $-CR^4=Y$, $-CR^4=CR^4-Y$, -L-Y or –Y; wherein Y is an optionally substituted cyclic hydrocarbyl group, preferably optionally substituted aryl or heteroaryl; and L is a divalent alkylenyl chain of 3 to 10 carbon atoms, having alternating double and single bonds, optionally substituted by one or more R^4; and R^4 is H or has the meaning of R^2, preferably wherein R^4 is H.

Preferably, at least one of T^1 or T^2 is $-CR^4=Y$, and Y is:



in which * marks the point of attachment to $-CR^4=$;

X^2 is S, O or $C(R^6)_2$;

W is S, O or $C(R^6)_2$ (preferably S);

R^5 is H, aliphatic, heteroaliphatic, aryl, heteroaryl , -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)OR^0$, $-C(=S)R^0$, $-C(=S)OR^0$, $-OC(=O)R^0$, $-OC(=S)R^0$, $-C(=O)SR^0$, $-SC(=O)R^0$, $-NH_2$, $-NR^0R^{00}$, $-NR^0C(O)R^0$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-CF_2-R^0$, $-SF_5$, silyl or hydrocarbyl with 1 to 40 C atoms and which optionally comprises one or more hetero atoms, wherein aliphatic, heteroaliphatic, aryl, heteroaryl, silyl or hydrocarbyl are optionally substituted, and wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C1-40 hydrocarbyl (preferably optionally substituted aliphatic, heteroaliphatic, aryl or heteroaryl);

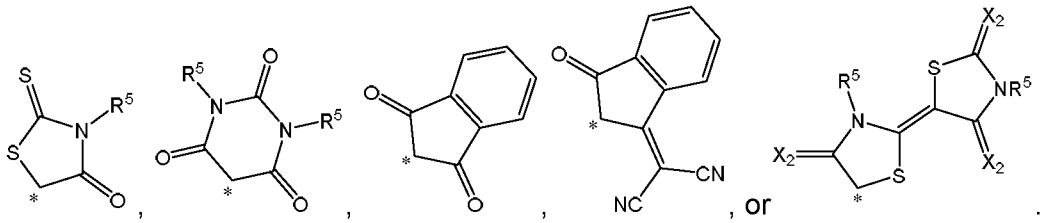
R^6 is, at each occurrence, independently, H, halo, aliphatic, heteroaliphatic, aryl, heteroaryl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)OR^0$, $-C(=S)R^0$, $-C(=S)OR^0$, $-OC(=O)R^0$, $-OC(=S)R^0$, $-C(=O)SR^0$, $-SC(=O)R^0$, $-NH_2$, $-NR^0R^{00}$, $-NR^0C(O)R^0$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-CF_2-R^0$, $-SF_5$, silyl or hydrocarbyl with 1 to 40 C atoms and which optionally comprises one or more hetero atoms, wherein aliphatic, heteroaliphatic, aryl, heteroaryl, silyl or hydrocarbyl are optionally substituted, and wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C1-40 hydrocarbyl;

 may be present or absent and represents a fused mono-, bi- or tri- cyclic hydrocarbyl group, preferably aryl or heteroaryl, optionally substituted by one or more R_7, wherein R^7 has the meaning of R^2;

R^8 is, at each occurrence, independently, halo, aryl, heteroaryl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)OR^0$, $-C(=S)R^0$, $-C(=S)OR^0$, $-OC(=O)R^0$, $-OC(=S)R^0$, $-C(=O)SR^0$, $-SC(=O)R^0$, $-NH_2$, $-NR^0R^{00}$, $-NR^0C(O)R^0$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-CF_2-R^0$, $-SF_5$, silyl or hydrocarbyl with 1 to 40 C atoms and which optionally comprises one or more hetero atoms, wherein aryl, heteroaryl, silyl or hydrocarbyl are optionally substituted, and wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C1-40 hydrocarbyl; and

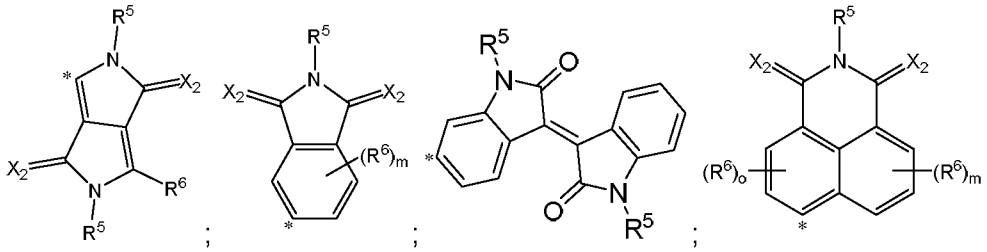
n is 0-4.

Preferably, at least one of T^1 or T^2 is $-CR^4=Y$, and Y is:



Preferably, T^1 or T^2 are both $-CR^4=Y$ and Y is as defined above.

Preferably, at least one of T^1 and T^2 is $-CR^4=CR^4-Y$ or –Y and Y is:



m is 0-3 and o is 0-2 and R^5, R^6 and X_2 are as defined above. In preferred embodiments, X_2 is O.

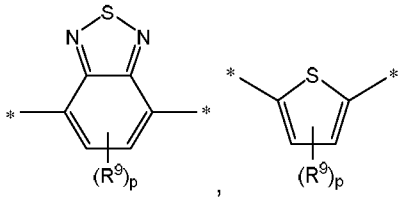
In any of the above embodiments of Y, R^5 is preferably C_{1-12} aliphatic, preferably C_{1-12} alkyl, more preferably C_{1-8} alkyl.

Within any of the structures described above for a compound of Formula (I), preferably a and b are both 1.

Within any of the structures described above for a compound of Formula (I), each occurrence of B^1 and B^2 may preferably be, independently, mono-, bi- or tri-cyclic aryl or

heteroaryl, unsubstituted or substituted by one or more groups R^3, wherein the aryl or heteroaryl group may optionally include a non-aromatic carbocyclic or heterocyclic ring fused thereto.

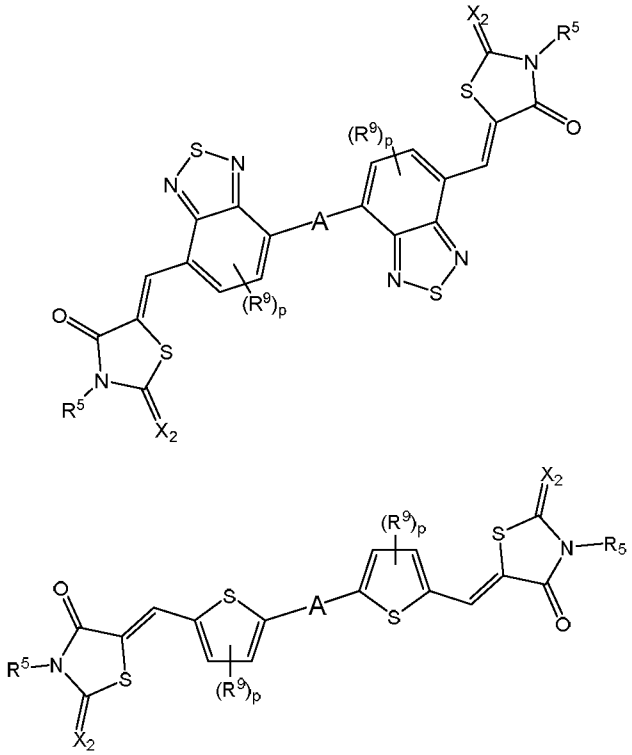
Preferably, one or more occurrences of B^1 and B^2 is:

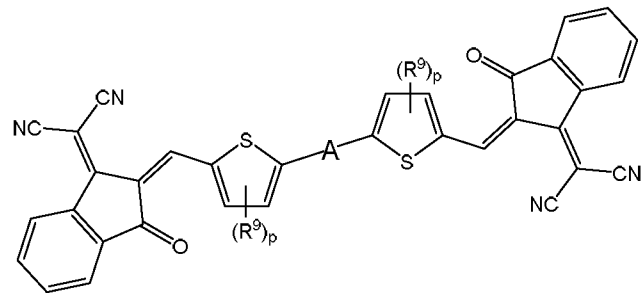


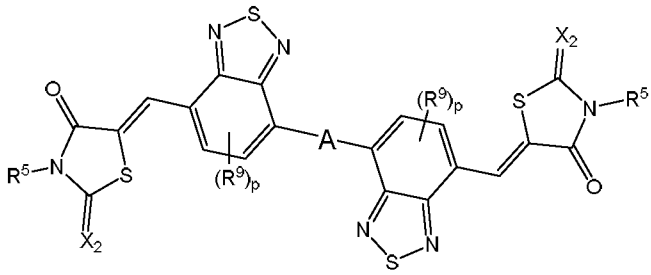
wherein p is 0, 1 or 2; and

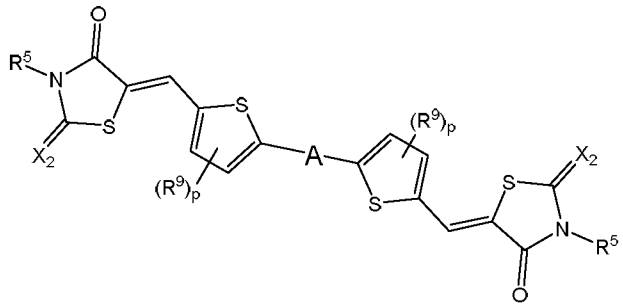
R^9 is, at each occurrence, independently, halo, aryl, heteroaryl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)OR^0$, $-C(=S)R^0$, $-C(=S)OR^0$, $-OC(=O)R^0$, $-OC(=S)R^0$, $-C(=O)SR^0$, $-SC(=O)R^0$, $-NH_2$, $-NR^0R^{00}$, $-NR^0C(O)R^0$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-CF_2-R^0$, $-SF_5$, silyl or hydrocarbyl with 1 to 40 C atoms and which optionally comprises one or more hetero atoms, wherein aryl, heteroaryl, silyl or hydrocarbyl are optionally substituted, and wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C1-40 hydrocarbyl.

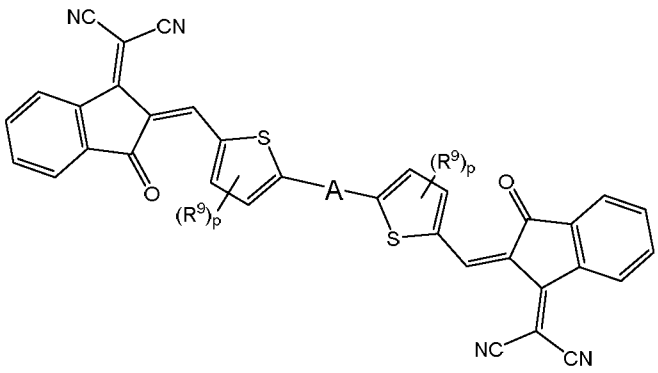
A compound of Formula (I) as defined herein, may preferably be selected from:



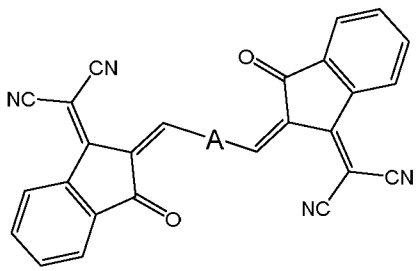






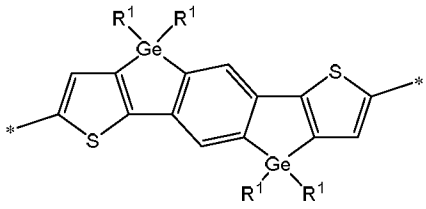


or



,

preferably wherein A is: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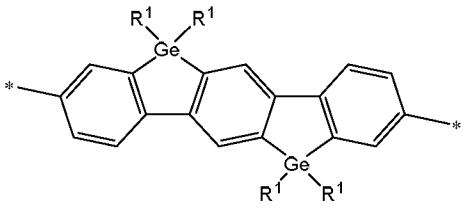
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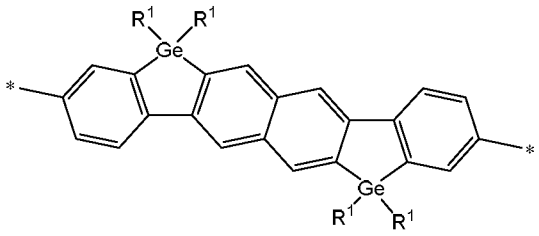
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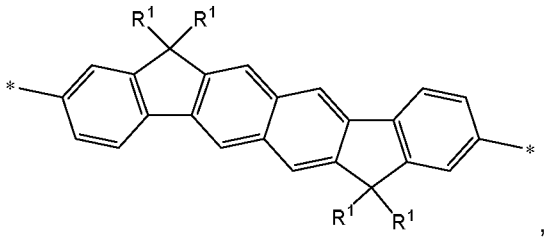
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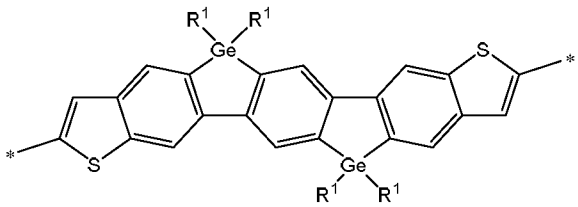
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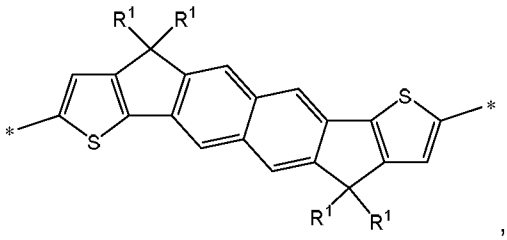
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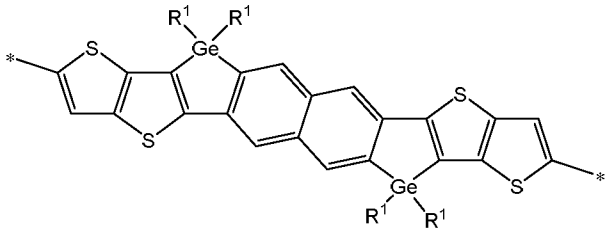
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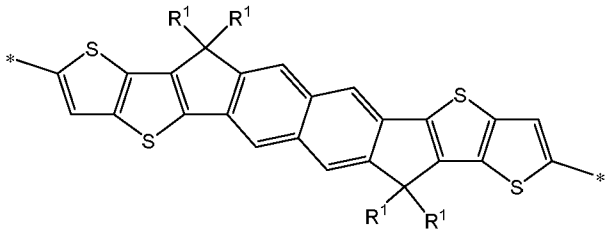
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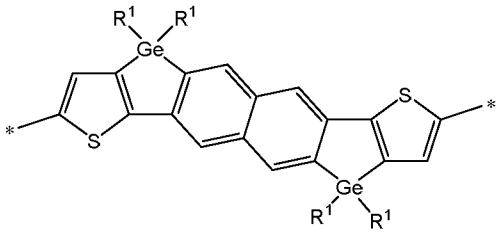
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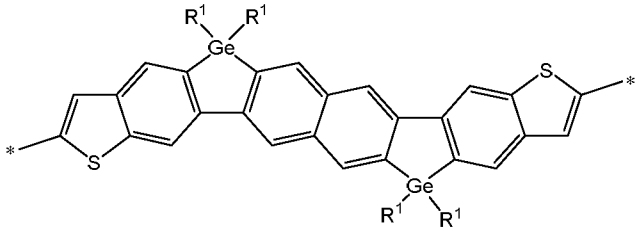
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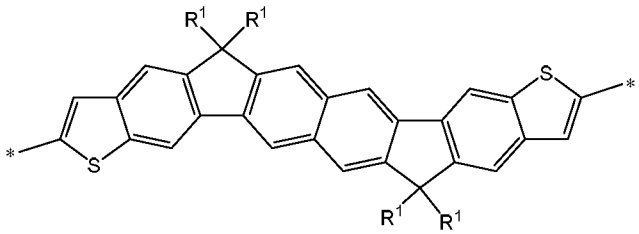
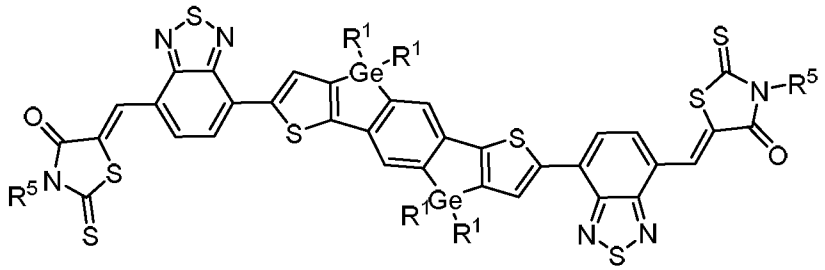
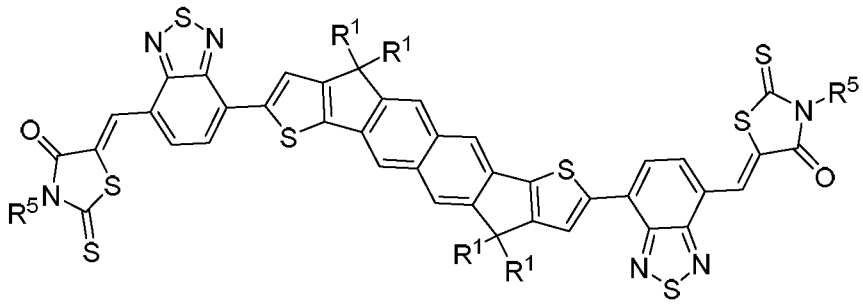
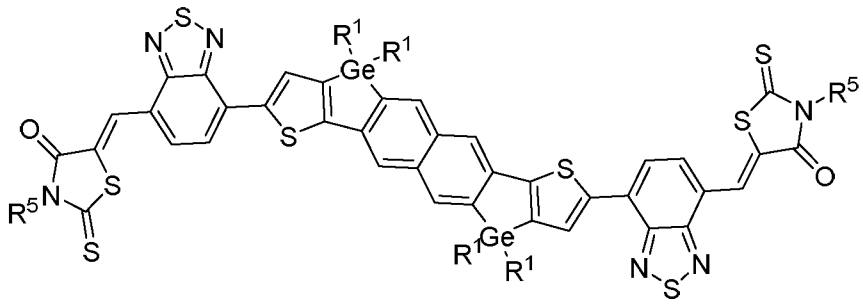
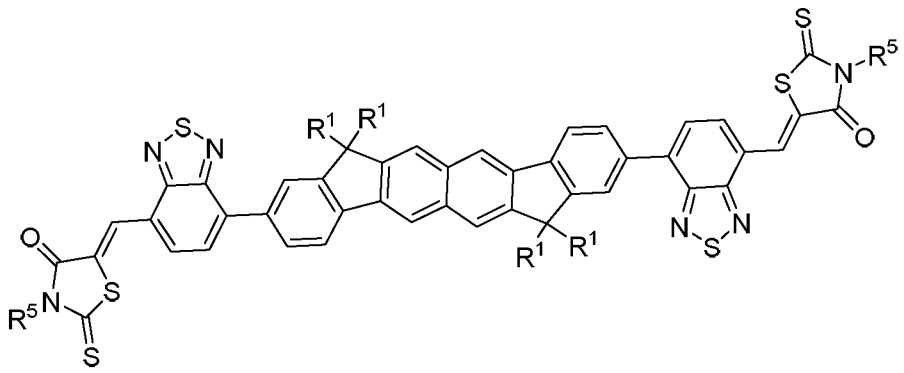

, optionally substituted by one or more groups R^2.

A compound of Formula (I) as defined herein, may preferably be selected from:









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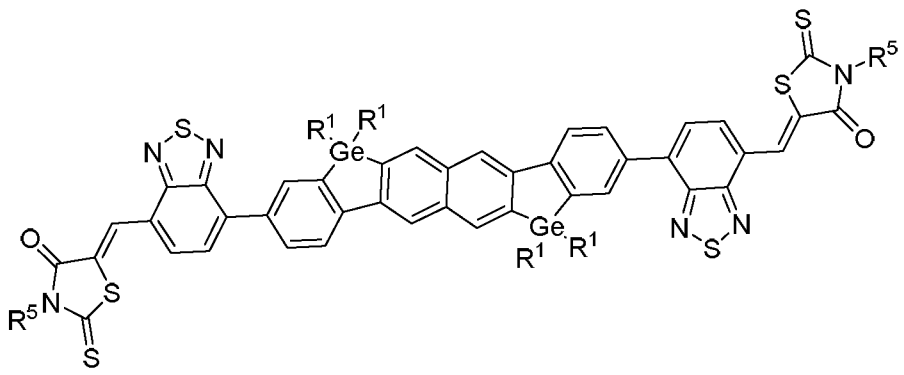


.

Preferably, R^1 is C_{1-8} aliphatic, preferably $-C_8H_{17}$ or $-CH_2C(C_2H_5)HC_4H_9$ and R^5 is methyl or ethyl (preferably ethyl).

In a second aspect the invention provides a composition comprising an organic electron acceptor compound of the first aspect of the invention and an organic electron donor compound. The composition preferably further comprises one or additional organic electron acceptor compounds.

Preferably, one electron acceptor compound is a compound of Formula (I) as defined in respect of the first aspect of the invention and a second electron acceptor compound that is a compound

(i) having an electron affinity and ionization potential between that of the electron donor and the first electron acceptor, for example such that there is an exothermic charge transfer on exciton dissociation, and it does not provide a source for charge trapping;

(ii) intimately mixing with the first acceptor, rather than phase separating, thus preventing pinning of the open circuit voltage to the lowest ionization potential component;

(iii) not disrupting or suppressing the molecular organisation of the donor phase; and/or

(iv) facilitating charge transport, improves charge carrier collection and extends device lifetime. The second electron acceptor compound may be a small molecule, for example a compound having a molecular weight of 1000Da or less. Preferably both the first and the second electron acceptor compounds are a compound of formula (I) as defined herein, provided that the first and electron acceptor compounds of formula (I) are not the same.

Preferably, the composition comprises a first electron acceptor compound and a second electron acceptor compound, wherein the second electron acceptor compound has an electron affinity and ionization potential between that of the electron donor and the first electron acceptor compound. Alternatively, the composition comprises a first electron acceptor compound and a second electron acceptor compound, wherein the first electron acceptor compound has an electron affinity and ionization potential between that of the electron donor and the second electron acceptor compound.

Preferably, the composition comprises a first electron acceptor compound and a second electron acceptor compound, wherein the second electron acceptor compound has an electron affinity and ionization potential between that of the electron donor and the first electron acceptor compound. Alternatively, the composition comprises a first electron

acceptor compound and a second electron acceptor compound, wherein the first electron acceptor compound has an electron affinity and ionization potential between that of the electron donor and the second electron acceptor compound.

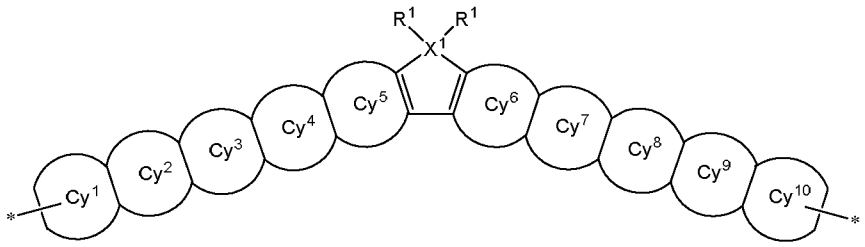
Preferably, one electron acceptor compound (for example, a first electron acceptor compound) is a compound of Formula (I) as defined in respect of the first aspect of the invention and the composition also comprises an organic electron acceptor compound (for example, a second electron acceptor compound) of Formula (IA)

$$T^1\text{-}(B^1)_a\text{-}(A)\text{-}(B^2)_b\text{-}T^2$$

Formula (IA)

wherein

A is a divalent conjugated fused ring system containing aromatic groups directly conjugated to groups B^1 and B^2, and having the structure:



wherein:

X_1 is C, Ge or Si;

R^1 is, at each occurrence, independently, H, or optionally substituted $C_{1\text{-}30}$ aliphatic, aryl or heteroaryl;

$Cy^{1\text{-}10}$ are, at each occurrence, independently, absent or a 5 or 6-membered ring having 0, 1 or 2 ring heteroatoms, or a fused polycyclic (for example, bicyclic or tricyclic) ring optionally having one or more ring heteroatoms, provided that at least one of $Cy^{1\text{-}5}$ and at least one of $Cy^{6\text{-}10}$ is not absent, and wherein each of $Cy^{1\text{-}10}$, when present, is optionally substituted by one or more groups R^2;

R^2 is, at each occurrence, independently, halo, $C_{1\text{-}30}$ aliphatic, aryl, heteroaryl, =O, =S, $=R^0$, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)OR^0$, $-C(=S)R^0$, $-C(=S)OR^0$, $-OC(=O)R^0$, $-OC(=S)R^0$, $-C(=O)SR^0$, $-SC(=O)R^0$, $-NH_2$, $-NR^0R^{00}$, $-NR^0C(O)R^0$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-CF_2\text{-}R^0$, $-SF_5$, silyl or hydrocarbyl with 1 to 40 C atoms and which optionally comprises one or more hetero atoms, wherein $C_{1\text{-}30}$ aliphatic, aryl, heteroaryl, silyl or hydrocarbyl are optionally substituted, and

wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C_{1-40} hydrocarbyl; or two R^2, with the intervening atoms form an optionally substituted fused ring, having 0, 1 or 2 ring heteroatoms;

each occurrence of B^1 and B^2 is, independently, $-CY^1=CY^2-$, $-C\equiv C-$, or a cyclic hydrocarbyl group with 5 to 30 ring atoms optionally including one or more heteroatoms, preferably aryl or heteroaryl, wherein each occurrence of B^1 and B^2 is, independently, unsubstituted or substituted by one or more R^3, wherein R^3 has the meaning of R^2;

Y^1 and Y^2 are, independently, H, F, Cl or CN;

a and b are, independently of each other, 0, 1 or 2; and

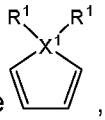
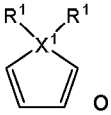
T^1 and T^2 are, independently of each other, an electron deficient group conjugated to group B^1 or B^2, respectively, or wherein when a and/or b are 0, T^1 and T^2 are, independently of each other, an electron deficient group conjugated to group A, respectively; and

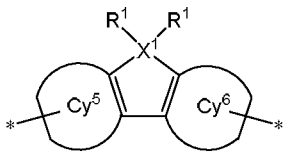
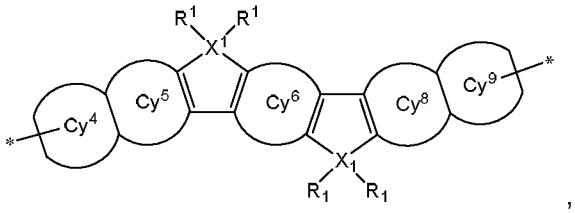
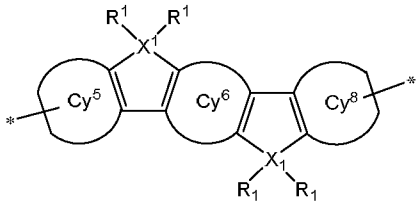
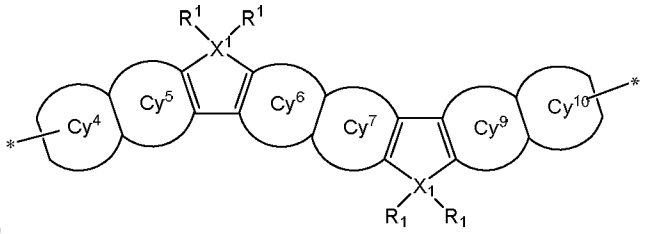
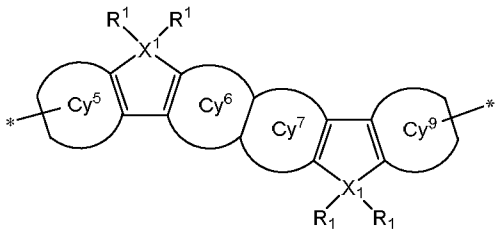
wherein A contains an optionally substituted aromatic ring having 0, 1, 2 or more ring heteroatoms directly bonded to groups B^1 and B^2, respectively, or wherein when a and/or b are 0, A contains an optionally substituted aromatic ring having 0, 1, 2 or more ring heteroatoms directly bonded to groups T^1 and T^2, respectively.

