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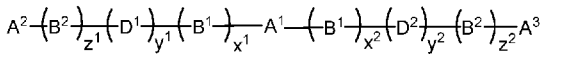

(I)

(57) Abstract: A compound of formula (I), A1 is a divalent heteroaromatic electron-accepting group; $A^2$ and $A^3$ are each independently a monovalent electron-accepting group; $D^1$ and $D^2$ independently in each occurrence is an electron-donating group; $B^1$ and $B^2$ independently in each occurrence is a bridging group; $x^1$ and $x^2$ are each independently 0, 1, 2 or 3; $y^1$ and $y^2$ are each independently at least 1; and $z^1$ and $z^2$ are each independently 0, 1, 2 or 3,with the proviso that at least one of $z^1$ and $z^2$ is at least 1. The compound of formula (I) may be used as an electron-accepting material in an organic photodetector.

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# PHOTORESPONSIVE NONFULLERENE ACCEPTORS OF THE A-D-A'-D-A TYPE FOR USE IN OPTOELECTRONIC DEVICES

## BACKGROUND

Embodiments of the present disclosure relate to electron-accepting compounds and more specifically, but not by way of limitation, to compounds containing electron-accepting and electron donating units, the compounds being suitable for use as an electron-accepting material in a photoresponsive device.

Electron-accepting non-fullerene compounds are known.

Yoon et al, "Effects of Electron Donating and Electron-Accepting Substitution on Photovoltaic Performance in Benzothiadiazole-Based A–D–A′–D–A-Type Small-Molecule Acceptor Solar Cells" ACS Appl. Energy Mater. 2020, 3, 12, 12327–12337 discloses A–D–A′–D–A-type acceptors for use in solar cells.

Gao et al, "Non-fullerene acceptors with nitrogen-containing six-membered heterocycle cores for the applications in organic solar cells" Solar Energy Materials and Solar Cells 225, 2021, 111046 discloses non-fullerene acceptors with pyrazine or pyridazine as the cores.

Wang et al, "Near-infrared absorbing non-fullerene acceptors with unfused D-A-D core for efficient organic solar cells" Organic Electronics 92, 2021, 106131 discloses a D-A-D core employing 3-bis(4-(2-ethylhexyl)-thiophen-2-yl)-5,7-bis(2ethylhexyl)benzo-[1,2:4,5-*c*′]-dithiophene-4,8-dione (BDD) unit as the A moiety and 4,4-dialkyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (CPDT) unit as the D moiety.

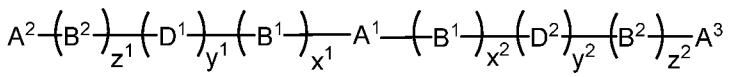
CN110379926 discloses an organic solar cell based on a benzodithiazole near-infrared receptor.

CN112608333 discloses a small molecule based on a bisthiadiazole carbazole derivative.

CN112259687 discloses a ternary fullerene organic solar cell.

## SUMMARY

In some embodiments, the present disclosure provides a compound of formula (I):



(I)

wherein:

$A^1$ is a divalent heteroaromatic electron-accepting group;

$A^2$ and $A^3$ are each independently a monovalent electron-accepting group;

$D^1$ and $D^2$ independently in each occurrence is an electron-donating group;

$B^1$ and $B^2$ independently in each occurrence is a bridging group;

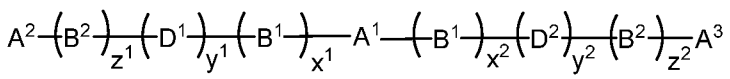
$x^1$ and $x^2$ are each independently 0, 1, 2 or 3;

$y^1$ and $y^2$ are each independently at least 1; and

$z^1$ and $z^2$ are each independently 0, 1, 2 or 3,

with the proviso that at least one of $z^1$ and $z^2$ is at least 1.

In some embodiments, the present disclosure provides a compound of formula (I):



(I)

wherein:

$A^1$ is a divalent heteroaromatic electron-accepting group comprising at least 3 fused rings;

$A^2$ and $A^3$ are each independently a monovalent electron-accepting group;

$D^1$ and $D^2$ independently in each occurrence is an electron-donating group;

$B^1$ and $B^2$ independently in each occurrence is a bridging group;

$x^1$ and $x^2$ are each independently 0, 1, 2 or 3;

$y^1$ and $y^2$ are each independently at least 1; and

$z^1$ and $z^2$ are each independently 0, 1, 2 or 3,

with the proviso that at least one of $x^1$, $x^2$, $z^1$ and $z^2$ is at least 1.

## DESCRIPTION OF DRAWINGS

The disclosed technology and accompanying figures describe some implementations of the disclosed technology.

Figure 1 illustrates an organic photoresponsive device according to some embodiments;

Figure 2 shows absorption spectra of a compound according to an embodiment of the present disclosure and an unbridged comparative compound;

Figure 3 shows external quantum efficiencies vs wavelength of an organic photodetector containing a compound according to an embodiment of the present disclosure and an organic photodetector containing an unbridged comparative compound; and

Figure 4 shows dark current density vs voltage for the devices of Figure 3.

The drawings are not drawn to scale and have various viewpoints and perspectives. The drawings are some implementations and examples. Additionally, some components and/or operations may be separated into different blocks or combined into a single block for the purposes of discussion of some of the embodiments of the disclosed technology. Moreover, while the technology is amenable to various modifications and alternative forms, specific embodiments have been shown by way of example in the drawings and are described in detail below. The intention, however, is not to limit the technology to the particular implementations described. On the contrary, the technology is intended to cover all modifications, equivalents, and alternatives falling within the scope of the technology as defined by the appended claims.

## DETAILED DESCRIPTION

Unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise," "comprising," and the like are to be construed in an inclusive sense, as

opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to." Additionally, the words "herein," "above," "below," and words of similar import, when used in this application, refer to this application as a whole and not to any particular portions of this application. Where the context permits, words in the Detailed Description using the singular or plural number may also include the plural or singular number respectively. The word "or," in reference to a list of two or more items, covers all of the following interpretations of the word: any of the items in the list, all of the items in the list, and any combination of the items in the list. References to a layer “over” another layer when used in this application means that the layers may be in direct contact or one or more intervening layers are may be present. References to a layer “on” another layer when used in this application means that the layers are in direct contact. References to a specific atom include any isotope of that atom unless specifically stated otherwise.

The teachings of the technology provided herein can be applied to other systems, not necessarily the system described below. The elements and acts of the various examples described below can be combined to provide further implementations of the technology. Some alternative implementations of the technology may include not only additional elements to those implementations noted below, but also may include fewer elements.

These and other changes can be made to the technology in light of the following detailed description. While the description describes certain examples of the technology, and describes the best mode contemplated, no matter how detailed the description appears, the technology can be practiced in many ways. As noted above, particular terminology used when describing certain features or aspects of the technology should not be taken to imply that the terminology is being redefined herein to be restricted to any specific characteristics, features, or aspects of the technology with which that terminology is associated. In general, the terms used in the following claims should not be construed to limit the technology to the specific examples disclosed in the specification, unless the Detailed Description section explicitly defines such terms. Accordingly, the actual scope of the technology encompasses not only the disclosed examples, but also all equivalent ways of practicing or implementing the technology under the claims.

To reduce the number of claims, certain aspects of the technology are presented below in certain claim forms, but the applicant contemplates the various aspects of the technology in any number of claim forms.

In the following description, for the purposes of explanation, numerous specific details are set forth in order to provide a thorough understanding of implementations of the disclosed technology. It will be apparent, however, to one skilled in the art that embodiments of the disclosed technology may be practiced without some of these specific details.

A compound of formula (I) as described herein may be provided in a bulk heterojunction layer of a photoresponsive device, preferably a photodetector, in which the bulk heterojunction layer is disposed between an anode and a cathode.

The bulk heterojunction layer comprises or consists of an electron-donating material and an electron-accepting compound of formula (I) as described herein.

In some embodiments, the bulk heterojunction layer contains two or more accepting materials and / or two or more electron-accepting materials.

In some embodiments, the weight of the electron-donating material(s) to the electron-accepting material(s) is from about 1:0.5 to about 1:2, preferably about 1:1.1 to about 1:2.

Preferably, the electron-donating material has a type II interface with the electron-accepting material, i.e. the electron-donating material has a shallower HOMO and LUMO that the corresponding HOMO and LUMO levels of the electron-accepting material. Preferably, the compound of formula (I) has a HOMO level that is at least 0.05 eV deeper, optionally at least 0.10 eV deeper, than the HOMO of the electron-donating material.

Optionally, the gap between the HOMO level of the electron-donating material and the LUMO level of the electron-accepting compound of formula (I) is less than 1.4 eV.

Unless stated otherwise, HOMO and LUMO levels of materials as described herein are as measured by square wave voltammetry (SWV).

In SWV, the current at a working electrode is measured while the potential between the working electrode and a reference electrode is swept linearly in time. The difference current between a forward and reverse pulse is plotted as a function of potential to yield a voltammogram. Measurement may be with a CHI 660D Potentiostat.

The apparatus to measure HOMO or LUMO energy levels by SWV may comprise a cell containing 0.1 M tertiary butyl ammonium hexafluorophosphate in acetonitrile; a 3 mm

diameter glassy carbon working electrode; a platinum counter electrode and a leak free Ag/AgCl reference electrode.

Ferrocene is added directly to the existing cell at the end of the experiment for calculation purposes where the potentials are determined for the oxidation and reduction of ferrocene versus Ag/AgCl using cyclic voltammetry (CV).

The sample is dissolved in toluene (3 mg / ml) and spun at 3000 rpm directly on to the glassy carbon working electrode.

LUMO = 4.8-E ferrocene (peak to peak average) - E reduction of sample (peak maximum).

HOMO = 4.8-E ferrocene (peak to peak average) + E oxidation of sample (peak maximum).

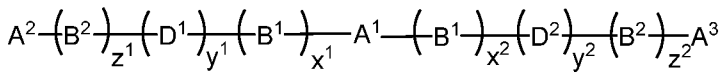
A typical SWV experiment runs at 15 Hz frequency; 25 mV amplitude and 0.004 V increment steps. Results are calculated from 3 freshly spun film samples for both the HOMO and LUMO data.

Preferably, the compound of formula (I) has an absorption peak greater than 1000 nm, more preferably greater than 1100 nm or 1200 nm.

Unless stated otherwise, absorption spectra of materials as described herein are measured using a Cary 5000 UV-VIS-NIR Spectrometer. Measurements were taken from 300 nm to 2500 nm using a PbSmart NIR detector for extended photometric range with variable slit widths (down to 0.01 nm) for optimum control over data resolution.

Absorption data are obtained by measuring the intensity of transmitted radiation through a solution sample. Absorption intensity is plotted vs. incident wavelength to generate an absorption spectrum. Solution absorption may be measured from a 0.015 mg / ml solution in a quartz cuvette and comparing to a cuvette containing the solvent only.

In some embodiments, the electron-accepting compound has formula (I):



(I)

$D^1$ and $D^2$ independently in each occurrence is an electron-donating group.

$A^1$, $A^2$ and $A^3$ are each independently an electron-accepting group.

$B^1$ and $B^2$ in each occurrence are independently a bridging group.

$x^1$ and $x^2$ are each independently 0, 1, 2 or 3, preferably 0 or 1.

$y^1$ and $y^2$ are each independently at least 1, preferably 1, 2 or 3, more preferably 1.

$z^1$ and $z^2$ are each independently 0, 1, 2 or 3, preferably 1.

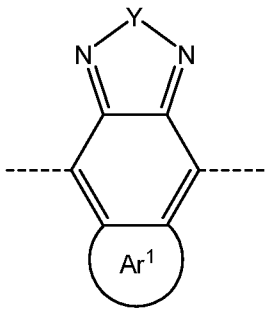
Each of the electron-accepting groups $A^1$, $A^2$ and $A^3$ has a lowest unoccupied molecular orbital (LUMO) level that is deeper (i.e., further from vacuum) than the LUMO of either of the electron-donating groups $D^1$ or $D^2$, preferably at least 1 eV deeper. The LUMO levels of electron-accepting groups and electron-donating groups may be as determined by modelling the LUMO level of these groups, in which each bond to adjacent group is replaced with a bond to a hydrogen atom. Modelling may be performed using Gaussian09 software available from Gaussian using Gaussian09 with B3LYP (functional) and LACVP* (Basis set).

Preferably, $A^1$ comprises at least 3 fused rings.

Acceptor Unit $A^1$

$A^1$ may be a polycyclic heteroaromatic group which is unsubstituted or substituted with one or more substituents.

A preferred group, $A^1$ of formula (I) is a group of formula (II):




(II)

wherein:

$Ar^1$ is a monocyclic or polycyclic aromatic or heteroaromatic group; and

Y is O, S, $NR^4$ or $R^1$-C=C-$R^1$ wherein $R^1$ in each occurrence is independently H or a substituent wherein two substituents $R^1$ may be linked to form a monocyclic or polycyclic ring; and $R^4$ is H or a substituent.

$R^2$ groups wherein $R^2$ in each occurrence is independently a substituent.

Preferred $R^2$ groups are selected from

F;

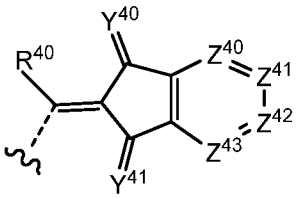
CN;

$NO_2$;

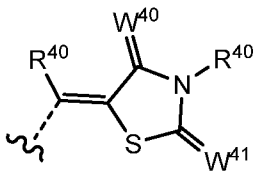
$C_{1-20}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$ wherein $R^7$ is a $C_{1-12}$ hydrocarbyl, COO or CO and one or more H atoms of the alkyl may be replaced with F;

an aromatic or heteroaromatic group, preferably phenyl, which is unsubstituted or substituted with one or more substituents; and

a group selected from




or




wherein $Z^{40}$, $Z^{41}$, $Z^{42}$ and $Z^{43}$ are each independently $CR^{13}$ or N wherein $R^{13}$ in each occurrence is H or a substituent, preferably a $C_{1-20}$ hydrocarbyl group; $Y^{40}$ and $Y^{41}$ are each independently O, S, $NX^{71}$ wherein $X^{71}$ is CN or $COOR^{40}$; or $CX^{60}X^{61}$ wherein $X^{60}$ and $X^{61}$ is independently CN, $CF_3$ or $COOR^{40}$; $W^{40}$ and $W^{41}$ are each independently O, S, $NX^{71}$ or $CX^{60}X^{61}$ wherein $X^{60}$ and $X^{61}$ is independently CN, $CF_3$ or $COOR^{40}$; and $R^{40}$ in each occurrence is H or a substituent, preferably H or a $C_{1-20}$ hydrocarbyl group. Exemplary substituents of an aromatic or heteroaromatic group $R^2$ are F, CN, $NO_2$, and $C_{1-12}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, COO or CO and one or more H atoms of the alkyl may be replaced with F.

$R^7$ as described anywhere herein may be, for example, $C_{1-12}$ alkyl, unsubstituted phenyl; or phenyl substituted with one or more $C_{1-6}$ alkyl groups.

If a C atom of an alkyl group as described anywhere herein is replaced with another atom or group, the replaced C atom may be a terminal C atom of the alkyl group or a non-terminal C-atom.

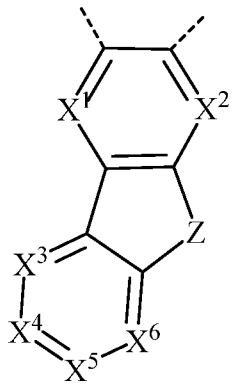
By "non-terminal C atom" of an alkyl group as used anywhere herein means a C atom other than the C atom of the methyl group at the end of an n-alkyl chain or the C atoms of the methyl groups at the ends of a branched alkyl chain.

If a terminal C atom of a group as described anywhere herein is replaced then the resulting group may be an anionic group comprising a countercation, e.g., an ammonium or metal countercation, preferably an ammonium or alkali metal cation.

A C atom of an alkyl substituent group which is replaced with another atom or group as described anywhere herein is preferably a non-terminal C atom, and the resultant substituent group is preferably non-ionic.

Exemplary monocyclic heteroaromatic groups $Ar^1$ are oxadiazole, thiadiazole, triazole and 1,4-diazine which is unsubstituted or substituted with one or more substituents. Thiadiazole is particularly preferred.

Exemplary polycyclic heteroaromatic groups $Ar^1$ are groups of formula (V):




(V)

$X^1$ and $X^2$, are each independently selected from N and $CR^3$ wherein $R^3$ is H or a substituent, optionally H or a substituent $R^2$ as described above.

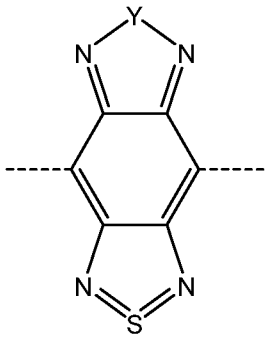
$X^3$, $X^4$, $X^5$ and $X^6$ are each independently selected from N and $CR^3$ with the proviso that at least one of $X^3$, $X^4$, $X^5$ and $X^6$ is $CR^3$.

Z is selected from O, S, $SO_2$, $NR^4$, $PR^4$, $C(R^3)_2$, $Si(R^3)_2$ C=O, C=S and $C=C(R^5)_2$ wherein $R^3$ is as described above; $R^4$ is H or a substituent; and $R^5$ in each occurrence is an electron-withdrawing group.

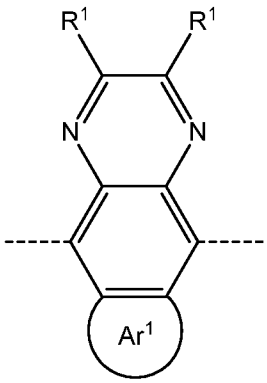
Optionally, each $R^4$ of any $NR^4$ or $PR^4$ described anywhere herein is independently selected from H; $C_{1-20}$ alkyl wherein one or more non-adjacent C atoms other than the C atom bound to N or P may be replaced with O, S, $NR^7$, COO or CO and one or more H atoms of the alkyl may be replaced with F; and phenyl which is unsubstituted or substituted with one or more substituents, optionally one or more $C_{1-12}$ alkyl groups wherein one or more non-adjacent C atoms of the alkyl may be replaced with O, S, $NR^7$, COO or CO and one or more H atoms of the alkyl may be replaced with F.

Preferably, each $R^5$ is CN, $COOR^{40}$; or $CX^{60}X^{61}$ wherein $X^{60}$ and $X^{61}$ is independently CN, $CF_3$ or $COOR^{40}$ and $R^{40}$ in each occurrence is H or a substituent, preferably H or a $C_{1-20}$ hydrocarbyl group.

