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(71) Applicant *(for MG only)*: **CAMBRIDGE DISPLAY TECHNOLOGY LIMITED** [GB/GB]; Unit 12, Cardinal Park, Cardinal Way, Godmanchester Cambridgeshire PE29 2XG (GB).

(71) Applicant: **SUMITOMO CHEMICAL CO., LTD** [JP/JP]; 27-1, Shinkawa 2-chome, Chuo-ku, Tokyo, Tokyo 1048260 (JP).

(72) Inventor: **GARDNER, Ben**; c/o Cambridge Display Technology Limited, Unit 12, Cardinal Park, Cardinal Way, Godmanchester Cambridgeshire PE29 2XG (GB).

(74) Agent: **GILANI, Anwar**; Venner Shipley LLP, Cambridge Business Park, Cowley Road, Cambridge CB4 0WZ (GB).

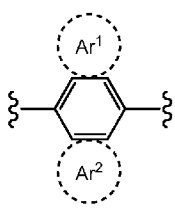
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(54) Title: PHOTOACTIVE MATERIAL



(I)

(57) Abstract: A material comprising an electron-accepting unit of formula (I), wherein Ar^1 is a 5- or 6-membered aromatic or heteroaromatic ring or is absent; Ar^2 is a 5- or 6-membered aromatic or heteroaromatic ring or is absent; and wherein the electron-accepting unit of formula (I) is substituted with at least one electron-withdrawing group. The material further comprises an electron-donating unit D comprising a fused or unfused furan or thiophene. The material may be a polymer comprising repeat units of formula (I). The material may be a non-polymeric compound. An organic photodetector may contain a bulk heterojunction layer containing an electron acceptor or an electron donor wherein at least one of the electron acceptor and electron donor contains unit of formula (I).

PHOTOACTIVE MATERIAL

BACKGROUND

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

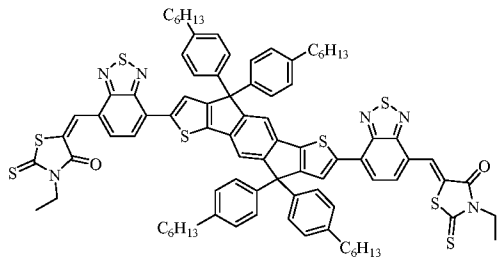
US20180366668A1 relates to visibly transparent, near-infrared absorbing donor-acceptor materials and devices.

KR101986593B1 discloses novel organic semiconductor compounds for organic electronic devices having a central benzothiadiazole or benzotriazole in which thiazolidine or indane functional group is introduced.

CN108218887A relates to fluorine-substituted benzoheterocycle conjugated materials for organic photovoltaic and organic field effect transistor applications.

CN108912125A relates to non-fullerene acceptors comprising a pyrrolo-pyrrole nucleus for organic solar cell applications.

CN106065020A relates to the preparation of a polymer solar battery small molecule receptor according to the following formula:



Brabec et. al., "Visible and Near-Infrared Imaging with Non-fullerene-based Photodetectors", Adv. Mat. Tech. (2018), 3(7), p1-7, is directed to an organic photodiode comprising P3HT and rhodanine-benzothiadiazole coupled indacenodithiophene (IDTBR).

Zhang et. al., "A2-A1-D-A1-A2 Type Non-fullerene Acceptors based on methoxy substituted benzotriazole with three different end-capped groups for P3HT-based organic solar cells", J. Mat. Chem. C, (2018), 6, p10902-10909 is directed to compounds BTA100, BTA101 and BTA103.

Xiao et. al., "A2–A1–D–A1–A2 Type Non-Fullerene Acceptors with 2-(1,1-Dicyanomethylene)rhodanine as the Terminal Groups for Poly(3-hexylthiophene)Based Organic Solar Cells", App. Mat and Interfaces, (2018), 10(40), p34427-34434 Is directed to compounds BT3 and BTA3.

CN103936970B relates to conjugated polymers containing carbazole-benzene 1,4-dithiapentalenefor for solar cell applications.

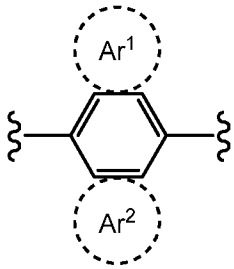
WO2020048939 relates to organic semiconducting compounds containing a polycyclic unit for organic photovoltaic devices and organic photodetectors.

WO2019206926 relates to organic semiconducting polymers containing a polycyclic acceptor-donor-acceptor repeat unit for organic photovoltaic devices and organic photodetectors

W02019091995 relates to organic semiconducting compounds containing an asymmetrically dihalogenated electron-deficient for organic photovoltaic devices and organic photodetectors.

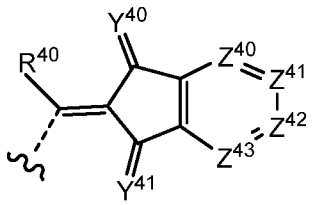
SUMMARY

According to some embodiments, the present disclosure provides a material comprising an electron-accepting unit of formula (I):

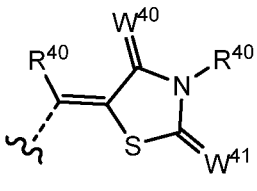


(I)

wherein Ar^1 is a 5- or 6-membered aromatic or heteroaromatic ring or is absent; Ar^2 is a 5- or 6-membered aromatic or heteroaromatic ring or is absent; and wherein the electron-accepting unit of formula (I) is substituted with at least one group of formula (Xa) or (Xb):



(Xa)



(Xb)

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;

Y^{40} and Y^{41} are each independently O, S, NX^{70} wherein X^{70} is CN or $COOR^{40}$; or $CX^{60}X^{61}$ wherein X^{60} or X^{61} is independently CN, CF_3 or $COOR^{40}$;

W^{40} and W^{41} are each independently O, S, NX^{70} wherein X^{70} is CN or $COOR^{40}$; or $CX^{60}X^{61}$ wherein X^{60} or X^{61} is independently CN, CF_3 or $COOR^{40}$; and

R^{40} in each occurrence is H or a substituent;

and wherein the material further comprises an electron-donating unit D comprising a fused or unfused furan or thiophene.

Optionally, each group of formula (Xa) or (Xb) is an electron-withdrawing group.

Optionally, no more than two of Z^{40}, Z^{41}, Z^{42} and Z^{43} are N. Preferably, each of Z^{40}, Z^{41}, Z^{42} and Z^{43} are CR^{13}.

In the case where R^{13} is a substituent, it may independently in each occurrence be selected from F, CF_3, CN, NO_2 and C_{1-12} alkyl wherein one or more non-adjacent, non-terminal C atoms may be replaced with O, S, CO or COO and one or more H atoms may be replaced with F.

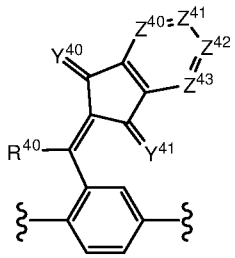
Preferably, each R^{13} is independently H or F.

In the case where R^{40} is a substituent, it may independently in each occurrence be selected from C_{1-12} alkyl wherein one or more non-adjacent, non-terminal C atoms may be replaced with O, S, CO or COO and one or more H atoms may be replaced with F.

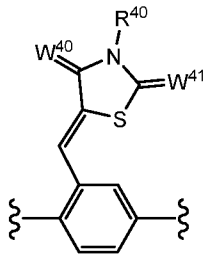
Preferably, R^{40} in each occurrence is H.

Preferably, the only substituent or substituents of the unit of formula (I) are the one or more groups of formula (Xa) or (Xb).

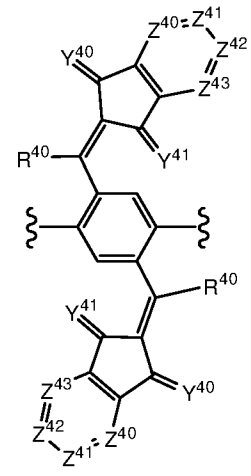
In the case where the unit of formula (I) is substituted with one or more substituents other than (Xa) or (Xb), the one or more further substituents are optionally selected from F, CN, CF_3, NO_2, $COOR^{40}$; NX^{70} wherein X^{70} is CN or $COOR^{40}$; C_{1-12} alkyl wherein one or more non-adjacent, non-terminal C atoms may be replaced with O, S, CO or COO and one or more H atoms 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, non-terminal C atoms may be replaced with O, S, COO or CO and one or more H atoms of the alkyl may be replaced with F. The one or more further substituents may be substituents of the central benzene ring of formula (I); Ar^1 if present; and / or Ar^2, if present. Optionally, the unit of formula (I) is selected from formulae (I-1) – (I-11):



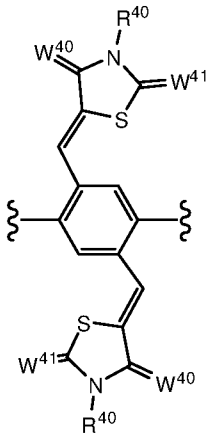
(I-1)



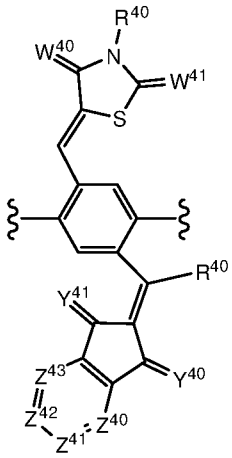
(I-2)



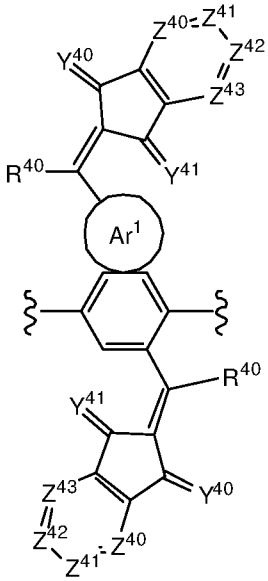
(I-3)



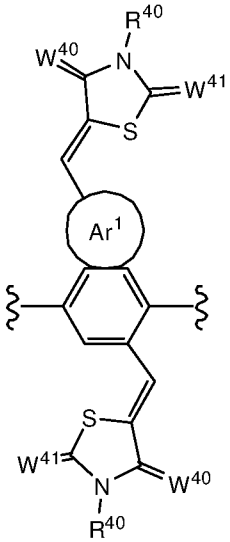
(I-4)



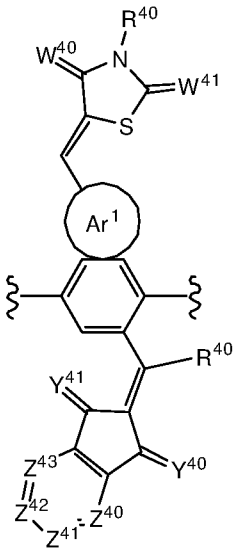
(I-5)