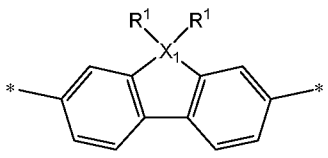
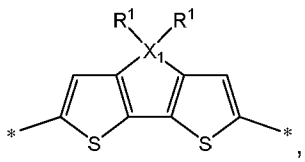
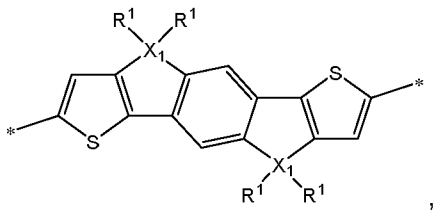
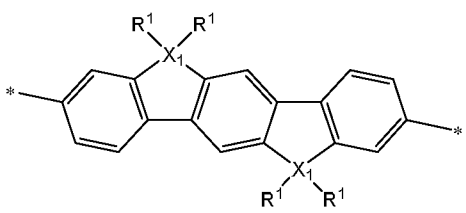
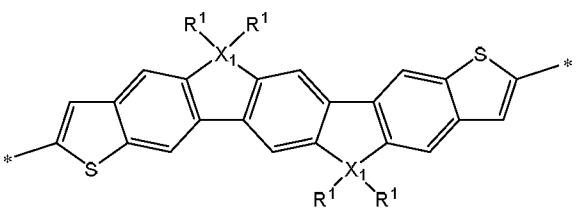
It will be appreciated that each occurrence of ——* represents the bond to B^1 and B^2, respectively. Where any one or more of Cy^{1-10} is absent, the point of attachment to B^1 and B^2 is instead on the next adjacent one of Cy^{1-10} that is not absent. For example, if Cy^1 is absent, but Cy^2 is present, the bond between A and B^1 will be between Cy^2 and B^1. Where a or b, respectively, is not 0, the one of Cy^{1-10} which is bonded to B^1 or B^2, respectively, is an optionally substituted aromatic ring having 0, 1, 2 or more ring heteroatoms . When a and/or b is 0, the one of Cy^{1-10} which is bonded to T^1 or T^2, respectively, is an optionally substituted aromatic ring having 0, 1, 2 or more ring heteroatoms directly bonded to groups T^1 and T^2, respectively.

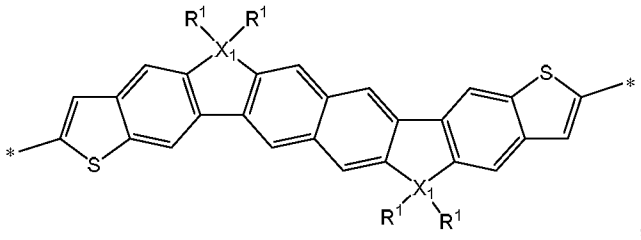
Cy^{1-10} are preferably, at each occurrence, independently, absent or a 5 or 6-membered ring having 0, 1 or 2 ring heteroatoms, each optionally substituted by one or more groups R^2, provided that at least one of Cy^{1-5} and at least one of Cy^{6-10} is not absent.

Preferably the one of Cy^{1-5} and at the one of Cy^{6-10} that are directly bonded to groups B^1 and B^2, or wherein when a and/or b are 0, the one of Cy^{1-5} and at the one of Cy^{6-10} that are directly bonded to groups T^1 and T^2, are each independently a 5 or 6-membered aromatic ring having 0, 1 or 2 ring heteroatoms (preferably phenyl or thiophenyl), each optionally substituted by one or more groups R^2.

Any one or more of Cy^{1-10} may have the structure  , wherein X_1 is C, Ge or Si. Each of Cy^{1-10} is preferably, independently, absent,  or a 5 or 6-membered aromatic ring having 0, 1 or 2 ring heteroatoms (preferably phenyl or thiophenyl), each optionally substituted by one or more groups R^2. For example, in a compound of Formula (IA) as defined herein, A may preferably be selected from:

 ,  ,  ,  , or  wherein Cy^{4-10} are as defined above. Preferably, Cy^{4-10} are at each occurrence, independently a 5 or 6-membered aromatic ring having 0, 1 or 2 ring heteroatoms (preferably phenyl or thiophenyl), each optionally substituted by one or more groups R^2. Preferably A may be selected from:

 ,  ,  ,  ,  ,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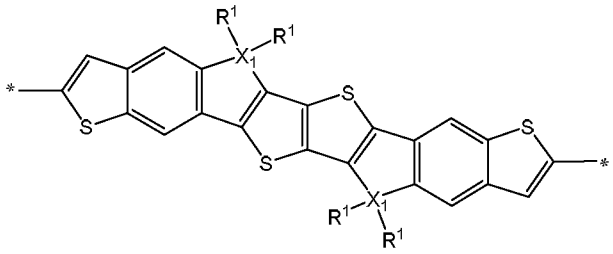
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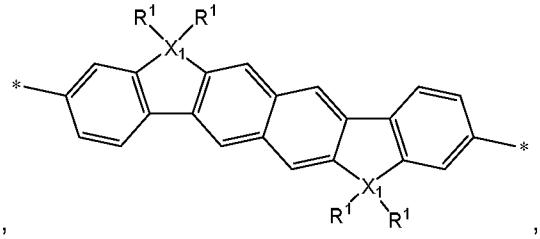
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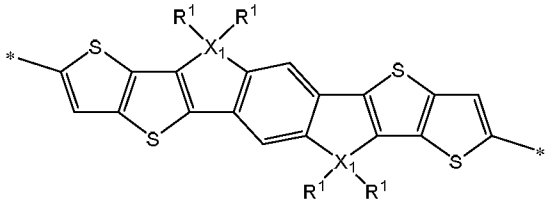
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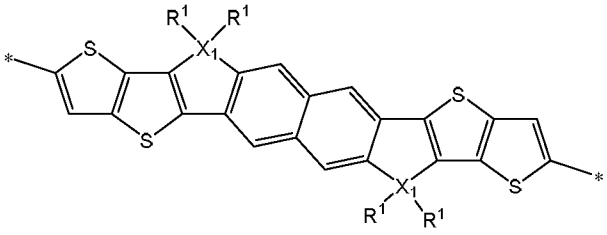
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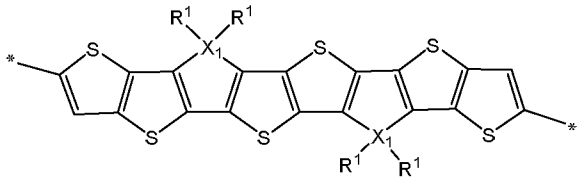
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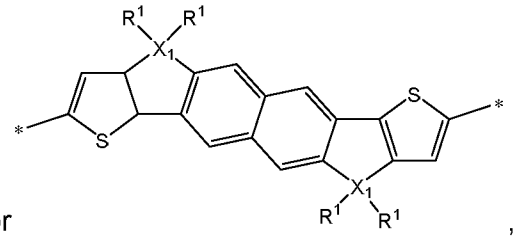
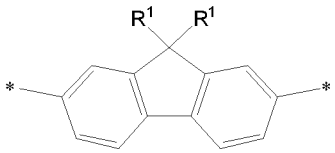

,

optionally substituted by one or more groups R^2, preferably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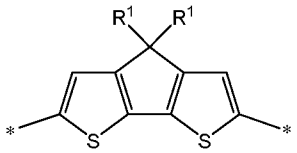
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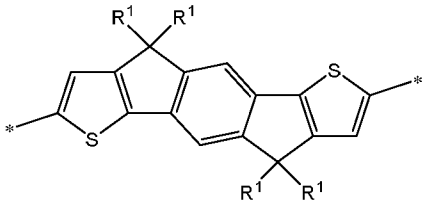
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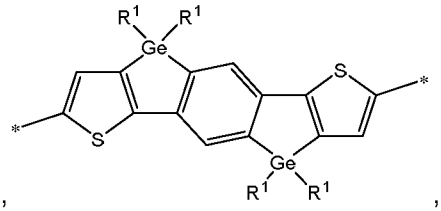
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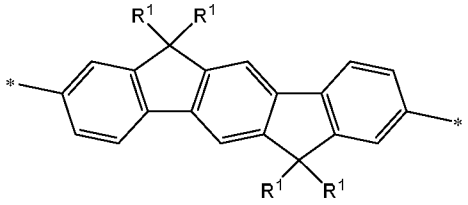
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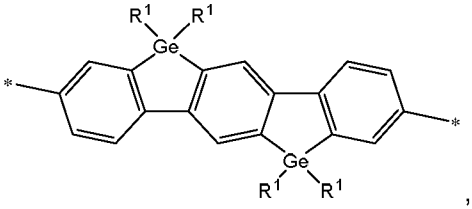
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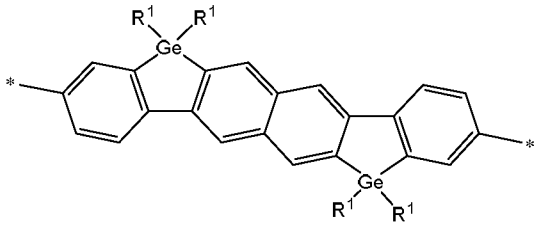
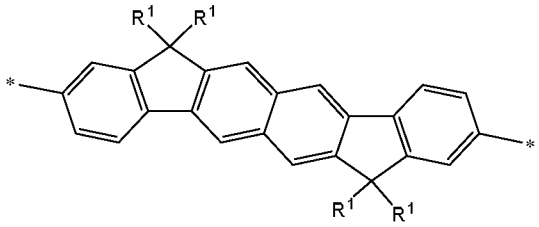
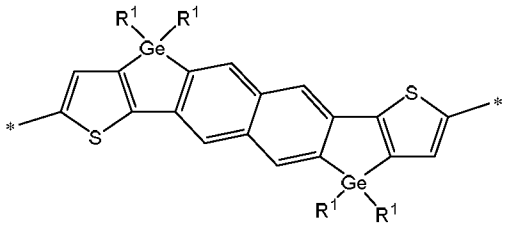
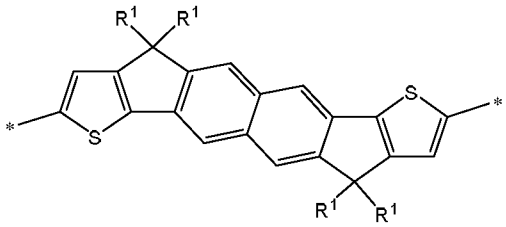
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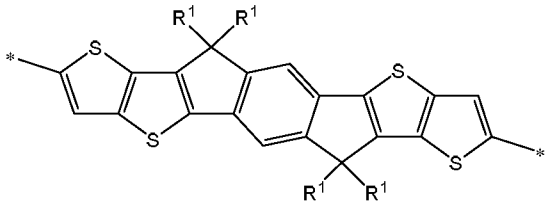

optionally substituted by one or more groups R^2.

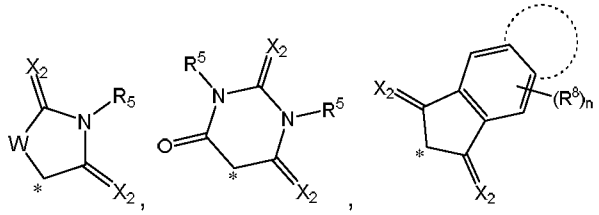
Preferably X_1 is C or Ge.

In any of the structures illustrated above, R^1 may, at each occurrence, independently, be C_{1-30} aliphatic or aryl optionally substituted with C_{1-10} aliphatic, preferably C_{6-10} aliphatic (for example, linear or branched C_8 aliphatic) or aryl (for example, phenyl) substituted with C_{1-6} aliphatic.

In any of the structures illustrated above, R^2 may, at each occurrence, independently, be H, optionally substituted C_{1-30} aliphatic, aryl or heteroaryl, preferably C_{1-30} aliphatic or aryl substituted with C_{1-10} aliphatic, preferably C_{6-8} aliphatic (for example, linear or branched C_8 aliphatic) or aryl (for example, phenyl) substituted with C_{1-6} aliphatic.

Within any of the structures described above for a compound of Formula (IA), T^1 and T^2 may be, independently of each other, $-CR^4=Y$, $-CR^4=CR^4-Y$, -L-Y or –Y; Y is an optionally substituted cyclic hydrocarbyl group, preferably optionally substituted aryl or heteroaryl; and L is a divalent alkylenyl chain of 3 to 10 carbon atoms, having alternating double and single bonds, optionally substituted by one or more R^4; and R^4 is H or has the meaning of R^2, preferably wherein R^4 is H.

Preferably, at least one of T^1 or T^2 is $-CR^4=Y$, and Y is:



in which * marks the point of attachment to -CR^4=;

X^2 is S, O or $C(R^6)_2$;

W is S, O or $C(R^6)_2$;

R^5 is H, halo, aliphatic, heteroaliphatic, aryl, heteroaryl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, -$C(=O)NR^0R^{00}$, -$C(=O)X^0$, -$C(=O)R^0$, -$C(=O)OR^0$, -$C(=S)R^0$, -$C(=S)OR^0$, -$OC(=O)R^0$, -$OC(=S)R^0$, -$C(=O)SR^0$, -$SC(=O)R^0$, -NH_2, -NR^0R^{00}, -$NR^0C(O)R^0$, -SH, -SR^0, -SO_3H, -SO_2R^0, -OH, -NO_2, -CF_3, -CF_2-R^0, -SF_5, silyl or hydrocarbyl with 1 to 40 C atoms and which optionally comprises one or more hetero atoms, wherein aliphatic, heteroaliphatic, aryl, heteroaryl, silyl or hydrocarbyl are optionally substituted, and wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C1-40 hydrocarbyl (preferably optionally substituted aliphatic, heteroaliphatic, aryl or heteroaryl);

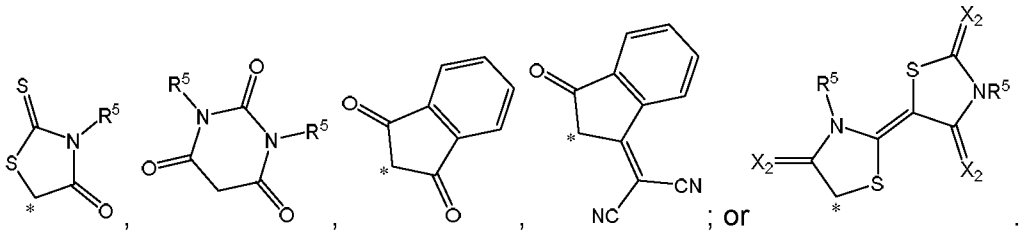
R^6 is, at each occurrence, independently, H, halo, aliphatic, heteroaliphatic, aryl, heteroaryl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, -$C(=O)NR^0R^{00}$, -$C(=O)X^0$, -$C(=O)R^0$, -$C(=O)OR^0$, -$C(=S)R^0$, -$C(=S)OR^0$, -$OC(=O)R^0$, -$OC(=S)R^0$, -$C(=O)SR^0$, -$SC(=O)R^0$, -NH_2, -NR^0R^{00}, -$NR^0C(O)R^0$, -SH, -SR^0, -SO_3H, -SO_2R^0, -OH, -NO_2, -CF_3, -CF_2-R^0, -SF_5, silyl or hydrocarbyl with 1 to 40 C atoms and which optionally comprises one or more hetero atoms, wherein aliphatic, heteroaliphatic, aryl, heteroaryl, silyl or hydrocarbyl are optionally substituted, and wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C1-40 hydrocarbyl;

 may be present or absent and represents a fused mono-, bi- or tri- cyclic hydrocarbyl group, preferably aryl or heteroaryl, optionally substituted by one or more R_7, wherein R^7 has the meaning of R^2;

R^8 is, at each occurrence, independently, halo, aryl, heteroaryl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, -$C(=O)NR^0R^{00}$, -$C(=O)X^0$, -$C(=O)R^0$, -$C(=O)OR^0$, -$C(=S)R^0$, -$C(=S)OR^0$, -$OC(=O)R^0$, -$OC(=S)R^0$, -$C(=O)SR^0$, -$SC(=O)R^0$, -NH_2, -NR^0R^{00}, -$NR^0C(O)R^0$, -SH, -SR^0, -SO_3H, -SO_2R^0, -OH, -NO_2, -CF_3, -CF_2-R^0, -SF_5, silyl or hydrocarbyl with 1 to 40 C atoms and which optionally comprises one or more hetero atoms, wherein aryl, heteroaryl, silyl or hydrocarbyl are optionally substituted, and wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C1-40 hydrocarbyl; and

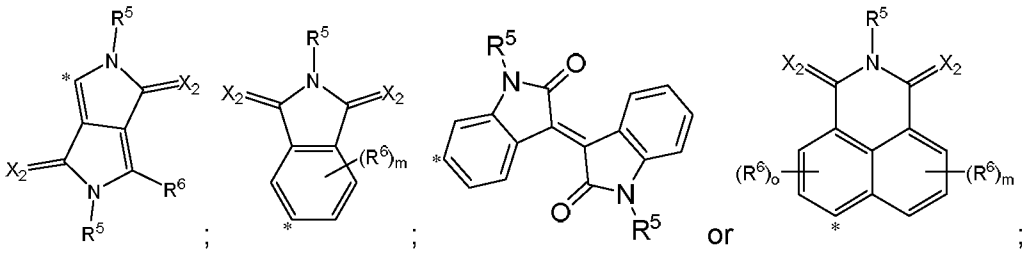
n is 0-4.

Preferably, at least one of T^1 or T^2 is $-CR^4=Y$, and Y is:



Preferably, T^1 or T^2 are both $-CR^4=Y$ and Y is as defined above.

Preferably, at least one of T^1 and T^2 is $-CR^4=CR^4-Y$ or $-Y$ and Y is:



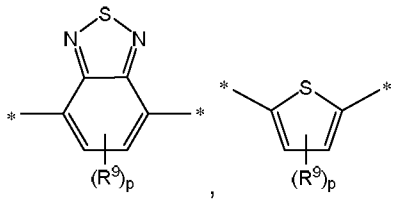
m is 0-3 and o is 0-2; and R^5, R^6 and X_2 are as defined above. In preferred embodiments, X_2 is O.

In any of the above embodiments of Y, R^5 is preferably C_{1-12} aliphatic, preferably C_{1-12} alkyl, more preferably C_{1-8} alkyl.

Within any of the structures described above for a compound of Formula (IA), preferably a and b are, independently, 1 or 2, more preferably a and b are both 1.

Within any of the structures described above for a compound of Formula (IA), each occurrence of B^1 and B^2 may preferably be, independently, mono-, bi- or tri-cyclic aryl or heteroaryl group, unsubstituted or substituted by one or more groups R^3, wherein the aryl or heteroaryl group may optionally include a non-aromatic carbocyclic or heterocyclic ring fused thereto.

Preferably, one or more occurrences of B^1 and B^2 is:



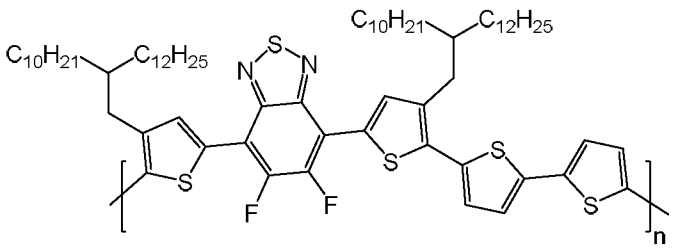
wherein p is 0, 1 or 2; and

R^9 is, at each occurrence, independently, halo, aryl, heteroaryl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)OR^0$, $-C(=S)R^0$, $-C(=S)OR^0$, $-OC(=O)R^0$, $-OC(=S)R^0$, $-C(=O)SR^0$, $-SC(=O)R^0$, $-NH_2$, $-NR^0R^{00}$, $-NR^0C(O)R^0$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-CF_2-R^0$, $-SF_5$, silyl or hydrocarbyl with 1 to 40 C atoms and which optionally comprises one or more hetero atoms, wherein aryl, heteroaryl, silyl or hydrocarbyl are optionally substituted, and wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C1-40 hydrocarbyl.

Alternatively, one electron acceptor compound is a compound of Formula (I) as defined in respect of the first aspect of the invention and the composition also comprises an organic electron acceptor compound as depicted in Figure 5.

In a composition according to any embodiment of the second aspect of the invention, the electron donor is preferably a polymer or a small molecule, e.g. a small molecule light absorber.

Preferably, the electron donor is poly(3-hexylthiophene-2,5-diyl) or a polymer of structure



, wherein n is 1-20000 (referred to herein as Y4). Other exemplary electron donor compounds include the polymeric compounds disclosed in WO 2013/000532, US 2015/0255725 and US 2015/0108409, the entire contents of which are herein incorporated by reference in their entirety.

A composition of the invention may be provided, for example, in the form of a bulk material or a film, for example a thin film. As would be understood by a skilled person, a thin film is a film with a thickness of about 100μm or less, preferably from about 5nm to about 100μm, more preferably from about 5 to about 500nm.

In a third aspect, the invention provides an optical or electronic device comprising a composition according to the second aspect of the invention. Preferably, the device is a photovoltaic cell (optionally an organic solar cell), an organic transistor, a light emitting diode, a photodetector or a photocatalytic device. The device may further comprise an anode and a cathode. The composition may forms an active layer between the anode and the cathode. Preferably, the device is an organic solar cell comprising a bulk heterojunction active layer comprising the composition according to the first aspect of the invention. Preferably, the device further comprises a hole transport layer and an electron transport layer.

In a fourth aspect, the invention provides a process for producing a composition according to the second aspect of the invention, the process comprising:

selecting a first organic electron acceptor compound;

optionally selecting a second organic electron acceptor compound

selecting an organic electron donor; and

blending the compounds to provide the composition.

Preferably, the process comprises select a first organic electron acceptor and a second organic electron acceptor, wherein the first and second organic electron acceptors and the organic electron donor are selected such that the second electron acceptor compound has an electron affinity and ionization potential between that of the electron donor and the first electron acceptor compound.

In a fifth aspect, the invention provides a process for producing a device according to the third aspect of the invention, comprising

providing a substrate; and

depositing a composition according to the second aspect of the invention on a surface of the substrate to form an active layer. Preferably, the process further comprises depositing an electrode on the active layer.

DESCRIPTION OF THE FIGURES

Figure 1 (a to b) shows exemplary electron acceptor compounds.

Figure 2 shows solution UV-vis absorption spectra for O-GeIDTBR and O-IDTBR.

Figure 3 shows thin film UV-vis absorption spectra for O-GeIDTBR and O-IDTBR.

Figure 4 shows *J-V* data for a glass/ITO/ZnO/P3HT:IDTBR(1:1)/MoO_3/Ag device.

Figure 5 (a to g) shows further exemplary electron acceptor compounds that may be used in devices described herein.

DETAILED DESCRIPTION OF THE INVENTION

Here we present new non-fullerene electron acceptors with good efficiency as a result of the high extinction coefficients of these compounds. In addition, these acceptor compounds have a higher lying LUMO energy level compared to, for example IDTBR, which generates a larger open circuit voltage in devices.

The air stability of our devices comprising these acceptor compounds is dramatically improved relative to the current highest performance polymer-fullerene devices, demonstrating the potential of these materials for commercial OPV applications in the future.

As used herein, the terms “donor” or “donating” and “acceptor” or “accepting” will be understood to mean an electron donor or electron acceptor, respectively. “Electron donor” will be understood to mean a chemical entity that donates electrons to another compound or another group of atoms of a compound. “Electron acceptor” will be understood to mean a chemical entity that accepts electrons transferred to it from another compound or another group of atoms of a compound. (see also U.S. Environmental Protection Agency, 2009, Glossary of technical terms, http://www.epa.gov/oust/cat/TUMGLOSS.HTM, or “Glossary of terms used in physical organic chemistry (IUPAC recommendations 1994)” in Pure and Applied Chemistry, 1994, 66, 1077, pages 1109-1110).

It will be appreciated that any organic electron acceptor compound referenced in any aspect or embodiment of the invention as described herein is preferably a non-fullerene organic electron acceptor compound, i.e. an organic compound comprising no fullerene components.

An organic electron donor compound referenced in any aspect or embodiment of the invention as described herein is preferably a non-fullerene organic electron donor compound, i.e. an organic compound comprising no fullerene components.

Preferably, a composition of the invention does not contain any fullerene components.

In a ternary composition of the invention, or an optical or electronic device comprising a ternary composition of the invention, there are a number of considerations to optimise the parameters of the device. This enables the photovoltaic parameters to be improved over those of a binary device. In relation to the second electron acceptor compound, preferably it may be selected such that it has one or more of the following properties:

(i) it has an electron affinity and ionization potential between that of the electron donor and the first electron acceptor, such that there is an exothermic charge transfer on exciton dissociation, and it does not provide a source for charge trapping;

(ii) it intimately mixes with the first acceptor, rather than phase separates, thus preventing pinning of the open circuit voltage to the lowest ionization potential component;

(iii) it does not disrupt or suppress the molecular organisation of the donor phase; and

(iv) it facilitates charge transport, improves charge carrier collection and extends device lifetime.

Preferably, the second electron compound may be a compound having energy levels that satisfy the following: a lower electron affinity than the primary acceptor, to facilitate an energy cascade heterojunction leading to larger open circuit voltages than can be obtained with just the first acceptor; an ionisation potential that is not too large to inhibit hole transfer to the electron donor; and a bandgap at a wavelength which can contribute to the cell external quantum efficiency.

Preferably, the surface energy of the electron acceptor (either the first electron acceptor or the second electron acceptor) with the lowest ionisation affinity should be in-between that of the electron donor and other electron acceptor.