$A^1$ groups of formula (II) are preferably selected from groups of formulae (IIa) and (IIb):




(IIa)



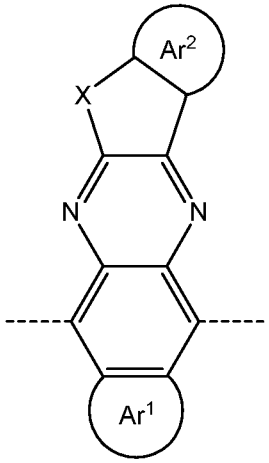

(IIb)

For compounds of formula (IIb), the two $R^1$ groups may or may not be linked.

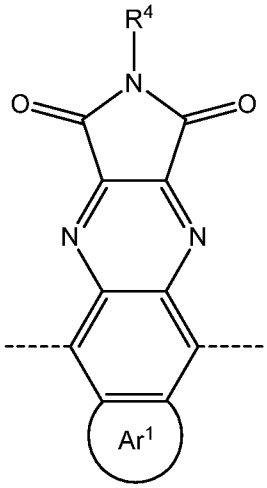
Preferably, when the two $R^1$ groups are not linked each $R^1$ is independently selected from H; F; CN; $NO_2$; $C_{1-20}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, CO, COO, $NR^4$, $PR^4$, or $Si(R^3)_2$ wherein $R^3$ and $R^4$ are as described above and one or more H atoms may be replaced with F; and aryl or heteroaryl, preferably phenyl, which may

be unsubstituted or substituted with one or more substituents. Substituents of the aryl or heteroaryl group may be selected from one or more of F; CN; $NO_2$; and $C_{1-20}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, CO, COO and one or more H atoms may be replaced with F.

Preferably, when the two $R^1$ groups are linked, the group of formula (IIb) has formula (IIb-1) or (IIb-2):




(IIb-1)

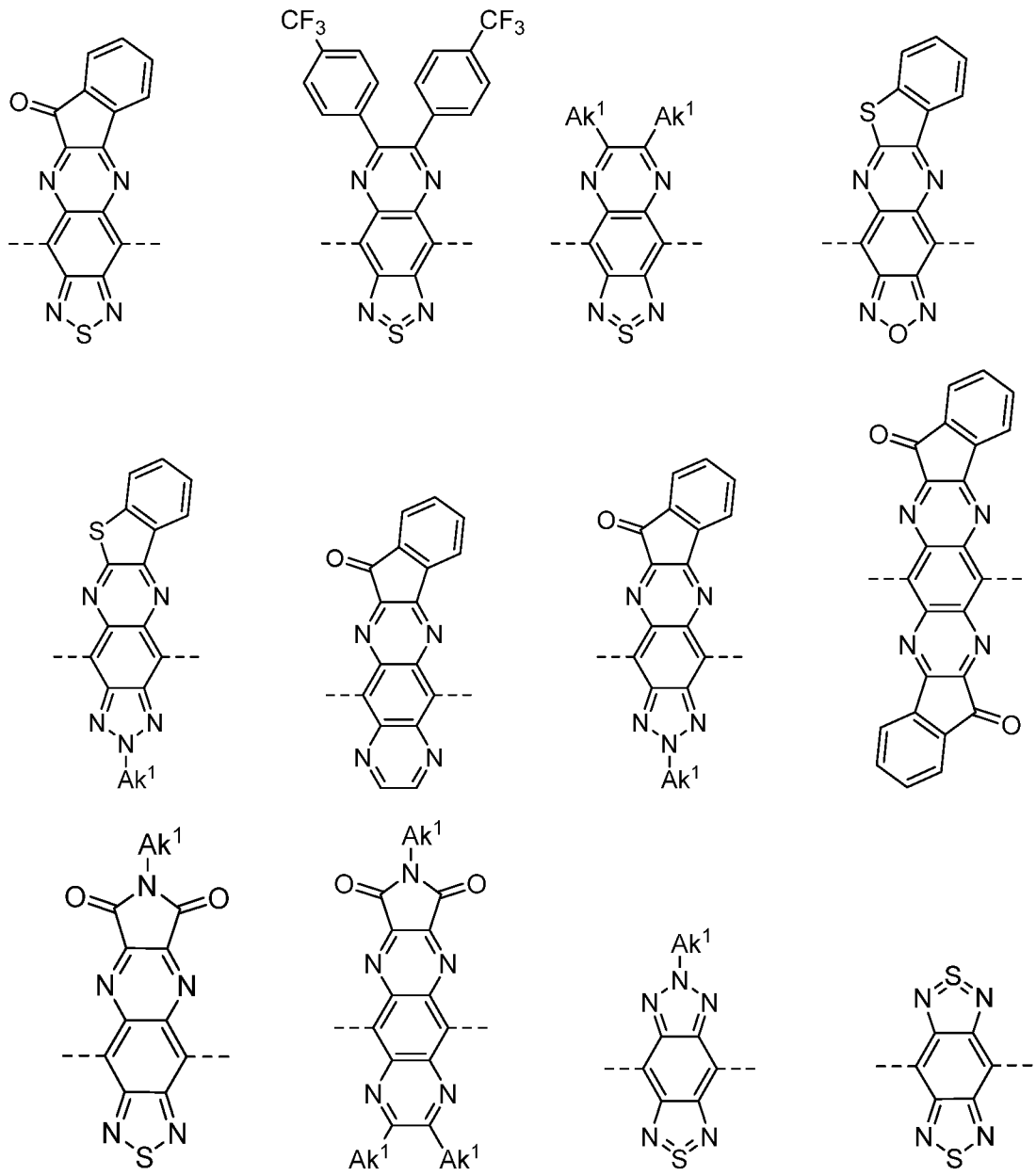



(IIb-2)

$Ar^2$ is an aromatic or heteroaromatic group, preferably benzene, which is unsubstituted or substituted with one or more substituents. $Ar^2$ may be unsubstituted or substituted with one or more substituents $R^2$ as described above.

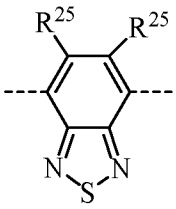
X is selected from O, S, $SO_2$, $NR^4$, $PR^4$, $C(R^3)_2$, $Si(R^3)_2$ C=O, C=S and $C=C(R^5)_2$ wherein $R^3$, $R^4$ and $R^5$ are as described above.

Exemplary electron-accepting groups of formula (II) include, without limitation:

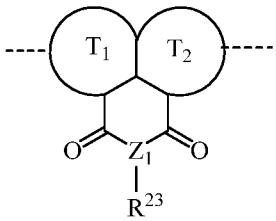


wherein $Ak^1$ is a $C_{1-20}$ alkyl group

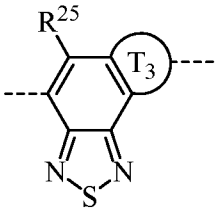
Divalent electron-accepting groups other than formula (II) are optionally selected from formulae (IVa)-(IVj):



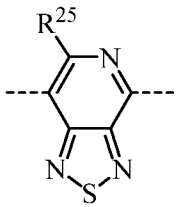
(IVa)



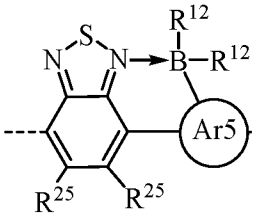
(IVb)



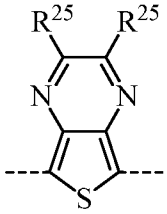
(IVc)



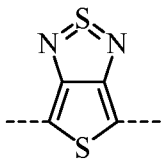
(IVd)



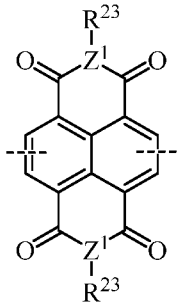
(IVe)



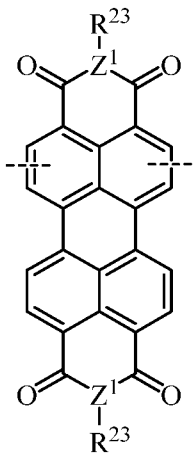
(IVf)



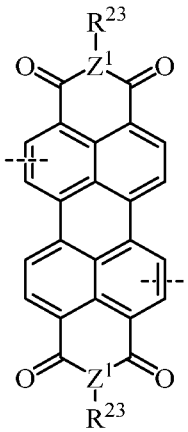
(IVg)



(IVh)



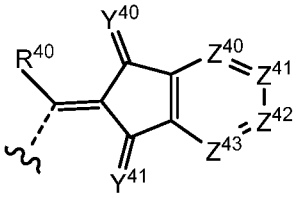
(IVi)



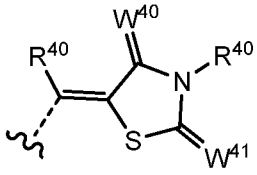
(IVj)

$R^{23}$ in each occurrence is a substituent, optionally $C_{1-12}$ alkyl wherein one or more non-adjacent C atoms other than the C atom attached to $Z^1$ may be replaced with O, S, $NR^7$, COO or CO and one or more H atoms of the alkyl may be replaced with F.

$R^{25}$ in each occurrence is independently H; F; CN; $NO_2$; $C_{1-12}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, COO or CO and one or more H atoms of the alkyl may be replaced with F; an aromatic group, optionally phenyl, which is unsubstituted or substituted with one or more substituents selected from F and $C_{1-12}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, COO or CO; or




or




wherein $Z^{40}$, $Z^{41}$, $Z^{42}$ and $Z^{43}$ are each independently $CR^{13}$ or N wherein $R^{13}$ in each occurrence is H or a substituent, preferably a $C_{1-20}$ hydrocarbyl group;

$Y^{40}$ and $Y^{41}$ are each independently O, S, $NX^{71}$ wherein $X^{71}$ is CN or $COOR^{40}$; or $CX^{60}X^{61}$ wherein $X^{60}$ and $X^{61}$ is independently CN, $CF_3$ or $COOR^{40}$;

$W^{40}$ and $W^{41}$ are each independently O, S, $NX^{71}$ wherein $X^{71}$ is CN or $COOR^{40}$; or $CX^{60}X^{61}$ wherein $X^{60}$ and $X^{61}$ is independently CN, $CF_3$ or $COOR^{40}$; and

$R^{40}$ in each occurrence is H or a substituent, preferably H or a $C_{1-20}$ hydrocarbyl group.

$Z^1$ is N or P.

$T^1$, $T^2$ and $T^3$ each independently represent an aryl or a heteroaryl ring, optionally benzene, which may be fused to one or more further rings. Substituents of $T^1$, $T^2$ and $T^3$, where present, are optionally selected from non-H groups of $R^{25}$.

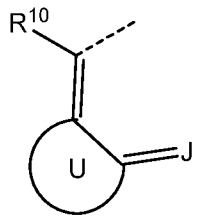
$R^{12}$ in each occurrence is a substituent, preferably a $C_{1-20}$ hydrocarbyl group.

$Ar^5$ is an arylene or heteroarylene group, optionally thiophene, fluorene or phenylene, which may be unsubstituted or substituted with one or more substituents, optionally one or more non-H groups selected from $R^{25}$.

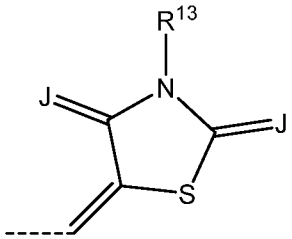
Electron-Accepting Groups $A^2$ and $A^3$

The monovalent acceptor Groups $A^2$ and $A^3$ may each independently be selected from any such units known to the skilled person. $A^2$ and $A^3$ may be the same or different, preferably the same.

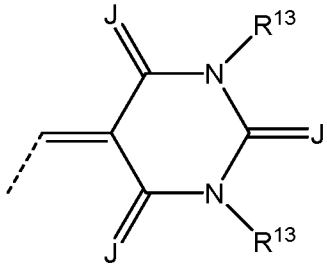
Exemplary monovalent acceptor units include, without limitation, units of formulae (IIIa)-(IIIq)



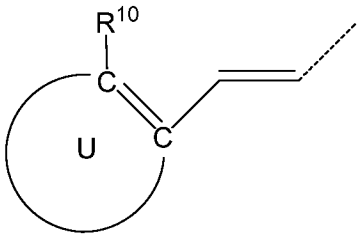

(IIIa)



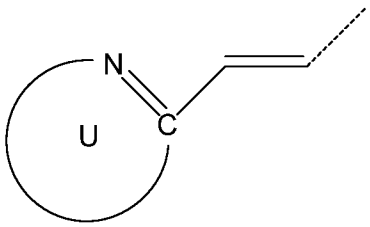

(IIIb)



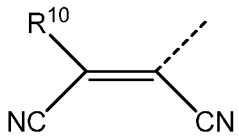

(IIIc)



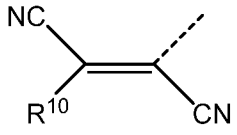

(IIId)



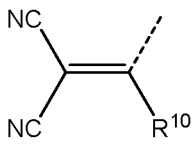

(IIIe)




(IIIf)

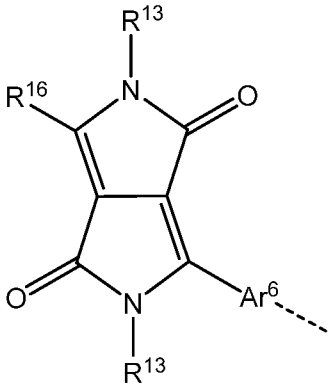



(IIIg)

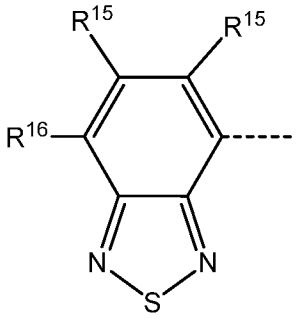



(IIIh)

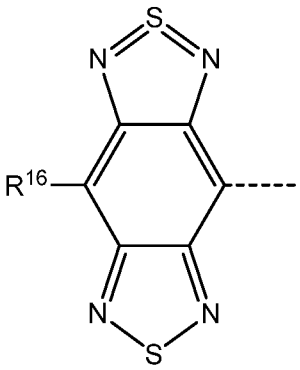
(IIIi)



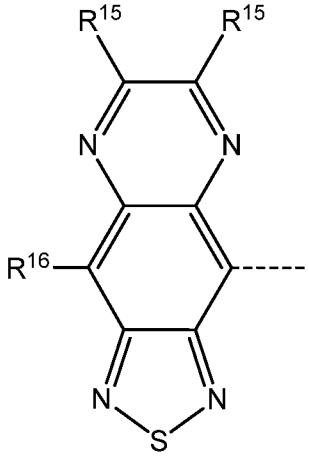
(IIIj)



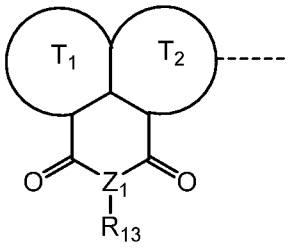
(IIIk)



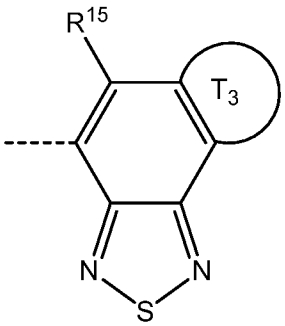
(IIIl)



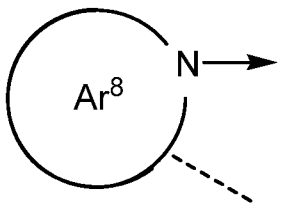
(IIIm)



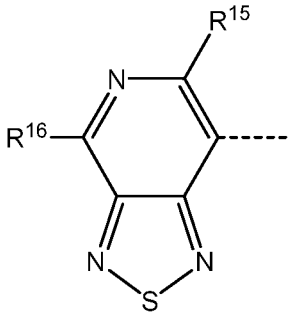
(IIIn)

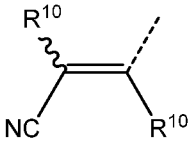


(IIIo)



(IIIp)





(IIIq)

U is a 5- or 6-membered ring which is unsubstituted or substituted with one or more substituents and which may be fused to one or more further rings.

The N atom of formula (IIIe) may be unsubstituted or substituted.

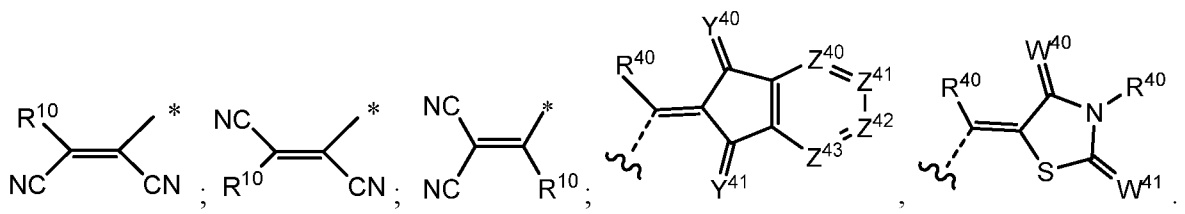
$R^{10}$ is H or a substituent, preferably a substituent selected from the group consisting of $C_{1-12}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, COO or CO and one or more H atoms of the alkyl may be replaced with F; and an aromatic group, optionally phenyl, which is unsubstituted or substituted with one or more substituents selected from F and $C_{1-12}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, COO or CO.

Preferably, $R^{10}$ is H.

J is O or S, preferably O.

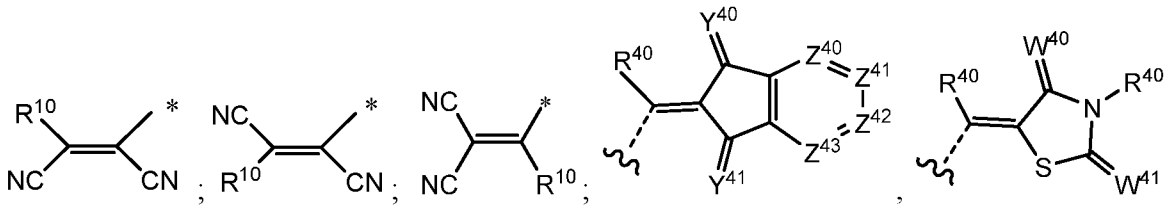
$R^{13}$ in each occurrence is a substituent, optionally $C_{1-12}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, COO or CO and one or more H atoms of the alkyl may be replaced with F.

$R^{15}$ in each occurrence is independently H; F; $C_{1-12}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, COO or CO and one or more H atoms of the alkyl may be replaced with F; aromatic group $Ar^2$, optionally phenyl, which is unsubstituted or substituted with one or more substituents selected from F and $C_{1-12}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, COO or CO; or a group selected from:



$R^{16}$ is H or a substituent, preferably a substituent selected from:

$-(Ar^3)_w$ wherein $Ar^3$ in each occurrence is independently an unsubstituted or substituted aryl or heteroaryl group, preferably thiophene, and w is 1, 2 or 3;



and

$C_{1-12}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, COO or CO and one or more H atoms of the alkyl may be replaced with F.