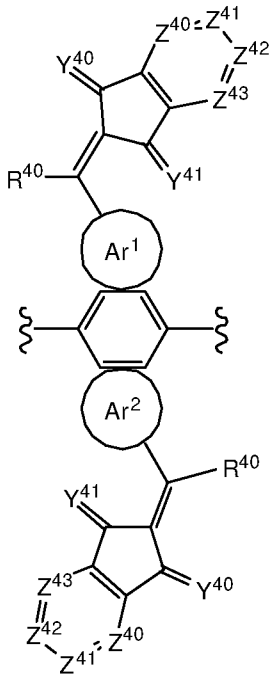
(I-6)



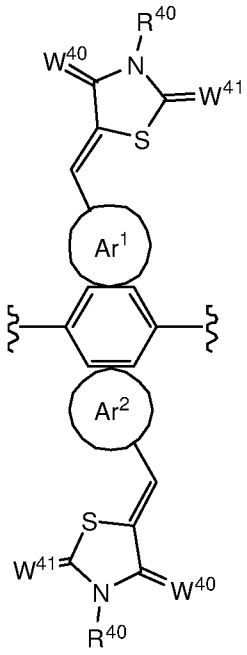
(I-7)



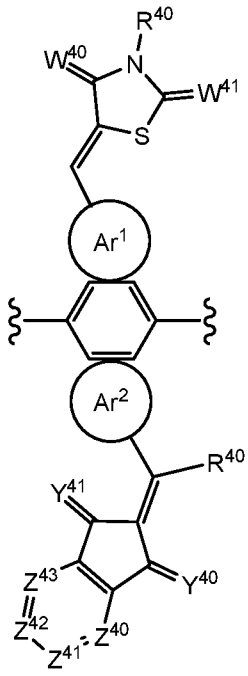
(I-8)



(I-9)



(I-10)

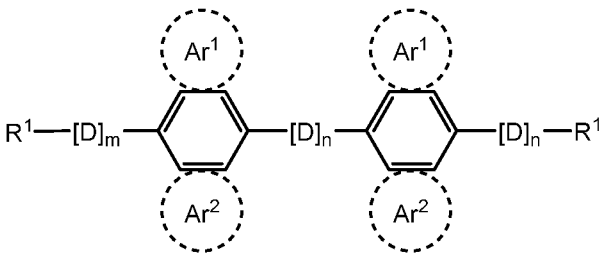


(I-11)

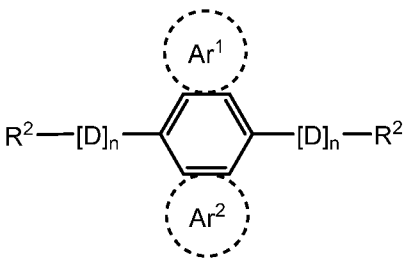
It will be understood that Ar^1 and Ar^2 of (I-6) to (I-11) as represented by a circle having a solid line, rather than a dashed line, are present in these units.

Optionally, Ar^1 and Ar^2, where present is independently a 5- or 6-membered heteroaromatic ring containing at least one N atom.

In some embodiments, the material is a non-polymeric compound. Optionally, the non-polymeric compound has formula (Ia) or (Ib):



(Ia)



(Ib)

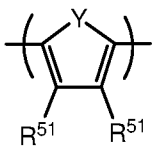
wherein n is at least 1; m is 0, 1, 2 or 3; D in each occurrence is independently an electron-donating unit comprising a fused or unfused furan or thiophene which may be unsubstituted

or substituted with one or more substituents; and R^1 and R^2 independently in each occurrence is H or a substituent.

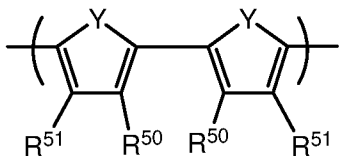
It will be understood that a group of formula –C(=Xa)-R^{40} and –C(=Xb)-R^{40} shown linked to an Ar^1 or Ar^2 group of formula (Ia) or (Ib) is bound directly to the central benzene ring if that Ar^1 or Ar^2 group is absent.

In some embodiments, the material is a polymer; the unit of formula (I) is an electron-accepting repeat unit of formula (I); and the electron-donating unit D is an electron-donating repeat unit.

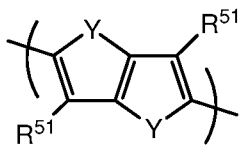
Optionally, D of a non-polymeric compound or a repeat unit D of a polymer as described herein is selected from formulae (IIa) – (IIm):



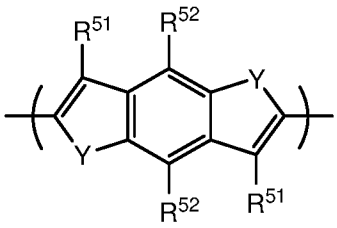
(IIa)



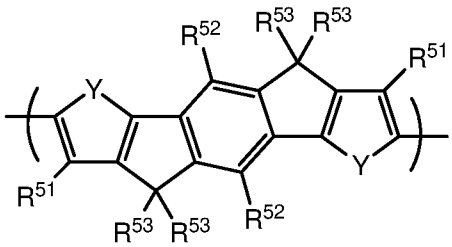
(IIb)



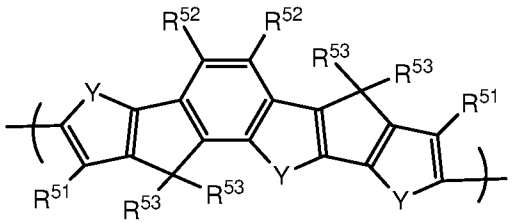
(IIc)

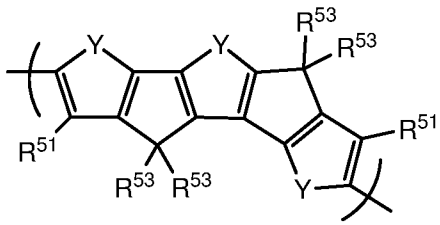


(IId)

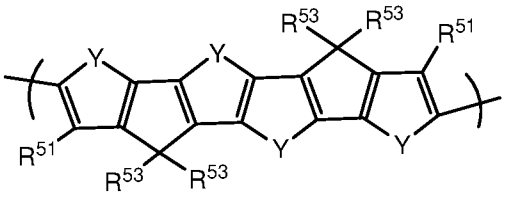


(IIe)

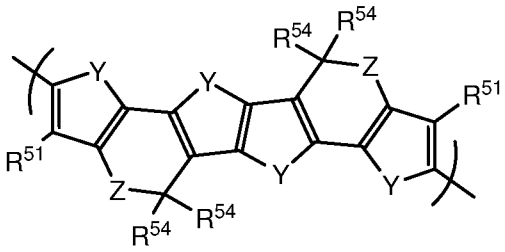




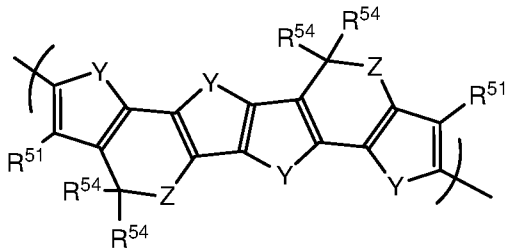
(IIf)



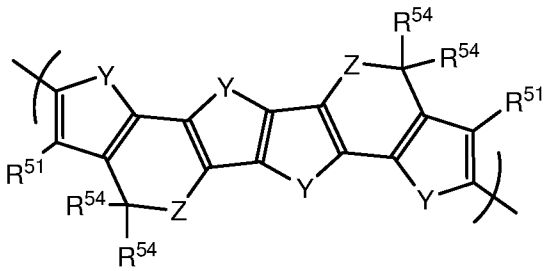
(IIg)



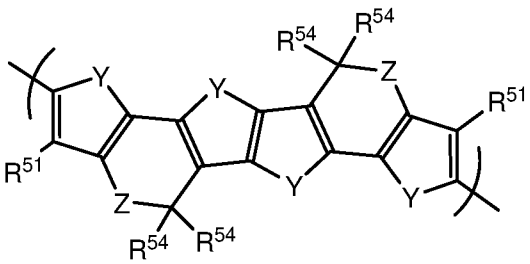
(IIh)



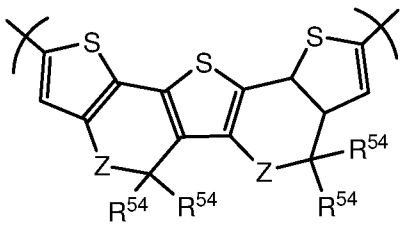
(IIi)



(IIj)



(IIk)

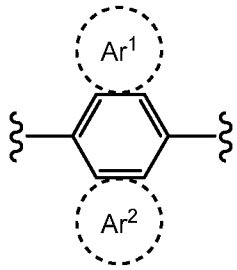


(III)

(IIm)

wherein Y in each occurrence is independently O or S; Z in each occurrence is independently O, S, NR^{55} or $C(R^{54})_2$; R^{50}, R^{51}, R^{52}, R^{54} and R^{55} independently in each occurrence is H or a substituent wherein R^{50} groups may be linked to form a ring; and R^{53} independently in each occurrence is a substituent.

According to some embodiments, the present disclosure provides a polymer comprising a repeat unit of formula (I):



(I)

wherein Ar^1 is a 5- or 6-membered aromatic or heteroaromatic ring or is absent; Ar^2 is a 5- or 6-membered aromatic or heteroaromatic ring or is absent; and wherein the repeat unit of formula (I) is substituted with at least one group of formula (Xa) or (Xb) as described above.

Optionally, the repeat unit of formula (I) may have formula (I-1) – (I-11) as described above.

Optionally the polymer may comprise an electron-donating repeat unit D comprising a fused or unfused furan or thiophene. The electron-donating repeat unit may be selected from formulae (IIa) – (IIm) as described herein.

According to some embodiments, the present disclosure provides a composition comprising an electron donor and an electron acceptor wherein at least one of the electron donor and electron acceptor is a material comprising an electron-accepting unit of formula (I) as described herein.

In some embodiments, the electron acceptor of the composition is the material comprising an electron-accepting unit of formula (I) as described herein. Optionally according to these embodiments, the electron acceptor is a non-polymeric compound as described herein.

In some embodiments, the electron donor is the material comprising an electron-accepting unit of formula (I) as described herein. Optionally, the electron donor is a polymer as described herein.

According to some embodiments, the present disclosure provides an organic electronic device comprising an active layer comprising a material or composition as described herein.

Optionally, 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 as described herein.

Optionally, the organic photoresponsive device is an organic photodetector.

According to some embodiments, the present disclosure provides a photosensor comprising a light source and an organic photodetector as described herein, wherein the photosensor is configured to detect light emitted from a light source. Optionally, the light source emits light having a peak wavelength of at least 750 nm.

According to some embodiments, the present disclosure provides a formulation comprising a material, polymer or composition as described herein dissolved or dispersed in one or more solvents.

According to some embodiments, the present disclosure provides a method of forming an organic electronic device as described herein, wherein formation of the active layer comprises deposition of a formulation as described herein onto a surface and evaporation of the one or more solvents.

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.

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.

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.