Measurements of Ionisation potential and electron affinity can be obtained by many standard techniques known to a skilled person in the art including, for example, cyclic voltammetry, ultraviolet photoelectron spectroscopy and inverse photoelectron spectroscopy.

Exemplary second electron acceptor compounds are set out in Figure 5.

As used herein, the term “n-type” or “n-type semiconductor” will be understood to mean an extrinsic semiconductor in which the conduction electron density is in excess of the mobile hole density, and the term “p-type” or “p-type semiconductor” will be understood to mean an extrinsic semiconductor in which mobile hole density is in excess of the conduction electron

density (see also, J. Thewlis, Concise Dictionary of Physics, Pergamon Press, Oxford, 1973).

As used herein, the term "conjugated" will be understood to mean a compound (for example a small molecule or a polymer) that contains mainly C atoms with sp2-hybridisation (or optionally also sp-hybridisation), and wherein these C atoms may also be replaced by hetero atoms. In the simplest case this is for example a compound with alternating C—C single and double (or triple) bonds, but is also inclusive of compounds with aromatic units like for example 1,4-phenylene. The term "mainly" in this connection will be understood to mean that a compound with naturally (spontaneously) occurring defects, which may lead to interruption of the conjugation, is still regarded as a conjugated compound. In the original meaning a conjugated system is a molecular entity whose structure may be represented as a system of alternating single and multiple bonds: e.g. CH_2=CH–CH=CH_2, CH_2=CH–C≡N. In such systems, conjugation is the interaction of one p-orbital with another across an intervening σ-bond in such structures. (In appropriate molecular entities d-orbitals may be involved.) The term is also extended to the analogous interaction involving a p-orbital containing an unshared electron pair, e.g. :Cl–CH=CH_2. Accordingly, a conjugated system is a system of connected p-orbitals with delocalized electrons in molecules with alternating single and multiple bonds. A conjugated system has a region of overlapping p-orbitals, bridging the adjacent single bonds. They allow a delocalization of electrons across all the adjacent aligned p-orbitals. The conjugated system may be cyclic, acyclic, linear, branched or mixed. A conjugated system according to the present invention is a system which may be partly or completely conjugated.

In the context used herein, a small molecule may be a compound having a molecular weight of 1000Da or less.

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

The term "aliphatic" includes both saturated and unsaturated, nonaromatic, straight chain (*i.e.*, unbranched), branched, acyclic, and cyclic (*i.e.*, carbocyclic) hydrocarbons, which are optionally substituted with one or more functional groups. As will be appreciated by one of ordinary skill in the art, "aliphatic" is intended herein to include, but is not limited to, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, and cycloalkynyl moieties containing from 1 to 40

carbon atoms, preferably 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms. Heteroaliphatic is an aliphatic group where one or more carbon atoms are replaced with a heteroatom, such as O, N, S, P etc.

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

The term "carbyl group" as used above and below denotes any monovalent or multivalent organic radical moiety which comprises at least one carbon atom either without any non-carbon atoms (like for example -C≡C-), or optionally combined with at least one non-carbon atom such as N, O, S, P, Si, Se, As, Te or Ge (for example carbonyl etc.). The term "hydrocarbyl group" denotes a carbyl group that does additionally contain one or more H atoms and optionally contains one or more hetero atoms like for example N, O, S, P, Si, Se, As, Te or Ge.

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

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

The carbyl or hydrocarbyl group may be a saturated or unsaturated acyclic group, or a saturated or unsaturated cyclic group. Unsaturated acyclic or cyclic groups are preferred, especially aryl, alkenyl and alkynyl groups (especially ethynyl). Where the C_1-C_{40} carbyl or hydrocarbyl group is acyclic, the group may be linear or branched.

The C_1-C_{40} carbyl or hydrocarbyl group includes for example: a C_1-C_{40} alkyl group, a C_2-C_{40} alkenyl group, a C_2-C_{40} alkynyl group, a C_3-C_{40} allyl group, a C_4-C_{40} alkyldienyl group, a C_4-C_{40} polyenyl group, a C_6-C_{18} aryl group, a C_6-C_{40} alkylaryl group, a C_6-C_{40} arylalkyl group, a C_4-C_{40} cycloalkyl group, a C_4-C_{40} cycloalkenyl group, and the like. Preferred among the foregoing groups are a C_1-C_{20} alkyl group, a C_2-C_{20} alkenyl group, a C_2 –C_{20} alkynyl group, a C_3-C_{20} allyl group, a C_4-C_{20} alkyldienyl group, a C_5-C_{12} aryl group, a C_6 –C_{20} arylalkyl group,

a 5 to 20 membered heteroaryl and a C_4-C_{20} polyenyl group, respectively. Also included are combinations of groups having carbon atoms and groups having hetero atoms, like e.g. an alkynyl group, preferably ethynyl, that is substituted with a silyl group, preferably a trialkylsilyl group.

Further preferred carbyl and hydrocarbyl groups include straight-chain, branched or cyclic alkyl with 1 to 40, preferably 1 to 25 C-atoms, which is unsubstituted, mono- or polysubstituted by F, Cl, Br, I or CN, and wherein one or more non-adjacent CH_2 groups are optionally replaced, in each case independently from one another, by -O-, -S-, -NH-, -NR^0-, -SiR^0R^{00}-, -CO-, -COO-, -OCO-, -O-CO-O-, -S-CO-, -CO-S-, -SO_2-, -CO-NR^0-, -NR^0-CO-, -NR^0-CO-NR^{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, wherein Y^1 and Y^2 are independently of each other H, F, Cl, Br, I or CN, and R^0 and R^{00} are independently of each other H or an optionally substituted aliphatic or aromatic hydrocarbon with 1 to 20 C atoms. Preferred carbyl and hydrocarbyl groups are aliphatic and heteroaliphatic groups.

Halogen is F, Cl, Br or I.

As used herein, an alkyl group is a straight chain or branched, cyclic or acyclic, substituted or unsubstituted group containing from 1 to 40 carbon atoms, from 1 to 25 carbon atoms, from 1 to 20 carbon atoms, from 1 to 18 carbon atoms, from 1 to 12 carbon atoms or from 1 to 8 carbon atoms, inclusive. An alkyl group may optionally be substituted at any position.

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

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

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

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

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

Aromatic rings are cyclic aromatic groups that may have 0, 1 or 2 or more, preferably 0, 1 or 2 ring heteroatoms. Aromatic rings may be optionally substituted and/or may be fused to one or more aromatic or non-aromatic rings, which may contain 0, 1, 2, or more ring heteroatoms, to form a polycyclic ring system.

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

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

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

Preferred heteroaryl groups include, without limitation, 5-membered rings like pyrrole, pyrazole, silole, imidazole, 1,2,3-triazole, 1,2,4-triazole, tetrazole, furan, thiophene, selenophene, oxazole, isoxazole, 1,2-thiazole, 1,3-thiazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,3,4-thiadiazole, 6-membered rings like pyridine, pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, 1,2,4-triazine, 1,2,3-triazine, 1,2,4,5-tetrazine, 1,2,3,4-tetrazine,

1,2,3,5-tetrazine, and fused systems like carbazole, indole, isoindole, indolizine, indazole, benzimidazole, benzotriazole, purine, naphthimidazole, phenanthrimidazole, pyridimidazole, pyrazinimidazole, quinoxalinimidazole, benzoxazole, naphthoxazole, anthroxazole, phenanthroxazole, isoxazole, benzothiazole, benzofuran, isobenzofuran, dibenzofuran, quinoline, isoquinoline, pteridine, benzo-5,6-quinoline, benzo-6,7-quinoline, benzo-7,8-quinoline, benzoisoquinoline, acridine, phenothiazine, phenoxazine, benzopyridazine, benzopyrimidine, quinoxaline, phenazine, naphthyridine, azacarbazole, benzocarboline, phenanthridine, phenanthroline, thieno[2,3b]thiophene, thieno[3,2b]thiophene, dithienothiophene, dithienopyridine, isobenzothiophene, dibenzothiophene, benzothiadiazothiophene, or combinations thereof. The heteroaryl groups may be substituted with alkyl, alkoxy, thioalkyl, fluoro, fluoroalkyl or further aryl or heteroaryl substituents.

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

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

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

As used herein, the term “fused” refers to a cyclic group, for example an aryl or heteroaryl group, in which two adjacent ring atoms , together with additional atoms, forms a fused ring to give a polycyclic (for example, a bicyclic) ring system.

Any of the above groups (for example, those referred to herein as “optionally substituted”, including aryl, heteroaryl, carbyl and hydrocarbyl groups) may optionally comprise one or more substituents, preferably selected from silyl, sulpho, sulphonyl, formyl, amino, imino, nitrilo, mercapto, cyano, nitro, halogen, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-NR^0R^{00}$, C_{1-12}alkyl, C_{1-12}alkenyl, C_{1-12}alkynyl, C_{6-12} aryl, heteroaryl having 5 to 12 ring atoms, C_{1-12} alkoxy, hydroxy, C_{1-12} alkylcarbonyl, C_{1-12} alkoxy-carbonyl, C_{1-12} alkylcarbonlyoxy or C_{1-12} alkoxycarbonyloxy wherein one or more H atoms are optionally replaced by F or Cl and/or combinations thereof; wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C1-40 hydrocarbyl. The optional substituents may

comprise all chemically possible combinations in the same group and/or a plurality (preferably two) of the aforementioned groups (for example amino and sulphonyl if directly attached to each other represent a sulphamoyl radical).

Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of the words, for example "comprising" and "comprises", mean "including but not limited to", and are not intended to (and do not) exclude other components.

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

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

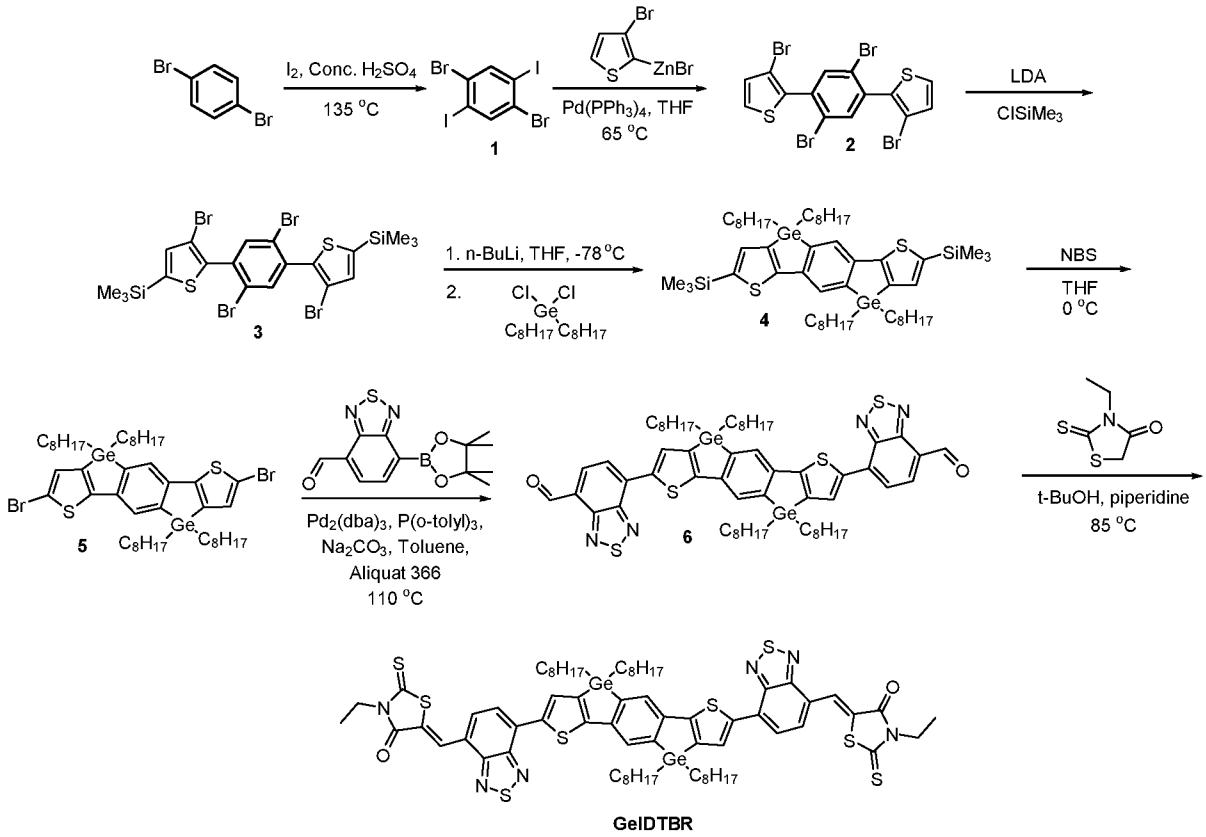
It will be appreciated that many of the features described above, particularly of the preferred embodiments, are inventive in their own right and not just as part of an embodiment of the present invention. Independent protection may be sought for these features in addition to or alternative to any invention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

EXAMPLES

UV-Vis spectroscopy was performed using a UV-1601 Shimadzu UV-Vis spectrometer.

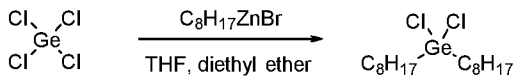
Example 1 – Synthesis of O-GeIDTBR

O-GeIDTBR was synthesised according to scheme 1 and the experimental procedures below.



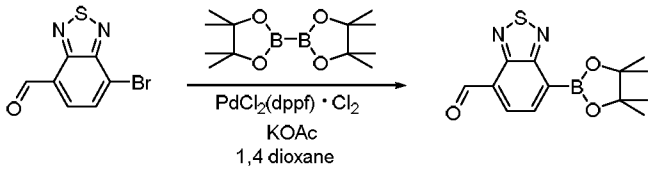
Scheme 1

Dichlorobis(octyl)germane



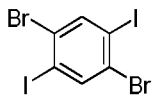
Perchlorogermane (21.5g, 100 mmol) was diluted in 100 mL of anhydrous THF and cooled to 0°C. A 1 M solution of (octyl)magnesium bromide (200 mL, 200 mmol) in diethyl ether was added dropwise over one hour. The reaction mixture was stirred overnight, whilst warming up to room temperature. 200 mL of *n*-hexane were added to the reaction mixture and large amounts of precipitate form. The precipitate is filtered-off and the solvent removed from the filtrate on the rotary evaporator. The cloudy viscous oil is distilled under reduced pressure. The dichlorobis(octyl)germane (16.7 g, 45.1 mmol) was recovered as a colourless oil in the temperature range of 100 to 140°C at 0.4 mbar. ^{1}H NMR (400 MHz, $CDCl_3$): *δ*: 1.78-1.68 (m, 4H), 1.51-1.19 (m, 24H), 0.94-0.83 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 31.83, 31.63, 29.10, 29.03, 28.06, 24.27, 22.66, 14.13.

7-(boronic acid pinacol ester)-2,1,3-benzothiadiazole-4-carboxaldehyde



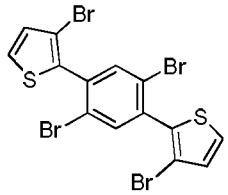
7-bromo-2,1,3-benzothiadiazole-4-carboxaldehyde (2 g, 8.23 mmol) was added to bis(pinacolato)diboron (4.8 g, 18.92 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (336 mg, 0.41 mmol), and KOAc (4.85 g, 49.36 mmol). The flask was sealed and heated to 80°C under high vacuum for an hour. The reaction vessel was filled with nitrogen and 25 ml of degassed anhydrous 1,4-dioxane was added and stirred at 80 °C overnight. The reaction was quenched by adding water, and the resulting mixture was extracted into ethyl acetate. The organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure to yield dark brown solid. The solid was triturated with heptane, filtered through celite and the solvent was evaporated to give the crude product as a yellow colored solid (1.18g, Yield - 50%). ^{1}H NMR (400 MHz, $CHCl_3$): δ 10.85 (s, 1H), 8.35 (d, *J* = 6.8 Hz, 1H), 8.22 (d, *J* = 6.8 Hz, 1H), 1.42 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 189.51, 137.58, 130.66, 129.30, 84.91, 24.92.

1) 1,4-dibromo-2,5-diiodobenzene



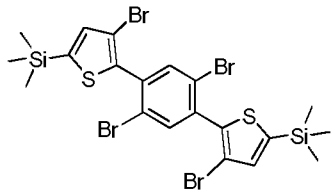
20 g (85 mmol) of 1,4-dibromobenzene were dissolved in 250 mL of concentrated sulphuric acid at 80°C. Iodine (47.3 g, 187 mmol) was added to the reaction flask in several portions. After complete addition the reaction temperature was increased to 130°C and the mixture was heated during 2 days. The reaction mixture was cooled to room temperature and carefully poured into ice-water. The black solid was filtered-off and extensively washed with water, before it was dissolved in warm chlorobenzene (300 mL). The organic chlorobenzene layer was washed several times with a concentrated aqueous sodium thiosulfate solution and water. The organic layer was separated and dried over anhydrous magnesium sulphate. The solution was concentrated and then precipitated into well stirred methanol. The formed solid was filtered off and the title compound was recovered as a white solid (23.3 g, 48 mmol, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.04 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 142.44, 129.34, 101.48. MS (EI): *m/z* calcd for $C_6H_2Br_2I_2$ (M^+) 488, 486, 490, 489 found 488, 486, 490, 489.

2) 2,2'-(2,5-dibromo-1,4-phenylene)bis(3-bromothiophene)



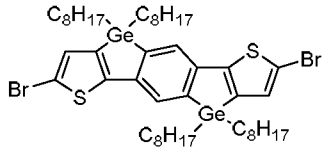
To an oven dried round bottom flask was added **1** (14.5 g, 29.8 mmol) and tetrakistriphenylphosphinepalladium(0) (1.7 g, 1.5 mmol) before a 0.5 M (3-bromothiophen-2-yl)zinc(II) bromide solution in THF (125 mL, 62.5 mmol) was added. The reaction mixture was stirred and heated at 65 °C (oil bath temperature) overnight. The mixture was cooled to room temperature and poured into 150 mL of saturated aqueous ammonium chloride solution. The precipitate was filtered off and washed with water, acetone and diethyl ether. Compound **2** was recovered as an off-white solid (11.6 g, 20.8 mmol, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (s, 2H), 7.44 (d, J = 5.3 Hz, 2H), 7.11 (d, J = 5.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.63, 136.11, 135.17, 130.51, 126.97, 123.53, 111.79, 77.16. HRMS (EI): *m/z* calcd for $C_{14}H_6Br_4S_2$ (M^+) 557.6603 found 557.6603.

3) (5,5'-(2,5-dibromo-1,4-phenylene)bis(4-bromothiophene-5,2-diyl))bis(trimethylsilane)



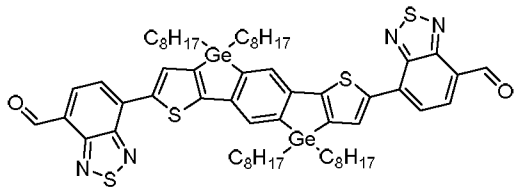
2,2'-(2,5-dibromo-1,4-phenylene)bis(3-bromothiophene) **2** (11 g, 19.7 mmol) was dissolved in anhydrous THF (400 mL) and cooled to -78°C. A 1.8 M solution of lithium diisopropylamide in THF/heptanes/ethylbenzene (33 mL, 59.4 mmol) was added slowly to the reaction. The temperature was kept at all times below -70°C. After complete addition the reaction was stirred during 1 hour at -78°C and then quenched by the addition of chlorotrimethylsilane (8.8 mL, 69.3 mmol). The reaction mixture was warmed to room temperature and stirred for another 30 minutes. The solvent was removed under reduced pressure and the crude product plugged through a silica pad using petroleum ether (60-80°C) as eluent. The solvent was evaporated and the product recrystallized from ethyl acetate to afford **3** as white needles (11.7 g, 16.7 mmol, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 2H), 7.17 (s, 2H), 0.36 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 139.8, 136.5, 136.3, 136.1, 123.0, 112.6, 0.30. MS (EI): *m/z* calcd for $C_{20}H_{22}Br_4S_2Si_2$ (M^+) 701.7, 699.7, 703.7, 702.7 found 701.7, 699.7, 703.7, 702.7.

4 and 5) 2,7-dibromo-4,4,9,9-tetrakis(octyl)-4,9-dihydro-benzo[1'',2'':4,5;4'',5'':4',5'] bisgermolo[3,2-b:3',2'-b']dithiophene



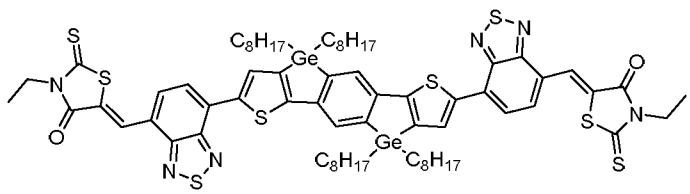
In an oven dried three-necked round bottom flask, compound **3** (3 g, 4.27 mmol) was dissolved in 60 mL of anhydrous THF and cooled to -90°C. In a second dry three-necked round bottom flask were introduced 30 mL of anhydrous THF, which were cooled down to -90°C before a 1.7 M solution of *tert*-butyllithium (20.7 mL, 35.11 mmol) in pentane was added. The solution containing compound **3** was added dropwise to the *t*-butyllithium solution, whilst maintaining the temperature below -85°C. After complete addition, the resulting dark brown solution was stirred during one hour at -90°C. Dichlorobis(octyl)germane (3.48 g, 9.40 mmol) diluted in 10 mL of dry THF was added dropwise to the reaction mixture. The resulting solution was stirred for additional three hours at low temperature, before the temperature was slowly raised to room temperature overnight. The reaction mixture was diluted with *n*-hexane and quenched by addition of 80 ml of saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted twice with *n*-hexane. The combined organic layers were washed with brine and dried over sodium sulfate. After solvent evaporation, the orange crude oil was purified by column chromatography on silica using *n*-hexane as eluent. The trimethylsilyl protecting groups were easily cleaved on the column and it was not possible to isolate the product. Therefore the crude product was dissolved in 100 mL of THF and cooled to 0°C. *N*-bromosuccinimide (1.8 g, 10.2 mmol) was added and the reaction was stirred during one hour. The reaction progress was followed by TLC and once the bromination had come to completion, the reaction mixture was diluted with 50 mL of *n*-hexane and quenched by the addition of 100 mL of water. The organic layer was separated and the aqueous layer extracted two more times with hexane (50 mL). The combined organic layers were dried over sodium sulfate and the solvent evaporated. The crude product was purified by column chromatography on silica gel using n-hexane as eluent. After solvent evaporation, compound **5** was recovered as an orange-yellow oily solid (0.700 g, 0.704 mmol, 10% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (s, 2H), 7.06 (s, 2H), 1.51-1.41 (m, 8H), 1.33-1.08 (m, 48H), 0.84-0.75 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.35, 142.73, 141.11, 140.90, 132.63, 125.71, 111.74, 32.91, 31.87, 29.26, 29.12, 25.42, 22.68, 14.50, 14.13. HRMS (ESI-ToF): *m/z* calcd for $C_{46}H_{72}Br_2Ge_2S_2$ (M+) 994, 992, 996, 990, 992 found 994, 992, 996, 990, 993.

6)



5 (0.343g, 0.345 mmol) and 7-(boronic acid pinacol ester)-2,1,3-benzothiadiazole-4-carboxaldehyde (0.250g, 0.862 mmol) were dissolved in anhydrous toluene (30 mL) along with a few drops of Aliquat 366, before being degassed for 2 hours. Tris(dibenzylideneacetone)dipalladium0 (0.0158 g, 0.0172 mmol) and tri(o-tolyl)phosphine (0.0105 g, 0.0345 mmol) were added to the solution before degassing for a further 30 mins. Degassed 2M sodium carbonate solution (1.38 mL, 2.758 mmol) was then added and the reaction was heated to 110 ^{0}C with stirring overnight, under an inert argon atmosphere. The mixture was then poured into H_2O, extracted with CH_2Cl_2, and the organic phase was washed with H_2O and brine, before drying over anhydrous magnesium sulphate. The resulting solid was purified by column chromatography over silica using CH_2Cl_2, and precipitated out from CH_2Cl_2/ methanol to yield **6** as a dark purple solid (0.186g, 0.160 mmol, 46.4% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.73 (s, 2H), 8.41 (s, 2H), 8.25 (d, J = 7.8 Hz, 2H), 8.05 (d, J = 8.0 Hz, 2H), 7.82 (s, 2H), 1.60-1.51 (m, 8H), 1.40-1.14 (m, 48H), 0.82 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.50, 158.54, 153.96, 144.97, 143.06, 141.84, 140.05, 133.71, 132.89, 126.80, 124.98, 123.40, 32.98, 31.88, 29.29, 29.15, 25.52, 22.67, 14.59, 14.10. HRMS (MALDI-ToF): *m/z* calcd for $C_{60}H_{78}Ge_2N_4O_2S_4$ (M+) 1160, 1158, 1162, 1161, 1156 found 1160, 1158, 1162, 1161, 1156.

O-GeIDTBR

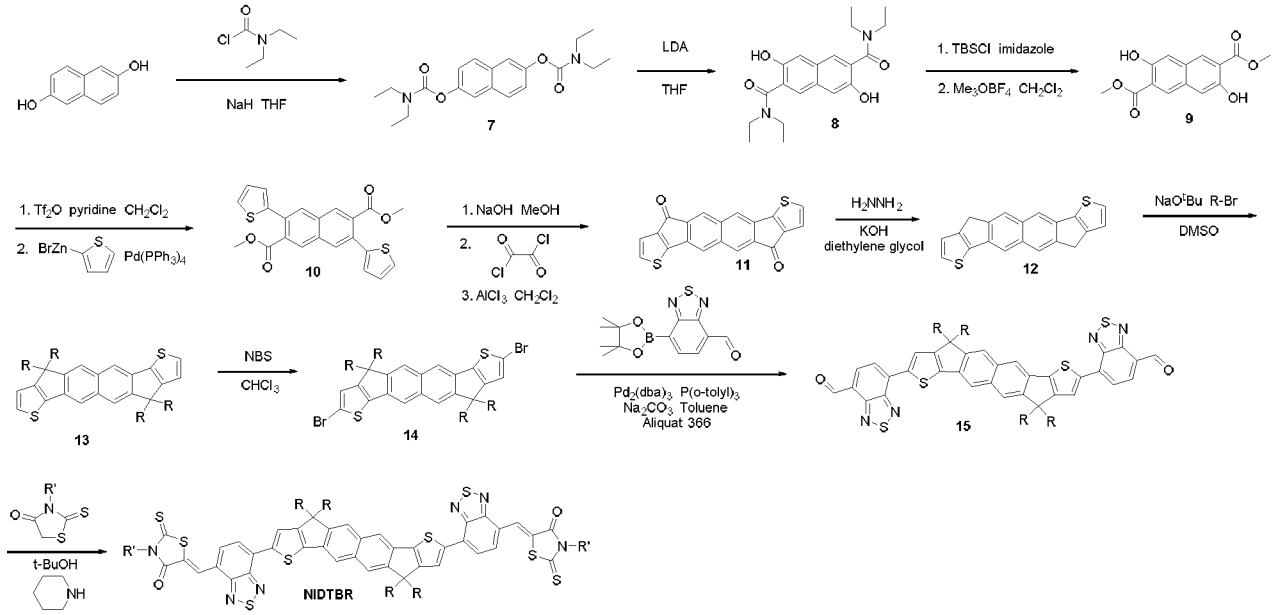


6 (0.150 g, 0.129 mmol) and 3-ethylrhodanine (0.062 g, 0.387 mmol) were dissolved in t-butanol (10 mL) and the mixture heated to 85 ^{0}C with stirring. 2 drops of piperidine were added and the mixture was heated at 85 ^{0}C with stirring overnight. The reaction mixture was then poured into water, extracted with CH_2Cl_2 and the organic phase was washed with water and brine and dried over anhydrous magnesium sulphate. The crude product was purified by flash column chromatography over silica with CH_2Cl_2 and precipitated from CH_2Cl_2/methanol and was then recrystallized from acetone to afford **O-GeIDTBR** as a dark blue solid (0.159 g,

0.110 mmol, 85.1% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 2H), 8.34 (s, 2H), 8.00 (d, J = 8.0 Hz, 2H), 7.79(s, 2H), 7.72 (d, J = 8.0 Hz, 2H), 4.25 (q, J = 8.0 Hz, 4H), 1.60-1.51 (m, 8H), 1.40-1.14 (m, 54H), 0.82 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.07, 167.57, 157.73, 154.59, 151.89, 144.86, 143.01, 141.81, 140.36, 132.84, 131.34, 130.12, 127.26, 126.68, 124.65, 124.42, 39.94, 32.98, 31.88, 29.30, 29.15, 25.53, 22.68, 14.59, 14.11, 12.33.