$Ar^6$ is a 5-membered heteroaromatic group, preferably thiophene or furan, which is unsubstituted or substituted with one or more substituents.

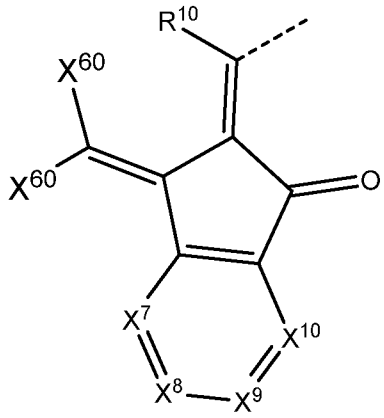
Substituents of $Ar^3$ and $Ar^6$, where present, are optionally selected from $C_{1-12}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, COO or CO and one or more H atoms of the alkyl may be replaced with F.

$T^1$, $T^2$ and $T^3$ are each independently as described above.

$Ar^8$ is a fused heteroaromatic group which is unsubstituted or substituted with one or more substituents, optionally one or more non-H substituents $R^{10}$, and which is bound to an aromatic C atom of $B^2$ and to a boron substituent of $B^2$.

Preferred groups $A^2$ and $A^3$ are groups having a non-aromatic carbon-carbon bond which is bound directly to $D^1$ or $D^2$ or, if present to $B^2$.

Preferably at least one of $A^2$ and $A^3$, preferably both of $A^2$ and $A^3$, are a group of formula (IIIa-1):



(IIIa-1)

wherein:

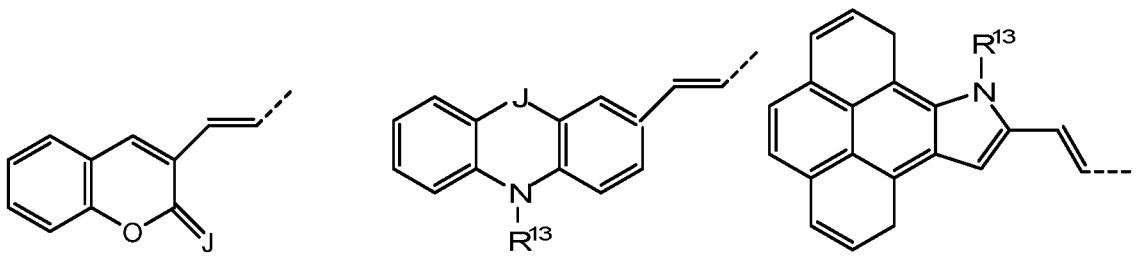
$R^{10}$ is as described above;

each $X^7$-$X^{10}$ is independently $CR^{12}$ or N wherein $R^{12}$ in each occurrence is H or a substituent selected from $C_{1-20}$ hydrocarbyl and an electron withdrawing group. Preferably, the electron withdrawing group is F, Cl, Br or CN, more preferably F, Cl or CN; and

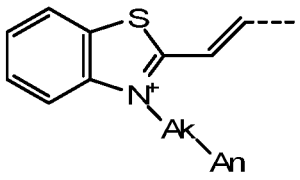
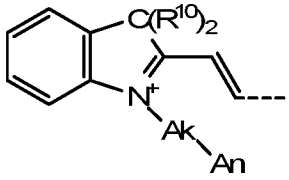
$X^{60}$ and $X^{61}$ is independently CN, $CF_3$ or $COOR^{40}$ wherein $R^{40}$ in each occurrence is H or a substituent, preferably H or a $C_{1-20}$ hydrocarbyl group. Preferably, $X^{60}$ and $X^{61}$ are each CN.

The $C_{1-20}$ hydrocarbyl group $R^{12}$ may be selected from $C_{1-20}$ alkyl; unsubstituted phenyl; and phenyl substituted with one or more $C_{1-12}$ alkyl groups.

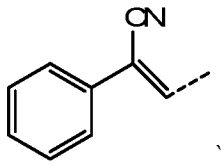
Exemplary groups of formula (IIId) include:



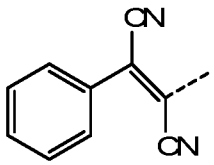
Exemplary groups of formula (IIIe) include:

An exemplary group of formula (IIIq) is:



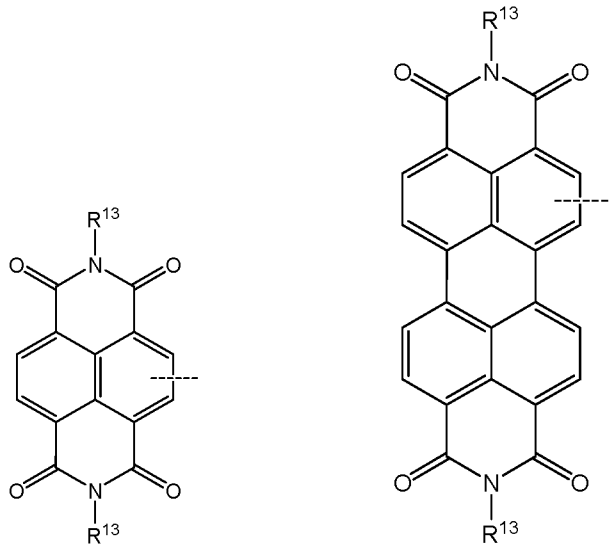
An exemplary group of formula (IIIg) is:



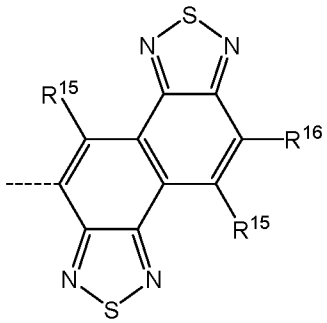
An exemplary group of formula (IIIj) is:

wherein Ak is a $C_{1-12}$ alkylene chain in which one or more C atoms may be replaced with O, S, $NR^7$, CO or COO; An is an anion, optionally $-SO_3^-$; and each benzene ring is independently unsubstituted or substituted with one or more substituents selected from substituents described with reference to $R^{10}$.

Exemplary groups of formula (IIIm) are:



An exemplary group of formula (IIIn) is:

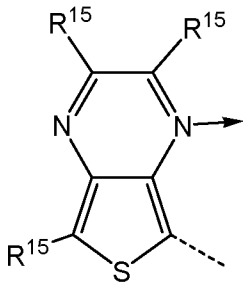
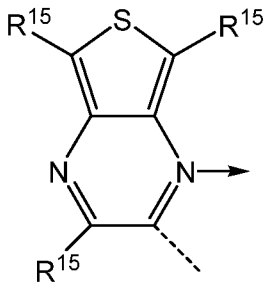
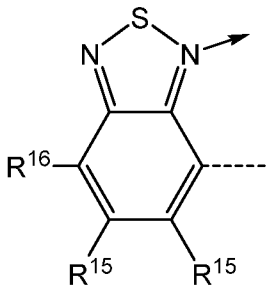


Groups of formula (IIIo) are bound directly to a bridging group $B^2$ substituted with a $-B(R^{14})_2$ wherein $R^{14}$ in each occurrence is a substituent, optionally a $C_{1-20}$ hydrocarbyl group; → is a bond to the boron atom $-B(R^{14})_2$ of $R^3$ or $R^6$; and --- is the bond to $B^2$.

Optionally, $R^{14}$ is selected from $C_{1-12}$ alkyl; unsubstituted phenyl; and phenyl substituted with one or more $C_{1-12}$ alkyl groups.

The group of formula (IIIo), the $B^2$ group and the $B(R^{14})_2$ substituent of $B^2$ may be linked together to form a 5- or 6-membered ring.

Optionally groups of formula (IIIo) are selected from:

Bridging units

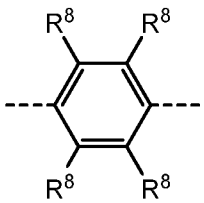
Bridging units $B^1$ and $B^2$ are preferably each selected from vinylene, arylene, heteroarylene, arylenevinylene and heteroarylenevinylene wherein the arylene and heteroarylene groups are monocyclic or bicyclic groups, each of which may be unsubstituted or substituted with one or more substituents.

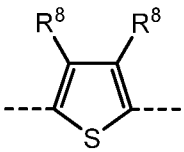
Bridging units $B^1$ and $B^2$ preferably are monocyclic or fused bicyclic arylene or heteroarylene groups, more preferably monocyclic or fused bicyclic heteroarylene groups.

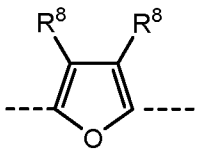
If $x^1$ and $x^2$ are each at least 1 then each $B^1$ is preferably the same.

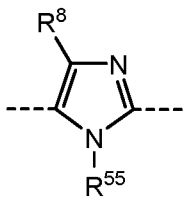
If $z^1$ and $z^2$ are each at least 1 then each $B^2$ is preferably the same.

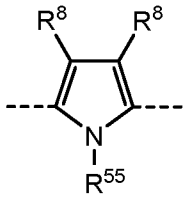
Optionally, $B^1$ and $B^2$ are independently selected from units of formulae (VIa) – (VIn):

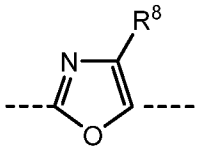

(VIa)


(VIb)


(VIc)


(VId)


(VIe)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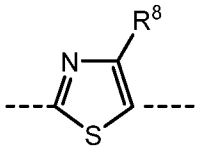
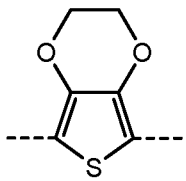
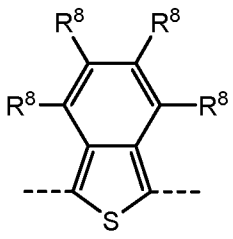
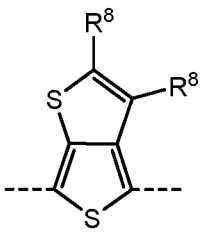

(VIg)

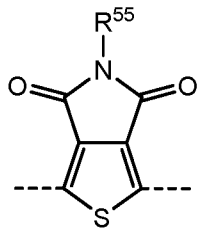

(VIh)



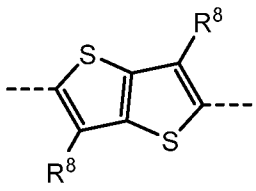
(VIi)



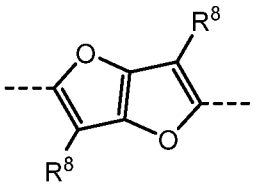
(VIj)



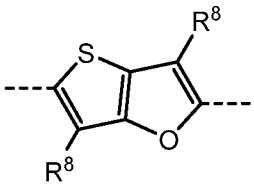
(VIk)



(VIl)



(VIm)



(VIn)

wherein $R^{55}$ is H or a substituent; $R^8$ in each occurrence is independently H or a substituent, preferably H or a substituent selected from F; CN; $NO_2$; $C_{1-20}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, COO or CO and one or more H atoms of the alkyl may be replaced with F; phenyl which is unsubstituted or substituted with one or more substituents; and $-B(R^{14})_2$ wherein $R^{14}$ in each occurrence is a substituent, optionally a $C_{1-20}$ hydrocarbyl group. $R^8$ groups of formulae (VIa), (VIb) and (VIc) may be linked to form a bicyclic ring, for example thienopyrazine.

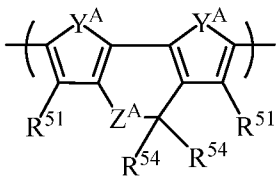
$R^8$ is preferably H, $C_{1-20}$ alkyl, $-COO-C_{1-19}$ alkyl, $C_{1-19}$ alkoxy or $C_{1-19}$ thioalkyl.

Electron-Donating Groups $D^1$ and $D^2$

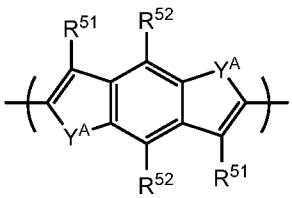
Electron-donating groups preferably are fused aromatic or heteroaromatic groups, more preferably fused heteroaromatic groups containing 3 or more rings. Particularly preferred electron-donating groups comprise fused thiophene or furan rings, optionally fused rings containing thiophene or furan rings and one or more rings selected from benzene, cyclopentadiene, tetrahydropyran, tetrahydrothiopyran and piperidine rings, each of said rings being unsubstituted or substituted with one or more substituents.

$D^1$ and $D^2$ may be the same or different. Preferably they are the same.

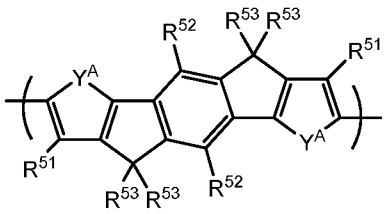
Exemplary electron-donating groups $D^1$ and $D^2$ include groups of formulae (VIIa)-(VIIp):



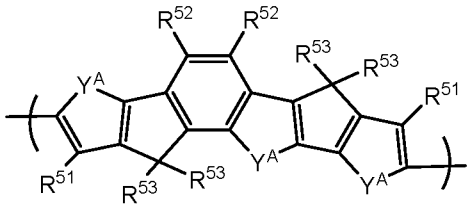
(VIIa)



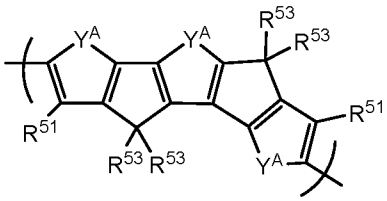
(VIIb)



(VIIc)



(VIId)



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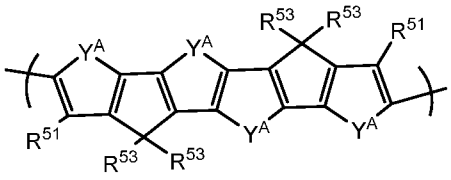

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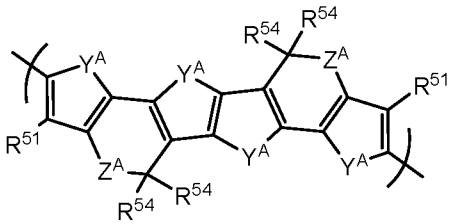
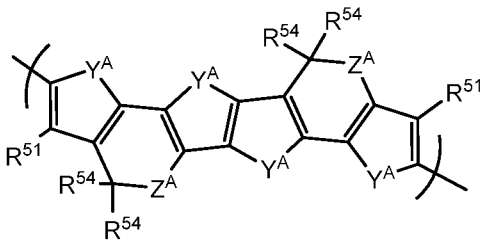
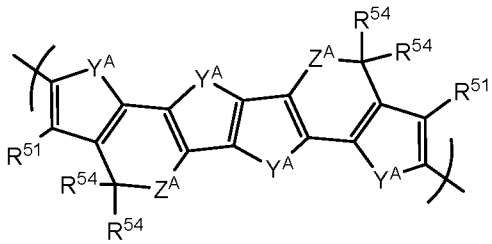
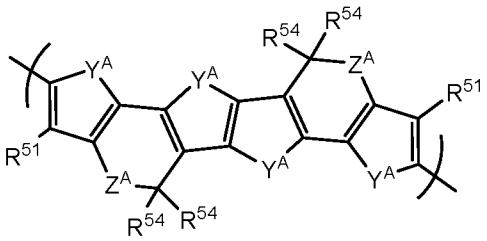


(VIIg)

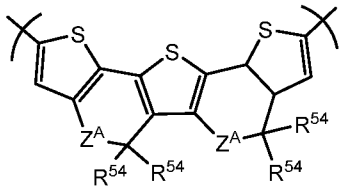




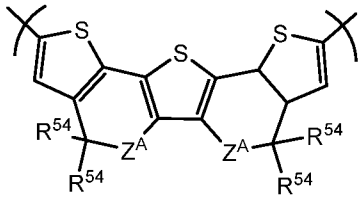
(VIIh)



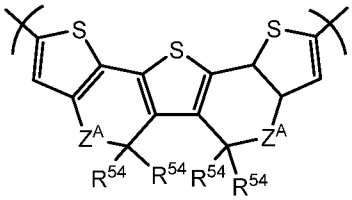
(VIIi)



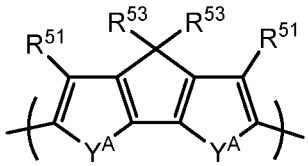
(VIIj)



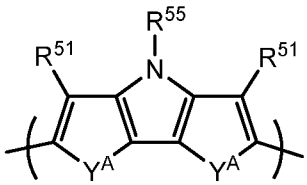
(VIIk)



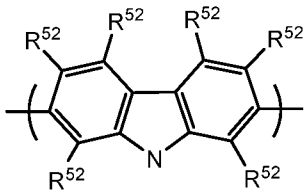
(VIIl)



(VIIm)



(VIIn)



(VIIo)

(VIIp)

wherein $Y^A$ in each occurrence is independently O, S or $NR^{55}$, $Z^A$ in each occurrence is O, CO, S, $NR^{55}$ or $C(R^{54})_2$; $R^{51}$, $R^{52}$ $R^{54}$ and $R^{55}$ independently in each occurrence is H or a substituent; and $R^{53}$ independently in each occurrence is a substituent.

Optionally, $R^{51}$ and $R^{52}$ independently in each occurrence are selected from H; F; $C_{1-20}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, COO or CO and

one or more H atoms of the alkyl may be replaced with F; and an aromatic or heteroaromatic group $Ar^3$ which is unsubstituted or substituted with one or more substituents.

In some embodiments, $Ar^3$ may be an aromatic group, e.g., phenyl.

The one or more substituents of $Ar^3$, if present, may be selected from $C_{1-12}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, COO or CO and one or more H atoms of the alkyl may be replaced with F.

Preferably, each $R^{54}$ is selected from the group consisting of:

H;

F;

linear, branched or cyclic $C_{1-20}$ alkyl wherein one or more non-adjacent C atoms may be replaced by O, S, $NR^7$, CO or COO wherein $R^7$ is a $C_{1-12}$ hydrocarbyl and one or more H atoms of the $C_{1-20}$ alkyl may be replaced with F; and

a group of formula $(Ak)u–(Ar^7)v$ wherein Ak is a $C_{1-20}$ alkylene chain in which one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, CO or COO; u is 0 or 1; $Ar^7$ in each occurrence is independently an aromatic or heteroaromatic group which is unsubstituted or substituted with one or more substituents; and v is at least 1, optionally 1, 2 or 3.