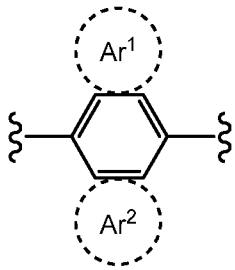
Each of the anode and cathode may independently be a single conductive layer or may comprise a plurality of layers.

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.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,

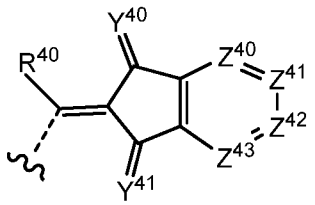
the substrate can be a wafer of silicon. The substrate is transparent if, in use, incident light is to be transmitted through the substrate and the electrode supported by the substrate.

The bulk heterojunction layer comprises an electron donor material and an electron acceptor material wherein at least one of the electron donor material and the electron acceptor material comprises an electron-accepting group of formula (I):

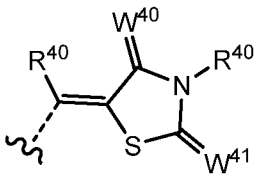


(I)

wherein Ar^1 is a 5- or 6-membered aromatic or heteroaromatic ring or is absent; Ar^2 is a 5- or 6-membered aromatic or heteroaromatic ring or is absent; and wherein the electron-accepting unit of formula (I) is substituted with at least one group of formula (Xa) or (Xb):



(Xa)



(Xb)

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;

Y^{40} and Y^{41} are each independently O, S, NX^{70} wherein X^{70} is CN or $COOR^{40}$; or $CX^{60}X^{61}$ wherein X^{60} or X^{61} is independently CN, CF_3 or $COOR^{40}$;

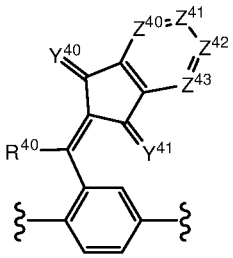
W^{40} and W^{41} are each independently O, S, NX^{70} wherein X^{70} is CN or $COOR^{40}$; or $CX^{60}X^{61}$ wherein X^{60} or X^{61} is independently CN, CF_3 or $COOR^{40}$; and

R^{40} in each occurrence is H or a substituent;

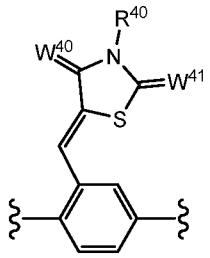
and wherein the material further comprises an electron-donating unit D comprising a fused or unfused furan or thiophene.

Preferably, each group of formula (Xa) or (Xb) is an electron-withdrawing group.

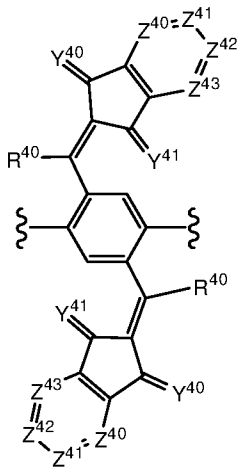
Preferably, the unit of formula (I) is selected from formula (I-1) – (I-11):



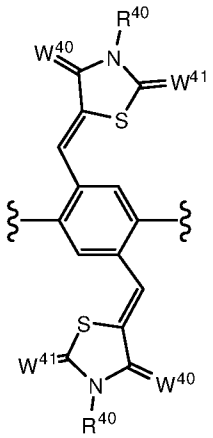
(I-1)



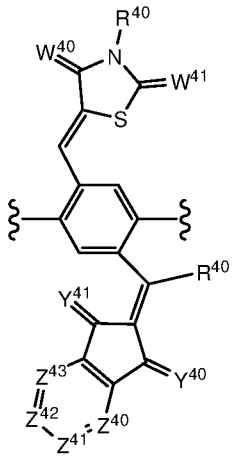
(I-2)



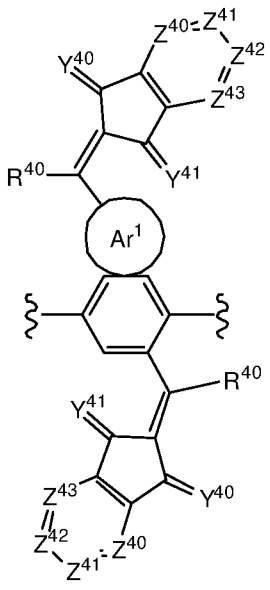
(I-3)



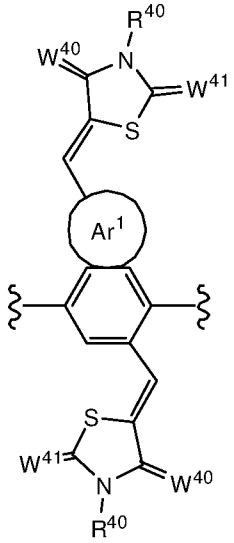
(I-4)



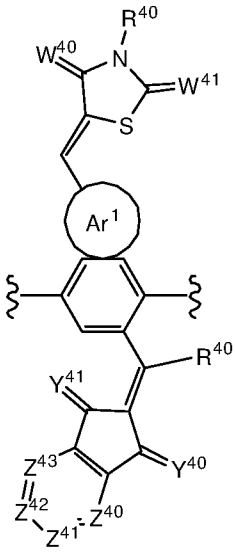
(I-5)



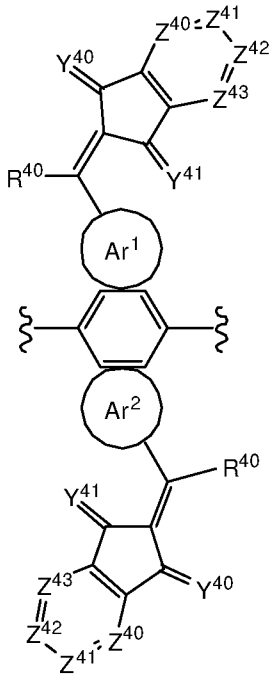
(I-6)



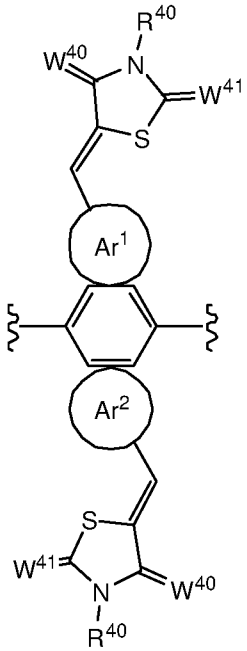
(I-7)



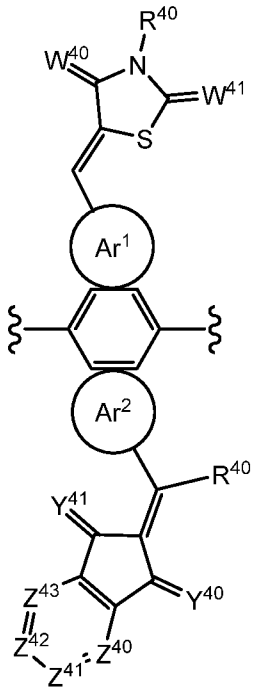
(I-8)



(I-9)



(I-10)



(I-11)

It will be understood that Ar^1 and Ar^2 of I-6 to I-11, as represented by a circle having a solid rather than a dashed line, are present in these units.

Preferably, each unit of formula (I) is bound directly to at least one electron-donating unit D comprising a fused or unfused furan or thiophene.

In some embodiments, the material comprising the unit of formula (I) has an absorption peak greater than 750 nm.

In some embodiments, the material comprising the unit of formula (I) has an absorption peak greater than 900 nm.

In some embodiments the material comprising the unit of formula (I) has an absorption peak in the range of 750-2000 nm, between 750-1400 nm, between 750-900 nm or 900-2000 nm.

Unless stated otherwise, absorption spectra of light-emitting materials as described herein are measured in water using a Cary 5000 UV-VIS-NIR Spectrometer. Measurements were taken from 175nm to 3300 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 solid (film) or solution sample. Absorption intensity is plotted vs. incident wavelength to generate an absorption spectrum. A method for measuring film absorption, may comprise dissolving the sample in toluene (15 mg / ml) and spin coating at 500 rpm directly on to a quartz substrate. Absorption is measured as compared to a blank substrate. A similar method may be used for measuring solution absorption but using a quartz cuvette.

The electron donor (p-type) material has a HOMO deeper (further from vacuum) than a LUMO of the electron acceptor (n-type) material. Optionally, the gap between the HOMO level of the p-type donor material and the LUMO level of the n-type acceptor material 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/AgCI 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/AgCI 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.

In some embodiments, the bulk heterojunction layer contains only one electron donor material and only one electron acceptor material, at least one of the donor and acceptor comprising an electron-accepting unit of formula (I).

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

In some embodiments, the weight of the donor material(s) to the acceptor material(s) is from about 1:0.5 to about 1:2, preferably about 1:1.1 to about 1:2.

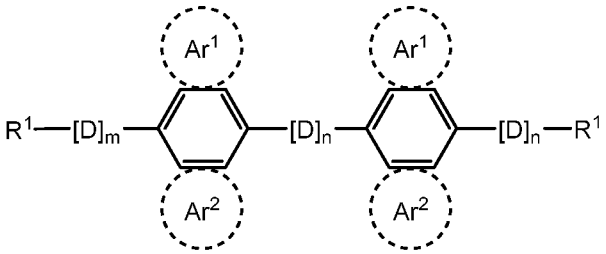
In some embodiments, the material comprising the group of formula (I) is a non-polymeric compound containing at least one unit of formula (I), optionally 1, 2 or 3 units of formula (I) and at least on electron-donating unit D. Preferably, the non-polymeric compound has a molecular weight of less than 5,000 Daltons, optionally less than 3,000 Daltons. Preferably, the non-polymeric compound contains no more than 3 groups of formula (I).

In some embodiments, the material comprising the group of formula (I) is a polymer comprising a repeat unit of formula (I) and an electron-donating repeat unit, more preferably alternating electron-accepting repeat units of formula (I) and electron-donating repeat units.

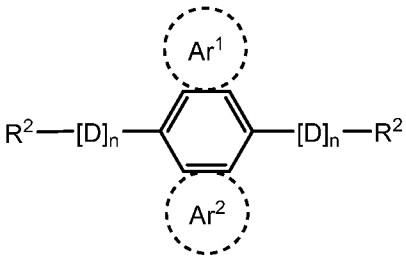
Preferably, the polystyrene-equivalent number-average molecular weight (Mn) measured by gel permeation chromatography of the polymer is in the range of about $5x10^3$ to $1x10^8$, and

preferably $1x10^4$ to $5x10^6$. The polystyrene-equivalent weight-average molecular weight (Mw) of the polymer may be $1x10^3$ to $1x10^8$, and preferably $1x10^4$ to $1x10^7$.

A non-polymeric compound comprising a unit of formula (I) may have formula (Ia) or (Ib):



(Ia)



(Ib)

wherein n is at least 1, optionally 1, 2 or 3; m is 0, 1, 2 or 3; D in each occurrence is independently an electron-donating unit comprising a fused or unfused furan or thiophene which may be unsubstituted or substituted with one or more substituents; R^1 and R^2 independently in each occurrence is H or a substituent; Ar^1 and Ar^2 are as described above; and where any of R^1, R^2, Ar^1 and Ar^2 occur more than once in formula (Ia) or (Ib), each occurrence can be the same or different.