Example 2 – Synthesis of EH-NIDTBR

EH-NIDTBR was synthesised according to scheme 2 and the experimental procedures below.



Scheme 2

Naphthalene-2,6-diyl bis(diethylcarbamate) (7)

10 g (1 equiv.) of naphthalene 2,6-diol were dissolved in THF and added to a stirred suspension of NaH (3 equiv.) in THF at 0°C. Then, the resulting suspension was stirred at 0°C for one hour before 23.7 mL of diethylcarbamoyl chloride (3 equiv.) were added dropwise. The reaction was allowed to warm up to room temperature and stirred overnight. Then, the reaction was carefully quenched by adding a few drops of water. Subsequently, the THF was removed by distillation and the residue was extracted with H_2O and ethyl acetate. The organic layer was washed with aq. KOH (1M) and H_2O, dried over $MgSO_4$ and evaporated. The retrieved product could be used without further purification. Yield: (~99%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.77 (d, 2H), 7.57 (dd, 2H), 7.28 (dd, 2H), 3.45 (m, 8H), 1.25 (m, 12H) ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 154.20, 148.74, 131.37, 128.51, 122.08, 118.19, 42.16, 41.82, 14.16, 13.29

N^2,N^2,N^6,N^6-tetraethyl-3,7-dihydroxynaphthalene-2,6-dicarboxamide (8)

Under an argon atmosphere, 162 mL of LDA solution (5 equiv.) were slowly added via syringe to a solution of 23.2 g (1.0 equiv.) of naphthalene-2,6-diyl bis(diethylcarbamate) in THF at –78 °C. The resulting mixture was allowed to warm to room temperature overnight while it turned deep green. Then, the reaction mixture was carefully quenched with HCl 2M solution, and the formed precipitate was filtered off and washed with Et_2O. After drying, a yield of (49 %) of a pale yellow solid were obtained which could be used without further purification. ^{1}H NMR (400 MHz, DMSO-d^6, δ): 9.72 (s, 2H), 7.46, (s, 2H), 7.12 (s, 2H), 3.45 (m, 4H), 3.13 (m, 4H), 1.16 (t, 6H), 1.00 (t, 6H)^{13}C NMR (100 MHz, DMSO-d^6, δ): 167.6, 149.4, 129.0, 128.1, 124.4, 109.3, 44.2, 42.3, 13.9, 12.9ESI-TOF-MS m/z: calc'd for $C_{20}H_{27}N_2O_4$ [M+] 359.1971; found, 359.1989.

Dimethyl 3,7-dihydroxynaphthalene-2,6-dicarboxylate (9)

N^2,N^2,N^6,N^6-tetraethyl-3,7-dihydroxynaphthalene-2,6-dicarboxamide (1 equiv.) were dissolved in DMF and imidazole (3.5 equiv.) was added. Then, TBSCl (3 equiv.) was added portionwise and the reaction mixture stirred at room temperature for 24 h. The reaction was quenched by pouring into water and the resulting white precipitate was filtered off, washed with copious amounts of water, and dried in vacuum. The crude product was dissolved in anhydrous DCM and $(CH_3)_3OBF_4$ (2.4 equiv.) was added in portions. After consumption of the amide was complete, as indicated by TLC (ca. 18 h), the reaction mixture was evaporated to dryness and methanol was added followed by a saturated solution of Na_2CO_3 and solid Na_2CO_3. The resulting mixture was filtered and acidified with HCl to a pH of 1. The formed solid was recovered by filtration as a first fraction, which could be used without further purification (34%). The organic layer was dried, evaporated and purified by silica gel filtration (chloroform as eluent) to yield a second fraction 49% yield was obtained in total. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 10.23 (s, 2H), 8.36 (s, 2H), 7.32 (s, 2H), 4.04 (s, 6H) ^{13}C NMR (100 MHz, $CDCl_3$, δ): only sparingly soluble in chloroform: 130.6 (CH, arom, naptht), 112.7 (CH, arom, naptht), 52.8 (CH_3)

3,7-Di(thiophen-2-yl)naphthalene-2,6-dicarboxylic acid dimethylester (10)

Dimethyl 3,7-dihydroxynaphthalene-2,6-dicarboxylate (1 equiv.) were dissolved (suspended) in DCM and a few drops of dry pyridine were added. Then, the reaction mixture was cooled to 0°C and (2.2 equiv.) of triflic anhydride were added dropwise. The reaction mixture was allowed to warm up to room temperature and was stirred overnight. Then, water and 2M HCl were added and the aqueous phase was subsequently extracted two times with DCM. The combined organic layers were extracted with sat. $NaHCO_3$ solution and brine, dried over $MgSO_4$ and evaporated to dryness. A white solid was retrieved which could be directly used for the next step. A mixture of the crude product, 2-thienylzinc bromide (2.5 equiv.) and $Pd(PPh_3)_4$ (0.05 equiv) was heated to reflux for 3 h. The reaction was allowed to cool to room temperature and sat. NH_4Cl solution was added, after which a white precipitate formed. The product was recovered by filtration, washed with water and methanol and dried in vacuum to give dimethyl 3,7-di(thiophen-2-yl)naphthalene-2,6-dicarboxylic acid dimethyl ester as a pale yellow solid (82%). ^1H NMR (400 MHz, $CDCl_3$, δ): 8.26 (s, 2H), 8.01 (s, 2H), 7.40 (dd, 2H), 7.12 (m, 4H), 3.81 (s, 6H). A ^{13}C NMR could not be recorded due to poor solubility.

4,10-Dihydro-naphtho[3'',2'':3,4;7'',6'':3',4'] dicyclopenta[2,1-b:2',1'-b'] dithiophene-4,10-dione (11)

To a solution of 3,7-di(thiophen-2-yl)naphthalene-2,6-dicarboxylic acid dimethylester (1 equiv.) in ethanol, a solution of sodium hydroxide (16 equiv.) was added. The reaction mixture was heated to reflux for 15 h. Then, the ethanol was removed on a rotary evaporator. The remaining aqueous solution was then acidified with concentrated hydrochloric acid. The precipitated product was isolated by filtration, washed with water and methanol and dried in vacuo. A crude yellow solid (98%) was obtained which could be used without further purification. To a suspension of 3,7-di(thiophen-2-yl)naphthalene-2,6-dicarboxylic acid (4 equiv.) in anhydrous DCM, oxalyl chloride (1 equiv.) was added, followed by dropwise addition of anhydrous DMF. The resultant mixture was stirred overnight at room temperature. Then, the solvents were removed in vacuo and after drying, the formed crude acid chloride (yellow solid) was redissolved in anhydrous DCM. This solution was then added dropwise (via cannula) to a suspension of anhydrous $AlCl_3$ (4.6 equiv.) in DCM which was cooled to 0°C. The reaction mixture was stirred overnight while being allowed to warm up to room temperature. Then, it was poured onto ice containing HCl. A red precipitate was formed which was collected by filtration and washed with 2M HCl solution, water and acetone. After drying in vacuo, a red solid was obtained. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.83 (s, 2H) 7.49 (s, 2H), 7.29 (d, J = 4.8Hz, 2H), 7.21 (d, J = 4.8Hz, 2H) A ^{13}C NMR spectrum could not be recorded due to poor solubility.

4,10-Dihydro-naphtho[3'',2'':3,4;7'',6'':3',4']-dicyclopenta[2,1-b:2',1'-b']-dithiophene (12)

A mixture of 4,10-dihydro-naphtho[3'',2'':3,4;7'',6'':3',4'] dicyclopenta[2,1-b:2',1'-b'] dithiophene-4,10-dione (1 equiv.), hydrazine monohydrate (20 equiv.) and KOH (20 equiv.) in diethylene glycol was heated at 180 ºC for 24 h, then poured into ice containing hydrochloric acid. The precipitate was collected by filtration and washed with water and acetone, and dried in vacuo to give the title compound as pale yellow solid. ^{1}H NMR (400 MHz, CDCl3, δ): 7.91 (s, 2H, Ar-H), 7.85 (s, 2H, Ar-H), 7.38 (d, J = 4.8Hz, 2H, Ar-H), 7.15 (d, J = 4.8Hz, 2H, Ar-H), 3.88 (s, 4H, CH_2). A ^{13}C NMR spectrum could not be recorded due to poor solubility.

4,4,10,10-tetrakis-(2-ethylhexyl)-4,10-dihydro-naphtho[3'',2'':3,4;7'',6'':3',4']-dicyclopenta[2,1-b:2',1'-b']-dithiophene (13)

To a suspension of 4,10-dihydro-naphtho[3'',2'':3,4;7'',6'':3',4']-dicyclopenta[2,1-b:2',1'-b']-dithiophene (1 equiv.) in anhydrous DMSO was added sodium tert-butoxide (6 equiv.) in parts. The reaction mixture was heated at 80 ºC for 1 h, followed by the addition of 1-bromohexadecane (6 equiv.) dropwise. After complete addition, the resultant mixture was heated at 85-90 ºC for 5 h, then poured into ice-water. The resulting brown solution was extracted with dichloromethane (three times) and the organic layer was dried over magnesium sulfate and evaporated to dryness. The received brown oil was purified by column chromatography on silica, eluting with hexanes, to give a colourless oil (10%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.73 (s, 2H, Ar-H), 7.64 (s, 2H, Ar-H), 7.30 (d, J = 4.8 Hz, 2H, Ar-H), 7.00 (d, J = 4.8 Hz, 2H, Ar-H), 1.99 (m, 8H, CH2), 1.05-0.45 (m, 60H, CH, CH_2 and CH_3) ^{13}C NMR (100 MHz, $CDCl_3$, δ): 151.7, 141.4, 136.5, 131.5, 127.3, 122.6, 121.9, 116.2, 77.3, 77.0, 76.7, 53.2, 44.6, 35.0, 28.5, 27.2, 22.8, 14.1, 10.6. MALDI-TOF-MS: m/z: calc'd for $C_{52}H_{76}S_2$ [$C_{52}H_{76}S_2$+ = M+] 764.5; found, 764.8.

2,8-Dibromo-4,4,10,10-tetrakis-(2-ethylhexyl)-4,10-dihydro-naphtho[3'',2'':3,4;7'',6'':3',4']-dicyclopenta[2,1-b:2',1'-b']-dithiophene (14)

A solution of 4,4,10,10-tetrakis-(2-ethylhexyl)-4,10-dihydro-naphtho[3'',2'':3,4;7'',6'':3',4'] dicyclopenta[2,1-b:2',1'-b']-dithiophene (1 equiv.) in chloroform was cooled to 0°C under argon in the absence of light. N-bromosuccinimide (4.4 equiv.) dissolved in chloroform was added in portions and the reaction progress was monitored by TLC. After full conversion had been detected, the reaction mixture was extracted with water, dried over magnesium

sulphate and evaporated to dryness. The crude was purified by column chromatography (using hexanes as mobile phase). This yielded a colourless oil (81%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.66 (s, 2H, Ar-H), 7.63 (s, 2H, Ar-H), 7.02 (s, 2H, Ar-H), 1.96 (m, 8H, CH_2), 1.05-0.46 (m, 60H, CH, CH_2 and CH_3). MALDI-TOF-MS: m/z: calc'd for $C_{52}H_{74}Br_2S_2$ [$C_{52}H_{74}Br_2S_2^+$ = MH^+] 922.4; found, 922.8.

(15)

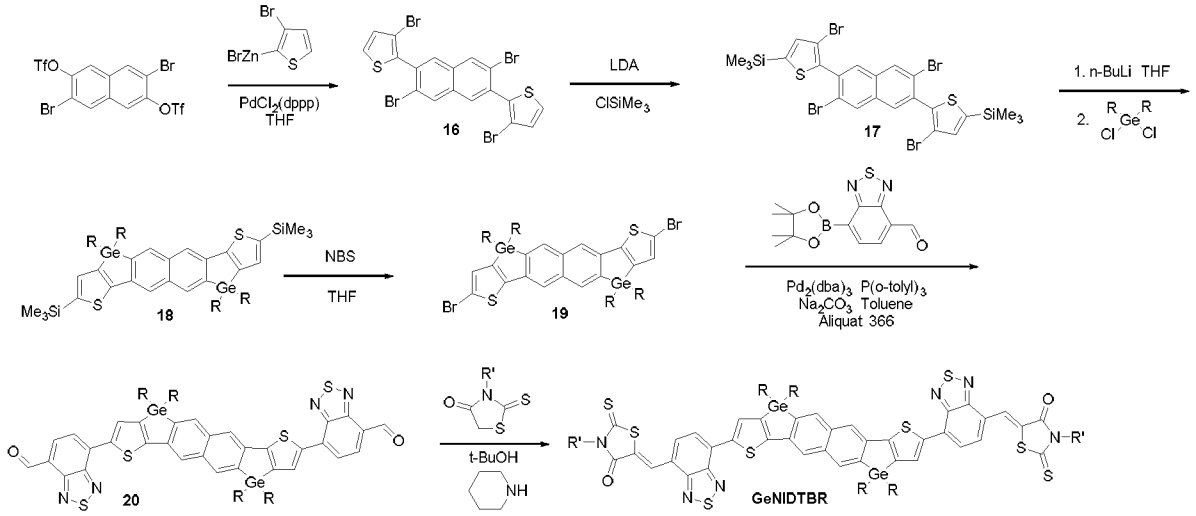
2,8-Dibromo-4,4,10,10-tetrakis-(2-ethylhexyl)-4,10-dihydro-naphtho[3'',2'':3,4;7'',6'':3',4']-dicyclopenta[2,1-b:2',1'-b']-dithiophene (1 equiv.) and 7-(boronic acid pinacol ester)-2,1,3-benzothiadiazole-4-carboxaldehyde (2.5 equiv.) were dissolved in anhydrous toluene along with a few drops of Aliquat 366, before being degassed for 2 hours. Tris(dibenzylideneacetone)dipalladium0 (0.05 equiv.) and tri(o-tolyl)phosphine (0.1 equiv.) were added to the solution before degassing for a further 30 mins. Degassed 2M sodium carbonate solution (8 equiv.) was then added and the reaction was heated to 110 ^{0}C with stirring overnight, under an inert argon atmosphere. The mixture was then poured into H_2O, extracted with CH_2Cl_2, and the organic phase was washed with H_2O and brine, before drying over anhydrous magnesium sulphate. The resulting solid was purified by column chromatography over silica using CH_2Cl_2, and precipitated out from CH_2Cl_2/ methanol to yield **15**.

NIDTBR

15 (1 equiv.) and 3-ethylrhodanine (3 equiv.) were dissolved in t-butanol and the mixture heated to 85 ^{0}C with stirring. 2 drops of piperidine were added and the mixture was heated at 85 ^{0}C with stirring overnight. The reaction mixture was then poured into water, extracted with CH_2Cl_2 and the organic phase was washed with water and brine and dried over anhydrous magnesium sulphate. The crude product was purified by flash column chromatography over silica with CH_2Cl_2 and precipitated from CH_2Cl_2/methanol and was then recrystallized from anhydrous toluene to afford **NIDTBR**.

Example 3 – Synthesis of O-GeNIDTBR

O-GeNIDTBR was synthesised according to scheme 3 and the experimental procedures below.



Scheme 3

2,2'-(3,7-dibromonaphthalene-2,6-diyl)bis(3-bromothiophene) (16)

To an oven dried round bottom flask was added 3,7-dibromo-2,6-bis(trifluoromethanesulfonyloxy)naphthalene (1 equiv.) and (1,3-Bis(diphenylphosphino)propane)palladium(II) chloride (0.05 equiv.). Anhydrous THF was added to dissolve the solids and 0.5 M (3-bromothiophen-2-yl)zinc(II) bromide solution in THF (2 equiv.) was added dropwise to the resulting solution at 0 °C. The reaction mixture was stirred at room temperature overnight. The mixture was quenched with saturated aqueous ammonium chloride solution and THF was removed to precipitate the solid. The precipitate was filtered off and washed with water, methanol and acetone. The product was recovered as an off-white solid (56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 2H), 7.89 (s, 2H), 7.46 (d, 2H, J = 5.2 Hz), 7.14 (d, 2H, J = 5.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.5, 133.29, 132.67, 131.79, 131.17, 130.37, 126.57, 123.3, 111.92.

(5,5'-(3,7-dibromonaphthalene-2,6-diyl)bis(4-bromothiophene-5,2-diyl))bis(trimethylsilane) (17)

2,2'-(3,7-dibromonaphthalene-2,6-diyl)bis(3-bromothiophene) (1 equiv) was dissolved in anhydrous THF and cooled to -78°C. A 2 M solution of lithium diisopropylamide in THF/heptanes/ethylbenzene (3 equiv.) was added slowly to the reaction. After complete addition the reaction was stirred for an hour at -78°C and then quenched by the addition of chlorotrimethylsilane (4 equiv.). The reaction mixture was slowly warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure and

the crude product was filtered, washed with water followed by methanol to give the product as an off-white solid (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 2H), 7.86 (s, 2H), 7.22 (s, 2H), 0.4 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.06, 141.33, 136.5, 133.6, 132.61, 131.72, 123.06, 112.9, 0.12.

(19)

In an oven dried two-necked round bottom flask, (5,5'-(3,7-dibromonaphthalene-2,6-diyl)bis(4-bromothiophene-5,2-diyl))bis(trimethylsilane) (1 equiv.) was dissolved in anhydrous THF. In a second dry two-necked round bottom flask anhydrous THF was introduced, which was cooled down to -90°C before a 1.7 M solution of *tert*-butyllithium (8.2 equiv.) in pentane was added. The solution containing TMS protected reactant was added dropwise to the *t*-butyllithium solution at -90°C. After complete addition, the resulting dark brown solution was stirred for two hour at -90°C. Dichloro-di-n-octylgermane (2.2 equiv.) diluted in dry THF was added dropwise to the reaction mixture. The resulting solution was stirred for additional two hours at -90°C, before the temperature was slowly raised to room temperature overnight. The reaction mixture was diluted with petroleum ether and quenched by addition of saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted twice with petroleum ether. The combined organic layers were washed with brine and dried over magnesium sulfate. After solvent evaporation, the orange crude oil was purified by column chromatography on silica using petroleum ether as eluent. Solvent was removed under reduced pressure to give the intermediate product which was dissolved in THF and cooled to 0°C. *N*-bromosuccinimide (2.1 equiv. based on the crude intermediate) was added and the reaction was stirred for an hour. The reaction mixture was then diluted with petroleum ether and quenched by the addition of water. The organic layer was separated and the aqueous layer extracted twice with petroleum ether. The combined organic layers were dried over magnesium sulfate and the solvent evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent. After solvent evaporation, the product was recovered as yellow oil, which slowly crystallized into a solid on storage under refrigeration (16% yield).

(20)

19 (1 equiv.) and 7-(boronic acid pinacol ester)-2,1,3-benzothiadiazole-4-carboxaldehyde (2.5 equiv.) were dissolved in anhydrous toluene along with a few drops of Aliquat 366, before being degassed for 2 hours. Tris(dibenzylideneacetone)dipalladium0 (0.05 equiv.) and tri(o-tolyl)phosphine (0.1 equiv.) were added to the solution before degassing for a

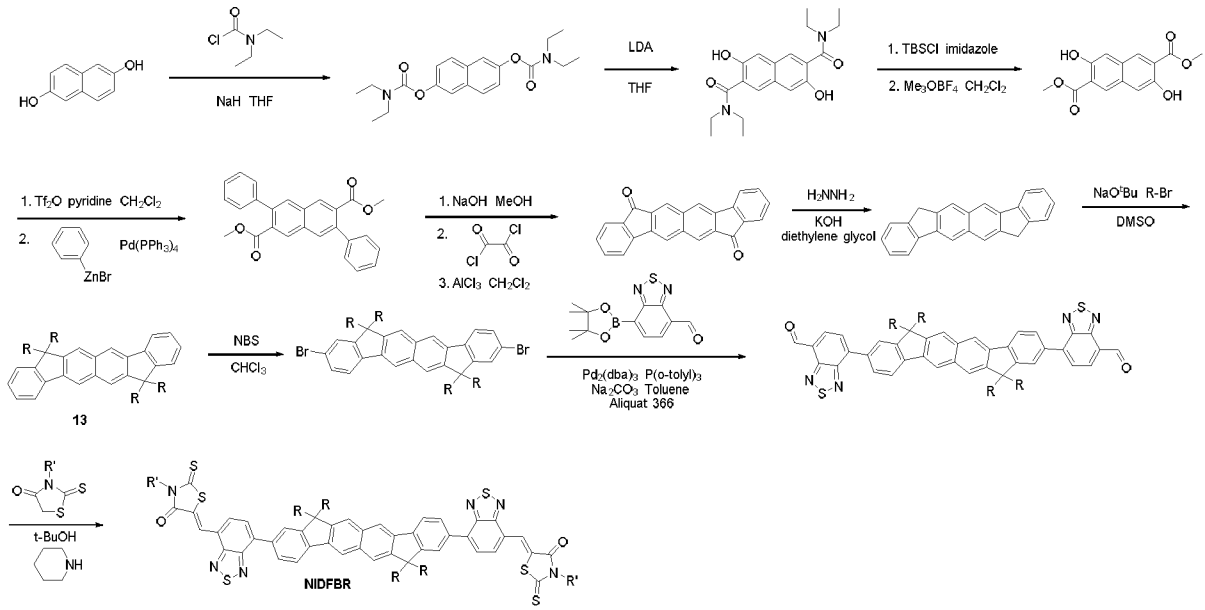
further 30 mins. Degassed 2M sodium carbonate solution (8 equiv.) was then added and the reaction was heated to 110 ^{0}C with stirring overnight, under an inert argon atmosphere. The mixture was then poured into H_2O, extracted with CH_2Cl_2, and the organic phase was washed with H_2O and brine, before drying over anhydrous magnesium sulphate. The resulting solid was purified by column chromatography over silica using CH_2Cl_2, and precipitated out from CH_2Cl_2/ methanol to yield **20**.

GeNIDTBR

20 (1 equiv.) and 3-ethylrhodanine (3 equiv.) were dissolved in t-butanol and the mixture heated to 85 ^{0}C with stirring. 2 drops of piperidine were added and the mixture was heated at 85 ^{0}C with stirring overnight. The reaction mixture was then poured into water, extracted with CH_2Cl_2 and the organic phase was washed with water and brine and dried over anhydrous magnesium sulphate. The crude product was purified by flash column chromatography over silica with CH_2Cl_2 and precipitated from CH_2Cl_2/methanol and was then recrystallized from anhydrous toluene to afford **GeNIDTBR**.

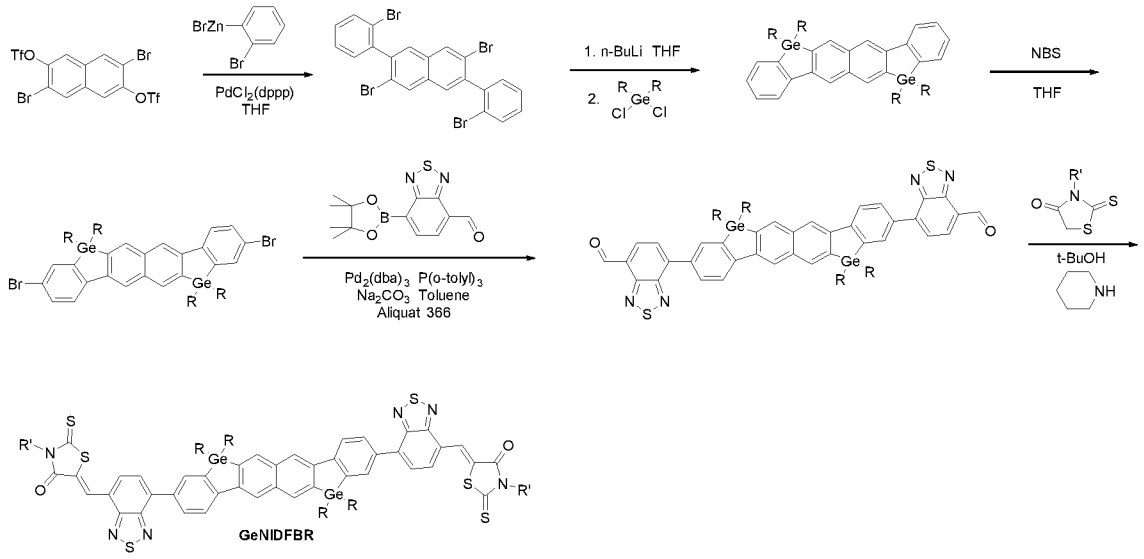
Example 4 – Synthesis of NIDFBR and GeNIDFBR

NIDFBR may be synthesised according to scheme 4, below.



Scheme 4

GeNIDFBR may be synthesised according to scheme 5, below.



Scheme 5

Example 5 – UV Measurements

Solution UV-Vis measurements of O-GeIDTBR and O-IDTBR were taken from 1.5 x 10^{-5} M solution in $CHCl_3$. UV-vis absorption spectra are shown in Figure 2 and measured values are in Table 1 below.