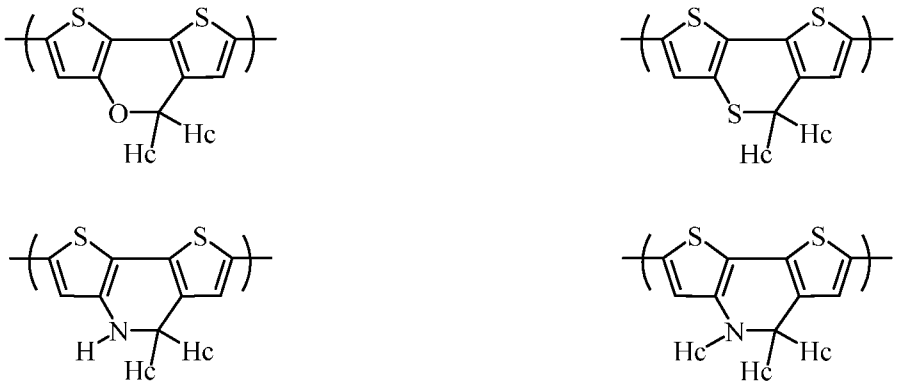
Substituents of $Ar^7$, if present, are preferably selected from F; Cl; $NO_2$; CN; and $C_{1-20}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, CO or COO and one or more H atoms may be replaced with F. Preferably, $Ar^7$ is phenyl.

Preferably, each $R^{51}$ is H.

Optionally, $R^{53}$ independently in each occurrence is selected from $C_{1-20}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, COO or CO and one or more H atoms of the alkyl may be replaced with F; and phenyl which is unsubstituted or substituted with one or more substituents, optionally one or more $C_{1-12}$ alkyl groups wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, COO or CO and one or more H atoms of the alkyl may be replaced with F.

Preferably, $R^{55}$ as described anywhere herein is H or $C_{1-30}$ hydrocarbyl group.

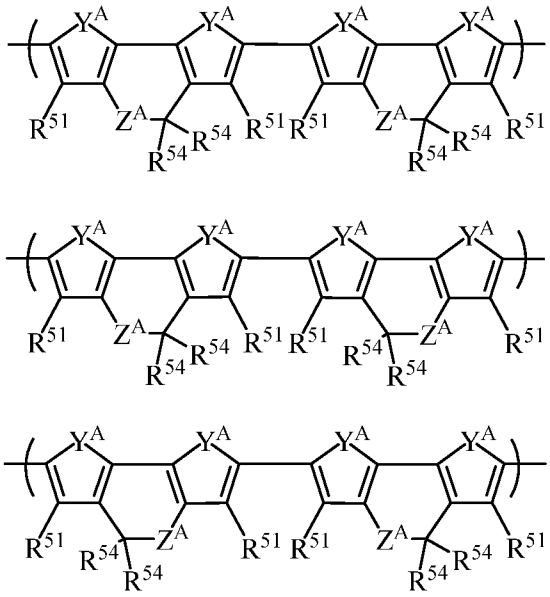
Preferably, $D^1$ and $D^2$ are each independently a group of formula (VIIa). Exemplary groups of formula (VIIa) include, without limitation:



wherein Hc in each occurrence is independently a $C_{1-20}$ hydrocarbyl group, e.g., $C_{1-20}$ alkyl, unsubstituted aryl, or aryl substituted with one or more $C_{1-12}$ alkyl groups. The aryl group is preferably phenyl.

In some embodiments, $y^1$ and $y^2$ are each 1.

In some embodiments, at least one of $y^1$ and $y^2$ is greater than 1. In these embodiments, the chain of $D^1$ and / or $D^2$ groups, respectively, may be linked in any orientation. For example, in the case where $D^1$ is a group of formula (VIIa) and $y^1$ is 2, $-[D^1]y^1$-may be selected from any of:



Electron-donating material

A bulk heterojunction layer as described herein comprises an electron-donating material and a compound of formula (I) or (X) as described herein.

Exemplary donor materials are disclosed in, for example, WO2013051676, the contents of which are incorporated herein by reference.

The electron-donating material may be a non-polymeric or polymeric material.

In a preferred embodiment the electron-donating material is an organic conjugated polymer, which can be a homopolymer or copolymer including alternating, random or block copolymers. The conjugated polymer is preferably a donor-acceptor polymer comprising alternating electron-donating repeat units and electron-accepting repeat units.

Preferred are non-crystalline or semi- crystalline conjugated organic polymers.

Further preferably the electron-donating polymer is a conjugated organic polymer with a low bandgap, typically between 2.5 eV and 1.5 eV, preferably between 2.3 eV and 1.8 eV. Optionally, the electron-donating polymer has a HOMO level no more than 5.5 eV from vacuum level. Optionally, the electron-donating polymer has a HOMO level at least 4.1 eV from vacuum level. As exemplary electron-donating polymers, polymers selected from conjugated hydrocarbon or heterocyclic polymers including polyacene, polyaniline, polyazulene, polybenzofuran, polyfluorene, polyfuran, polyindenofluorene, polyindole, polyphenylene, polypyrazoline, polypyrene, polypyridazine, polypyridine, polytriarylamine, poly(phenylene vinylene), poly(3-substituted thiophene), poly(3,4-bisubstituted thiophene), polyselenophene, poly(3-substituted selenophene), poly(3,4- bisubstituted selenophene), poly(bisthiophene), poly(terthiophene), poly(bisselenophene), poly(terselenophene), polythieno[2,3-b]thiophene, polythieno[3,2-b]thiophene, polybenzothiophene, polybenzo[1,2-b:4,5-b']dithiophene, polyisothianaphthene, poly(monosubstituted pyrrole), poly(3,4-bisubstituted pyrrole), poly-1,3,4-oxadiazoles, polyisothianaphthene, derivatives and co-polymers thereof may be mentioned.

Preferred examples of donor polymers are copolymers of polyfluorenes and polythiophenes, each of which may be substituted, and polymers comprising benzothiadiazole-based and thiophene-based repeating units, each of which may be substituted.

A particularly preferred donor polymer comprises donor unit (VIIa) provided as a repeat unit of the polymer, most preferably with an electron-accepting repeat unit, for example divalent electron-accepting units as described herein provided as polymeric repeat units.

Additional Electron-Accepting Materials

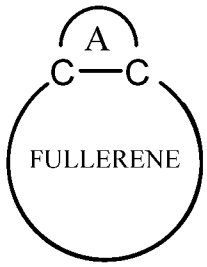
In some embodiments, the compound of formula (I) or (X) as described herein is the only electron-accepting material of a bulk heterojunction layer.

In some embodiments, the bulk heterojunction layer contains a compound of formula (I) or (X) and one or more further electron-accepting materials. The one or more further electron-accepting materials may be selected from non-fullerene acceptors and fullerenes.

Non-fullerene acceptors are described in, for example, Cheng et. al., "Next-generation organic photovoltaics based on non-fullerene acceptors", Nature Photonics volume 12, pages 131–142 (2018), the contents of which are incorporated herein by reference, and which include, without limitation, PDI, ITIC, ITIC, IEICO and derivatives thereof, e.g., fluorinated derivatives thereof such as ITIC-4F and IEICO-4F.

Exemplary fullerene electron-accepting compounds are $C_{60}$, $C_{70}$, $C_{76}$, $C_{78}$ and $C_{84}$ fullerenes or a derivative thereof, including, without limitation, PCBM-type fullerene derivatives including phenyl-$C_{61}$-butyric acid methyl ester ($C_{60}$PCBM), TCBM-type fullerene derivatives (e.g. tolyl-$C_{61}$-butyric acid methyl ester ($C_{60}$TCBM)), and ThCBM-type fullerene derivatives (e.g. thienyl-$C_{61}$-butyric acid methyl ester ($C_{60}$ThCBM).

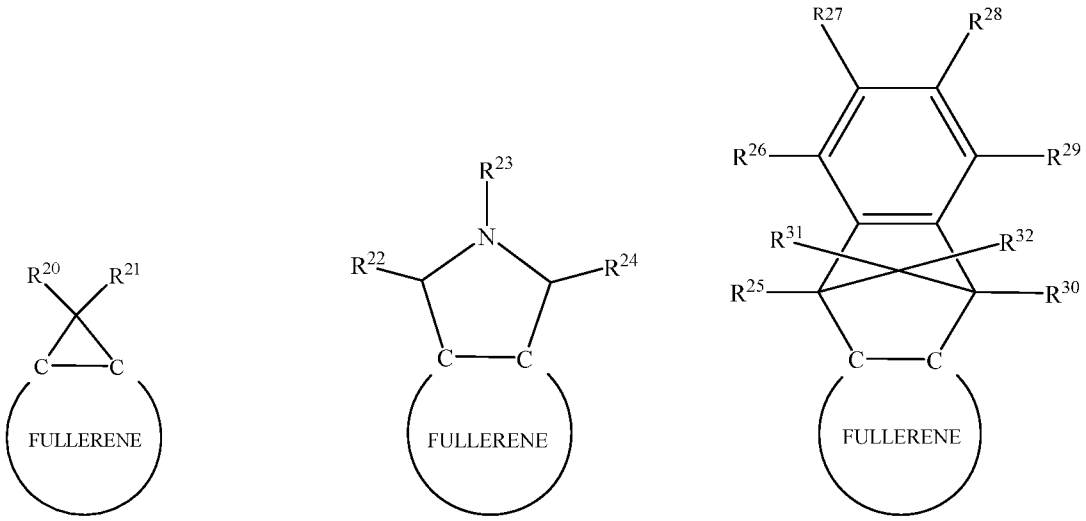
Fullerene derivatives may have formula (V):




(V)

wherein A, together with the C-C group of the fullerene, forms a monocyclic or fused ring group which may be unsubstituted or substituted with one or more substituents.

Exemplary fullerene derivatives include formulae (Va), (Vb) and (Vc):




(Va) (Vb) (Vc)

wherein $R^{20}$–$R^{32}$ are each independently H or a substituent.

Substituents $R^{20}$-$R^{32}$ are optionally and independently in each occurrence selected from the group consisting of aryl or heteroaryl, optionally phenyl, which may be unsubstituted or substituted with one or more substituents; and $C_{1-20}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, CO or COO and one or more H atoms may be replaced with F.

Substituents of aryl or heteroaryl, where present, are optionally selected from $C_{1-12}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, $NR^7$, CO or COO and one or more H atoms may be replaced with F.

Formulations

The bulk heterojunction layer may be formed by any process including, without limitation, thermal evaporation and solution deposition methods.

Preferably, the bulk heterojunction layer is formed by depositing a formulation comprising the electron-donating material(s), the electron-accepting material(s) and any other components of the bulk heterojunction layer dissolved or dispersed in a solvent or a mixture of two or more solvents. The formulation may be deposited by any coating or printing

method including, without limitation, spin-coating, dip-coating, roll-coating, spray coating, doctor blade coating, wire bar coating, slit coating, ink jet printing, screen printing, gravure printing and flexographic printing.

The one or more solvents of the formulation may optionally comprise or consist of benzene substituted with one or more substituents selected from chlorine, $C_{1-10}$ alkyl and $C_{1-10}$ alkoxy wherein two or more substituents may be linked to form a ring which may be unsubstituted or substituted with one or more $C_{1-6}$ alkyl groups, optionally toluene, xylenes, trimethylbenzenes, tetramethylbenzenes, anisole, indane and its alkyl-substituted derivatives, and tetralin and its alkyl-substituted derivatives.

The formulation may comprise a mixture of two or more solvents, preferably a mixture comprising at least one benzene substituted with one or more substituents as described above and one or more further solvents. The one or more further solvents may be selected from esters, optionally alkyl or aryl esters of alkyl or aryl carboxylic acids, optionally a $C_{1-10}$ alkyl benzoate, benzyl benzoate or dimethoxybenzene. In preferred embodiments, a mixture of trimethylbenzene and benzyl benzoate is used as the solvent. In other preferred embodiments, a mixture of trimethylbenzene and dimethoxybenzene is used as the solvent.

The formulation may comprise further components in addition to the electron-accepting material, the electron-donating material and the one or more solvents. As examples of such components, adhesive agents, defoaming agents, deaerators, viscosity enhancers, diluents, auxiliaries, flow improvers colourants, dyes or pigments, sensitizers, stabilizers, nanoparticles, surface-active compounds, lubricating agents, wetting agents, dispersing agents and inhibitors may be mentioned.

Organic Electronic Device

A polymer or composition as described herein may be provided as an active layer of an organic electronic device. In a preferred embodiment, a bulk heterojunction layer of an organic photoresponsive device, more preferably an organic photodetector, comprises a composition as described herein.

Figure 1 illustrates an organic photoresponsive device according to some embodiments of the present disclosure. The organic photoresponsive device comprises a cathode 103, an anode 107 and a bulk heterojunction layer 105 disposed between the anode and the cathode. The

organic photoresponsive device may be supported on a substrate 101, optionally a glass or plastic substrate.

Each of the anode and cathode may independently be a single conductive layer or may comprise a plurality of layers.

At least one of the anode and cathode is transparent so that light incident on the device may reach the bulk heterojunction layer. In some embodiments, both of the anode and cathode are transparent. The transmittance of a transparent electrode may be selected according to an emission wavelength of a light source for use with the organic photodetector.

Figure 1 illustrates an arrangement in which the cathode is disposed between the substrate and the anode. In other embodiments, the anode may be disposed between the cathode and the substrate.

The organic photoresponsive device may comprise layers other than the anode, cathode and bulk heterojunction layer shown in Figure 1. In some embodiments, a hole-transporting layer is disposed between the anode and the bulk heterojunction layer. In some embodiments, an electron-transporting layer is disposed between the cathode and the bulk heterojunction layer. In some embodiments, a work function modification layer is disposed between the bulk heterojunction layer and the anode, and/or between the bulk heterojunction layer and the cathode.

The area of the OPD may be less than about 3 $cm^2$, less than about 2 $cm^2$, less than about 1 $cm^2$, less than about 0.75 $cm^2$, less than about 0.5 $cm^2$ or less than about 0.25 $cm^2$. Optionally, each OPD may be part of an OPD array wherein each OPD is a pixel of the array having an area as described herein, optionally an area of less than 1 $mm^2$, optionally in the range of 0.5 $micron^2$ – 900 $micron^2$.

The substrate may be, without limitation, a glass or plastic substrate. The substrate can be an inorganic semiconductor. In some embodiments, the substrate may be silicon. For example, the substrate can be a wafer of silicon. The substrate is transparent if, in use, incident light is to be transmitted through the substrate and the electrode supported by the substrate.

The bulk heterojunction layer contains a polymer as described herein and an electron-accepting compound. The bulk heterojunction layer may consist of these materials or may

comprise one or more further materials, for example one or more further electron-donating materials and / or one or more further electron-accepting compounds.

Applications

A circuit may comprise the OPD connected to a voltage source for applying a reverse bias to the device and / or a device configured to measure photocurrent. The voltage applied to the photodetector may be variable. In some embodiments, the photodetector may be continuously biased when in use.

In some embodiments, a photodetector system comprises a plurality of photodetectors as described herein, such as an image sensor of a camera.

In some embodiments, a sensor may comprise an OPD as described herein and a light source wherein the OPD is configured to receive light emitted from the light source. In some embodiments, the light source has a peak wavelength of at least 900 nm or at least 1000 nm, optionally in the range of 1000-1500 nm.

The present inventors have found that a material comprising an electron-accepting unit of formula (I) may be used for the detection of light at longer wavelengths, particularly 1300-1400 nm.

In some embodiments, the light from the light source may or may not be changed before reaching the OPD. For example, the light may be reflected, filtered, down-converted or up-converted before it reaches the OPD.

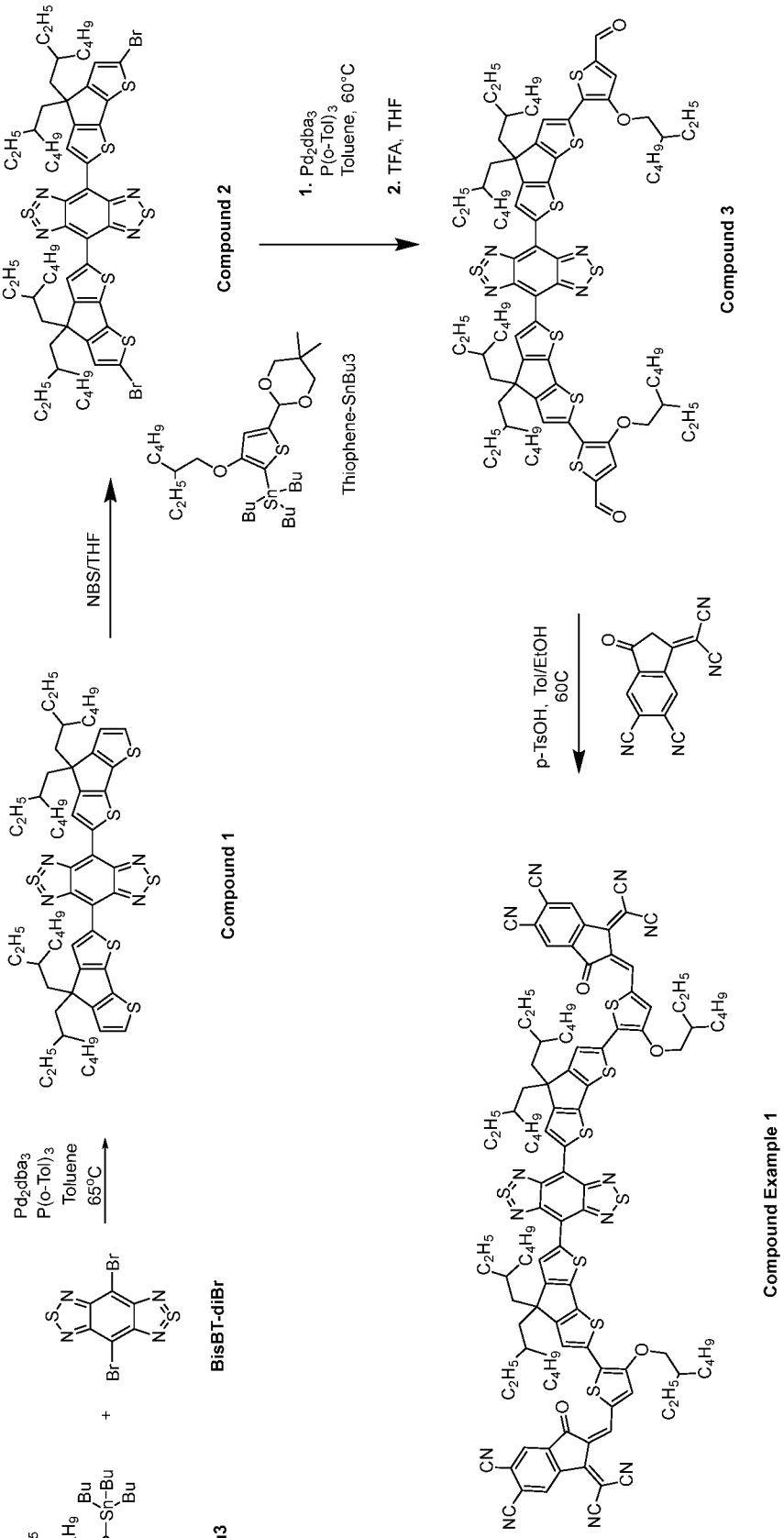
The organic photoresponsive device as described herein may be an organic photovoltaic device or an organic photodetector. An organic photodetector as described herein may be used in a wide range of applications including, without limitation, detecting the presence and / or brightness of ambient light and in a sensor comprising the organic photodetector and a light source. The photodetector may be configured such that light emitted from the light source is incident on the photodetector and changes in wavelength and/or brightness of the light may be detected, e.g., due to absorption by, reflection by and/or emission of light from an object, e.g. a target material in a sample disposed in a light path between the light source and the organic photodetector. The sample may be a non-biological sample, e.g. a water sample, or a biological sample taken from a human or animal subject. The sensor may be,

without limitation, a gas sensor, a biosensor, an X-ray imaging device, an image sensor such as a camera image sensor, a motion sensor (for example for use in security applications) a proximity sensor or a fingerprint sensor. A 1D or 2D photosensor array may comprise a plurality of photodetectors as described herein in an image sensor. The photodetector may be configured to detect light emitted from a target analyte which emits light upon irradiation by the light source or which is bound to a luminescent tag which emits light upon irradiation by the light source. The photodetector may be configured to detect a wavelength of light emitted by the target analyte or a luminescent tag bound thereto.