Preferably, R^1 in each occurrence is the same; R^2 in each occurrence is the same, Ar^1 of formula (Ia) in each occurrence is the same; and Ar^2 of formula (Ia) in each occurrence is the same.

Optionally, R^1 and R^2 are each independently selected from the group consisting of H; F; C_{1-20} alkyl wherein one or more non-adjacent, non-terminal C atoms may be replaced with O, S, 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, non-terminal C atoms may be replaced with O, S, COO or CO and one or more H atoms of the alkyl may be replaced with F.

In a preferred embodiment, Ar^1 and Ar^2, where present, are independently a 5- or 6-membered aromatic or heteroaromatic ring, which may be monocyclic or fused. Ar^1 and Ar^2 may each independently be unsubstituted or substituted with one or more substituents. Substituents may be selected from non-H groups of R^1 and R^2 as described above.

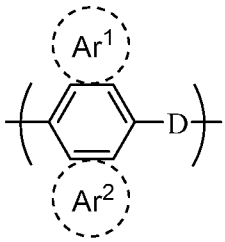
In a preferred embodiment, Ar^1 and Ar^2, where present, are independently a 5- or 6-membered heteroaromatic ring, wherein the beteroaromatic ring contains at least one N atom.

In a preferred embodiment, Ar^1 and Ar^2, where present, are independently a 5- or 6-membered heteroaromatic ring, wherein the beteroaromatic ring contains at least one N atom and one S atom.

In a preferred embodiment, Ar^1 and Ar^2, where present, are independently selected from a pyrrole, pyrazole, imidazole, oxazole, thiazole, thiazine, diazine including pyrimidine, pyridazine, pyrazine, thiadiazole, oxazine, and triazole.

In a more preferred embodiment, Ar^1 and Ar^2, where present, are independently selected from a diazine, thiadiazole and triazole.

A polymer comprising repeat units of formula (I) may contain the a repeating structure of formula (II), comprising the repeat unit of formula (I) and an adjacent electron donating repeat unit D:



(II)

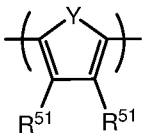
For an electron donor material or electron acceptor material containing an electron-accepting unit of formula (I) and an electron-donating unit D the, or each, unit of formula (I) has a LUMO level that is deeper (i.e. further from vacuum) than the, or each, electron-donating unit, preferably at least 1 eV deeper. The LUMO levels of an electron-donating unit and an electron-accepting unit of formula (I) may be as determined by modelling, respectively, the LUMO level of D-H or H-D-H and H-[Formula (I)]-H, respectively, i.e. by replacing the bond or bonds between D and formula (I) with a bond or bonds to a hydrogen atom. Modelling may be performed using Gaussian09 software available from Gaussian using Gaussian 09 with B3LYP (functional).

Preferably, a model compound of formula H-[Formula (I)]-H containing one or more electron-withdrawing groups of formula (Xa) or (Xb) deepens the LUMO by at least 0.2 eV as compared to the case where each Xa or Xb is H.

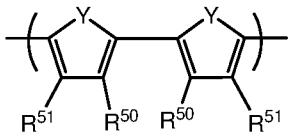
Electron-donating unit

Electron-donating units D are preferably in each occurrence a monocyclic or polycyclic heteroaromatic group which contains at least one furan or thiophene and which may be unsubstituted or substituted with one or more substituents. Preferred electron-donating units D are monocyclic thiophene or furan or a polycyclic donor wherein each ring of the polycyclic donor includes thiophene or furan rings and, optionally, one or more of benzene, cyclopentane, or a six-membered ring containing 5 C atoms and one of N and O atoms.

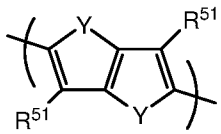
Optionally, electron donating units D are selected from formulae (IIa) – (IIm), or a combination thereof:



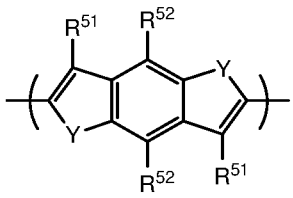
(IIa)



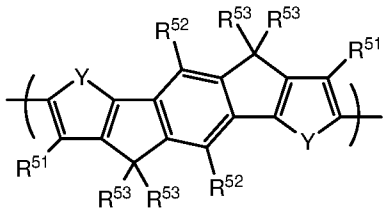
(IIb)



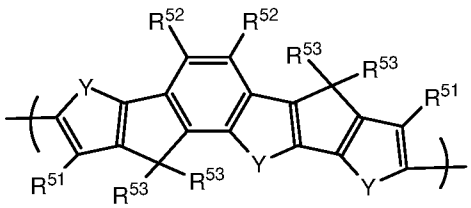
(IIc)

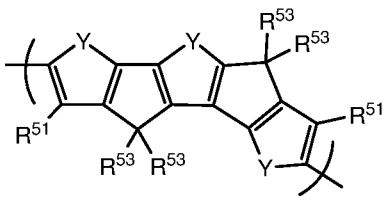


(IId)

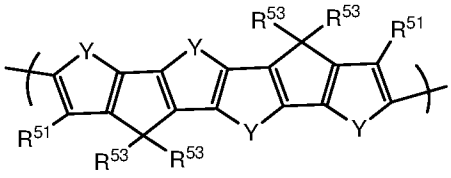


(IIe)

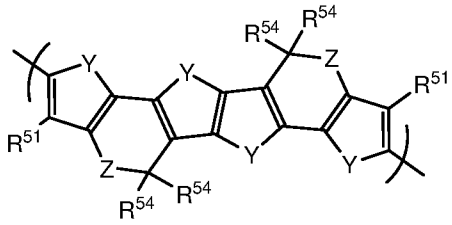




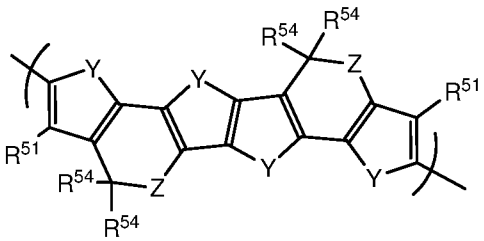
(IIf)



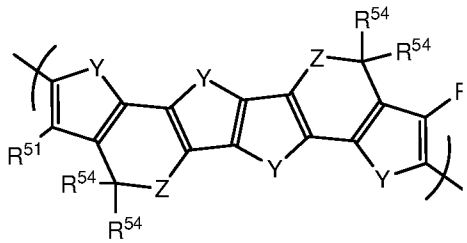
(IIg)



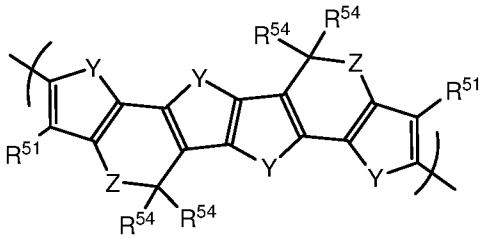
(IIh)



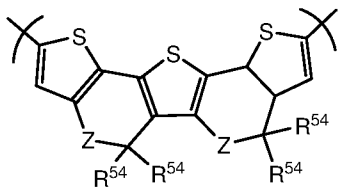
(IIi)



(IIj)



(IIk)



(III)

(IIm)

wherein Y in each occurrence is independently O or S, preferably S; Z in each occurrence is independently O, S, NR^{55}, or $C(R^{54})_2$; R^{50}, R^{51}, R^{52} and R^{54} independently in each occurrence is H or a substituent wherein R^{50} groups may be linked to form a ring; and R^{53} independently in each occurrence is a substituent.

In some embodiments, the electron-donating unit D is a single group of formula (IIa) – (IIm).

In some embodiments, the electron-donating unit D comprises a plurality of directly linked groups of formula (IIa) – (IIm). The directly linked groups may be the same or different and maybe linked in any orientation.

Optionally, R^{50}, R^{51} and R^{52} independently in each occurrence are selected from H; F; C_{1-20} alkyl wherein one or more non-adjacent, non-terminal C atoms may be replaced with O, S, 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 maybe 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, non-terminal C atoms may be replaced with O, S, COO or CO and one or more H atoms of the alkyl may be replaced with F.

By "non-terminal" C atom of an alkyl group as used herein is meant a C atom of the alkyl other than the methyl C atom of a linear (n-alkyl) chain or the methyl C atoms of a branched alkyl chain.

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

H;

linear, branched or cyclic C_{1-20} alkyl wherein one or more non-adjacent, non-terminal 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 $(Ak)u–(Ar^4)v$ wherein Ak is a C_{1-12} alkylene chain in which one or more C atoms may be replaced with O, S, CO or COO; u is 0 or 1; Ar^4 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.

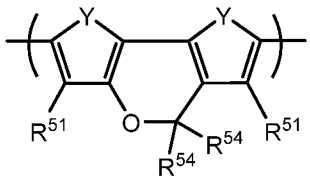
Preferably, each R^{51} is H.

Optionally, R^{53} independently in each occurrence is selected from C_{1-20} alkyl wherein one or more non-adjacent, non-terminal C atoms may be replaced with O, S, 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, non-terminal C atoms may be replaced with O, S, COO or CO and one or more H atoms of the alkyl may be replaced with F.

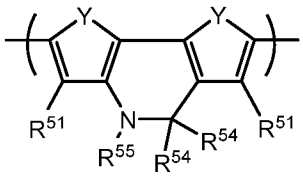
Preferably, R^{55} is a H or C_{1-30} hydrocarbyl group

Preferably, each R^{50} is a substituent.

In a preferred embodiment, the R^{50} groups are linked to form a group of formula $–Z-C(R^{54})_2-$ wherein Z is independently O, S, NR^{55}, or $C(R^{54})_2$, e.g. a group of formula (IIb-1) or (IIb-2):



(IIb-1)



(IIb-2)

Electron donor material

In the case where the material comprising the group of formula (I) is an electron-accepting material, it may be used with any electron donor material containing a group of formula (I) or any other electron donor material known to the person skilled in the art, including organic polymers and non-polymeric organic molecules.

In a preferred embodiment the electron donor material is an organic conjugated polymer, which can be a homopolymer or copolymer including alternating, random or block copolymers. Preferred are non-crystalline or semi- crystalline conjugated organic polymers. Further preferably the p-type organic semiconductor 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 p-type donor has a HOMO level no more than 5.5 eV from vacuum level. Optionally, the p-type donor has a HOMO level at least 4.1 eV from vacuum level.