	ε_{max} ($M^{-1}cm^{-1}$)	λ_{max} (nm)
O-GeIDTBR	137,000	622
O-IDTBR	98,500	650

Table 1

Thin film UV-Vis measurements of O-GeIDTBR and O-IDTBR were taken from films prepared from 10 mg/mL solution of the acceptors in chlorobenzene, with films annealed at 130 °C for 10 min. UV-vis absorption spectra are shown in Figure 3 and measured values are in Table 2 below.

	As cast λ_{max} (nm)	Annealed λ_{max} (nm)	Optical Eg (eV)
O-GeIDTBR	670	670	1.69
O-IDTBR	689	730	1.63

Table 2

Example 6 - Initial device data

Solar cells were fabricated using P3HT as the donor polymer. An inverted device architecture (glass/ITO/ZnO/P3HT:IDTBR(1:1)/MoO_3/Ag) was used for its improved environmental stability relative to conventional architecture, allowing for devices to be tested under ambient conditions. The active layer blends were spin-coated from chlorobenzene solution under ambient conditions without the use of additives. Some thermal annealing (10 min at 130 °C) was required to promote ordering of the polymer, as is typical in P3HT solar cells, as well as to induce acceptor crystallisation. Fig. 4 and Table 3 show *J-V* data for the the device with an active device area of 0.045 cm^2, which were measured under simulated AM1.5G illumination at 100 mW cm^{-2}. The acceptor yielded high open-circuit voltage (V_{oc}) values (0.7-0.8 V) relative to reference devices with $PC_{60}BM$ as the acceptor, which give 0.58 V.

	Jsc (mA cm-2)	Voc (V)	FF	PCE (%)
O-GeIDTBR	7.9	0.79	0.62	3.9

Table 3

Embodiments of the invention have been described by way of example only. It will be appreciated that variations of the described embodiments may be made which are still within the scope of the invention.

Claims:

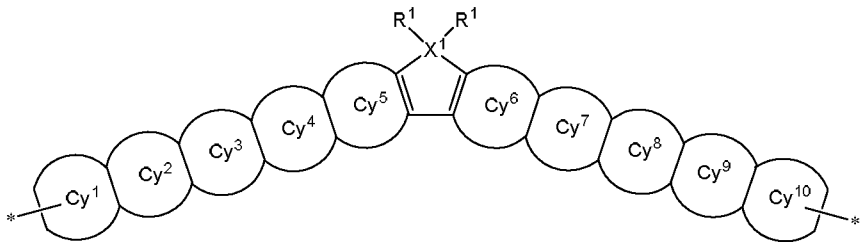
1. A compound of Formula (I)

$$T^1\text{-}(B^1)_a\text{-}(A)\text{-}(B^2)_b\text{-}T^2$$

Formula (I)

wherein

A is a divalent conjugated fused ring system having the structure:



wherein:

X_1 is C, Ge or Si;

R^1 is, at each occurrence, independently, H, or optionally substituted $C_{1\text{-}30}$ aliphatic, aryl or heteroaryl;

$Cy^{1\text{-}10}$ are, at each occurrence, independently, absent or a 5 or 6-membered ring having 0, 1 or 2 ring heteroatoms, or a fused polycyclic ring optionally having one or more ring heteroatoms, provided that at least one of $Cy^{1\text{-}5}$ and at least one of $Cy^{6\text{-}10}$ is not absent, and wherein each of $Cy^{1\text{-}10}$, when present, is optionally substituted by one or more groups R^2;

R^2 is, at each occurrence, independently, halo, $C_{1\text{-}30}$ aliphatic, aryl, heteroaryl, =O, =S, $=R^0$, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)OR^0$, $-C(=S)R^0$, $-C(=S)OR^0$, $-OC(=O)R^0$, $-OC(=S)R^0$, $-C(=O)SR^0$, $-SC(=O)R^0$, $-NH_2$, $-NR^0R^{00}$, $-NR^0C(O)R^0$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-CF_2\text{-}R^0$, $-SF_5$, silyl or hydrocarbyl with 1 to 40 C atoms and which optionally comprises one or more hetero atoms, wherein $C_{1\text{-}30}$ aliphatic, aryl, heteroaryl, silyl or hydrocarbyl are optionally substituted, and wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C1-40 hydrocarbyl; or two R^2, with the intervening atoms form an optionally substituted fused aromatic or non-aromatic ring, having 0, 1 or 2 ring heteroatoms;

and wherein within A it is required that:

(i) X_1 is Ge;

(ii) at least 2 adjacent $Cy^{1\text{-}4}$ or $Cy^{5\text{-}8}$ groups are both 6-membered rings; or

(ii) X_1 is Ge and at least 2 adjacent $Cy^{1\text{-}4}$ or $Cy^{5\text{-}8}$ groups are both 6-membered rings;

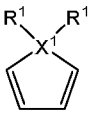
each occurrence of B^1 and B^2 is, independently, $-CY^1=CY^2-$, —C≡C—, or a cyclic hydrocarbyl group with 5 to 30 ring atoms optionally including one or more heteroatoms, preferably aryl or heteroaryl, wherein each occurrence of B^1 and B^2 is, independently, unsubstituted or substituted by one or more groups R^3, wherein R^3 has the meaning of R^2;

Y^1 and Y^2 are, independently, H, F, Cl or CN;

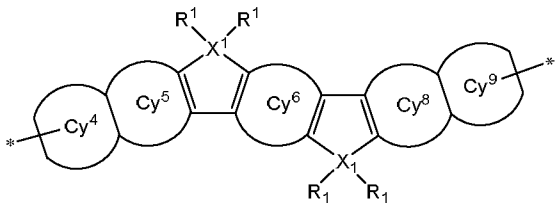
a and b are, independently of each other, 0, 1 or 2;

T^1 and T^2 are, independently of each other, an electron deficient group conjugated to group B^1 or B^2, respectively, or wherein when a and/or b are 0, T^1 and T^2 are, independently of each other, an electron deficient group conjugated to group A, respectively; and

wherein A contains an optionally substituted aromatic ring having 0, 1, 2 or more ring heteroatoms directly bonded to groups B^1 and B^2, respectively, or wherein when a and/or b are 0, A contains an optionally substituted aromatic ring having 0, 1, 2 or more ring heteroatoms directly bonded to groups T^1 and T^2, respectively.

2. The compound of claim 1, wherein each of Cy^{1-10} are, at each occurrence, independently, absent,  or a 5 or 6-membered aromatic ring having 0, 1 or 2 ring heteroatoms (preferably phenyl or thiophenyl) , each optionally substituted by one or more groups R^2.

3. The compound of claim 1 or 2, wherein A is: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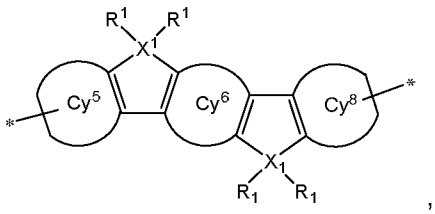
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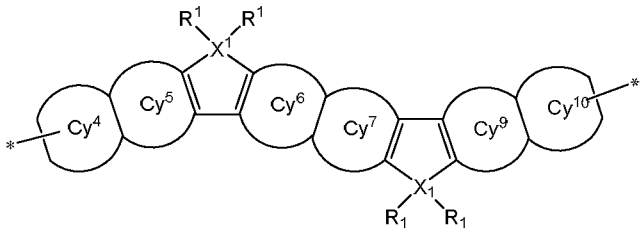
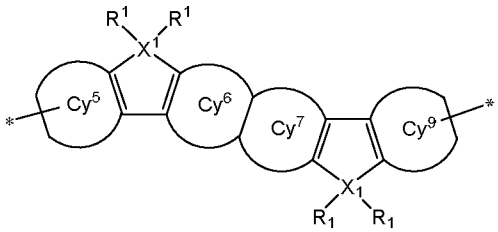
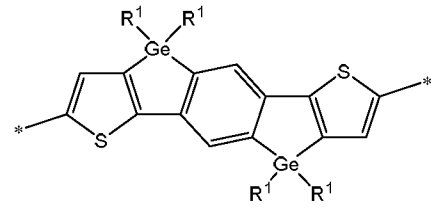

or


optionally wherein Cy^{1-10} are, at each occurrence, independently a 5 or 6-membered aromatic ring having 0, 1 or 2 ring heteroatoms, each optionally substituted by one or more groups R^2, optionally wherein A is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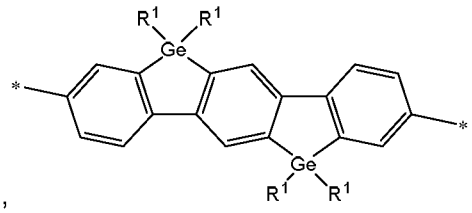
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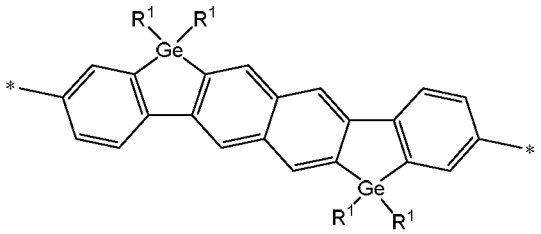
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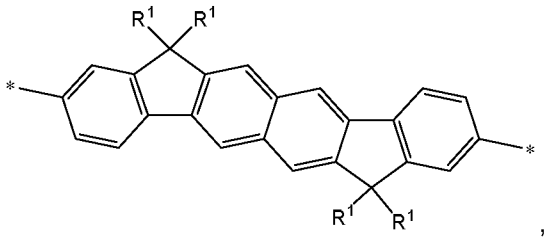
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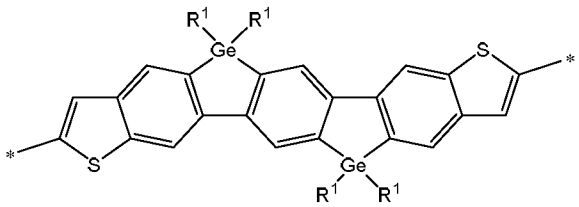
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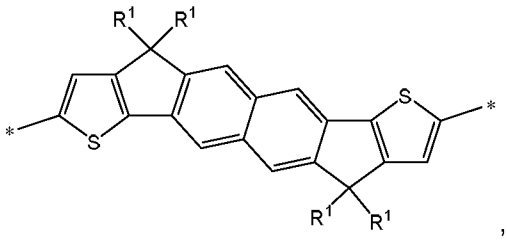
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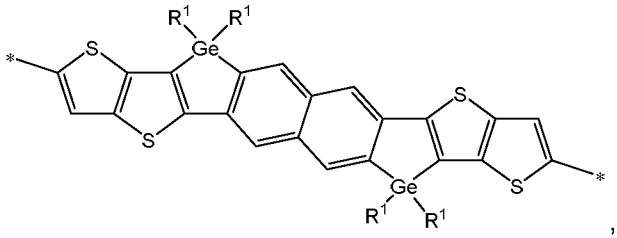
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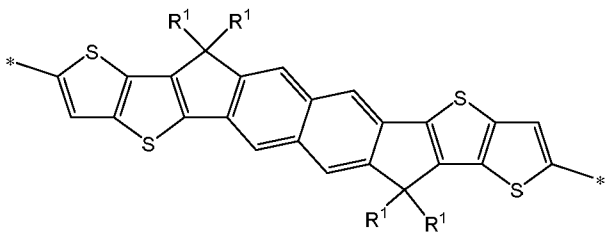
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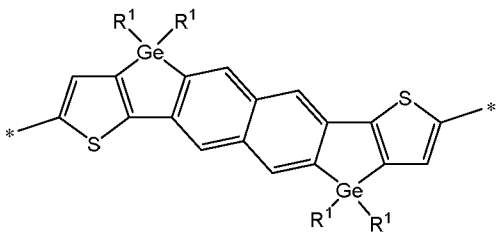
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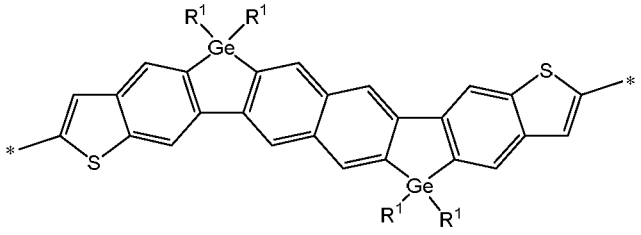
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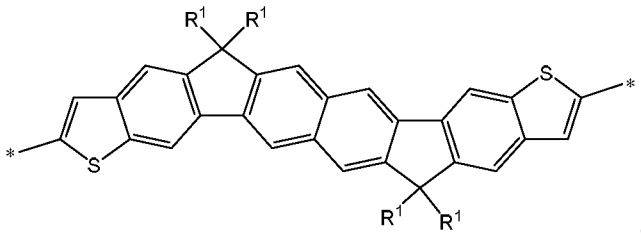

, each optionally substituted by one or more groups R^2.

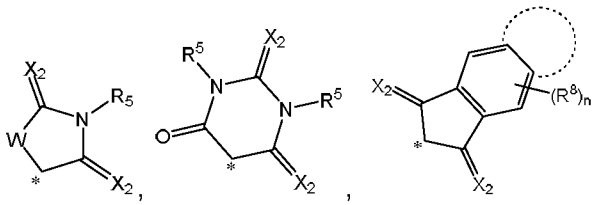
4. The compound of any one of the preceding claims, wherein T^1 and T^2 are, independently of each other, $-CR^4=Y$, $-CR^4=CR^4-Y$, -L-Y or –Y;

Y is an optionally substituted cyclic hydrocarbyl group, preferably optionally substituted aryl or heteroaryl; and

L is a divalent alkylenyl chain of 3 to 10 carbon atoms, having alternating double and single bonds, optionally substituted by one or more R^4; and

R^4 is H or has the meaning of R^2, preferably wherein R^4 is H.

5. The compound of claim 4, wherein at least one of T^1 or T^2 is $-CR^4=Y$, and Y is:



in which * marks the point of attachment to $-CR^4=$;

X^2 is S, O or $C(R^6)_2$;

W is S, O or $C(R^6)_2$;

R^5 is H, halo, aliphatic, heteroaliphatic, aryl, heteroaryl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)OR^0$, $-C(=S)R^0$, $-C(=S)OR^0$, $-OC(=O)R^0$, $-OC(=S)R^0$, $-C(=O)SR^0$, $-SC(=O)R^0$, $-NH_2$, $-NR^0R^{00}$, $-NR^0C(O)R^0$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-CF_2-R^0$, $-SF_5$, silyl or hydrocarbyl with 1 to 40 C atoms and which optionally comprises one or more hetero atoms, wherein aliphatic, heteroaliphatic, aryl, heteroaryl, silyl or hydrocarbyl are optionally substituted, and wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C1-40 hydrocarbyl, preferably optionally substituted aliphatic, heteroaliphatic, aryl or heteroaryl;

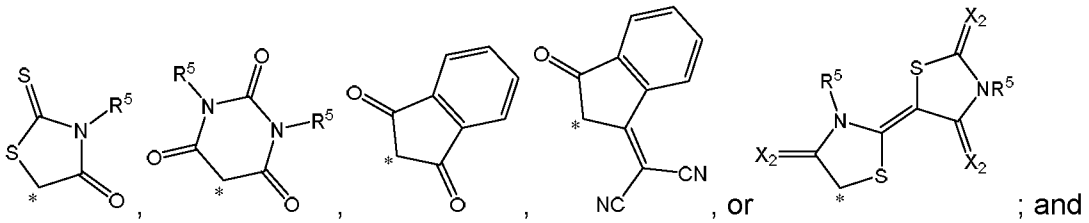
R^6 is, at each occurrence, independently, H, halo, aliphatic, heteroaliphatic, aryl, heteroaryl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)OR^0$, $-C(=S)R^0$, $-C(=S)OR^0$, $-OC(=O)R^0$, $-OC(=S)R^0$, $-C(=O)SR^0$, $-SC(=O)R^0$, $-NH_2$, $-NR^0R^{00}$, $-NR^0C(O)R^0$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-CF_2-R^0$, $-SF_5$, silyl or hydrocarbyl with 1 to 40 C atoms and which optionally comprises one or more hetero atoms, wherein aliphatic, heteroaliphatic, aryl, heteroaryl, silyl or hydrocarbyl are optionally substituted, and wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C1-40 hydrocarbyl;

 may be present or absent and represents a fused mono-, bi- or tri- cyclic hydrocarbyl group, preferably aryl or heteroaryl, optionally substituted by one or more R_7, wherein R^7 has the meaning of R^2;

R^8 is, at each occurrence, independently, halo, aryl, heteroaryl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)OR^0$, $-C(=S)R^0$, $-C(=S)OR^0$, $-OC(=O)R^0$, $-OC(=S)R^0$, $-C(=O)SR^0$, $-SC(=O)R^0$, $-NH_2$, $-NR^0R^{00}$, $-NR^0C(O)R^0$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-CF_2-R^0$, $-SF_5$, silyl or hydrocarbyl with 1 to 40 C atoms and which optionally comprises one or more hetero atoms, wherein aryl, heteroaryl, silyl or hydrocarbyl are optionally substituted, and wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C1-40 hydrocarbyl; and

n is 0-4.

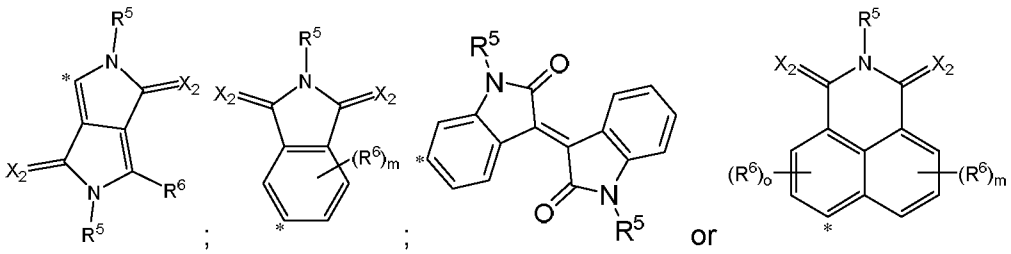
6. The compound of claim 5, wherein Y is:



, or ; and

R_5 is $C_{1\text{-}12}$ aliphatic.

7. The compound of any one of the preceding claims, wherein at least one of T^1 and T^2 is $-CR^4=CR^4-Y$ or –Y and Y is:

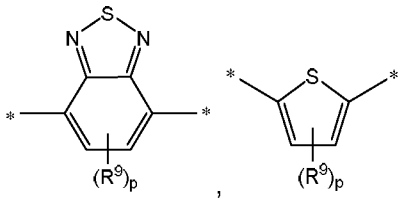


m is 0-3 and o is 0-2.

8. The compound of any one of the preceding claims, wherein a and b are both 1.

9. The compound of any one of the preceding claims, wherein each occurrence of B^1 and B^2 is, independently, mono-, bi- or tri-cyclic aryl or heteroaryl, unsubstituted or substituted by one or more groups R^3, wherein the aryl or heteroaryl group may optionally include a non-aromatic carbocyclic or heterocyclic ring fused thereto.

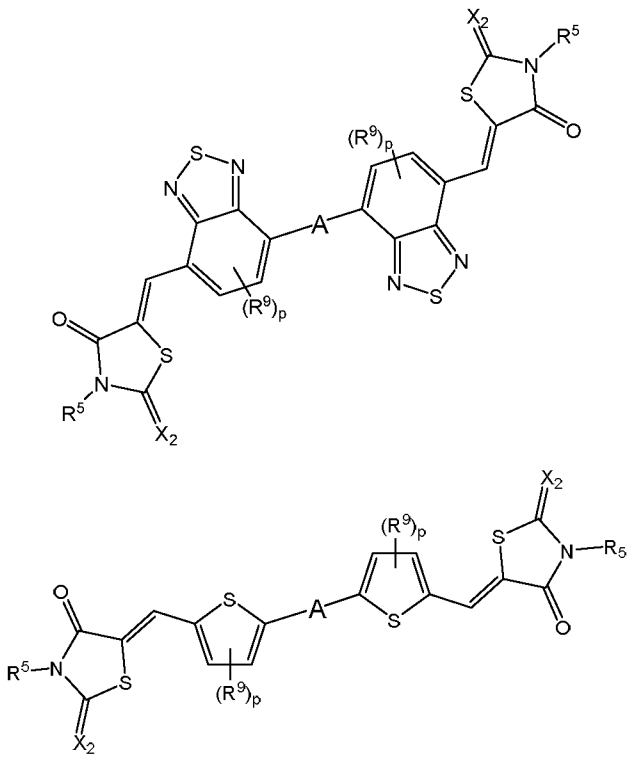
10. The compound of any one of the preceding claims, wherein one or more occurrences of B^1 and B^2 is:

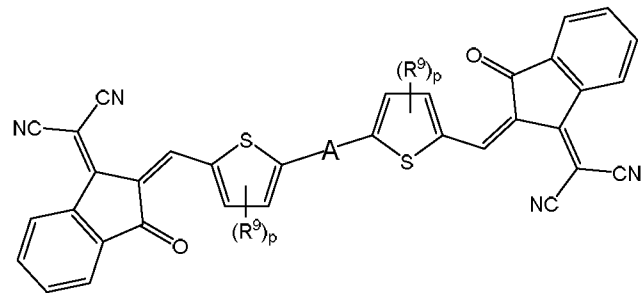


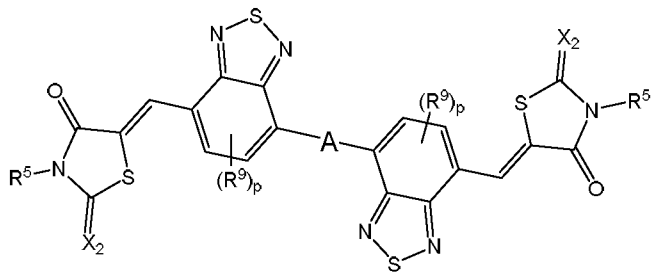
p is 0, 1 or 2; and

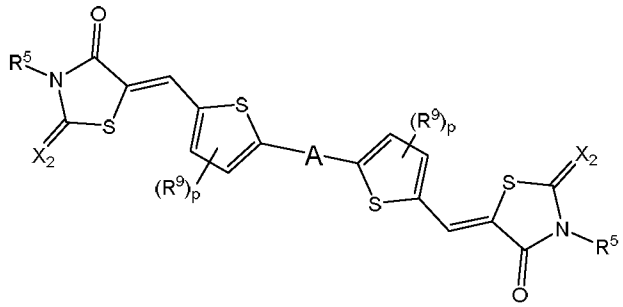
R^9 is, at each occurrence, independently, halo, aryl, heteroaryl, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, $-C(=O)X^0$, $-C(=O)R^0$, $-C(=O)OR^0$, $-C(=S)R^0$, $-C(=S)OR^0$, $-OC(=O)R^0$, $-OC(=S)R^0$, $-C(=O)SR^0$, $-SC(=O)R^0$, $-NH_2$, $-NR^0R^{00}$, $-NR^0C(O)R^0$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-CF_2-R^0$, $-SF_5$, silyl or hydrocarbyl with 1 to 40 C atoms and which optionally comprises one or more hetero atoms, wherein aryl, heteroaryl, silyl or hydrocarbyl are optionally substituted, and wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C1-40 hydrocarbyl.