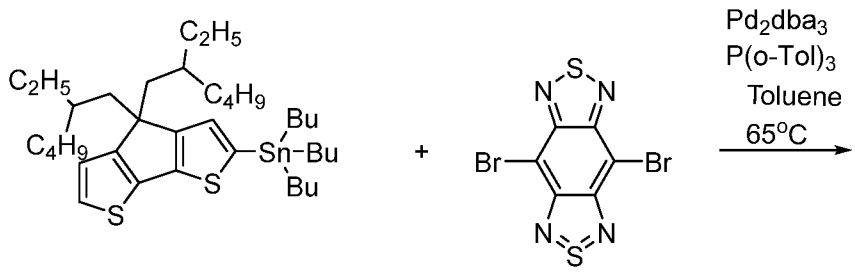
## EXAMPLES

Compound Example 1

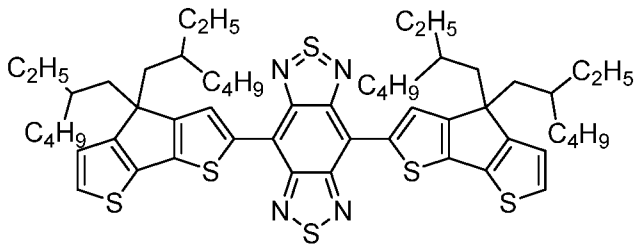
Compound Example 1 was prepared according to the following reaction scheme:


CPDT-SnBu3
BisBT-diBr
Pd2dba3
P(o-Tol)3
Toluene
65°C
Compound 1
NBS/THF
Compound 2
Thiophene-SnBu3
1. Pd2dba3
P(o-Tol)3
Toluene, 60°C
2. TFA, THF
Compound 3
p-TsOH, Tol/EtOH
60C
Compound Example 1

*Synthesis of Compound 1*



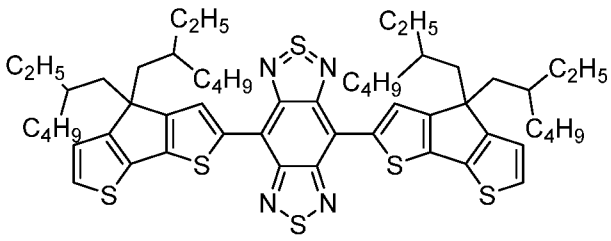

**CPDT-SnBu3** **BisBT-diBr**



**Compound 1**

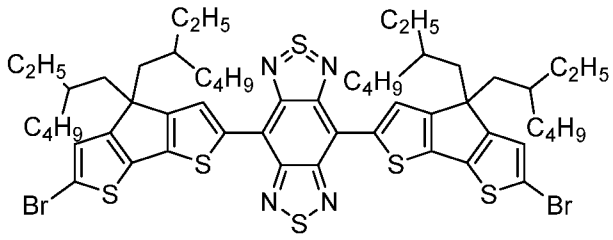
Toluene (60 ml) was added to CPDT-$SnBu_3$ (4.84 g, 7.00 mmol) and BisBT-diBr (1.15 g, 3.26 mmol) under nitrogen. The mixture was degassed for 15 minutes and tris(2-methylphenyl)phosphine (0.30 g, 0.98 mmol) and tris(dibenzylideneacetone) dipalladium (0.24 g, 0.26 mmol) were added and the mixture was degassed for additional 5 minutes. The mixture was heated at 70 °C for 30 minutes and then at 100 °C overnight. Upon completion, solvent was removed on a rotary evaporator and purification by column chromatography (silica gel; heptane/toluene)gave **Compound 1 (**2.37 g) as a dark brown oil.

*Synthesis of Compound 2*



**Compound 1**

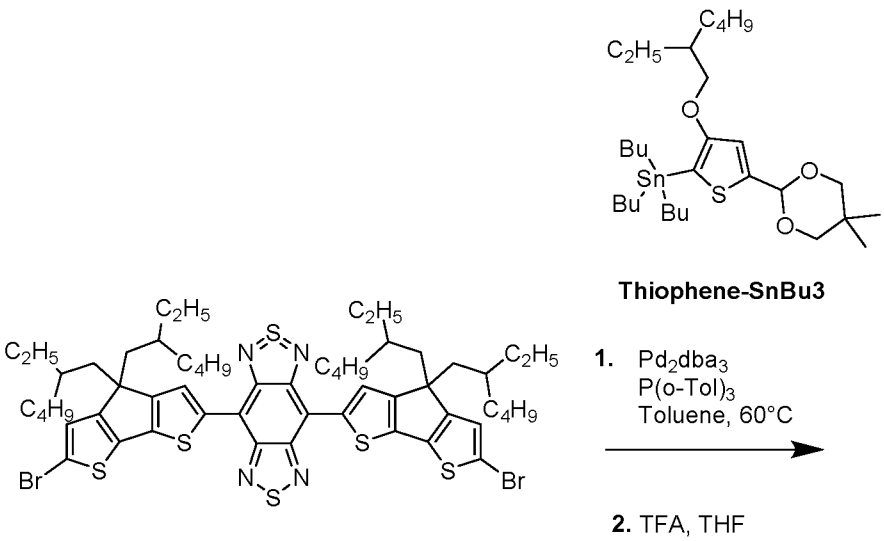
NBS/THF



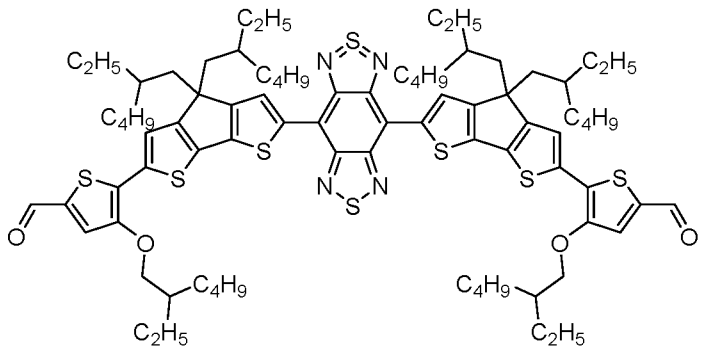
**Compound 2**

A solution of **Compound 1** (0.5 g, 0.50 mmol) in THF (5 ml) and cooled to -40 °C and N-bromosuccinimide (0.18 g, 1 mmol) was added portion-wise. The mixture was stirred at this temperature for 4.5 hours and quenched with 10 % sodium thiosulfate solution, extracted with heptane, dried over magnesium sulphate, and evaporated to give **Compound 2** as a black oil.

*Synthesis of Compound 3*



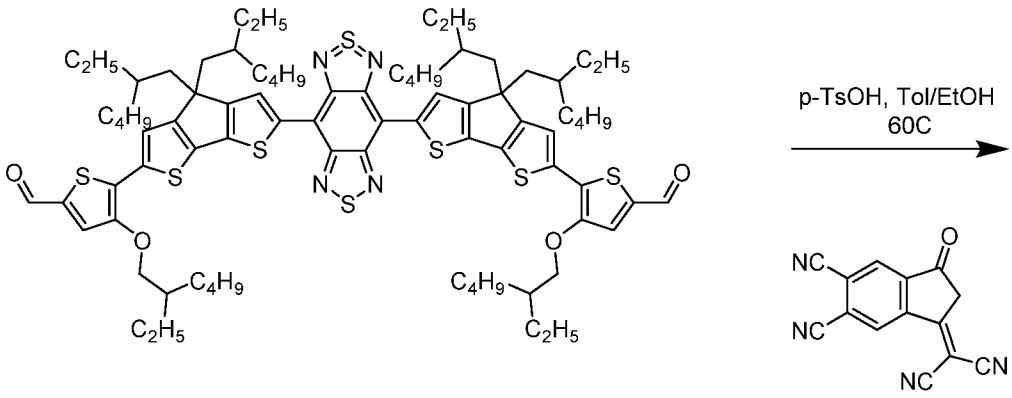

Compound 2



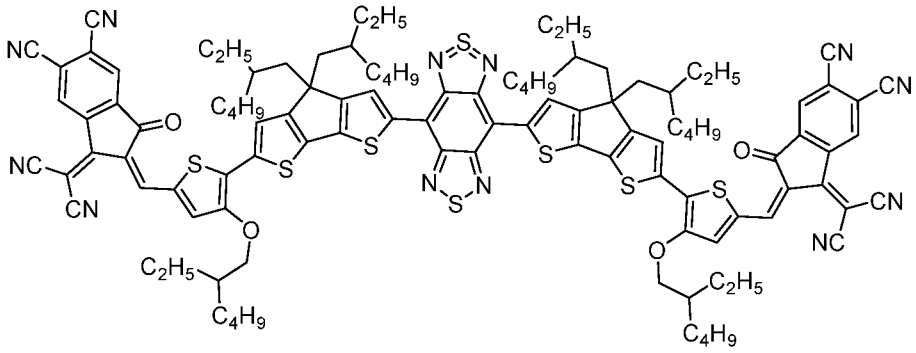
Compound 3

A solution of **Compound 2** (0.53 g, 0.46 mmol) and **Thiophene-SnBu3** (1.03 g, 1.67 mmol) in toluene (9 ml) was degassed for 15 minutes. Tris(2-methylphenyl)phosphine (0.04 g, 0.14 mmol) and tris(dibenzylideneacetone) dipalladium (0.03 g, 0.04 mmol) were added and the mixture was degassed for additional 5 minutes. The mixture was heated at 70 °C for 30min and then at 100 °C overnight. Upon completion it was diluted with toluene and extracted with water. The organic phase was placed in a flask,trifluoroacetic acid (4 ml) was added, and it was stirred for 30 minutes at room temperature and then at 40 °C for another 30 minutes. The reaction mixture was cooled to room temperature, water (10 ml) was added followed by a saturated solution of sodium hydrogen carbonate, it was transferred to separating funnel and further extracted with this solution. The organic phase was dried over magnesium sulphate, filtered and concentrated under vaccum to give a purple oil. Purification via column chromatography (silca-gel; heptane/toluene)gave **Compound 3** (0.25 g) as a purple solid.

*Synthesis of Compound 4*




**Compound 3** **IC2CN**



**Compound Example 1**

**Compound 3** (0.25 g, 0.17 mmol), **IC2CN** (0.21 g, 0.83 mmol) and para-toluenesulfonic acid (0.24 g, 1.24 mmol) were placed in a flask, toluene (6 ml) and ethanol (8 ml) were added, and the mixture was degassed for 15 minutes with nitrogen and heated at 70 °C overnight. After this time the mixture was filtered and the resulting solid was washed with hot ethanol, methanol and pentane. Purification via column chromatography (silica gel; toluene DCM and THF) gave **Compound Example 1** (0.07 g).

$^1$H NMR (300 MHz, THF-$d_8$): δ 9.28 (s, 2H), 8.98 (s,2H), 8.79 (s, 2H), 8.35 (s,2H), 7.97 (t, 2H), 7.83 (s, 2H), 4.35 (d, 4.7Hz, 4H), 2.22 (m, 8H), 1.96 (m, 2H), 1.49-1.44 (m, 9H), 1.12-0.93 (m, 54H), 0.75-0.60 (m, 27H).

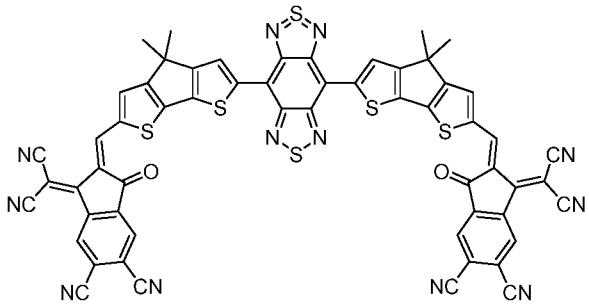
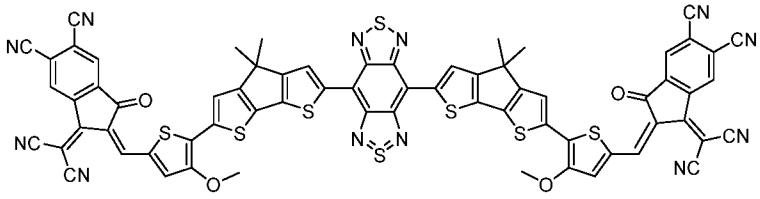
LCMS (APCI+ve): 1924.91 ([M+H]+).

Band gap and absorption spectra

Figure 2 shows the absorption spectra for Compound Example 1 and an unbridged comparative compound illustrated in Table 1 in o-dichlorobenzene solution.

With reference to Table 1, Compound Example 2 has a smaller HOMO-LUMO band gap as measured by square wave voltammetry than the Comparative Compound.

Table 1

| Structure | HOMO / eV | LUMO / eV | Eg / eV |
|---|---|---|---|
|  Comparative Compound | -5.41 | -4.15 | 1.26 |
|  Compound Example 2 | 5.13 | 4.10 | 1.03 |

Device Example 1

A device having the following structure was prepared:

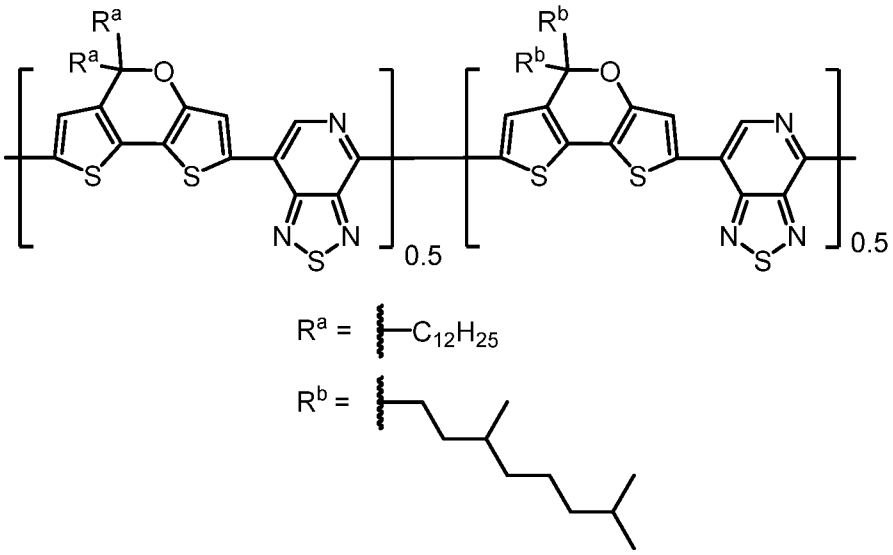
Cathode / Donor : Acceptor layer / Anode

A glass substrate coated with a layer of indium-tin oxide (ITO) was treated with polyethyleneimine (PEIE) to modify the work function of the ITO.

A mixture of a donor polymer and Compound Example 1 (acceptor) in a donor : acceptor mas ratio of 1:0.8 was deposited over the modified ITO layer by bar coating from a 15 mg / ml solution in o-dichlorobenzene. The film was dried at 80°C to form a ca. 500 nm thick bulk heterojunction layer

An anode stack of $MoO_3$ (10 nm) and ITO (50 nm) was formed over the bulk heterojunction by thermal evaporation ($MoO_3$) and sputtering (ITO).

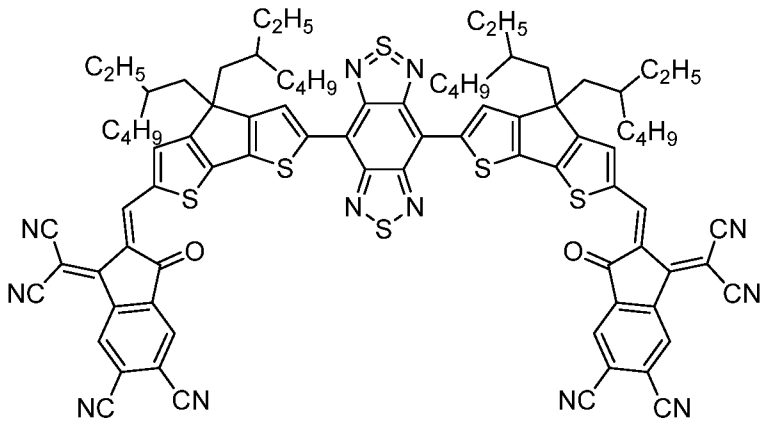
The donor polymer, shown below, has a donor repeat unit of formula (VIIa) and an acceptor repeat unit. The donor polymer may be prepared as described in WO2013/051676, the contents of which are incorporated herein by reference.




Donor Polymer 1

Comparative Device 1

For the purpose of comparison, Comparative Device 1 was prepared as described for Device Example 1 except that Comparative Compound 1 was used in placed of Compound Example 1 and the donor polymer / Comparative Compound 1 mixture was deposited from 1,2,4 Trimethylbenzene:methylbenzoate 50:50 v/v solvent mixture:



Comparative Compound 1

With reference to Figure 3, the exernal quantum efficiency of Device Example 1 is higher than that of Comparative Device at around 1400-1700 nm.

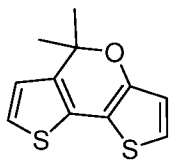
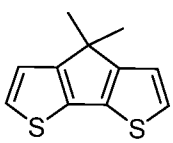
Dark current densities for Device Example 1 and Comparative Device 1 are shown in Figure 4.

Modelling Examples

All modelling as described in these examples was performed using Gaussian09 software available from Gaussian using Gaussian09 with B3LYP (functional).