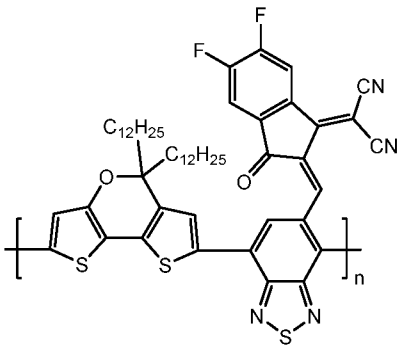
As exemplary p-type donor polymers, polymers selected from conjugated hydrocarbon or heterocyclic polymers including polyacene, polyaniline, polyazulene, polybenzofuran, polyfluorene, polyfuran, polyindenofluorene, polyindole, polyphenylene, polypyrazoline, polypyrene, polypyridazine, polypyridine, polytriarylamine, 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,

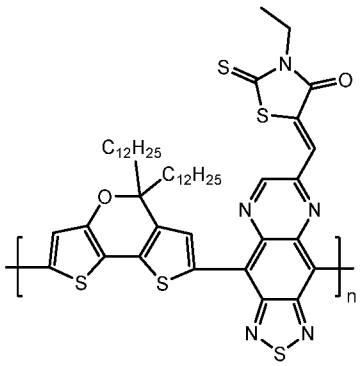
polythieno[3,2-b]thiophene, polybenzothiophene, polybenzo[1 ,2-b:4,5-b'jdithiophene, polyisothianaphthene, poly(monosubstituted pyrrole), poly(3,4-bisubstituted pyrrole), poly-1 ,3,4-oxadiazoles, polyisothianaphthene, derivatives and co-polymers thereof may be mentioned. Preferred examples of p-type donors 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. It is understood that the p-type donor may also consist of a mixture of a plurality of electron-donating materials.

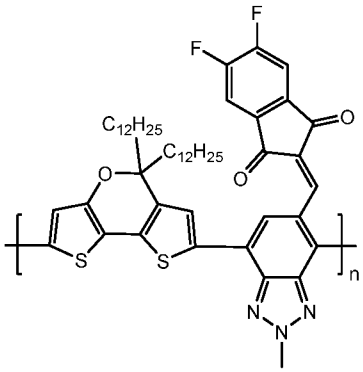
Optionally, the electron donor polymer comprises a repeat unit selected from formulae (IIa) – (IIm) as described above.

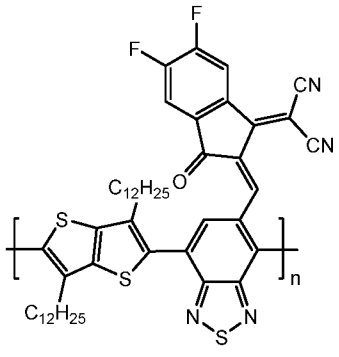
In a preferred embodiment, the repeat units of the electron donor polymer comprise or consist of a repeat unit of formula (I) and a repeat unit of formula (IIb-1) or (IIb-2) in an alternating arrangement as shown in formula (II).

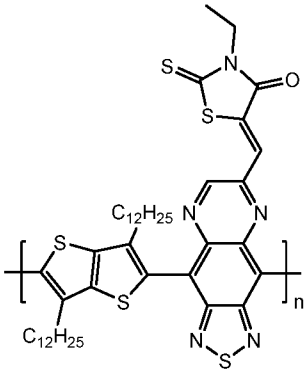
Exemplary electron-donor polymers comprising a repeat unit of formula (I) include polymers having a repeating structure selected from:

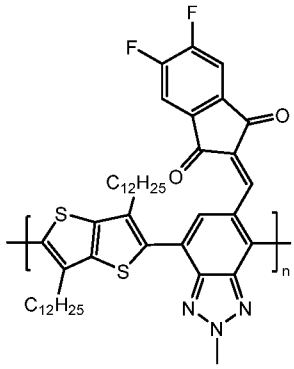


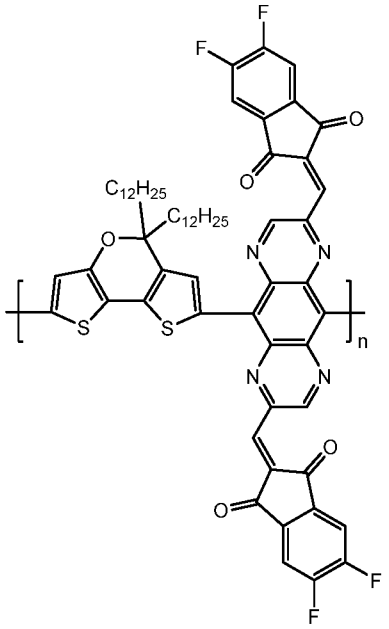




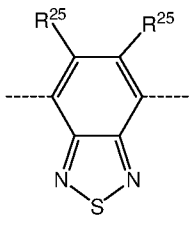




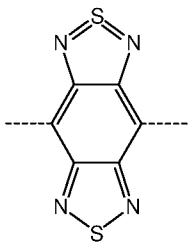




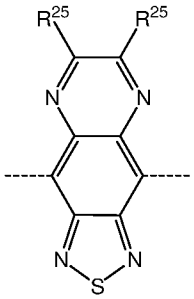
Optionally, in the case where the electron donor polymer does not contain a repeat unit of formula (I), it comprises a repeat unit selected from repeat units of formulae:



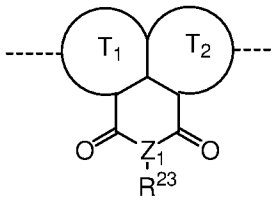
(XVIIIa)



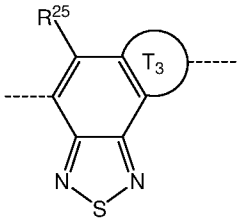
(XIXa)



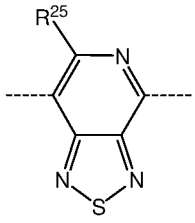
(XXa)



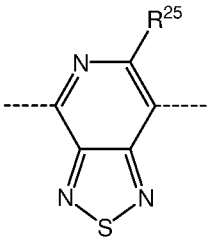
(XXIa)



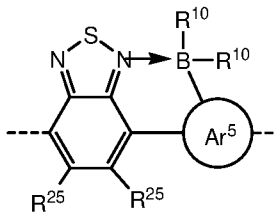
(XXIIa)



(XXIVa)



(XXVa)



(XXVIa)

R^{23} in each occurrence is a substituent, optionally C_{1-12} alkyl wherein one or more non-adjacent, non-terminal C atoms may be replaced with O, S, 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; C_{1-12} alkyl wherein one or more non-adjacent, non-terminal C atoms may be replaced with O, S, COO or CO and one or more H atoms of the alkyl may be replaced with F; or an 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, non-terminal C atoms may be replaced with O, S, COO or CO.

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^{10} 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}.

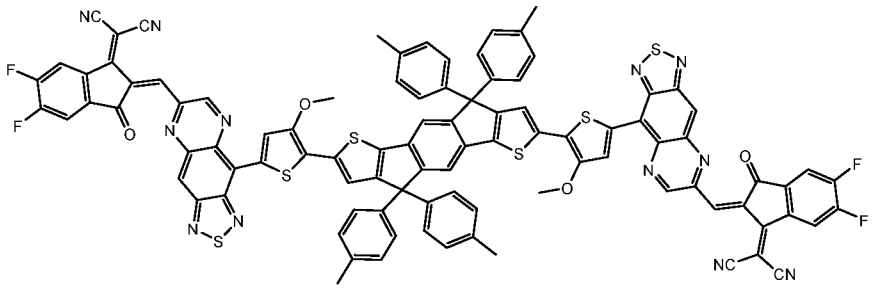
Exemplary donor materials are disclosed in, for example, WO2013/051676, the contents of which are incorporated herein by reference.

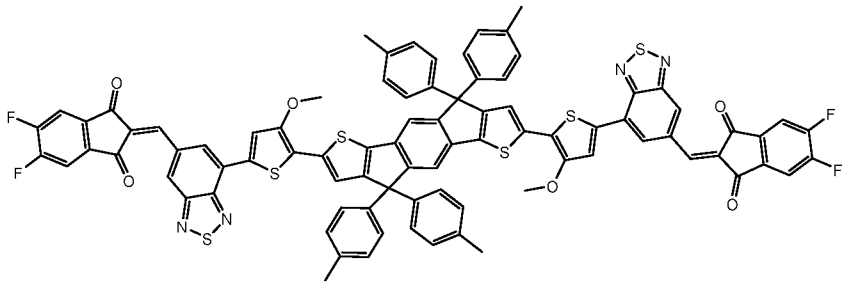
Electron acceptor material

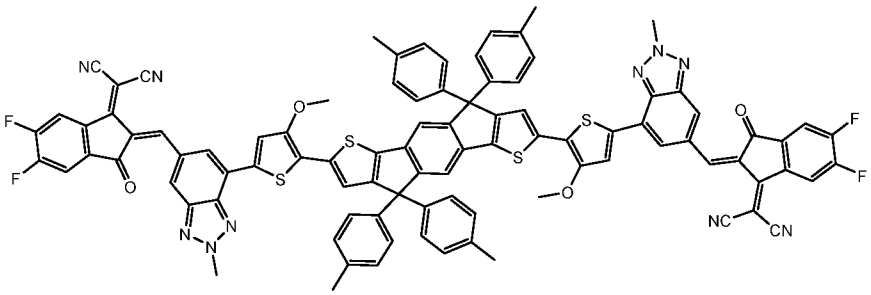
In the case where the material comprising the group of formula (I) is an electron-donor material, it may be used with any electron-accepting material containing a group of formula (I) or any other electron-accepting material known to the person skilled in the art.

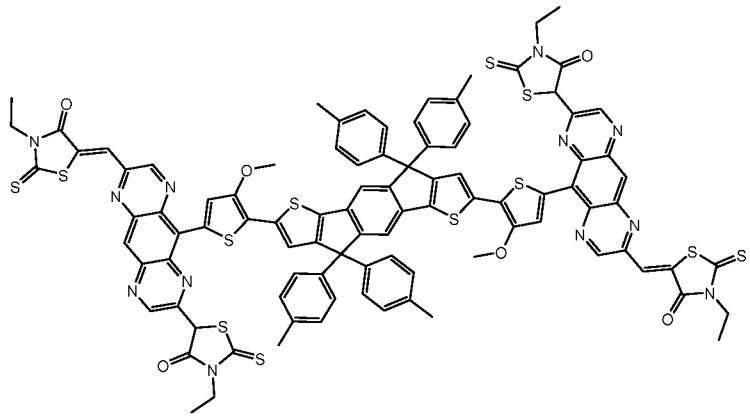
Exemplary electron-accepting materials are non-fullerene acceptors, which may or may not contain a unit of formula (I), and fullerenes.

Exemplary electron-accepting compounds containing at least one unit of formula (I) include:





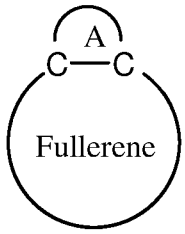




Non-fullerene acceptors which do not contain a unit of formula (I) are described in, for example, Cheng et al, "Next-generation Organic Photovoltaics based on Non-fullerene Acceptors", Nature Photonics (2018), 12, p131-142, the contents of which are incorporated herein by reference, and which include, without limitation, PDI, ITIC, IEICO and derivatives thereof.