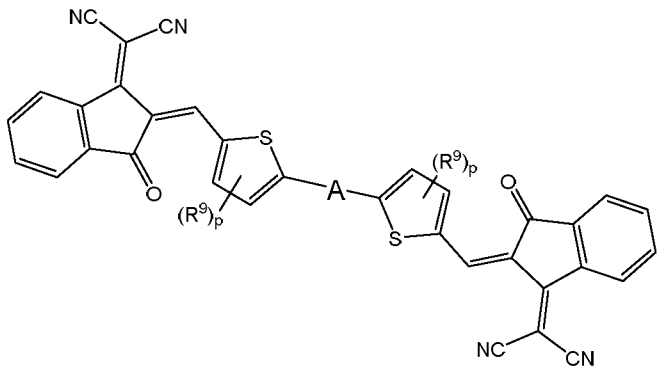
11. The compound of any one of the preceding claims, wherein the compound of formula (I) is











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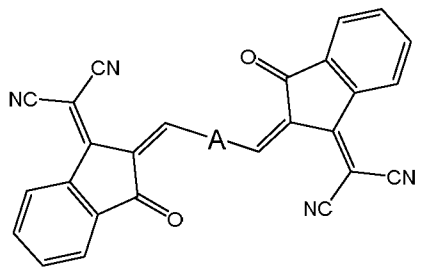

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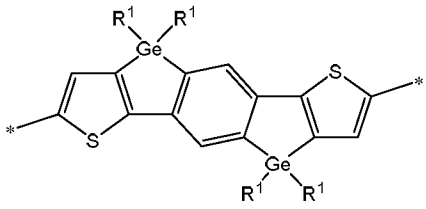
preferably wherein A is: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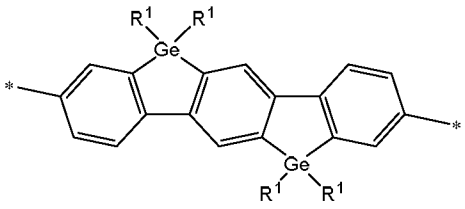
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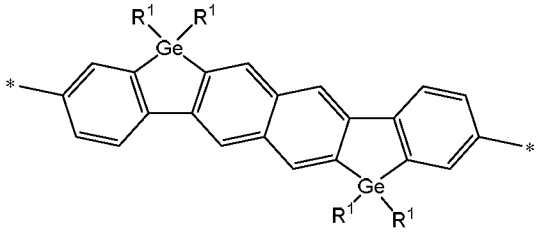
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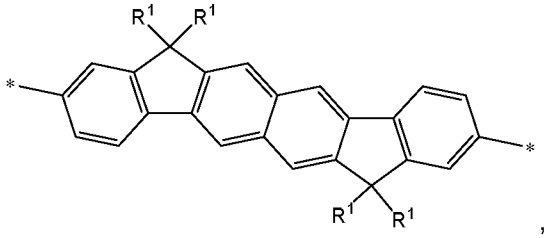
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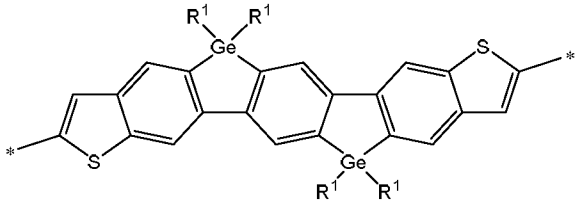
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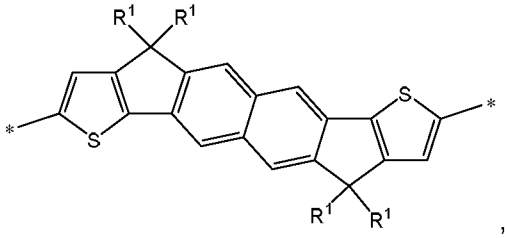
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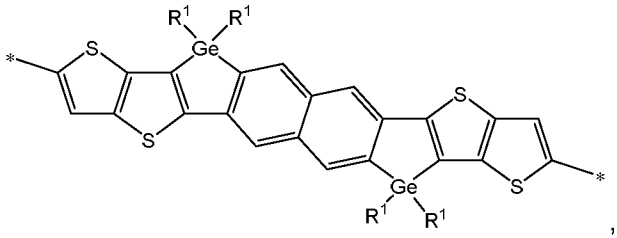
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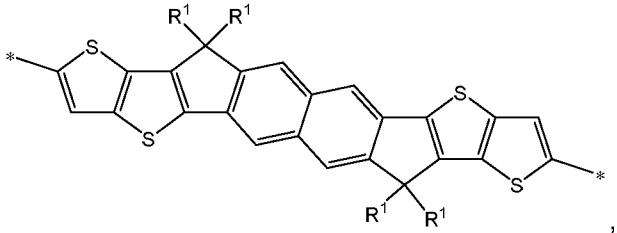
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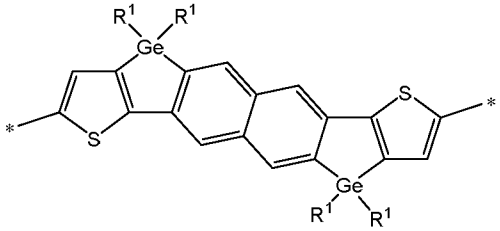
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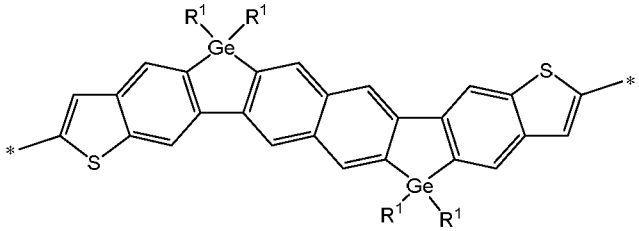
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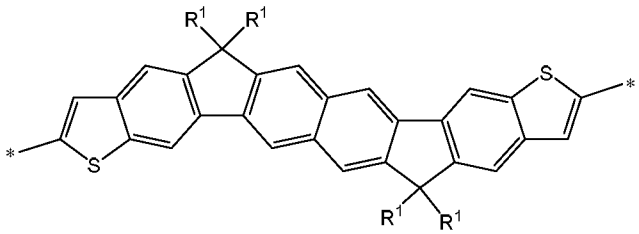
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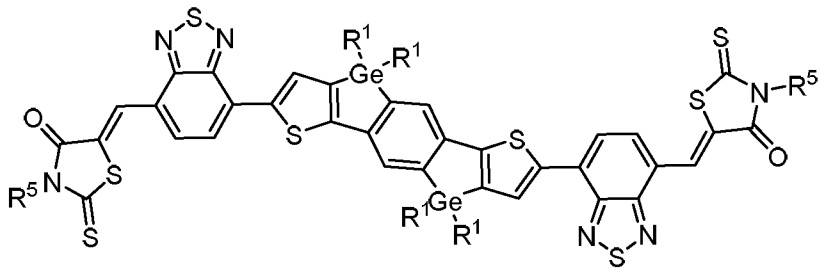
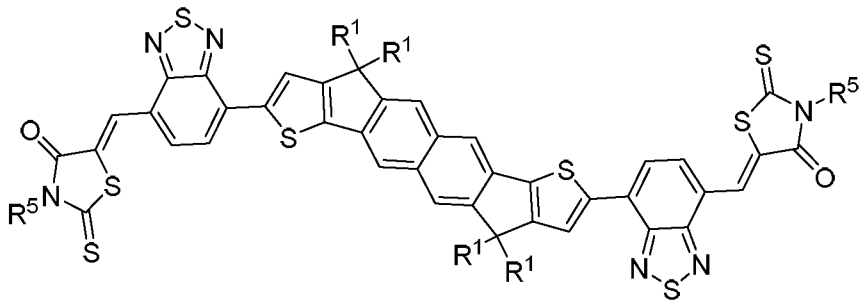
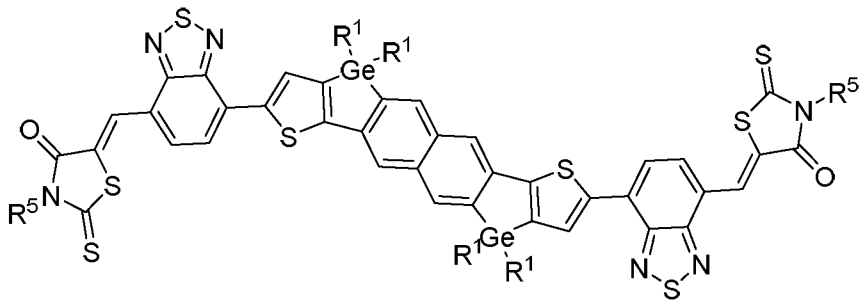
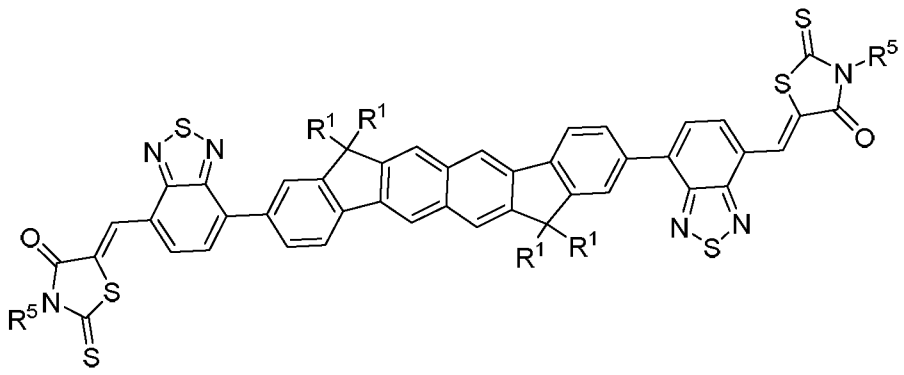
12. The compound of any one of the preceding claims, wherein the compound is









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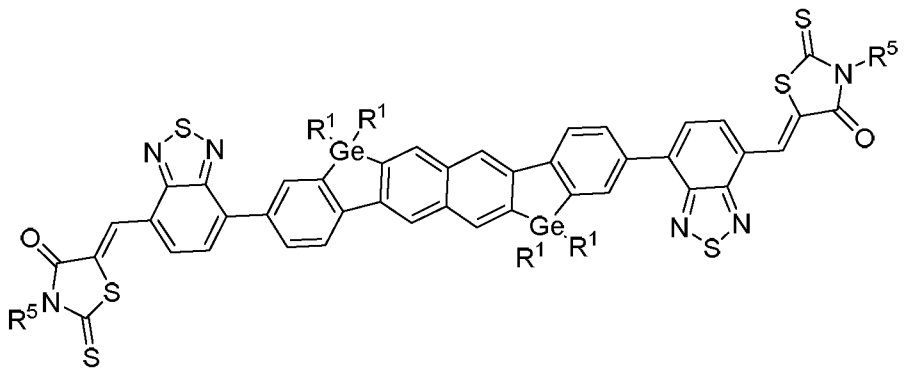


13. The compound of claim 12, wherein R^1 is $–C_8H_{17}$ or $–CH_2C(C_2H_5)HC_4H_9$ and R^5 is methyl or ethyl (preferably ethyl).

14. A composition comprising an organic electron acceptor compound as defined in any one of claims 1 to 12 and an organic electron donor compound.

15. The composition of claim 14 further comprising one or additional organic electron acceptor compounds.

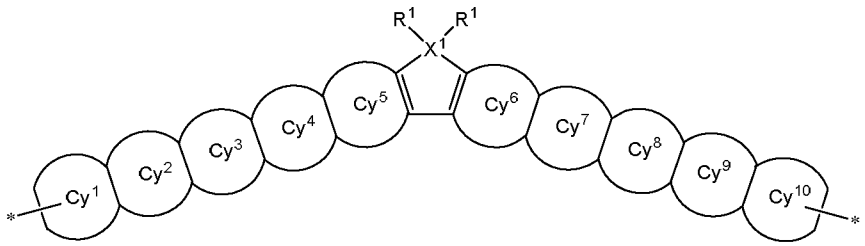
16. The composition of claim 15, wherein one electron acceptor compound is a compound of formula (I) as defined in any one of claims 1 to 13 and the composition also comprises an organic electron acceptor compound of Formula (IA)

$$T^1\text{-}(B^1)_a\text{-}(A)\text{-}(B^2)_b\text{-}T^2$$

Formula (IA)

wherein

A is a divalent conjugated fused ring system containing aromatic groups directly conjugated to groups B^1 and B^2, and having the structure:



wherein:

X_1 is C, Ge or Si;

R^1 is, at each occurrence, independently, H, optionally substituted $C_{1\text{-}30}$ aliphatic, aryl or heteroaryl;

$Cy^{1\text{-}10}$ are, at each occurrence, independently, absent or a 5 or 6-membered ring having 0, 1 or 2 ring heteroatoms, or a fused polycyclic (for example, bicyclic or tricyclic) ring optionally having one or more ring heteroatoms, provided that at least one of $Cy^{1\text{-}5}$ and at least one of $Cy^{6\text{-}10}$ is not absent, and wherein each of $Cy^{1\text{-}10}$, when present, is optionally substituted by one or more groups R^2;

R^2 is, at each occurrence, independently, halo, optionally substituted $C_{1\text{-}30}$ aliphatic, aryl, heteroaryl, =O, =S, $=R^0$, -CN, -NC, -NCO, -NCS, -OCN, -SCN, $-C(=O)NR^0R^{00}$, -

$C(=O)X^0$, $-C(=O)R^0$, $-C(=O)OR^0$, $-C(=S)R^0$, $-C(=S)OR^0$, $-OC(=O)R^0$, $-OC(=S)R^0$, $-C(=O)SR^0$, $-SC(=O)R^0$, $-NH_2$, $-NR^0R^{00}$, $-NR^0C(O)R^0$, -SH, $-SR^0$, $-SO_3H$, $-SO_2R^0$, -OH, $-NO_2$, $-CF_3$, $-CF_2-R^0$, $-SF_5$, silyl or hydrocarbyl with 1 to 40 C atoms and which optionally comprises one or more hetero atoms, wherein aryl, heteroaryl, silyl or hydrocarbyl are optionally substituted, and wherein X^0 is halogen and R^0 and R^{00} are, independently, H or optionally substituted C_{1-40} hydrocarbyl; or two R^2, with the intervening atoms form an optionally substituted fused ring, having 0, 1 or 2 ring atoms;

each occurrence of B^1 and B^2 is, independently, $-CY^1=CY^2-$, -C≡C-, or a cyclic hydrocarbyl group with 5 to 30 ring atoms, optionally including one or more heteroatoms, preferably aryl or heteroaryl, wherein each occurrence of B^1 and B^2 is, independently, unsubstituted or substituted by one or more R^3, wherein R^3 has the meaning of R^2;

Y^1 and Y^2 are, independently, H, F, Cl or CN;

a and b are, independently of each other, 0, 1 or 2; and

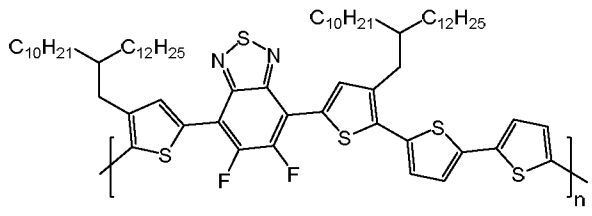
T^1 and T^2 are, independently of each other, an electron deficient group conjugated to group B^1 or B^2, respectively, or wherein when a and/or b are 0, T^1 and T^2 are, independently of each other, an electron deficient group conjugated to group A, respectively; and

wherein A contains an optionally substituted aromatic ring having 0, 1, 2 or more ring heteroatoms directly bonded to groups B^1 and B^2, respectively, or wherein when a and/or b are 0, A contains an optionally substituted aromatic ring having 0, 1, 2 or more ring heteroatoms directly bonded to groups T^1 and T^2, respectively; and

wherein the first and second electron acceptor compounds are not the same.

17. The composition of claim 14, 15 or 16, wherein the electron donor is a polymer or small molecule light absorber.

18. The composition of claim 17, wherein the electron donor is poly(3-hexylthiophene-2,5-diyl) (P3HT) or a polymer of structure



, wherein n is 1-20000.

19. The composition of any one of claims 14 to 18, wherein the composition comprises a first electron acceptor compound and a second electron acceptor compound and wherein the second electron acceptor compound has an electron affinity and ionization potential between that of the electron donor and the first electron acceptor compound.

20. The composition of any one of the claims 14 to 19, wherein the composition is provided in the form of a bulk material or a film.

21. An optical or electronic device comprising a composition according to any one claims 14 to 18.

22. The device of claim 21, wherein the device is a photovoltaic cell (optionally an organic solar cell), an organic transistor, a light emitting diode, a photodetector or a photocatalytic device.

23. The device of claim 22, wherein the device further comprises an anode and a cathode.

24. The device of claim 23, wherein the composition forms an active layer between the anode and the cathode.

25. The device of any one of claims 21 to 24, wherein the device is an organic solar cell comprising a bulk heterojunction active layer comprising the composition according to any one of claims 14 to 19.

26. The device of any one of claims 21 to 25, wherein the device further comprises a hole transport layer and an electron transport layer.

27. A process for producing a composition according to any one of claims 14 to 20, the process comprising:

selecting a first organic electron acceptor compound;

optionally selecting a second organic electron acceptor compound

selecting an organic electron donor; and

blending the compounds to provide the composition.

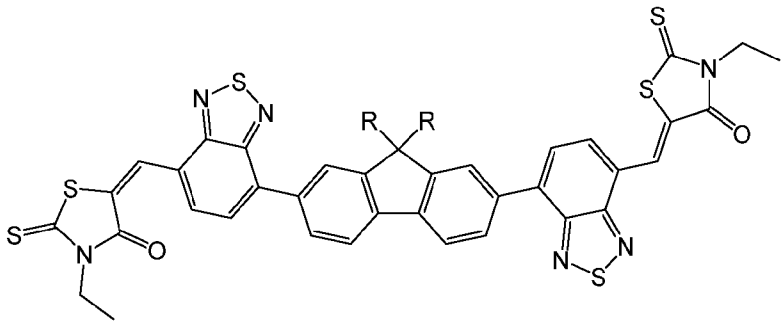
28. A process for producing a device as claimed in any of claims 21 to 26, comprising providing a substrate; and

depositing a composition according to any one of claims 14 to 20 on a surface of the substrate to form an active layer.

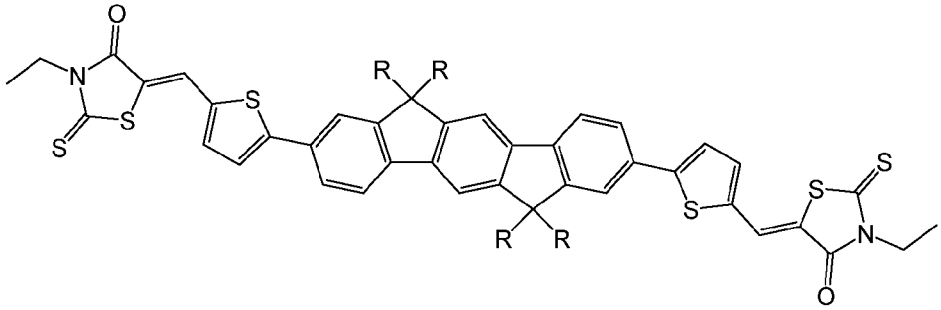
29. The process of claim 28, wherein the process further comprises depositing an electrode on the active layer.

30. A compound, composition, device or process as substantially described herein with reference to or as illustrated in one or more of the examples or accompanying figures.

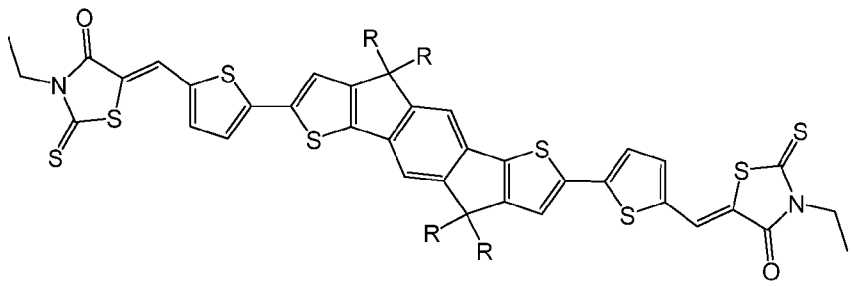
FIG. 1a



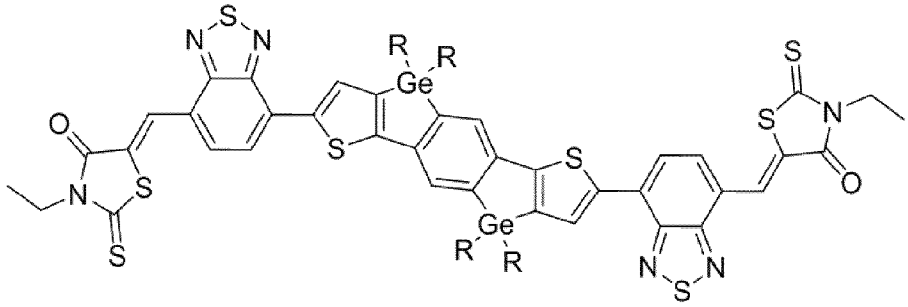
O-FBR (R = n-octyl)
EH-FBR (R = 2-ethylhexyl)



O-IDFBR (R = n-octyl)
EH-IDFBR (R = 2-ethylhexyl)

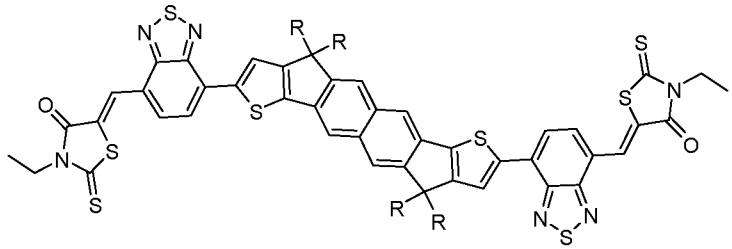


O-IDTBR (R = n-octyl)
EH-IDTBR (R = 2-ethylhexyl)

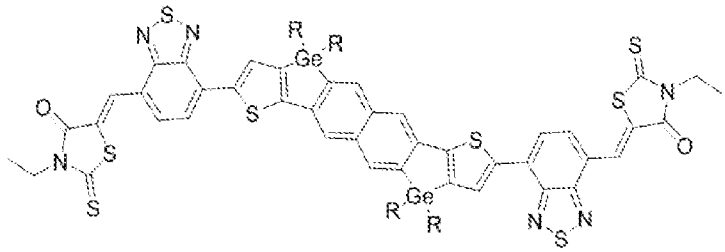


O-GeIDTBR (R = n-octyl)
EH-GeIDTBR (R = 2-ethylhexyl)

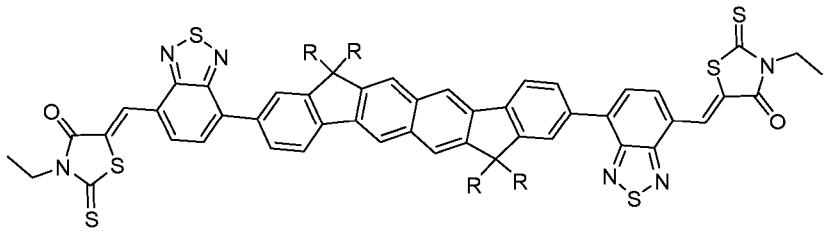
FIG. 1b



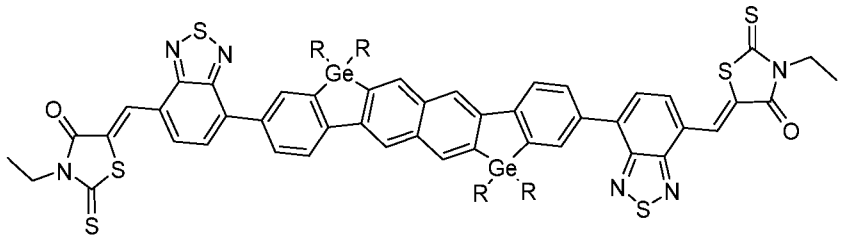
O-NIDTBR (R = n-octyl)
EH-NIDTBR (R = 2-ethylhexyl)



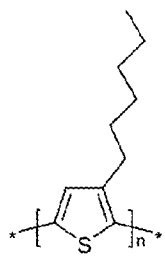
O-GeNIDTBR (R = n-octyl)
EH-GeNIDTBR (R = 2-ethylhexyl)



O-NIDFBR (R = n-octyl)
EH-NIDFBR (R = 2-ethylhexyl)



O-GeNIDFBR (R = n-octyl)
EH-GeNIDFBR (R = 2-ethylhexyl)



P3HT

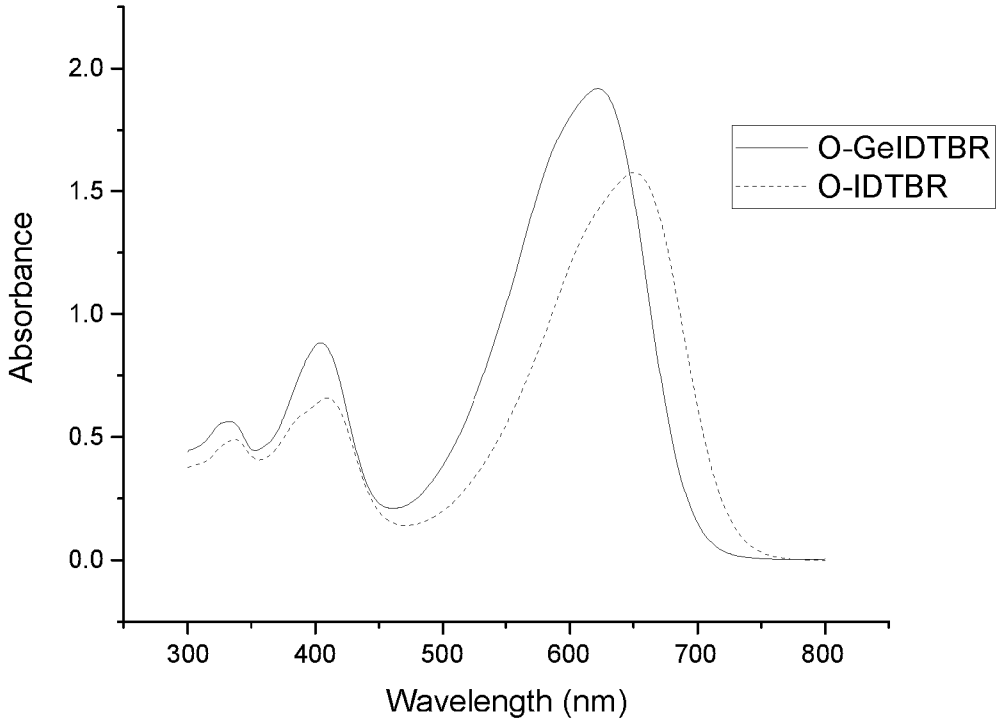
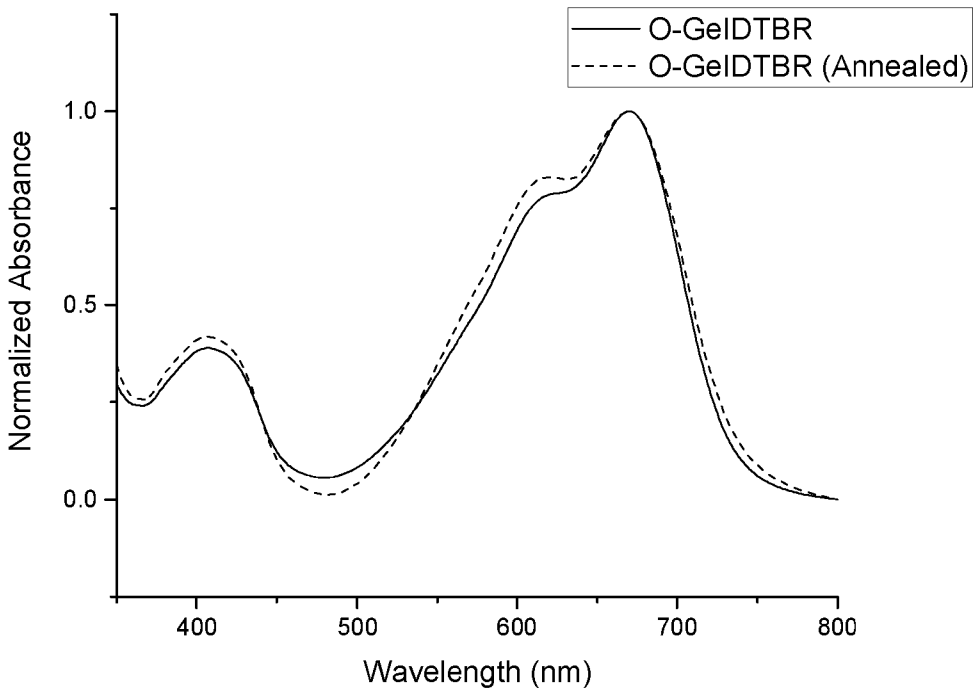

2.0
1.5
1.0
0.5
0.0
Absorbance
300
400
500
600
700
800
Wavelength (nm)
O-GeIDTBR
O-IDTBR

FIG. 2


O-GeIDTBR
O-GeIDTBR (Annealed)
Normalized Absorbance
1.0
0.5
0.0
400
500
600
700
800
Wavelength (nm)

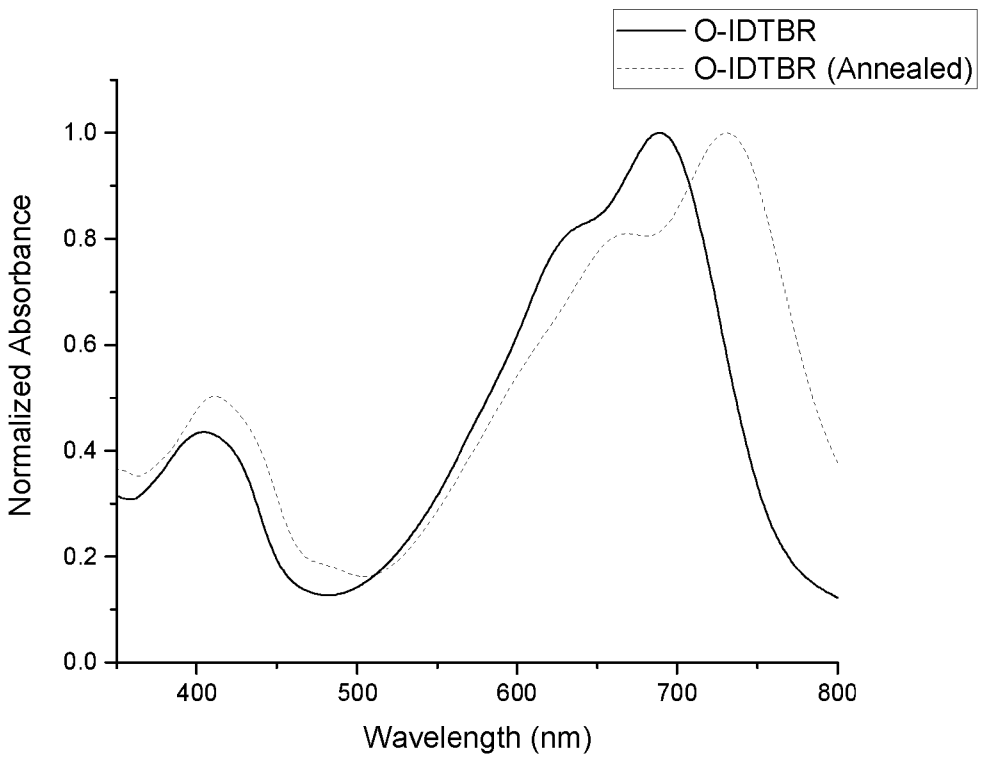

O-IDTBR
O-IDTBR (Annealed)
Normalized Absorbance
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
800
Wavelength (nm)