HOMO and LUMO levels were modelled for individual donor and acceptor units. Results are set out in Tables 2-4

Table 2

| Donor units $D^1$, $D^2$ | HOMO / eV | LUMO / eV |
|---|---|---|
|  | -5.08 | -1.09 |
|  | -5.18 | -1.01 |

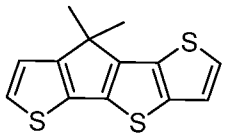
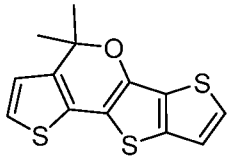
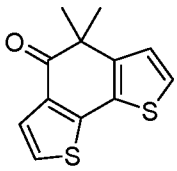
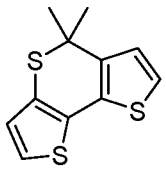
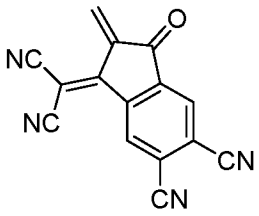
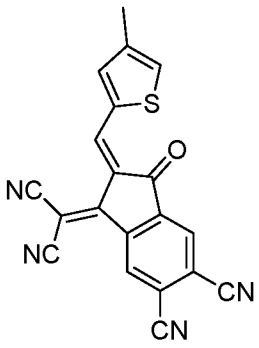
| | | |
|---|---|---|
|  | -5.06 | -1.25 |
|  | -4.97 | -1.32 |
|  | -5.74 | -1.87 |
|  | -5.27 | -1.33 |

Table 3

| Acceptor units $A^2$, $A^3$ | HOMO / eV | LUMO / eV |
|---|---|---|
|  | -7.95 | -4.23 |
|  | -6.32 | -3.34 |

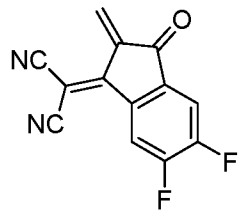
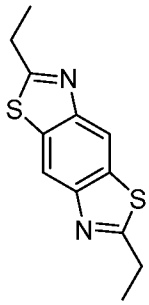
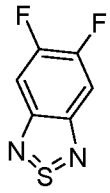
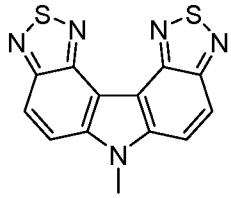
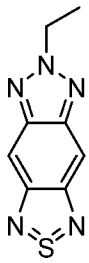
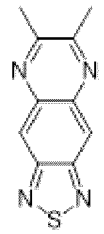
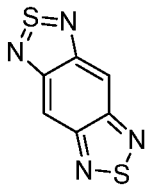
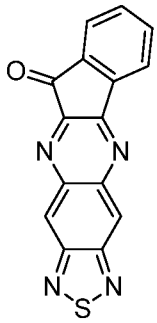
| | | |
|---|---|---|
|  | -7.39 | -3.57 |

Table 4

| Acceptor Unit A[1] | HOMO / eV | LUMO / eV |
|---|---|---|
|  | -6.02 | -1.25 |
|  | -6.95 | -2.60 |
|  | -5.72 | -2.15 |
|  | -5.80 | -2.82 |

| | | |
|---|---|---|
|  | -6.17 | -2.93 |
|  | -6.20 | -3.56 |
|  | -6.44 | -3.36 |

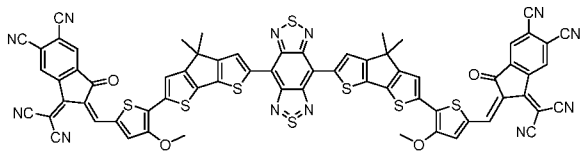
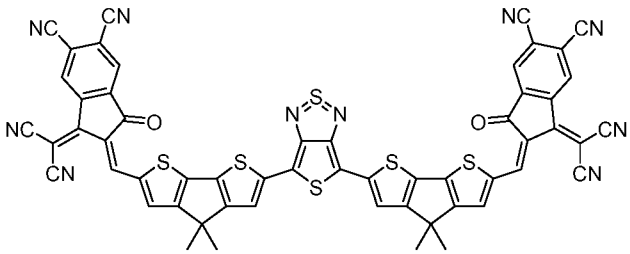
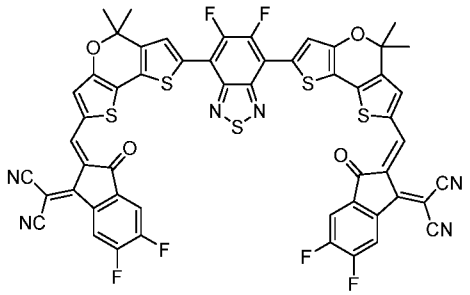
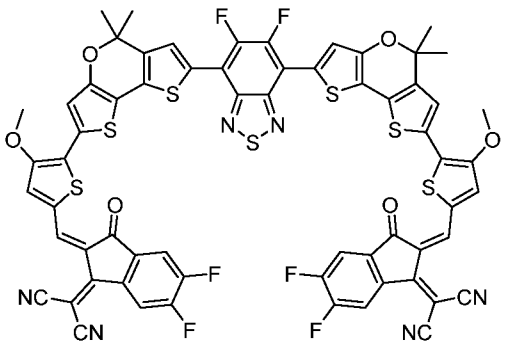
Acceptor units $A^1$ preferably have a modelled LUMO of at least 2.9 eV or at least 3.0 eV from vacuum level.

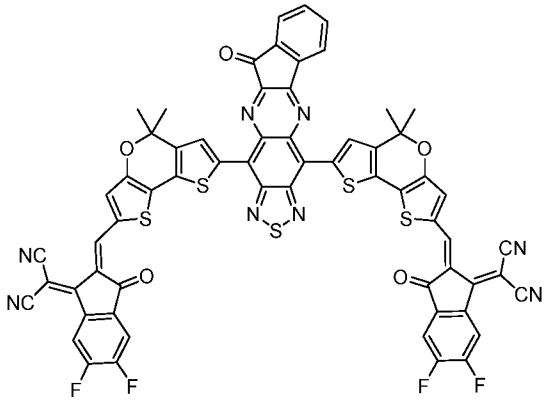
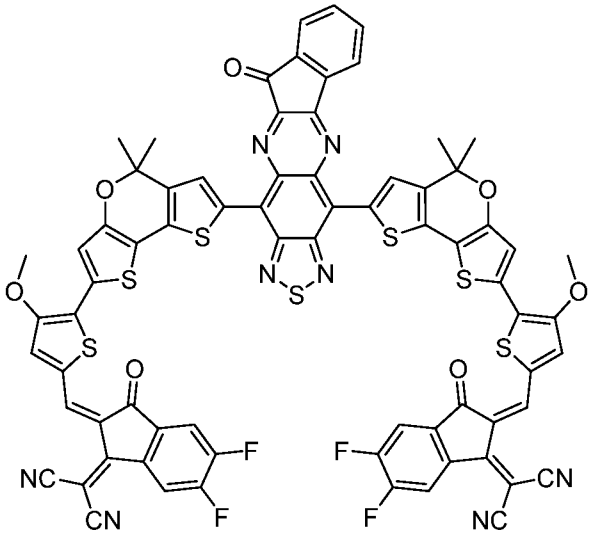
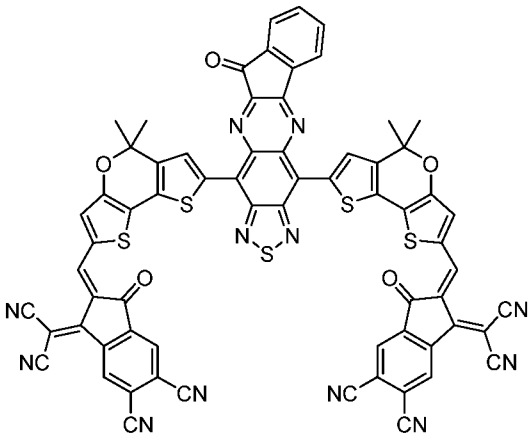
HOMO and LUMO levels were modelled for compounds of formula (I) in which there is no bridge between $A^2$ and $D^1$ ($z^1$=0) or between $A^3$ and $D^2$ ($z^2$=0).

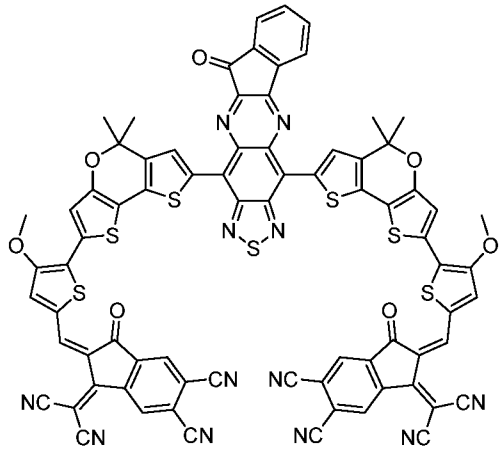
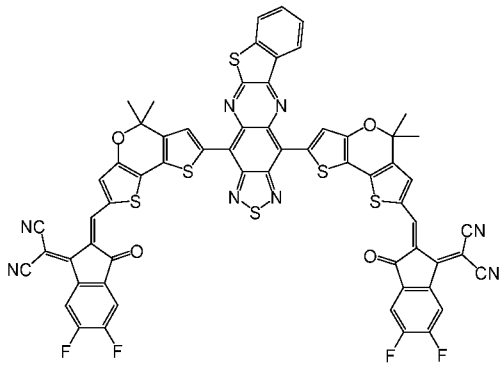
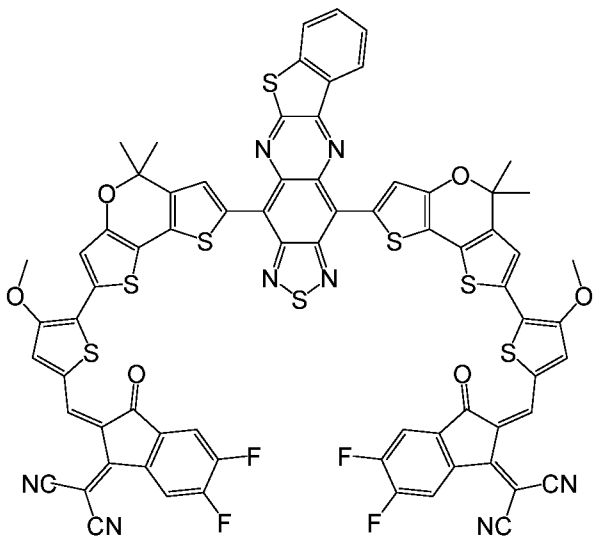
Results are set out in Table 5. S1f corresponds to oscillator strength of the transition from S1 (predicting absorption intensity), Eopt is the modelled optical gap.

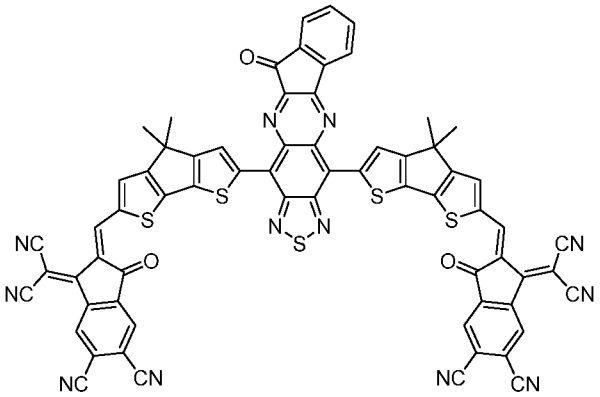
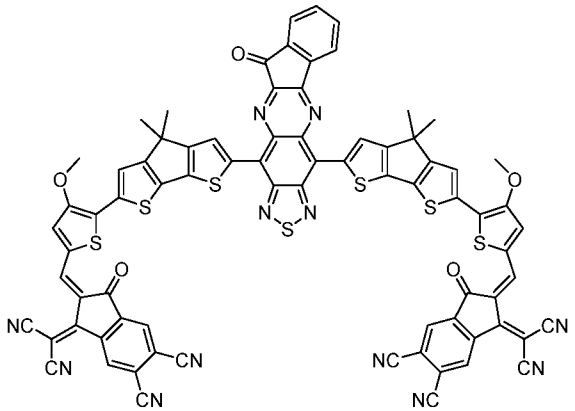
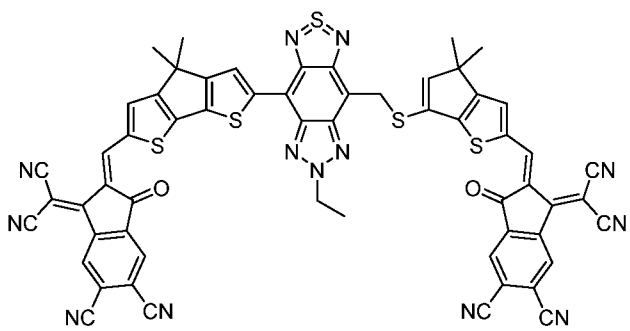
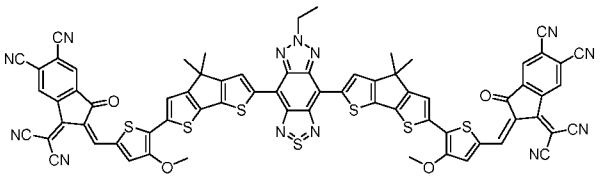
As shown above, Compound Example 1 has a smaller band gap, as measured by square wave voltammetry, than Comparative Compound 1. As shown in the first two entries of Table 5, this smaller band gap is also observed in the modelled energy levels for the corresponding model compounds, which differ from Compound Example 1 and Comparative Compound 1 only in that alkyl groups are methyl for simplicity of calculation. This is indicative of the accuracy of the model.

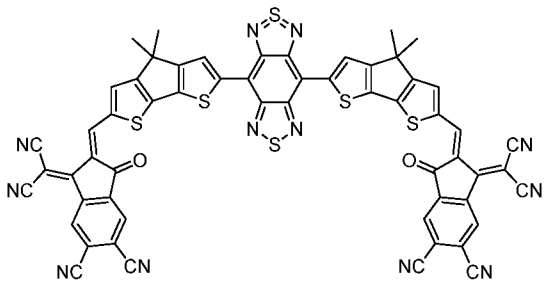
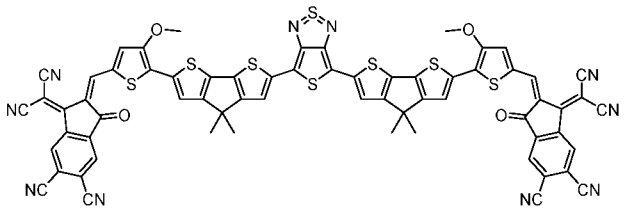
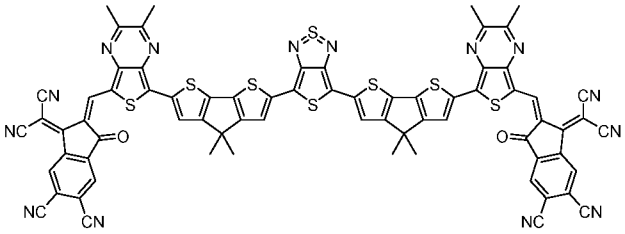
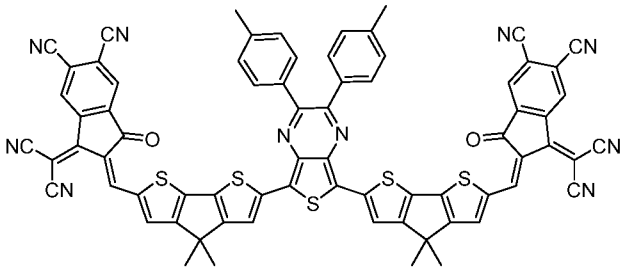
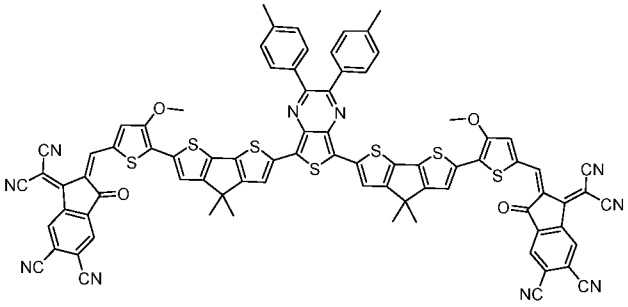
Table 5

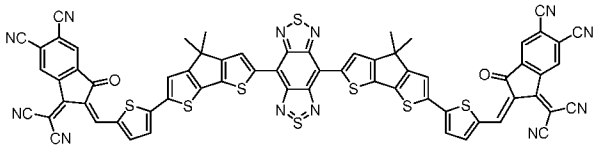
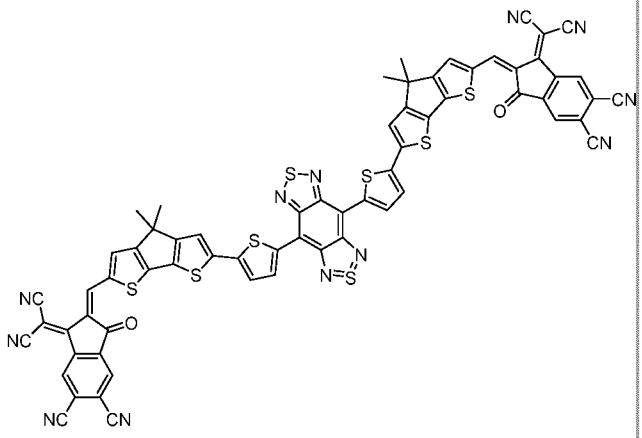
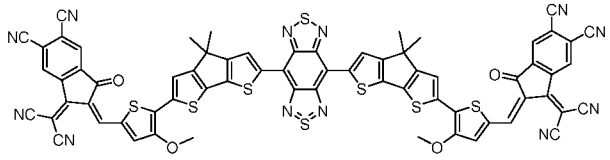
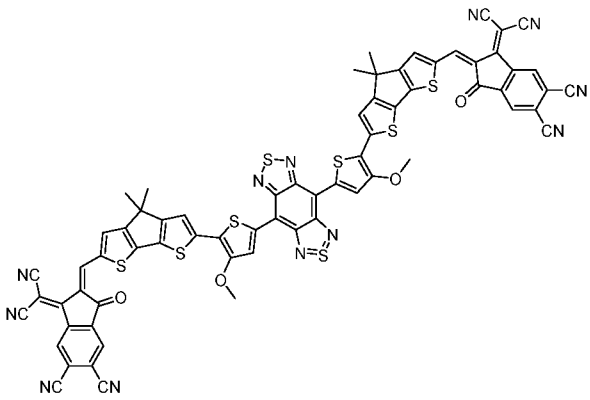
| Structure | HOMO / eV | LUMO / eV | Eg / nm | S1f | Eopt/ nm |
|---|---|---|---|---|---|
|  | -5.10 | -4.23 | 1424 | 2.32 | 1430 |
|  Comparative Compound | -5.59 | -4.35 | 1002 | 2.42 | 1025 |
|  Comparative Compound | -5.49 | -3.74 | 708 | 2.11 | 802 |
|  Comparative Compound | -5.02 | -3.51 | 821 | 2.03 | 937 |

| | | | | | |
|---|---|---|---|---|---|
|  Comparative Compound | -5.31 | -4.09 | 1016 | 1.08 | 1153 |
|  | -4.84 | -3.78 | 1165 | 1.23 | 1329 |
|  Comparative Compound | -5.62 | -4.38 | 1000 | 1.32 | 1123 |

| | | | | | |
|---|---|---|---|---|---|
|  | -5.11 | -4.05 | 1180 | 1.41 | 1327 |
|  | -5.25 | -4.02 | 1008 | 1.26 | 1119 |
|  | -5.08 | -3.61 | 1037 | 0.66 | 1238 |

| | | | | | |
|---|---|---|---|---|---|
|  Comparative Compound | -5.70 | -4.39 | 946 | 1.58 | 1062 |
|  | -5.18 | -4.08 | 1129 | 1.86 | 1129 |
|  Comparative Compound | -5.56 | -4.27 | 960 | 2.52 | 995 |
|  | -5.06 | -3.98 | 1155 | 3.62 | 1182 |

| | | | | | |
|---|---|---|---|---|---|
|  Comparative Compound | -5.63 | -4.57 | 1173 | 1.60 | 1209 |
|  | -5.07 | -4.03 | 1201 | 3.25 | 1217 |
|  | -5.20 | -4.19 | 1230 | 3.27 | 1238 |
|  Comparative Compound | -5.51 | -4.03 | 838 | 2.96 | 896 |
|  | -5.04 | -3.82 | 1016 | 3.55 | 1081 |

| | | | | | |
|---|---|---|---|---|---|
|  | -5.28 | -4.31 | 1280 | 2.16 | 1337 |
|  | -5.41 | -4.34 | 1168 | 2.08 | 1263 |
|  | -5.10 | -4.23 | 1424 | 2.32 | 1430 |
|  | -5.26 | -4.38 | 1419 | 1.97 | 1448 |

The effect of different bridging groups is illustrated in Table 6.