Exemplary fullerene electron acceptor materials 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-C61-butyric acid methyl ester (C_{60}PCBM), TCBM-type fullerene derivatives (e.g. tolyl-C61-butyric acid methyl ester (C_{60}TCBM)), and ThCBM-type fullerene derivatives (e.g. thienyl-C61-butyric acid methyl ester (C_{60}ThCBM).

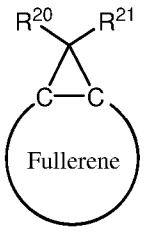
Fullerene derivatives may have formula (III):



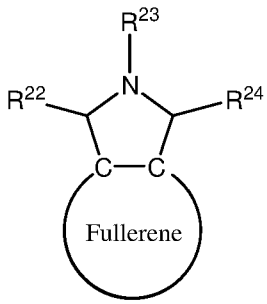
(III)

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.

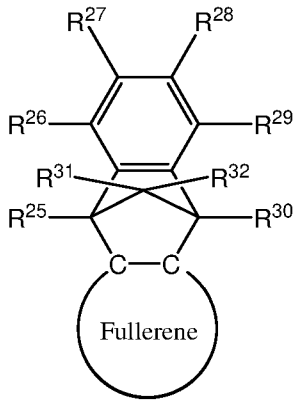
Exemplary fullerene derivatives include formulae (IIIa), (IIIb) and (IIIc):



(IIIa)



(IIIb)



(IIIc)

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, non-terminal C atoms may be replaced with O, S, 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, non-terminal C atoms may be replaced with O, S, CO or COO and one or more H atoms may be replaced with F.

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.

Electrodes

Each transparent electrode preferably has a transmittance of at least 70 %, optionally at least 80 %, to wavelengths in the range of 750-1000 nm or 1300-1400 nm. The transmittance 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.

Bulk heterojunction layer formation

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 donor material(s), the electron acceptor 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 acceptor, the electron donor 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.

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 750 nm, optionally in the range of 900-1000 nm. In some embodiments, the light source has a peak wavelength greater than 1000 nm, optionally in the range of 1300-1400 nm.

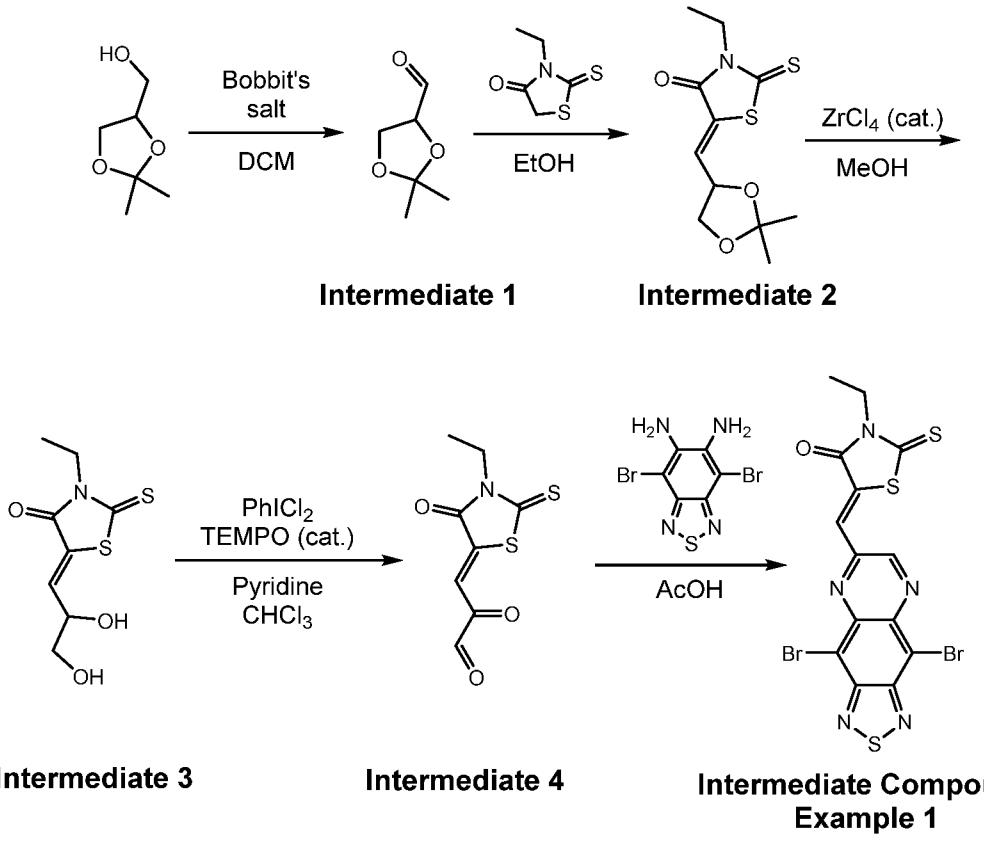
In some embodiments, the light from the light source may or may not be changed before reaching the OPD. For example, the light may be reflected, filtered, down-converted or up-converted before it reaches the OPD.

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.

EXAMPLES

Intermediate Compound Example 1



Intermediate 1

4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidinium tetrafluoroborate, (Bobitt's salt, 2.4 equiv.) is added to a solution of 1,2-isopropylideneglycerol and 2,6-lutidine (2.2 equiv.) in DCM under nitrogen. The reaction mixture is stirred for 4 hours and purified.

Intermediate 2

N-Ethylrhodanine (1 equiv.) is added to a solution of Intermediate 1 (1.1 equiv.) in ethanol and the solution is heated at reflux for 18 hrs. The reaction mixture is cooled to room temperature, the solid is filtered, washed with ethanol and diethyl ether and dried in vacuum.

Intermediate 3

$ZrCl_4$ (10 mol %) is added to a solution of Intermediate 2 in methanol and stirred for 3 hrs at 35 °C. The crude reaction mixture is purified by column chromatography.

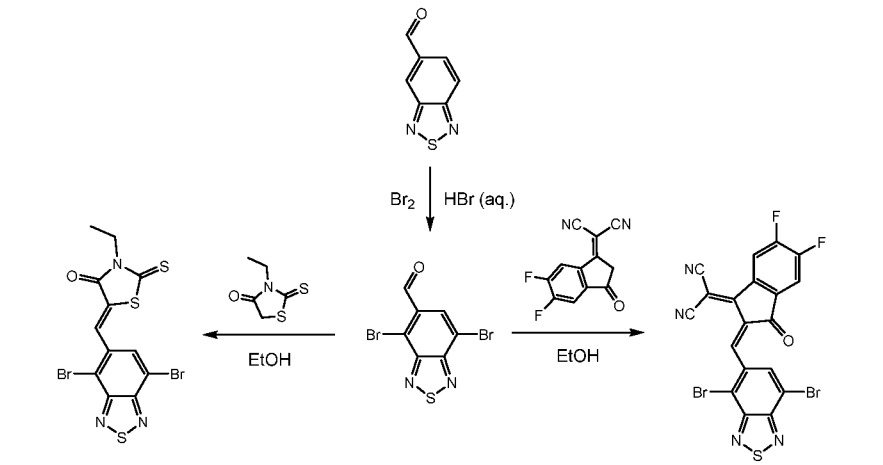
Intermediate 4

$PhICl_2$ (1.5 equiv.) is added to a solution of Intermediate 3 (1 equiv.), TEMPO (8 mol %) and pyridine (3 equiv.) in $CHCl_3$ at room temperature. The mixture is heated at 50 °C for 3 hrs, cooled and purified.

Intermediate Compound Example 1

Concentrated AcOH is added to a mixture of Intermediate 4 (1.0 equiv.) and 4,7-dibromobenzo[c][1,2,5]thiadiazole-5,6-diamine (1.0 equiv.). The mixture is heated to 80 °C overnight and cooled to room temperature. The solid is filtered, washed with water and methanol and dried under vacuum.

Intermediate Compound Examples 2 and 3



Intermediate 5

Bromine is added dropwise to a solution of 2,1,3-benzothiadiazole-5-carbaldehyde dissolved in 48 % HBr (aq,). The mixture is heated to 120 °C, cooled to room temperature and quenched with saturated aqueous $NaHSO_3$. The product is extracted with DCM and dried.

Intermediate Compound Example 2

N-Ethylrhodanine (1 equiv.) is added to a solution of Intermediate 5 (1.1 equiv.) in ethanol. The resulting solution is heated at reflux for 18 hrs, allowed to cool to room temperature and the solid is filtered, washed with ethanol and diethyl ether and dried in vacuum.

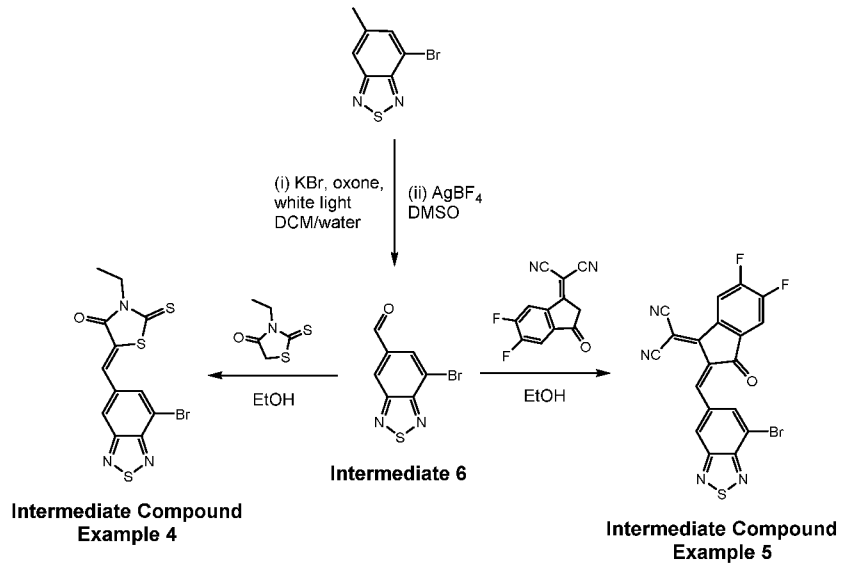
Intermediate Compound Example 3

Intermediate Compound Example 3 is prepared in a similar fashion to Intermediate Compound Example 2 using 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (1.1 equiv.) instead of N-ethylrhodanine.

Intermediate Compound Examples 1, 2 and 3 may be reacted to form polymeric or non-polymeric materials comprising an electron-accepting unit derived from these compounds and an electron donating unit.

A polymer comprising an electron-accepting repeat unit formed by polymerisation of Intermediate Compound Example 1, 2 or 3 may be formed by Suzuki polymerisation with a monomer for forming a electron-donating repeat unit, for example as disclosed in WO2013/051676, the contents of which are incorporated herein by reference.

Intermediate Compound Example 4 and 5



Intermediate 6

Preparation of Intermediate 6 is reported in Org. Lett. 2020, 22 (1), 270.