FIG. 3

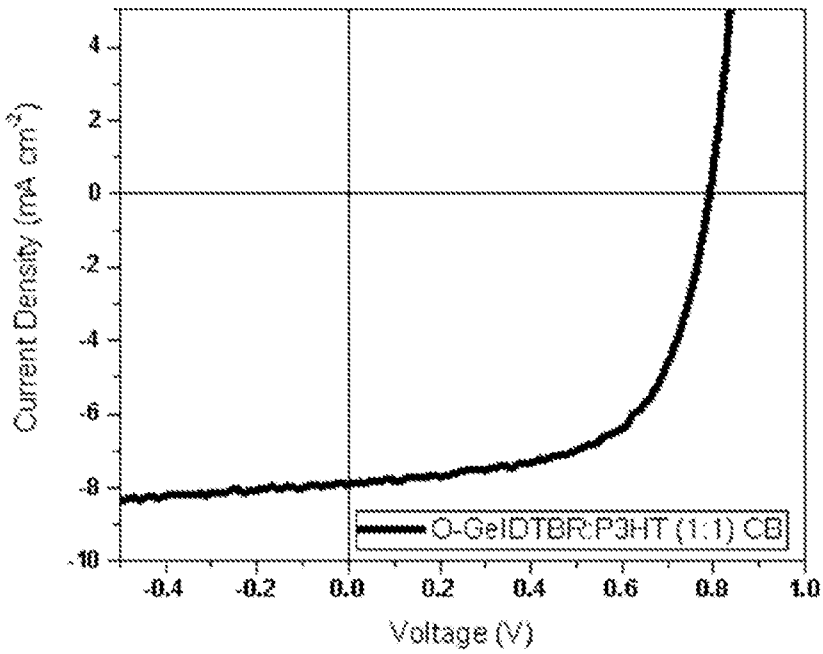
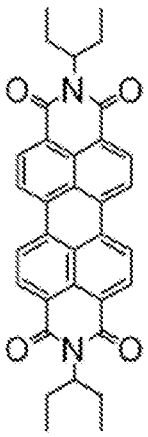
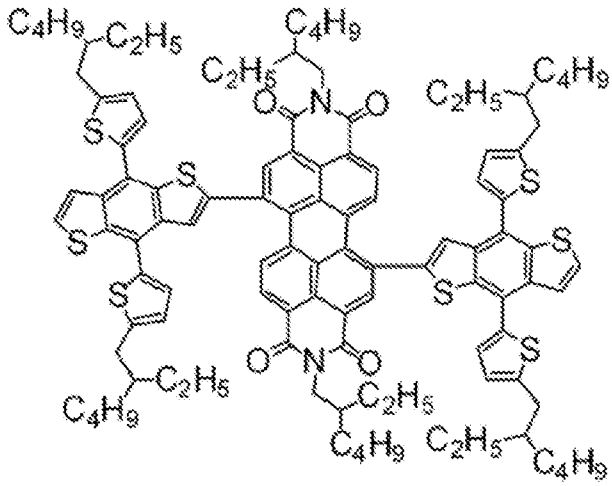

Current Density (mA cm^{-2})
4
2
0
-2
-4
-6
-8
-10
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
Voltage (V)
O-GeIDTBR:P3HT (1:1) CB

FIG. 4

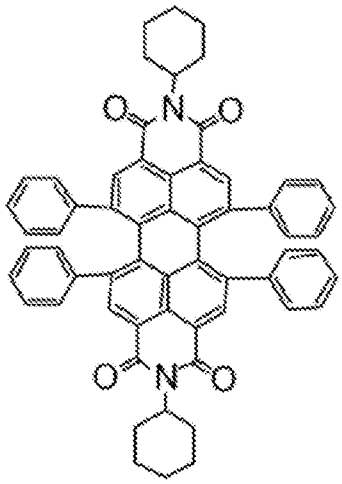
FIG. 5a



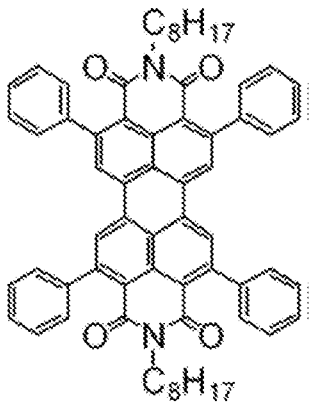
PDI 1



PDI 2

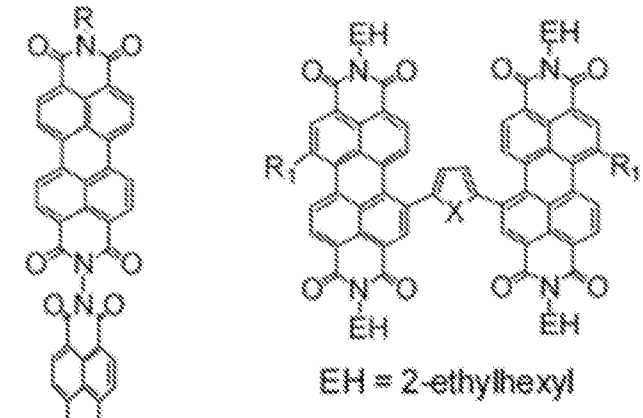


PDI 3



PDI 4

FIG. 5a (cont.)



5a: R= C_7H_{15} / C_7H_{15}

5b: R= C_9H_{11} / C_9H_{11}

PDI 5

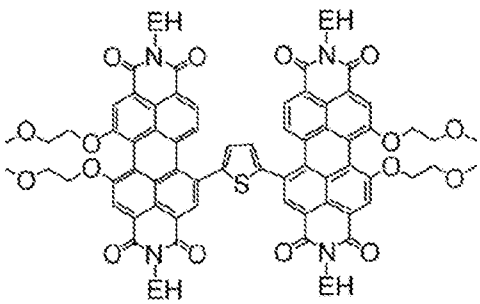
6a: X=S, Bis-PDI-T, R_1=H

6b: X=S, Bis-PDI-T-EG, R_1=

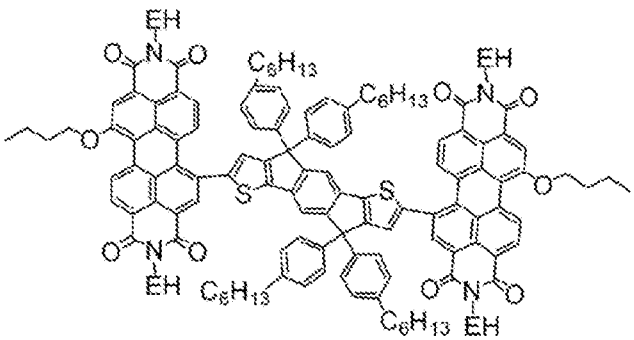
6c: X=S, Bis-PDI-T-MO, R_1=

6d: X=Se, Bis-PDI-Se-EG, R_1=

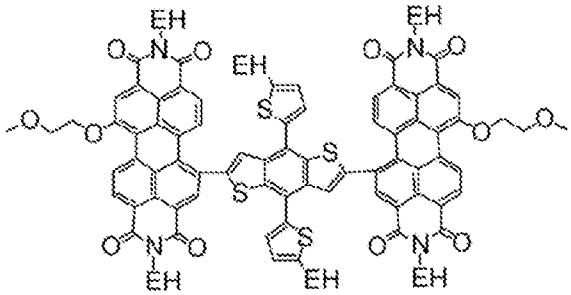
PDI 6



PDI 7 Bis-PDI-T-di-EG

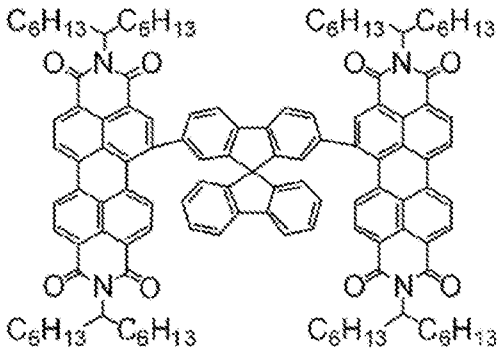


PDI 9

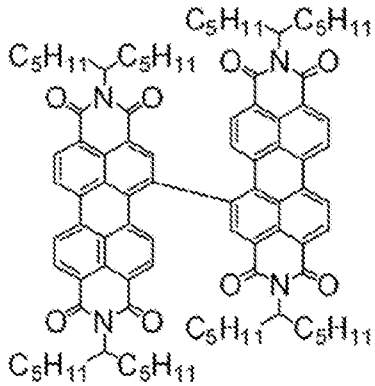


PDI 8 Bis-PDI-BDT-EG

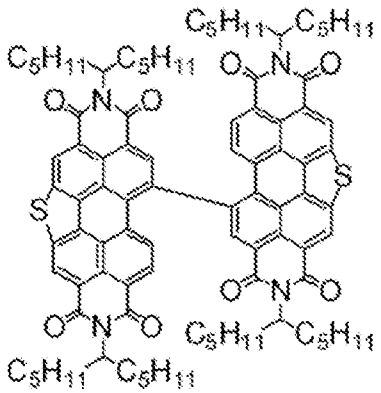
FIG. 5b



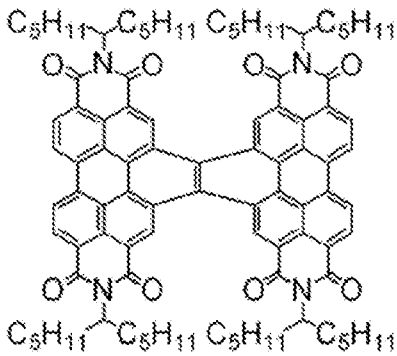
PDI 10



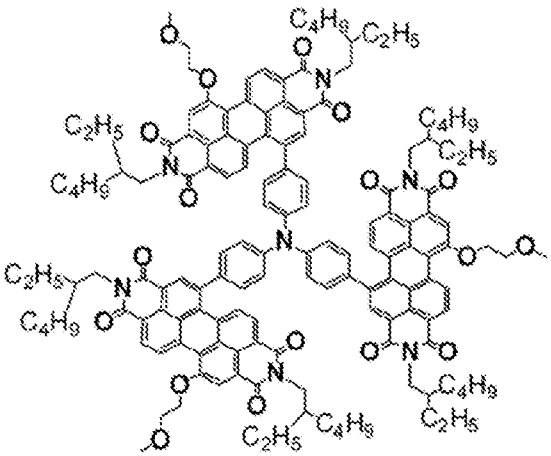
PDI 11



PDI 12

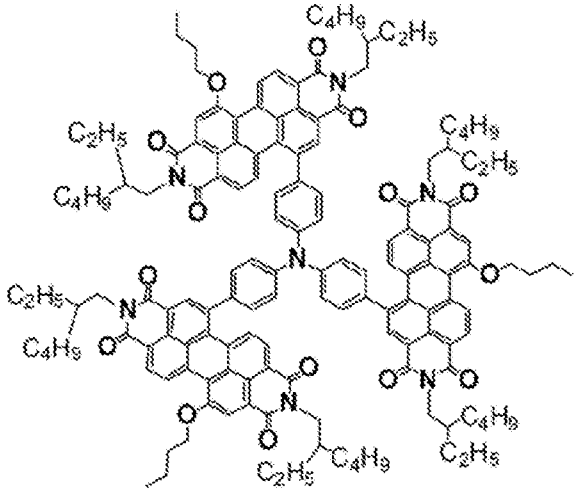


PDI 13



Tris-PDI-TPA-EG

PDI 14



PDI 15

FIG. 5b (cont.)

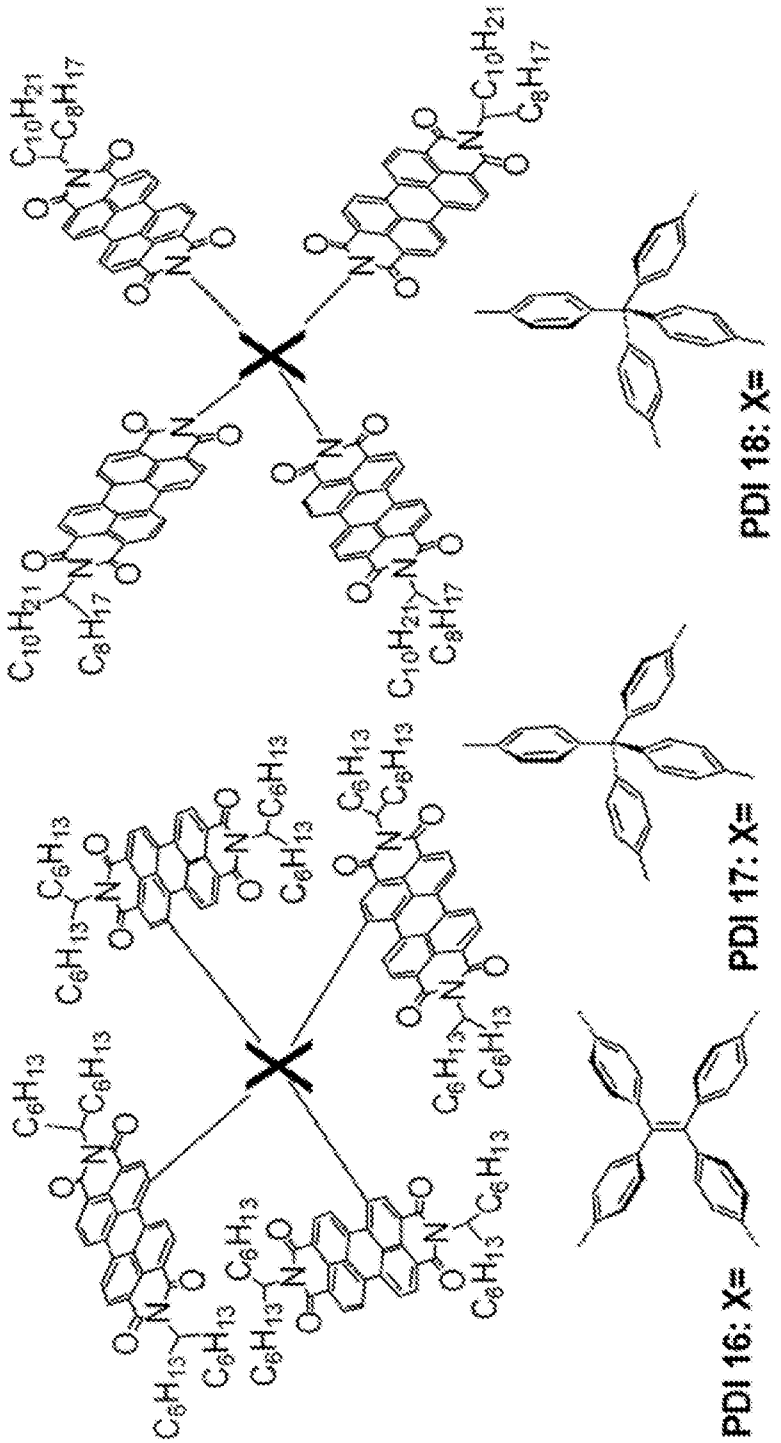


FIG. 5c

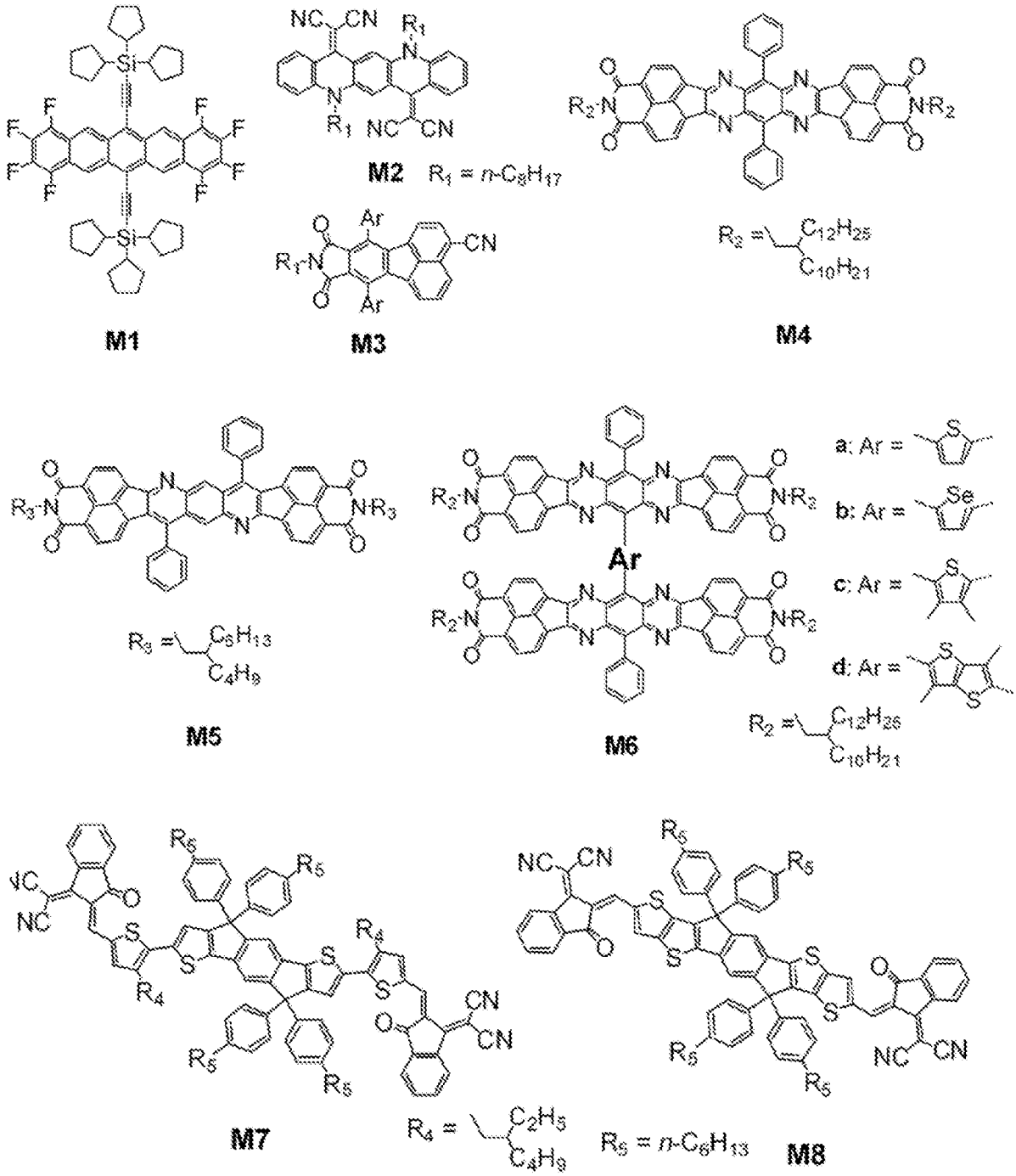
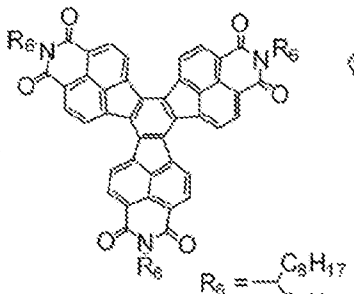
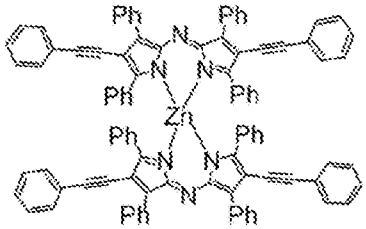

M1
M2 $R_1 = n\text{-}C_8H_{17}$
M3
M4
$R_2 =$ $C_{12}H_{25}$ $C_{10}H_{21}$
M5
$R_3 =$ C_5H_{13} C_4H_9
M6
a: Ar =
b: Ar =
c: Ar =
d: Ar =
$R_2 =$ $C_{12}H_{25}$ $C_{10}H_{21}$
M7
$R_4 =$ C_2H_5 C_4H_9
$R_5 = n\text{-}C_6H_{13}$
M8

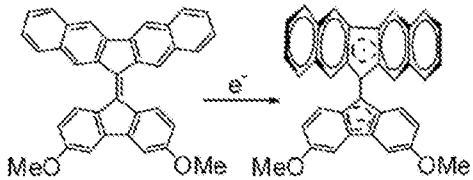
FIG. 5c (cont.)



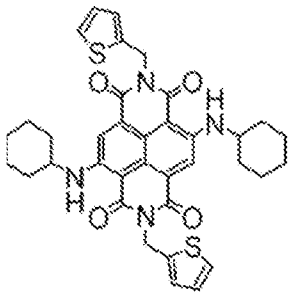
M9



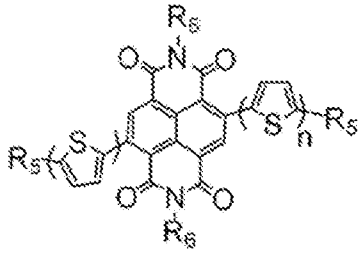
M10



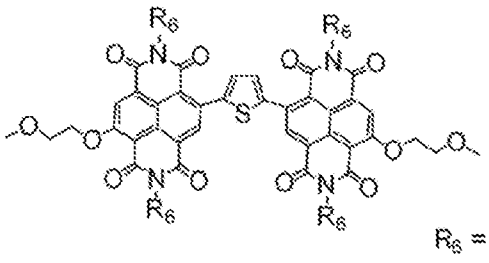
M11



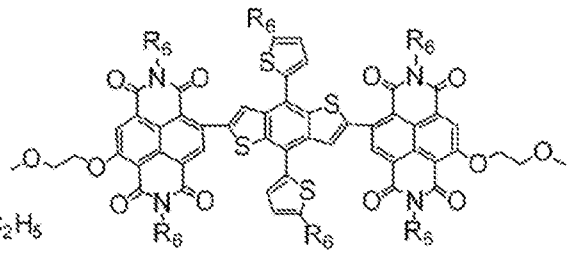
M12



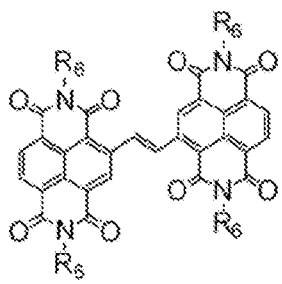
M13



M14

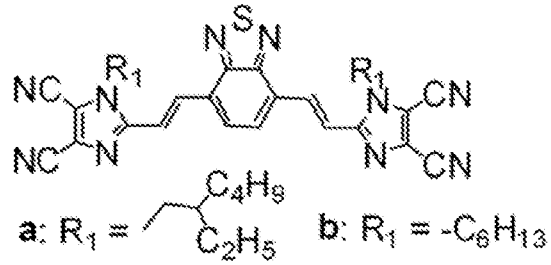


M15

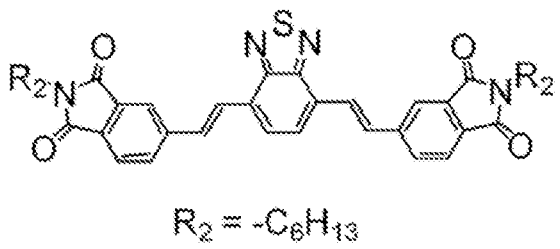


M16

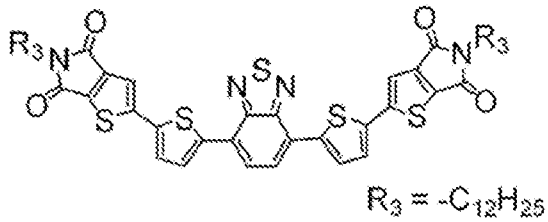
FIG. 5d



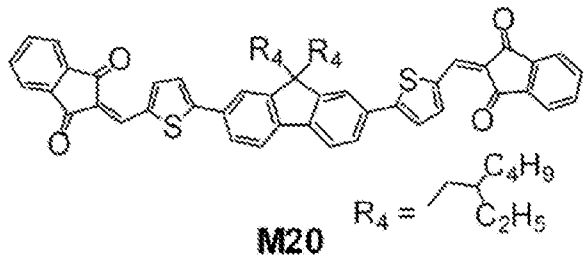
M17



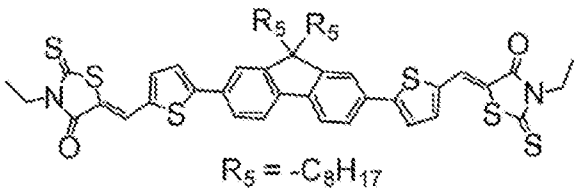
M18



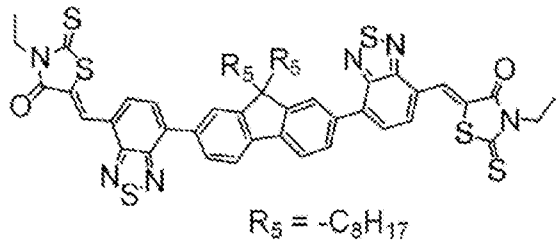
M19



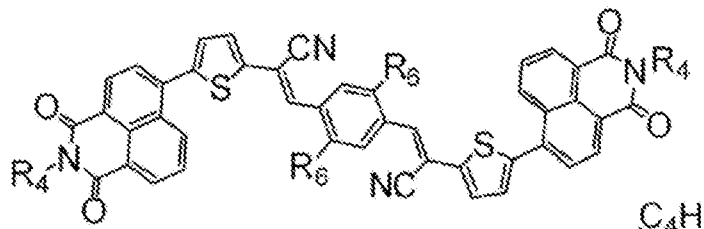
M20



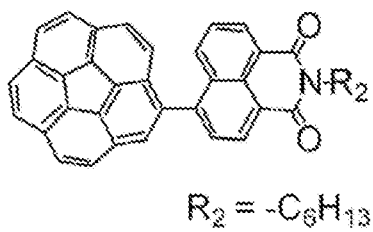
M21



M22

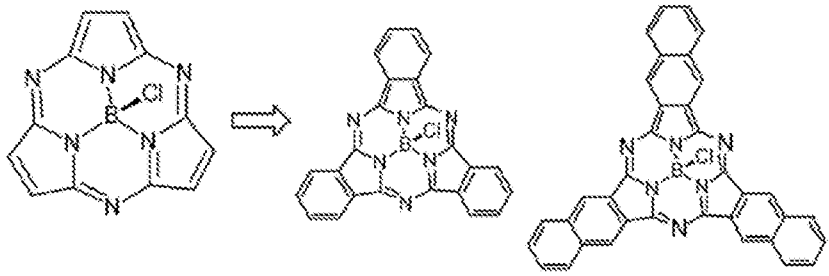


M23

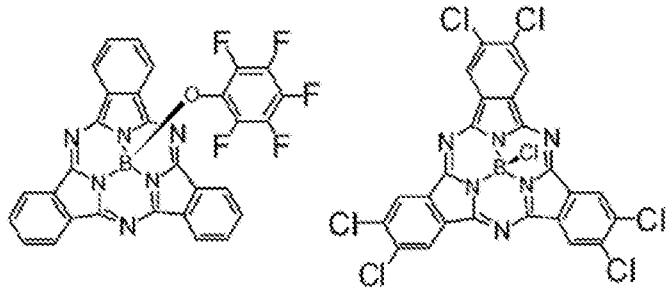


M24

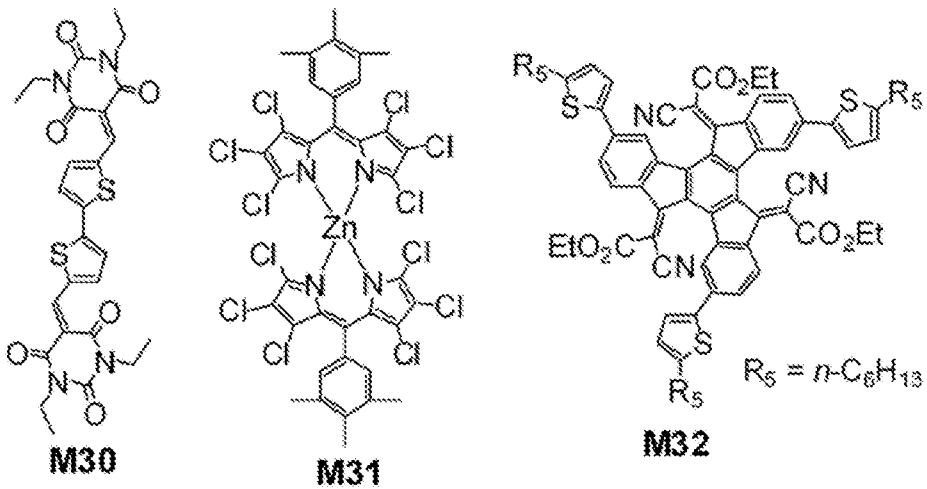
FIG. 5d (cont.)