Table 6

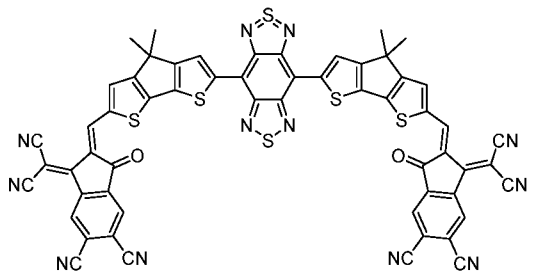
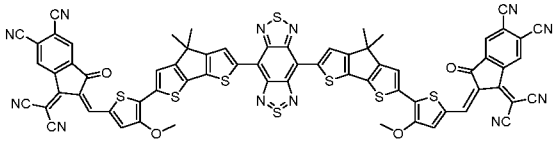
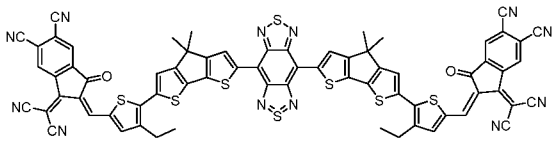
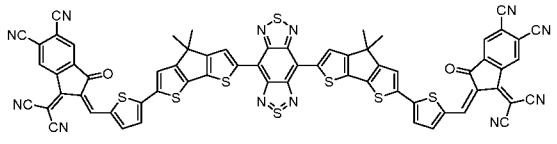
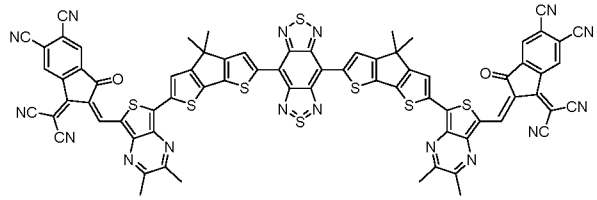
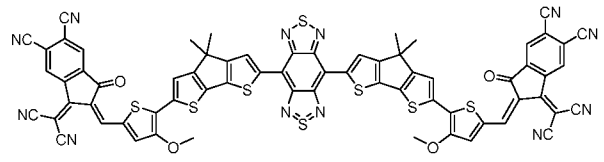
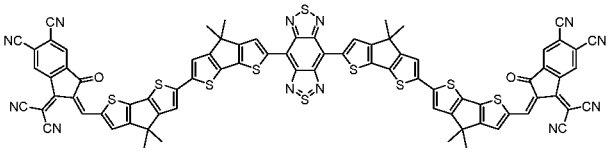
| Structure | HOMO / eV | LUMO / eV | Eg / nm | S1f | Eopt / nm |
|---|---|---|---|---|---|
|  | -5.63 | -4.57 | 1173 | 1.60 | 1209 |
|  | -5.10 | -4.23 | 1424 | 2.32 | 1430 |
|  | -5.21 | -4.26 | 1314 | 2.17 | 1367 |
|  | -5.28 | -4.31 | 1280 | 2.16 | 1337 |
|  | -5.23 | -4.38 | 1459 | 2.37 | 1450 |

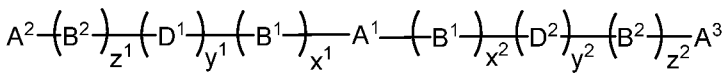
Table 7 compares a compound having a bridge and a donor group between acceptor groups and two donor groups between acceptor groups. Although band gaps are similar, the HOMO of the compound containing two donor groups is considerably shallower, which can be expected to result in lower compound stability.

Table 7

| Structure | HOMO / eV | LUMO /eV | Eg / nm | S1f | Eopt / nm |
|---|---|---|---|---|---|
|  | -5.10 | -4.23 | 1424 | 2.32 | 1430 |
|  Comparative Compound | -5.03 | -4.10 | 1347 | 2.61 | 1438 |

## CLAIMS

1. A compound of formula (I):



(I)

wherein:

$A^1$ is a divalent heteroaromatic electron-accepting group;

$A^2$ and $A^3$ are each independently a monovalent electron-accepting group;

$D^1$ and $D^2$ independently in each occurrence is an electron-donating group;

$B^1$ and $B^2$ independently in each occurrence is a bridging group;

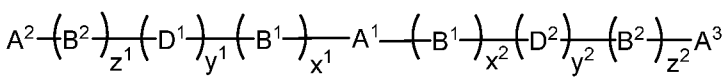
$x^1$ and $x^2$ are each independently 0, 1, 2 or 3;

$y^1$ and $y^2$ are each independently at least 1; and

$z^1$ and $z^2$ are each independently 0, 1, 2 or 3,

with the proviso that at least one of $z^1$ and $z^2$ is at least 1.

2. A compound of formula (I):



(I)

wherein:

$A^1$ is a divalent heteroaromatic electron-accepting group comprising at least 3 fused rings;

$A^2$ and $A^3$ are each independently a monovalent electron-accepting group;

$D^1$ and $D^2$ independently in each occurrence is an electron-donating group;

$B^1$ and $B^2$ independently in each occurrence is a bridging group;

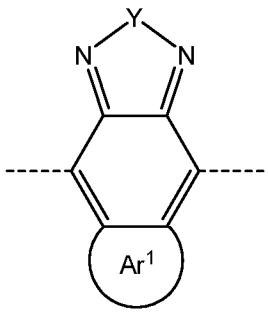
$x^1$ and $x^2$ are each independently 0, 1, 2 or 3;

$y^1$ and $y^2$ are each independently at least 1; and

$z^1$ and $z^2$ are each independently 0, 1, 2 or 3,

with the proviso that at least one of $x^1$, $x^2$, $z^1$ and $z^2$ is at least 1.

3. The compound according to claim 1 or 2 wherein $A^1$ is a group of formula (II):



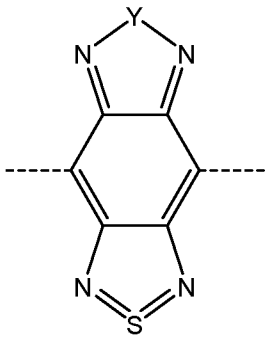

(II)

wherein:

$Ar^1$ is a monocyclic or polycyclic aromatic or heteroaromatic group; and

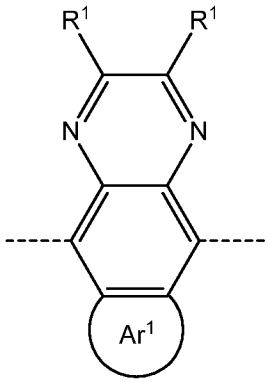
Y is O, S, $NR^4$ or $R^1$-C=C-$R^1$ wherein $R^1$ in each occurrence is independently H or a substituent wherein two substituents $R^1$ may be linked to form a monocyclic or polycyclic ring; and $R^4$ is H or a substituent.

4. The compound according to claim 3 wherein $A^1$ is a group of formula (IIa):




(IIa)

5. The compound according to claim 3 wherein the group of formula (II) has formula (IIb):



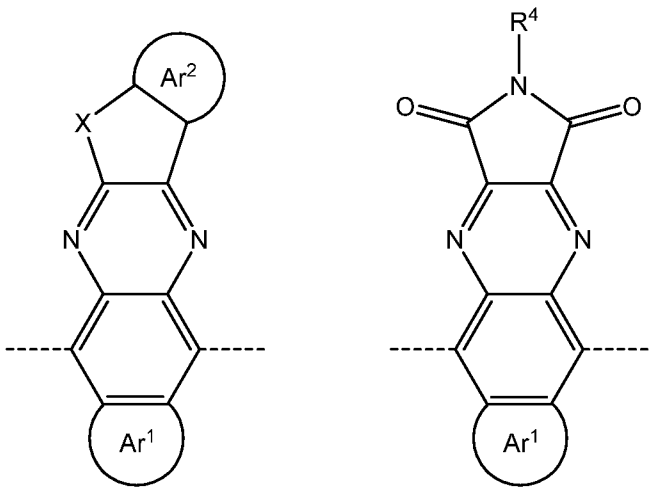
(IIb)

6. The compound according to claim 5 wherein the two $R^1$ groups are not linked.

7. The compound according to claim 6 wherein each $R^1$ is independently selected from H; F; CN; $NO_2$; $C_{1-20}$ alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, CO, COO, $NR^4$, $PR^4$, or $Si(R^3)_2$ and one or more H atoms may be replaced with F; and aryl or heteroaryl which may be unsubstituted or substituted with one or more substituents, wherein $R^3$ and $R^4$ are each independently H or a substituent.

8. The compound according to claim 5 wherein the two $R^1$ groups are linked.

9. The compound according to claim 8 wherein the compound of formula (IIb) has formula (IIb-1) or (IIb-2):



(IIb-1) (IIb-2)

wherein

$Ar^2$ is an aromatic or heteroaromatic group which is unsubstituted or substituted with one or more substituents; and

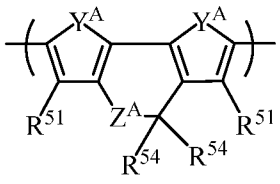
X is selected from O, S, $SO_2$, $NR^4$, $PR^4$, $C(R^3)_2$, $Si(R^3)_2$ C=O, C=S and $C=C(R^5)_2$ wherein $R^3$ and $R^4$ independently in each occurrence are selected from H and a substituent and $R^5$ independently in each occurrence is an electron-withdrawing group.

10. The compound according to claim 9 wherein $Ar^2$ is benzene which is unsubstituted or substituted with one or more substituents.

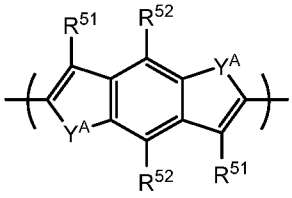
11. The compound according to any one of the preceding claims wherein at least one of $x^1$ and $x^2$ is at least 1 and $B^1$ in each occurrence is independently selected from vinylene, arylene, heteroarylene, arylenevinylene and heteroarylenevinylene, each of which is unsubstituted or substituted with one or more substituents.

12. The compound according to any one of the preceding claims wherein at least one of $z^1$ and $z^2$ is at least 1 and $B^2$ in each occurrence is independently selected from vinylene, arylene, heteroarylene, arylenevinylene and heteroarylenevinylene, each of which is unsubstituted or substituted with one or more substituents.

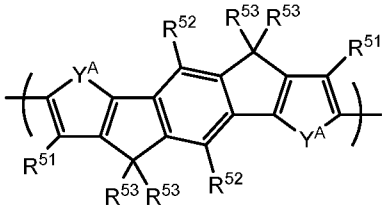
13. The compound according to any one of the preceding claims wherein $D^1$ and $D^2$ are each independently selected from units of formulae (VIIa)-(VIIp):



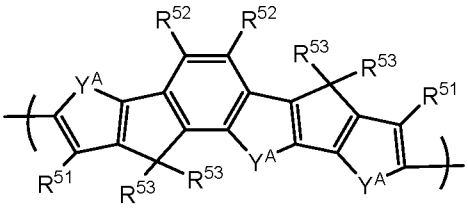

(VIIa)



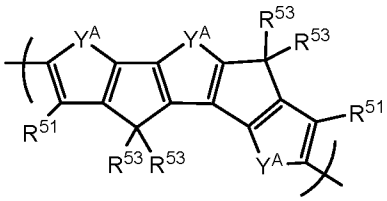
(VIIb)



(VIIc)



(VIId)



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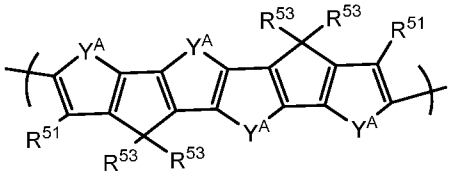

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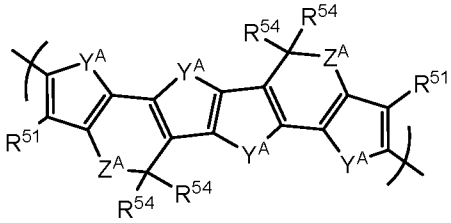
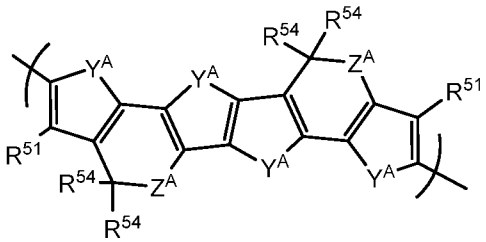


(VIIg)



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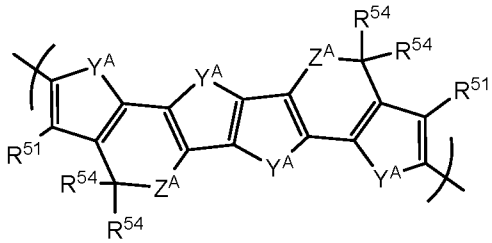
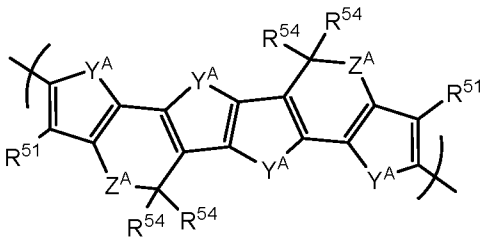
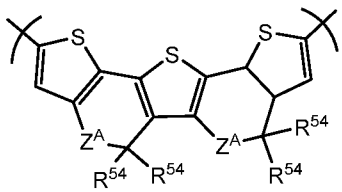


(VIIi)



(VIIj)



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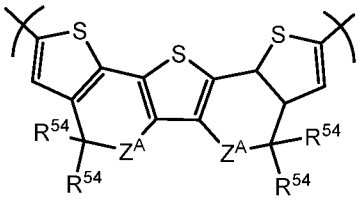
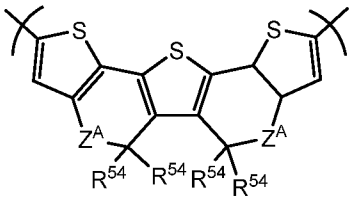


(VIIl)



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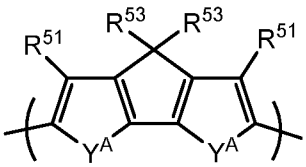

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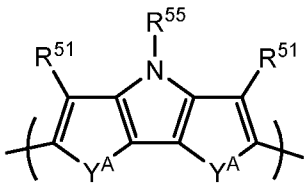

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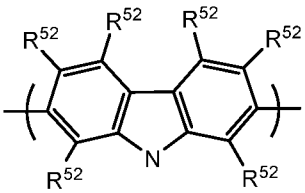
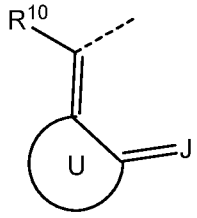


(VIIp)

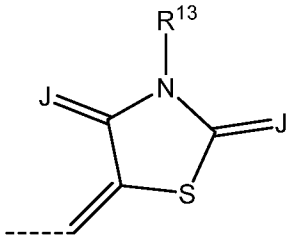
wherein $Y^A$ in each occurrence is independently O, S or $NR^{55}$, $Z^A$ in each occurrence is O, S, $NR^{55}$ or $C(R^{54})_2$; $R^{51}$, $R^{52}$ $R^{54}$ and $R^{55}$ independently in each occurrence is H or a substituent; and $R^{53}$ independently in each occurrence is a substituent.

14. The compound according to any one of the preceding claims wherein at least one of $A^2$ and $A^3$ comprises a non-aromatic carbon-carbon double bond and a carbon atom of the carbon-carbon double bond is bound directly to $D^1$ or $D^2$ or, if present, to $B^2$.