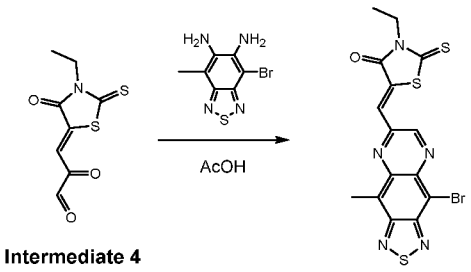
Intermediate Compound Example 4

N-Ethylrhodanine (1 equiv.) is added to a solution of Intermediate 6 (1.1 equiv.) in ethanol. The resulting solution is heated at reflux for 18 hrs, allowed to cool to room temperature and the solid is filtered, washed with ethanol and diethyl ether and dried in vacuum.

Intermediate Compound Example 5

Intermediate Compound Example 4 is prepared in a similar fashion to Intermediate Compound Example 4 using 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (1.1 equiv.) instead of N-ethylrhodanine

Intermediate Compound Example 6



Intermediate 4

Intermediate Compound Example 6

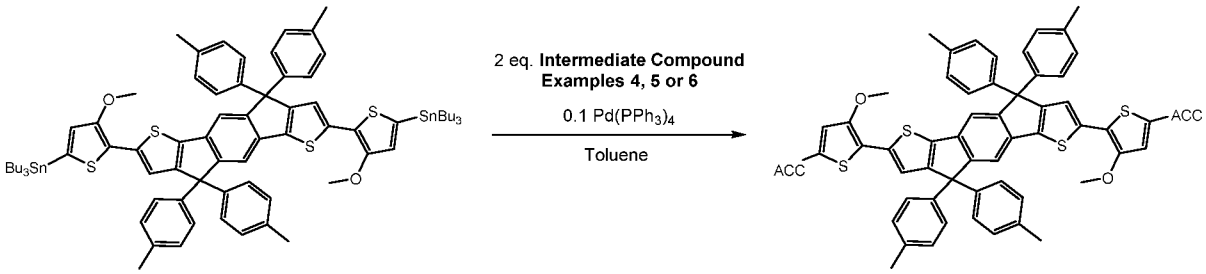
4-bromo-7-methylbenzo[c][1,2,5]thiadiazole-5,6-diamine is prepared following the reported procedure in US20190051781.

Intermediate Compound Example 6

Intermediate Compound Example 6 is prepared in a similar fashion to Intermediate Compound Example 1 using 4-bromo-7-methylbenzo[c][1,2,5]thiadiazole-5,6-diamine instead of 4,7-dibromobenzo[c][1,2,5]thiadiazole-5,6-diamine.

Intermediate Compound Examples 4, 5 and 6 may be reacted to form non-polymeric material comprising an electron-accepting unit derived from these compounds and an electron donating unit.

A non-polymeric material comprising an electron-accepting repeat unit formed by reaction of Intermediate Compound Example 4, 5 or 6 may be formed, for example as shown below.



Intermediate 7 **General Formula 1**

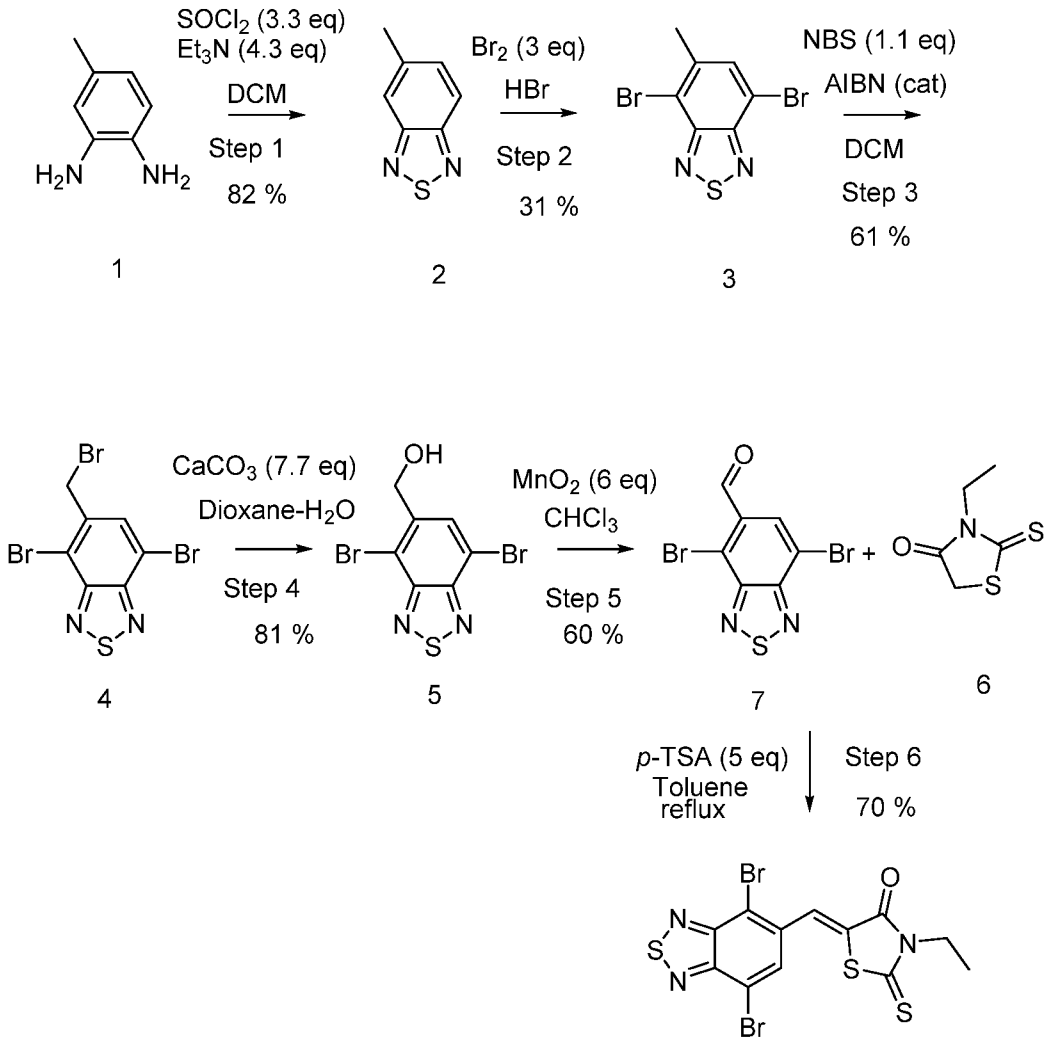
Intermediate 7

Synthesis of Intermediate 7 maybe prepared via standard lithiation and stannylation methods, analogous to that disclosed in for example US20190181348.

General Formula 1

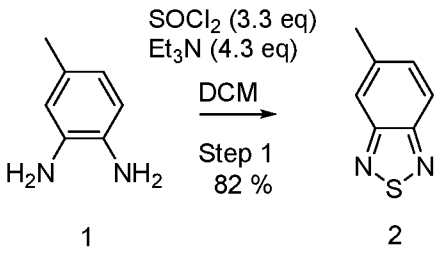
Intermediate 7 (1 equiv.), Intermediate Compound Example 4, 5 or 6 (2.2 equiv.) and $Pd(PPh_3)_4$ (0.1 equiv.) are dissolved in toluene under nitrogen and heated to 100 °C for 48 hours. The mixture is allowed to cool, poured into dilute aqueous KF, extracted with DCM and purified. This is analogous to that isclosed in for example CN104557968.

Intermediate Compound Example 7



Intermediate Compound Example 7

Synthesis of intermediate 2



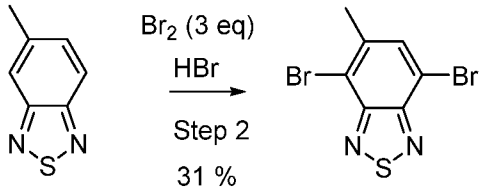
3,4-diaminotoluene (50 g, 0.409 mol) was dissolved in dichloromethane (1 L) in a 2 L 3-necked round-bottom flask, equipped with magnetic stirrer, nitrogen inlet and exhaust and the mixture was cooled to 10 ^{0}C with an ice bath. Triethylamine (242 mL, 1.75 mol) was added. Thionyl chloride (98.1 mL, 1.36 mol) was slowly added to the reaction mixture and stirred at room temperature. The reaction progress was monitored using thin layer chromatography and LC-MS.

After completion of the reaction, the reaction mixture was added to aqueous 1M sodium hydroxide solution (1L) and extracted with dichloromethane (3 x 500 mL). The organic layer was separated, dried over sodium sulphate and concentrated in a rotary evaporator to get 54 g of intermediate 2 with 96 % product mass in LC-MS.

The crude product was purified by column chromatography (60-120 mesh silica gel) and eluted with petroleum ether/ ethyl acetate (~ 4 % ethyl acetate in petroleum ether) to get 50 g of 5-methyl-2,1,3-benzothiadiazole with 99.65 % LCMS purity.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] 2.56 (s, *3*H), 7.45 (dd, *J* = 9.2 Hz & 1.6 Hz, 1H), 7.77 (d, *J* = 1.6 Hz, 1H), 7.89 (d, *J* = 9.2 Hz, 1H).

Synthesis of intermediate 3



2 3

To 5-methyl-2,1,3-benzothiadiazole (50 g, 0.332 mol) in HBr (320 mL) in a 2 L 3-necked round-bottom flask, equipped with overhead stirrer, reflux condenser, nitrogen inlet and exhaust was added bromine (51.2 mL, 0.996 mmol) in HBr (80 mL) was slowly added to the reaction. The reaction mass was heated to reflux temperature and stirred for 8 hours.

The reaction progress monitored by LCMS showed mono-bromide as major product. A further 3 equivalents of bromine were added and the reaction was continued for about 6 hours. After completion of the reaction, the reaction mixture was cooled to room temperature and carefully quenched with saturated sodium bisulfite solution to consume excess bromine. The solid obtained was filtered and washed with water.

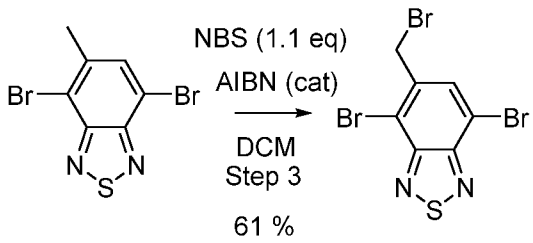
100 g of crude solid was obtained with 96.9% purity by GC-MS.

The crude product was purified by mixing it with acetonitrile (417 mL), heating at 75°C and adding toluene (167mL) added until dissolved.

The mixture was stirred at room temperature and the solid obtained was filtered to obtain 32 g of 4,7-dibromo-5-methyl-2,1,3-benzothiadiazole with 99.67% purity.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] 2.60 (s, 3H), 7.76 (s, 1H).

Synthesis of intermediate 4



3 4

To 4,7-dibromo-5-methyl-2,1,3-benzothiadiazole (30.0 g, 0.0974 mol) in chloroform (300 mL) in a 1 L 3-necked round-bottom flask, equipped with overhead stirrer, reflux condenser, nitrogen inlet and exhaust was added N-bromosuccinimide (19.0 g, 0.107 mol) and Azobisisobutyronitrile (799 mg, 4.87 mmol). The reaction mixture was refluxed overnight (~about 17 hours). The reaction progress was monitored using thin layer chromatography and after completion, the reaction mixture was concentrated to obtain 48 g of crude product with 81.72% purity of the desired product.