M25 M26 M27



M28 M29



M30 M31 M32

FIG. 5e

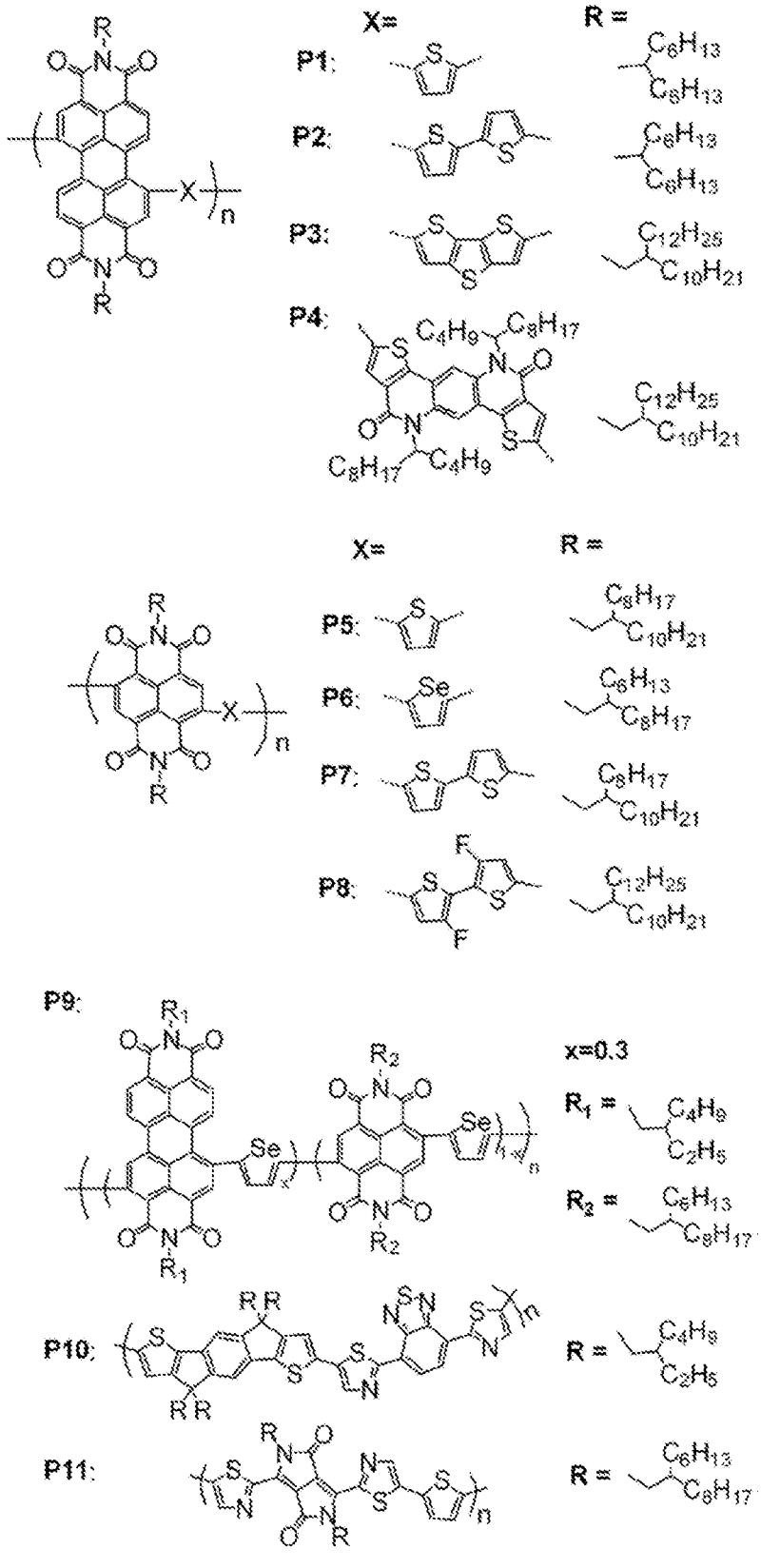
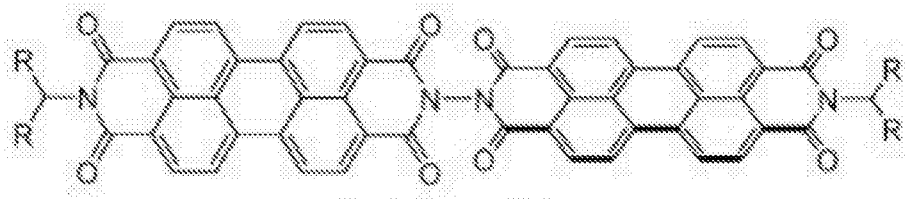
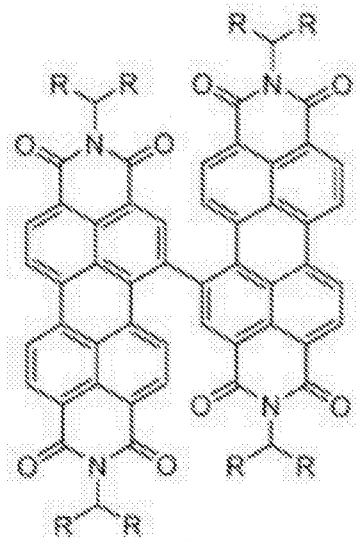


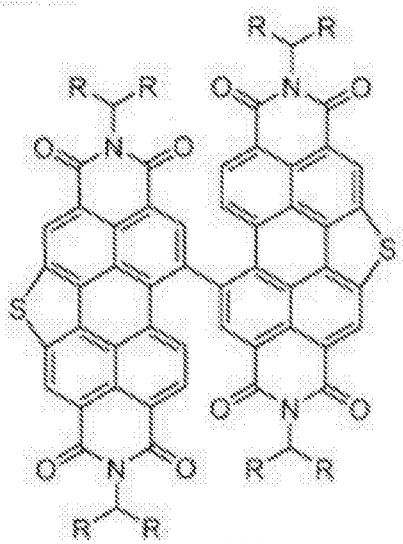
FIG. 5e (cont.)



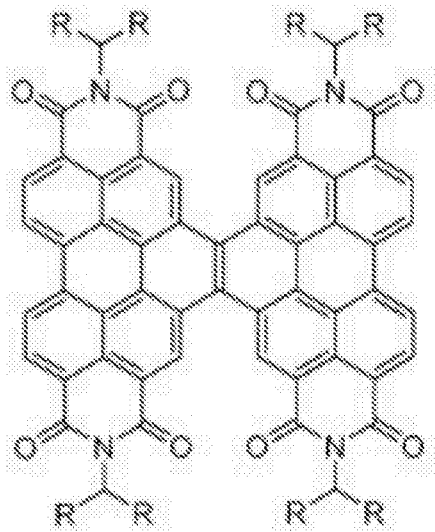
1.1a R = C_7H_{15}
1.1b R = C_5H_{11}



1.2
R = C_5H_{11}

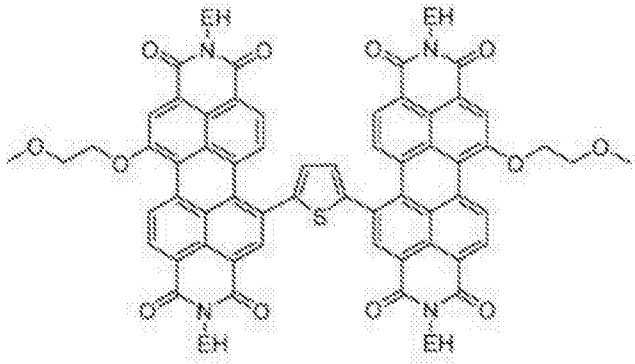


1.3
R = C_5H_{11}

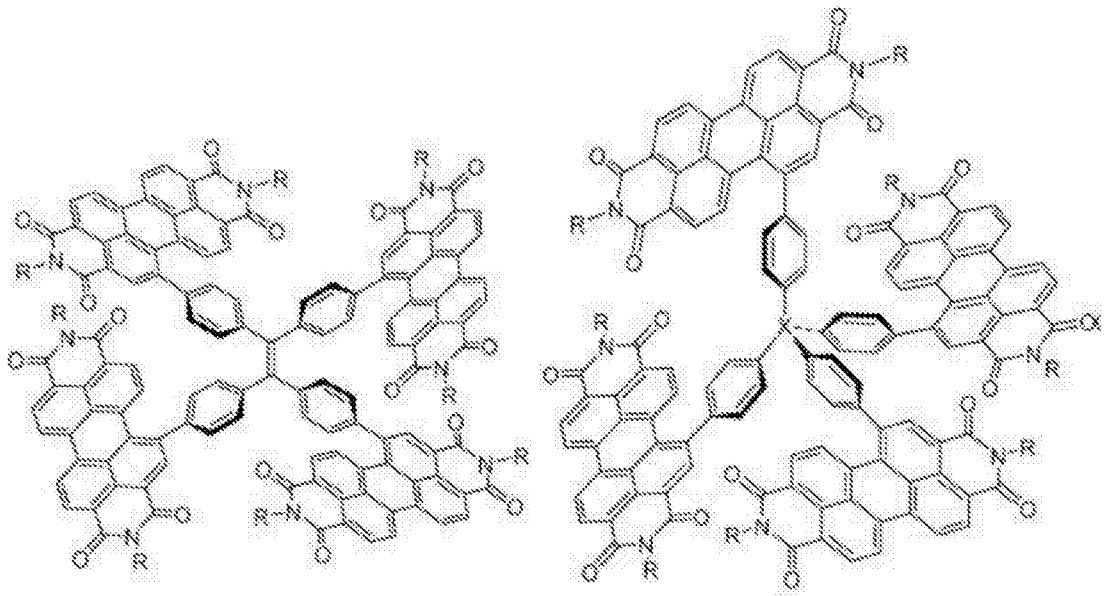


1.4
R = C_5H_{11}

FIG. 5f

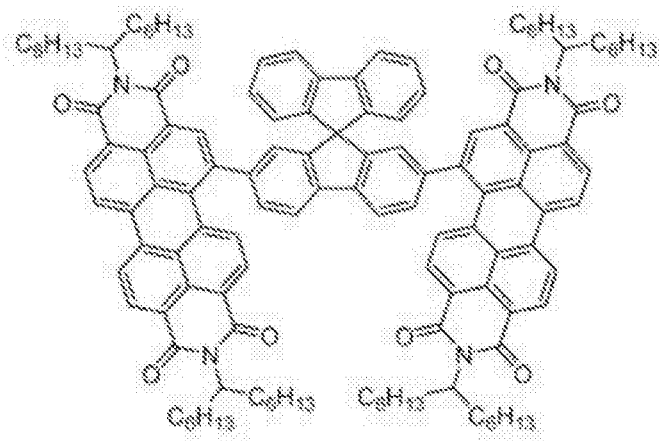


1.5



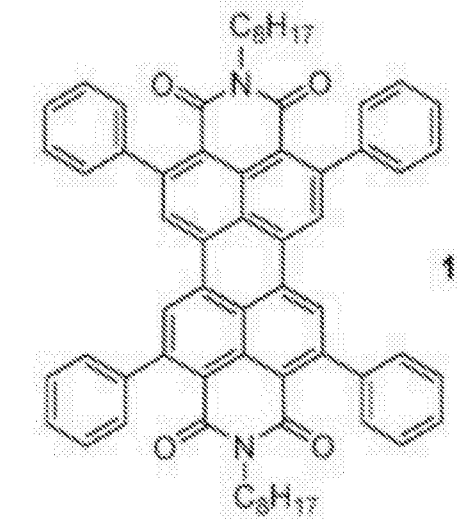
1.6, R = 

1.7a X = C
1.7b X = Si
R = 

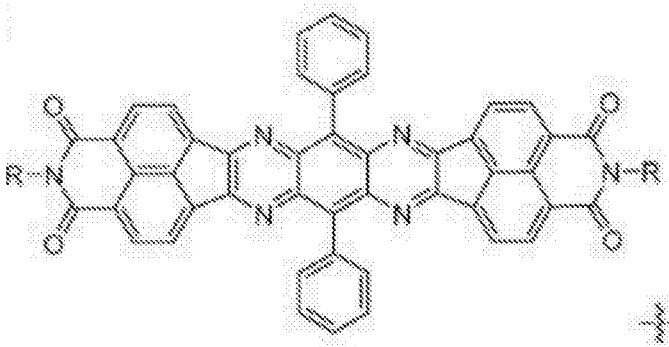


1.8

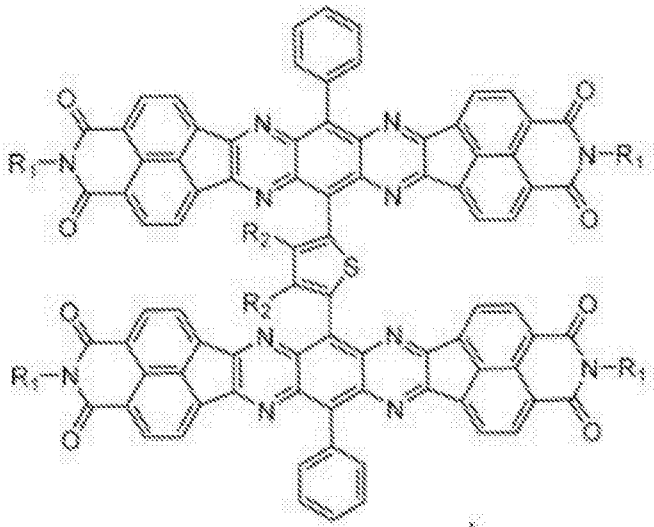
FIG. 5f (cont.)



1.9



1.10 R =



1.11a R_2 = H
1.11b R_2 = CH_3

R_1 =

FIG. 5g

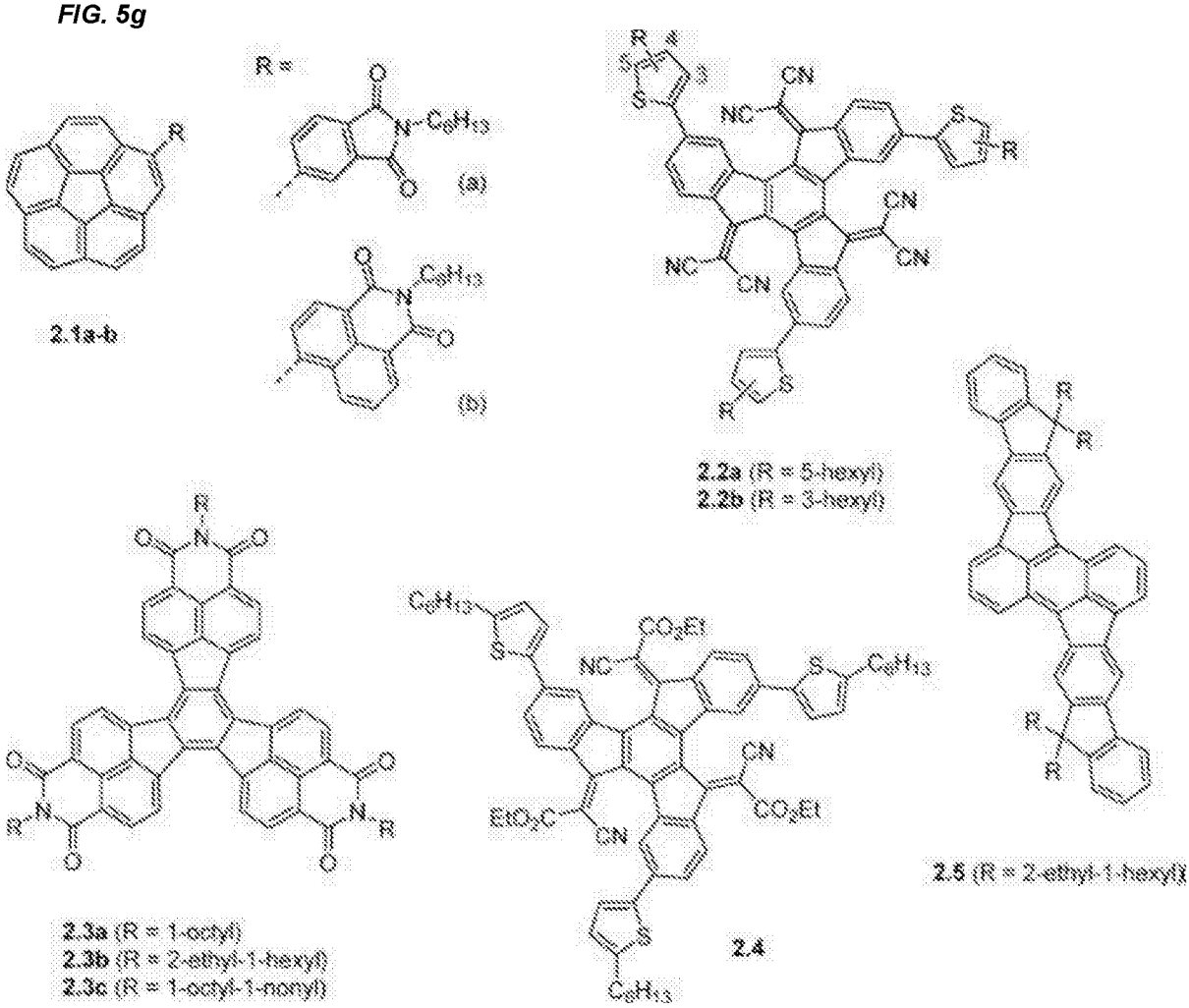
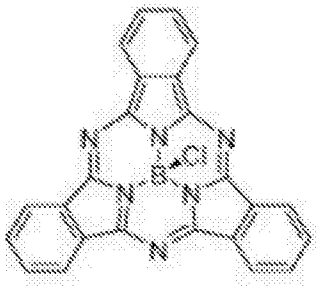
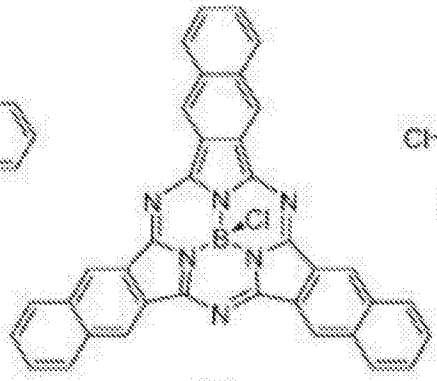

R =
(a)
(b)
2.1a-b
2.2a (R = 5-hexyl)
2.2b (R = 3-hexyl)
2.3a (R = 1-octyl)
2.3b (R = 2-ethyl-1-hexyl)
2.3c (R = 1-octyl-1-nonyl)
2.4
2.5 (R = 2-ethyl-1-hexyl)

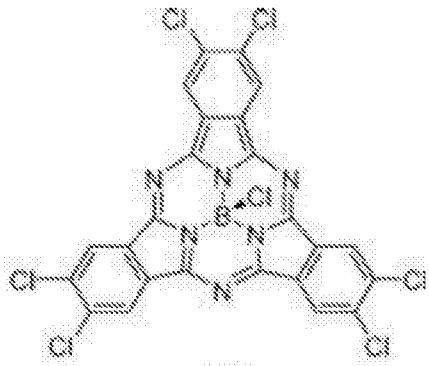
FIG. 5g (cont.)



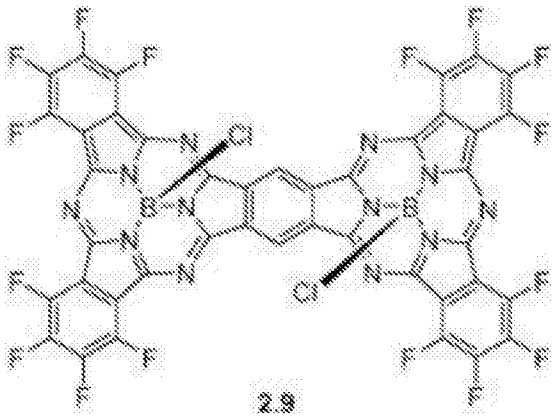
2.6



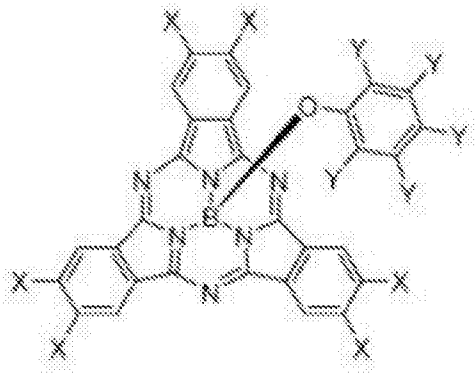
2.7



2.8



2.9



2.10a (X = Y = F)
2.10b (X = Cl, Y = H)

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2017/051258

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D417/14 C07D495/04 C07F7/30 H01L51/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D C07F H01L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	D.S. BROWN ET AL: "The crystal and molecular structure of 5,5-diphenyloctafluorogermanthrene, (C6H5)2GeC12F8", JOURNAL OF ORGANOMETALLIC CHEMISTRY., vol. 302, no. 3, 1 March 1986 (1986-03-01) , pages 343-350, XP055385506, CH ISSN: 0022-328X, DOI: 10.1016/0022-328X(86)80099-7 figure 3 ----- -/--	1,2

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

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
5 July 2017	25/07/2017

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

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YUSUKE YABUSAKI ET AL: "Versatile Synthesis of Blue Luminescent Siloles and Germoles and Hydrogen-Bond-Assisted Color Alteration", CHEMISTRY - A EUROPEAN JOURNAL, vol. 16, no. 19, 17 May 2010 (2010-05-17), pages 5581-5585, XP055385833, ISSN: 0947-6539, DOI: 10.1002/chem.200903408 compounds 15 and 16	1,2
X	HARTMUT BRAUER ET AL: "Palladium-catalyzed cycloaddition of alkynes (RC.tplbond.CR') with dimethylgermylene", SYNLETT, vol. 1991, no. 6, 1 June 1991 (1991-06-01) , pages 431-432, XP055385864, compounds 3d and 3e	1,2
X	WO 2014/026244 A1 (COMMW SCIENT IND RES ORG [AU]) 20 February 2014 (2014-02-20) whole document, specialy claims 1, 3-5, 49	1-30
X	WO 2015/190762 A2 (LG CHEMICAL LTD [KR]) 17 December 2015 (2015-12-17) whole document, specially claim 1 and compound [1-1-1] in p. 24	1-30
Y	SARAH HOLLIDAY ET AL: "A Rhodanine Flanked Nonfullerene Acceptor for Solution-Processed Organic Photovoltaics", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 137, no. 2, 21 January 2015 (2015-01-21), pages 898-904, XP055385912, US ISSN: 0002-7863, DOI: 10.1021/ja5110602 compound FBR in p. 899	1-30
Y	CHRISTIAN B. NIELSEN ET AL: "Non-Fullerene Electron Acceptors for Use in Organic Solar Cells", ACCOUNTS OF CHEMICAL RESEARCH., vol. 48, no. 11, 17 November 2015 (2015-11-17), pages 2803-2812, XP055385933, US ISSN: 0001-4842, DOI: 10.1021/acs.accounts.5b00199 compounds 3.1 to 3.5 and 3.7 in p. 2809	1-30

-/--

1

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	YUZE LIN ET AL: "High-Performance Electron Acceptor with Thienyl Side Chains for Organic Photovoltaics", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 138, no. 14, 13 April 2016 (2016-04-13), pages 4955-4961, XP055385947, US ISSN: 0002-7863, DOI: 10.1021/jacs.6b02004 compounds ITIC and ITIC-Th in p. 4956 -----	1-30
Y	LESLEY R. RUTLEDGE ET AL: "Design and Computational Characterization of Non-Fullerene Acceptors for Use in Solution-Processable Solar Cells", JOURNAL OF PHYSICAL CHEMISTRY. A, MOLECULES, SPECTROSCOPY,KINETICS, ENVIRONMENT AND GENERAL THEORY, vol. 118, no. 36, 11 September 2014 (2014-09-11), pages 7939-7951, XP055385967, US ISSN: 1089-5639, DOI: 10.1021/jp505867y Figure 1 in p. 7940 -----	1-30

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2017/051258

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014026244 A1	20-02-2014	NONE	
WO 2015190762 A2	17-12-2015	CN 106459080 A	22-02-2017
		KR 20150142609 A	22-12-2015
		WO 2015190762 A2	17-12-2015