15. The compound according to any one of the preceding claims wherein $A^2$ and $A^3$ are each independently selected from groups of formulae (IIIa)-(IIIq)



(IIIa)



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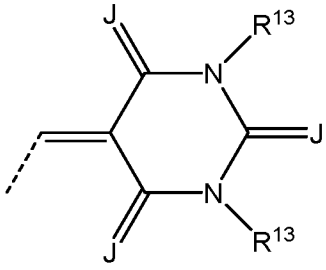

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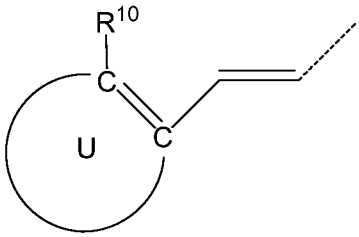

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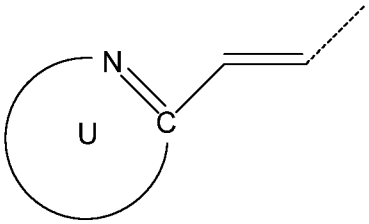

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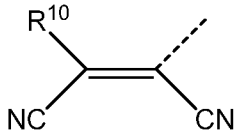

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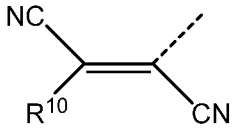

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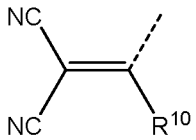

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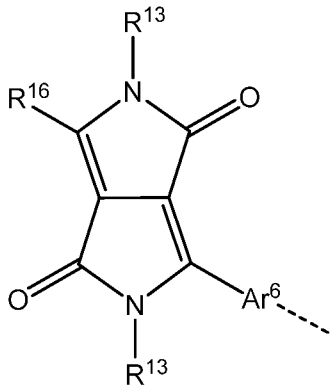
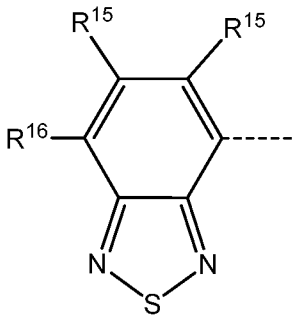


(IIIi)



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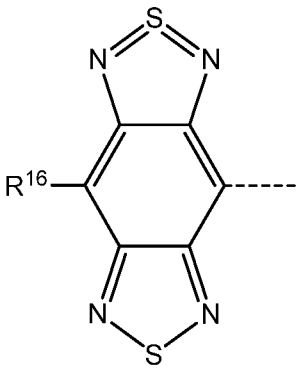
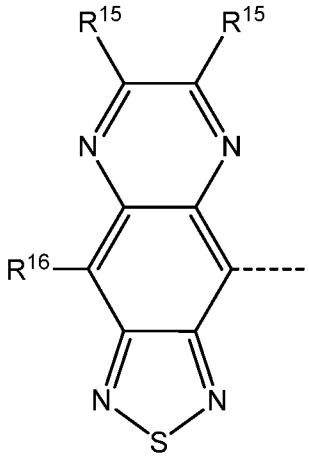
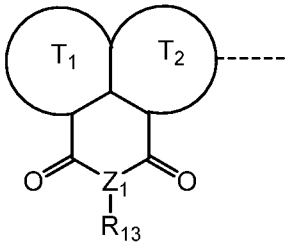


(IIIk)



(IIIl)



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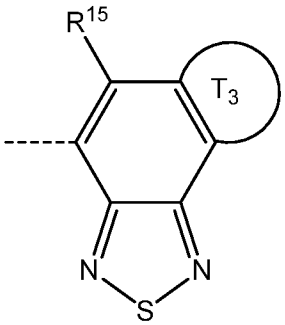

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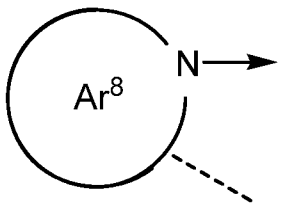
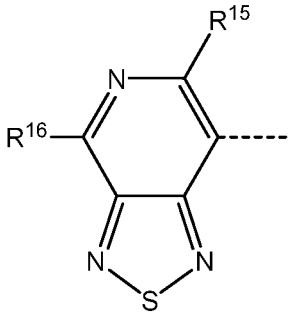


(IIIo)



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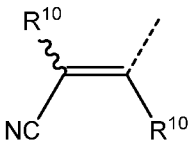


(IIIq)

wherein:

U is a 5- or 6-membered ring which is unsubstituted or substituted with one or more substituents and which may be fused to one or more further rings;

$R^{10}$ is H or a substituent;

J is O or S;

$R^{13}$ in each occurrence is a substituent;

$R^{15}$ in each occurrence is independently H or a substituent

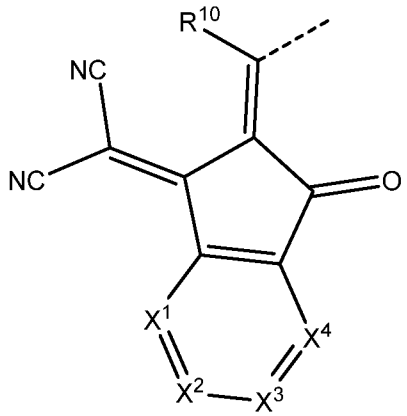
$R^{16}$ is a substituent;

$Ar^6$ is a 5-membered heteroaromatic group which is unsubstituted or substituted with one or more substituents;

$T^1$, $T^2$ and $T^3$ each independently represent an aryl or a heteroaryl ring which may be fused to one or more further rings and each of $T^1$, $T^2$ and $T^3$ is independently unsubstituted or substituted with one or more substituents; and

$Ar^8$ is a fused heteroaromatic group which is unsubstituted or substituted with one or more substituents and which is bound to an aromatic C atom of $B^2$ and to a boron substituent of $B^2$.

16. The compound according to claim 15 wherein at least one of $A^2$ and $A^3$ is a group of formula (IIIa-1):




(IIIa-1)

wherein:

each $X^1$-$X^4$ is independently $CR^{12}$ or N wherein $R^{12}$ in each occurrence is H or a substituent selected from $C_{1-20}$ hydrocarbyl and an electron withdrawing group.

17. The compound according to any one of the preceding claims wherein the polymer has an absorption peak of greater than 900 nm.

18. A composition comprising an electron-donating material and an electron-accepting material wherein the electron accepting material is a compound according to any one of the preceding claims.

19. An organic electronic device comprising an active layer comprising a compound or composition according to any one of the preceding claims.

20. An organic electronic device according to claim 19 wherein the organic electronic device is an organic photoresponsive device comprising a bulk heterojunction layer disposed between an anode and a cathode and wherein the bulk heterojunction layer comprises a composition according to claim 18.

21. An organic electronic device according to claim 20 wherein the organic photoresponsive device is an organic photodetector.

22. A photosensor comprising a light source and an organic photodetector according to claim 21, wherein the photosensor is configured to detect light emitted from the light source.

23. The photosensor according to claim 22, wherein the light source emits light having a peak wavelength of greater than 900 nm.

24. A formulation comprising a compound or composition according to any one of claims 1 to 18 dissolved or dispersed in one or more solvents.

25. A method of forming an organic electronic device according to any one of claims 19-21 wherein formation of the active layer comprises deposition of a formulation according to claim 24 onto a surface and evaporation of the one or more solvents.

**FIGURE 1**

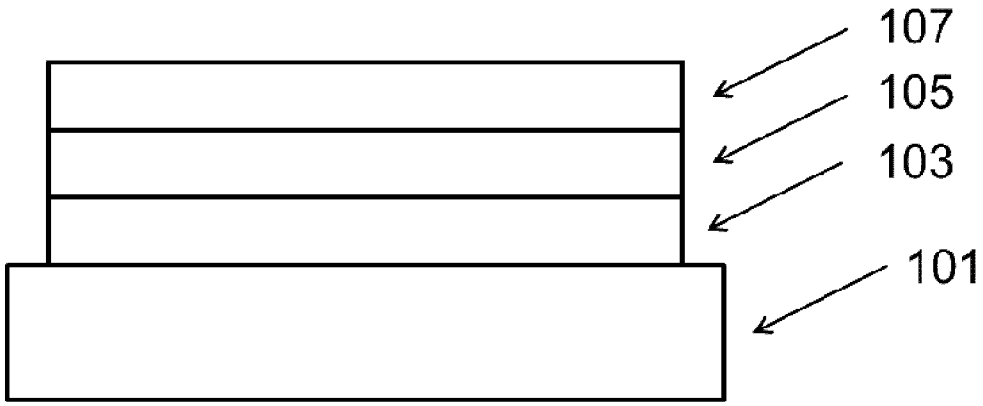



**FIGURE 2**

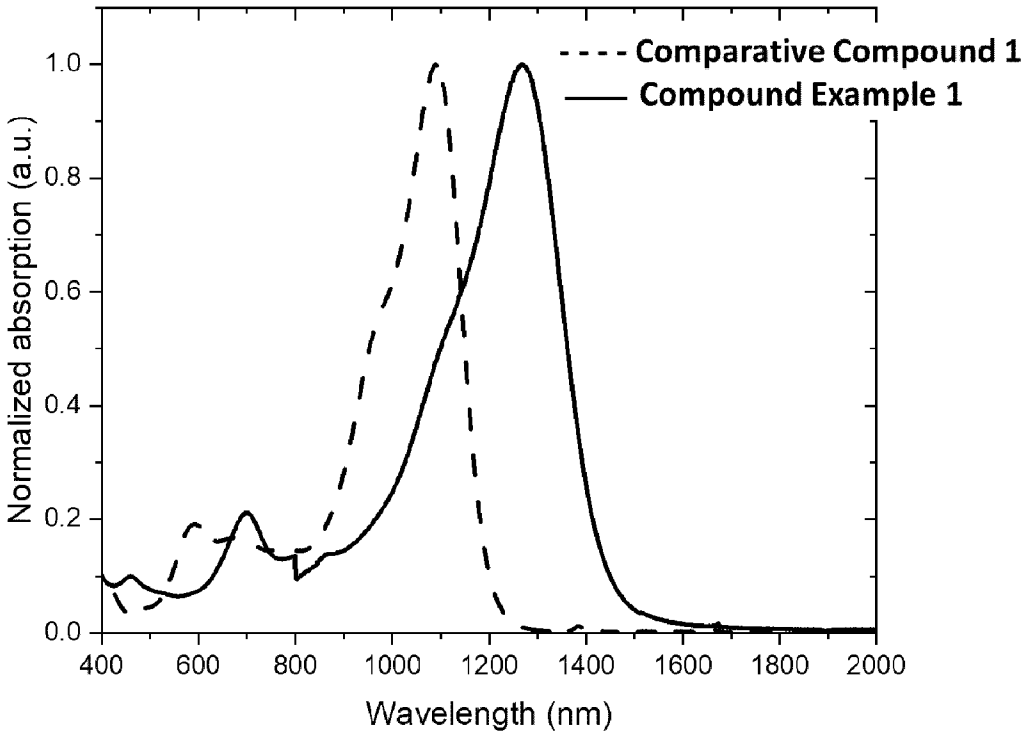


**FIGURE 3**

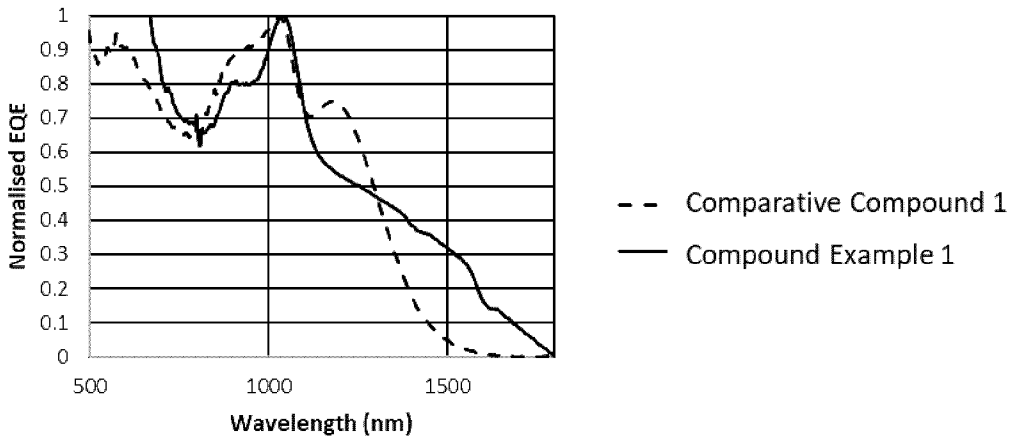
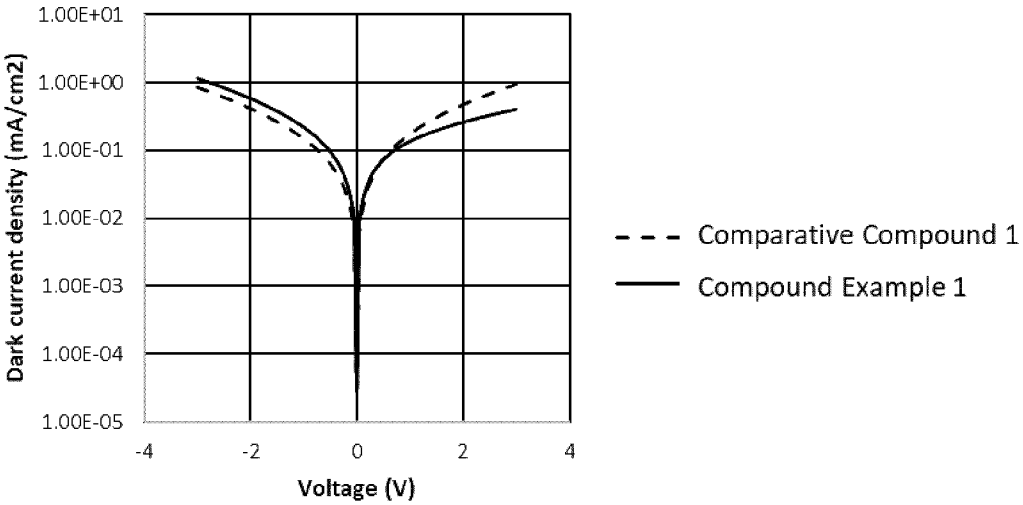



**FIGURE 4**



# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/072162

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D519/00 H01L51/00 H01L51/42
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

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, BIOSIS, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | US 2018/026200 A1 (PARK JUNGHYUN [KR] ET AL) 25 January 2018 (2018-01-25) | 1,11-25 |
| Y | Specific compound 1-3 and groups of compounds 1-5 to 1-8 wherein the group L1 of [Chemical Formula 1] is an acceptor group; claims 1, 8, 9 | 2-10 |

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

[x] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 17 October 2022 | 26/10/2022 |

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

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | ATA IBRAHIM ET AL: "The influence of the central acceptor unit on the optoelectronic properties and photovoltaic performance of A-D-A-D-A-type co-oligomers", ORGANIC CHEMISTRY FRONTIERS, vol. 4, no. 5, 10 February 2017 (2017-02-10), pages 755-766, XP055953296, DOI: 10.1039/C7QO00043J | 1,11-25 |
| Y | page 758, left-hand column, paragraph 2; figures 1, 2a versus 2b; compounds 3, 4 | 2-10 |
| Y | KR 2021 0027929 A (NAT UNIV PUSAN IND UNIV COOP FOUND [KR] ET AL.) 11 March 2021 (2021-03-11) compounds of paragraphs 103-109; claims | 2-10 |
| Y | CN 108 586 496 A (UNIV CHANGZHOU) 28 September 2018 (2018-09-28) compounds of paragraphs 14 and 15; claims | 2-10 |
| Y | CASTRO EDISON ET AL: "Low-Energy-Gap Organic Based Acceptor--Donor-Acceptor [pi]-Conjugated Small Molecules for Bulk-Heterojunction Organic Solar Cells : Organic [pi]-Conjugated Small Molecules for Organic Solar Cells", EUROPEAN JOURNAL OF ORGANIC CHEMISTRY, vol. 2015, no. 21, 5 June 2015 (2015-06-05), pages 4629-4634, XP055927017, DE ISSN: 1434-193X, DOI: 10.1002/ejoc.201500552 table 1; compound ECTBT (Scheme 1) | 2-10 |
| Y | IRFAN AHMAD ET AL: "Computational Designing of Low Energy Gap Small Molecule Acceptors for Organic Solar Cells", MEXICAN CHEMICAL SOCIETY JOURNAL, vol. 61, no. 4, 1 January 2017 (2017-01-01), pages 309-316, XP055953290, MX ISSN: 1870-249X, DOI: 10.29356/jmcs.v61i4.461 figures 1, 2; table 2 | 2-10 |
| 2 Y | CN 112 920 204 A (INST CHEMISTRY CAS) 8 June 2021 (2021-06-08) see other appl.; claims; compounds A1, A2 | 2-10 |
| 1 | -/-- | |

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/072162

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | TAOUALI W ET AL: "Theoretical design of new small molecules with a low band-gap for organic solar cell applications: DFT and TD-DFT study", COMPUTATIONAL MATERIALS SCIENCE, ELSEVIER, AMSTERDAM, NL, vol. 150, 1 April 2018 (2018-04-01), pages 54-61, XP085399892, ISSN: 0927-0256, DOI: 10.1016/J.COMMATSCI.2018.03.038 figure 1 (moiety M3); compound SM3 | 2-10 |
| Y | CN 112 608 333 A (UNIV SOUTH CHINA TECH) 6 April 2021 (2021-04-06) cited in the application figure 1 (on drawing page 1/3); compounds DBTeH-4F,-4Cl; DBTC6-4F, -4Cl | 2-10 |
| Y | WO 2018/140578 A1 (HARVARD COLLEGE [US]) 2 August 2018 (2018-08-02) first two compounds omn page 43; claim 15 | 2-10 |

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# INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2022/072162

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1-25 (partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims;; it is covered by claims Nos.:

**Remark on Protest**

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-25(partially)

In the two formulae (I) of independent compound claims 1 and 2 the D(onor) groups and the A(cceptor) groups are merely functionally defined and should have been structurally defined for a clear and unambiguous scope of the claims in the sense of Art. 6 PCT as the property whether a group is e.g. electron-donating depends on the presence of an acceptor and its relative potential and thus those chemical groups which are meant to be encompassed by the definition of the groups D and A cannot be determined with certainty. Furthermore, the B(ridging) groups are only defined in that they are bivalent but may mean any thinkable structural moiety. Even those bridging groups as structurally defined in present dependent claim 11 or 12, including optionally substituted moieties, may well be donors or acceptors thus overlapping in scope with the D and A groups. Therefore, the B groups encompass moieties which are not expected to be mere "linkers" and thus may disturb the "A-D-A'-D-A" concept of the presently claimed acceptor compounds.

These objections also apply to dependent compound claims 3-17 and further claims 18-25 (which refer to all the compound claims), because none of these claims provides a sufficient structural definition of the compounds encompassed in their scopes. Consequently, present claims 1-25 are not only unclearly defined in violation of Art. 6 PCT, but also relate to an extremely large number of possible compounds while support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of the compounds claimed, see the exemplified compounds given in the present description.

The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of said claims (PCT Guidelines 9.19 and 9.23). As there is no fall-back position in any of the dependent compound claims which could be seen as reasonable generalisation of the example compounds, only the example compounds could be searched completely. Consequently, the subject-matter of present claims 1-25 can be seen as (partially) searched insofar as it relates to the example compounds.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) PCT declaration be

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

overcome.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2022/072162

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
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| | | KR 20160101701 A | 25-08-2016 |
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| | | WO 2016133368 A2 | 25-08-2016 |
| KR 20210027929 A | 11-03-2021 | NONE | |
| CN 108586496 A | 28-09-2018 | NONE | |
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| CN 112608333 A | 06-04-2021 | NONE | |
| WO 2018140578 A1 | 02-08-2018 | NONE | |