The crude material was purified over silica column chromatography using petroleum ether and ethyl acetate to get three fractions.

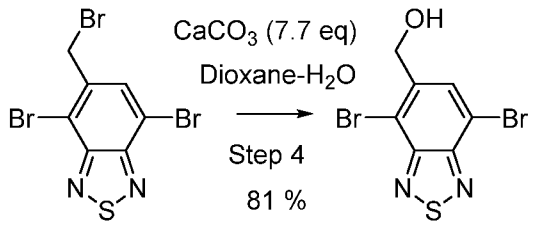
Fraction 1: 11 g with 70 % purity

Fraction 2: 9.0 g with 97.89 % purity

Fraction 3: 14.0 g with 98.70 % purity

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] 4.76 (s, 2H), 7.94 (s, 1H).

Synthesis of intermediate 5



4 5

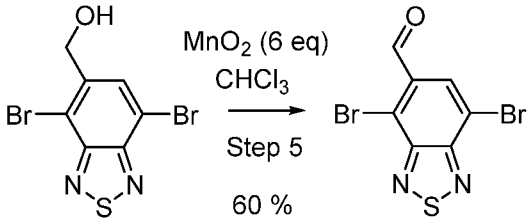
To 4,7-dibromo-5-(bromomethyl)-2,1,3-benzothiadiazole (25.0 g, 0.0646 mol) in 1,4 dioxane (400 mL) and water (400 mL) in a 2 L 3-necked round-bottom flask, equipped with overhead stirrer, reflux condenser, nitrogen inlet and exhaust was added calcium carbonate (49.7 g, 0.497 mol). The reaction mixture was refluxed for overnight under nitrogen atmosphere. The reaction progress was monitored using thin layer chromatography and after completion,

the mixture was acidified with 2N HCl and extracted with chloroform (1 L). The organic layer was concentrated to give 20.0 g of crude product with 96.88% purity by LC-MS.

The crude product (20 g) was triturated with ethyl acetate (10v) and filtered to get 17 g of (4,7-dibromo-2,1,3-benzothiadiazol-5-yl)methanol with 96.5 % HPLC purity.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] 2.19 (t, J = 6.0 Hz, 1H), 4.76 (d, J = 6.0 Hz, 2H), 8.17 (s, 1H).

Synthesis of Intermediate 7



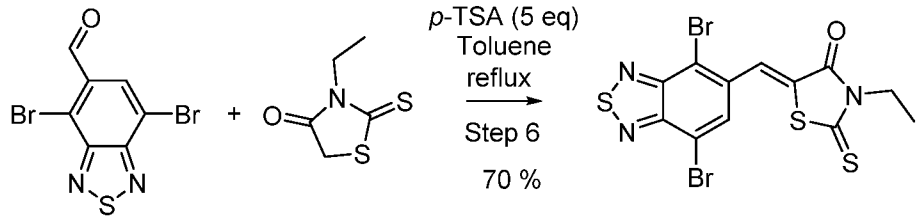
5 7

To (4,7-dibromo-2,1,3-benzothiadiazol-5-yl)methanol (20.0 g, 0.0617 mol) in chloroform (1.1L) in a 2 L multi-necked round-bottom flask, equipped with overhead stirrer, reflux condenser, nitrogen inlet and exhaust was added manganese dioxide (32.1 g, 0.370 mol). The reaction mixture was heated at 55 °C and stirred overnight. The reaction progress was monitored using thin layer chromatography. After completion of the reaction, the mixture was filtered through a celite bed. The pad was washed with chloroform (200 mL). The filtrate was concentrated to get 15.0 g of crude product with 97 % HPLC purity.

The crude material was purified by crystallization using DMF and water. The crude product (15 g) was heated in DMF (3v), and water was added until a slight turbidity remained. The mixture was allowed to slowly warm to room temperature, stirred overnight and the solid obtained was filtered to obtain 12 g of M1399 with 98.8 % HPLC purity.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] 8.35 (S, 1H), 10.55 (s, 1H).

Synthesis of Intermediate Compound 7



7 6 **Intermediate Compound 7**

To 4,7-dibromo-2,1,3-benzothiadiazole-5-carbaldehyde (6.0 g, 18.6 mmol) in toluene (300 mL) in a 500 mL 3-necked round-bottom flask, equipped with magnetic stirrer, reflux condenser, nitrogen inlet and exhaust was added 3-ethyl-2-sulfanylidene-1,3-thiazolidin-4-one (8.99 g, 55.8 mmol) and *p*-toluene sulfonic acid (18.5 g, 93.0 mmol).

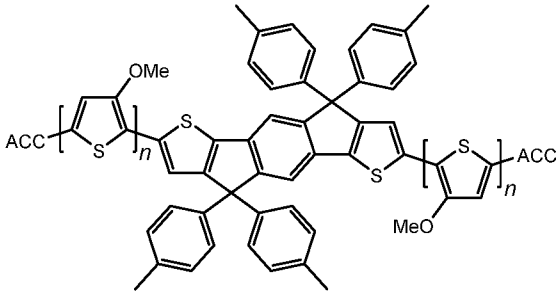
The reaction mixture was heated to 145°C (oil bath) for overnight. After completion of the reaction monitored using thin layer chromatography (9.5:0.5 hexane: ethyl acetate), the reaction mass was concentrated to get 8.2 g of crude material. The crude was passed through a silica column (silica 230-400 mesh) and the product was eluted at 6% ethyl acetate in hexane to get 7.6 g of the desired product with 97.86 % LCMS purity. The product was triturated using acetonitrile to get 7 g with 98.9 % LCMS purity. The material was further crystallized twice using hot ethyl acetate to obtain 6.0 g of Intermediate Compound 7 with 99.3 % HPLC purity.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] 1.35 (t, *J* = 7.2 Hz, 3H), 4.26 (q, *J* = 7.2 Hz, 2H), 7.99 (s, 1H), 8.12 (s, 1H).

Modelling Example 1

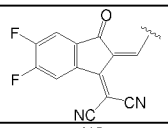
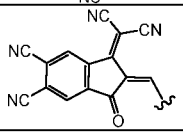
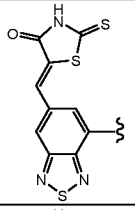
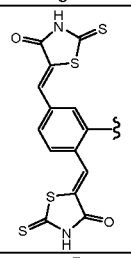
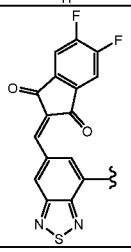
All modelling as described in these examples was performed using Gaussian09 software available from Gaussian using Gaussian09 with B3LYP (functional).

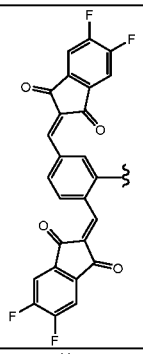
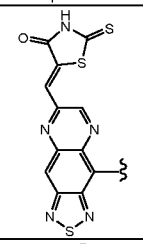
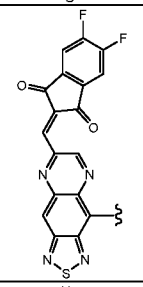
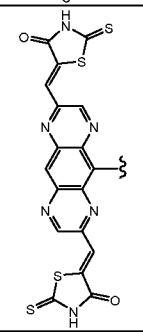
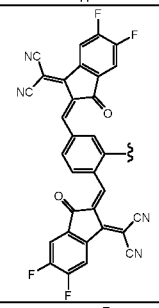
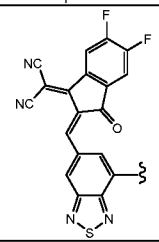
HOMO and LUMO levels for range of acceptor (A) of model compounds of General Formula 1 were modelled:

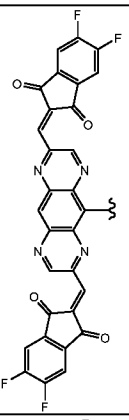
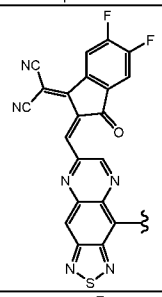
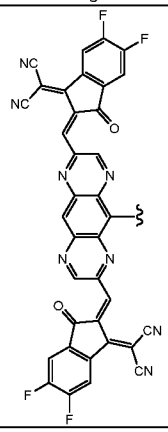


General Formula 1

Table 1

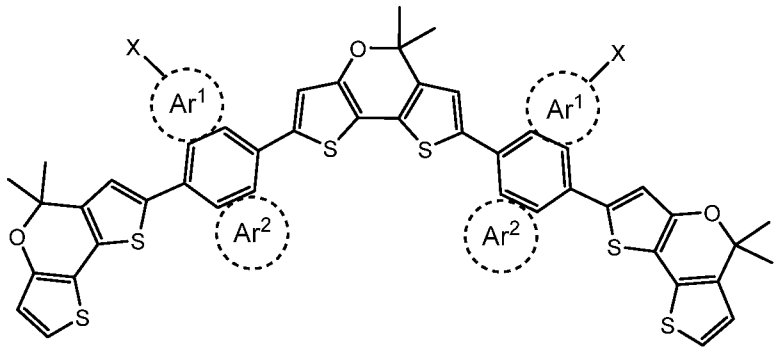
Entry	ACC	n	HOMO (eV)	LUMO (eV)	E_g (eV)	Abs (nm)
1A (Comparative)		0	–5.79	–3.57	2.21	562
1B (Comparative)		1	–5.44	–3.81	1.62	765
1C (Exemplary)		1	–4.60	–3.16	1.44	864
1D (Exemplary)		1	-4.69	-3.27	1.43	869
1E (Exemplary)		1	–4.45	–3.24	1.21	1029

1F (Exemplary)		1	-4.57	-3.37	1.20	1033
1G (Exemplary)		1	–4.67	–3.612	1.06	1170
1H (Exemplary)		1	–4.58	–3.56	1.02	1219
1I (Exemplary)		1	–4.73	–3.74	0.99	1250
1J (Exemplary)		1	-4.78	-3.86	0.93	1335
1K (Exemplary)		1	–4.57	–3.65	0.92	1355

1L (Exemplary)		1	–4.69	–3.78	0.91	1357
1M (Exemplary)		1	–4.64	–3.79	0.85	1460
1N (Exemplary)		1	–4.87	–4.03	0.83	1490

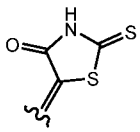
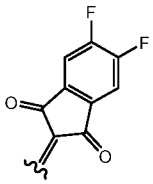
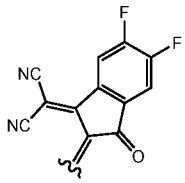
Modelling Example 2

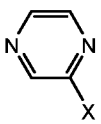
The effect of a range of groups X and the presence of groups Ar^1 and Ar^2 on the HOMO and LUMO of materials of formula (I) was modelled using model compounds of General Formula 2:

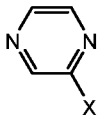
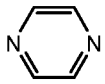


General Formula 2

Table 2

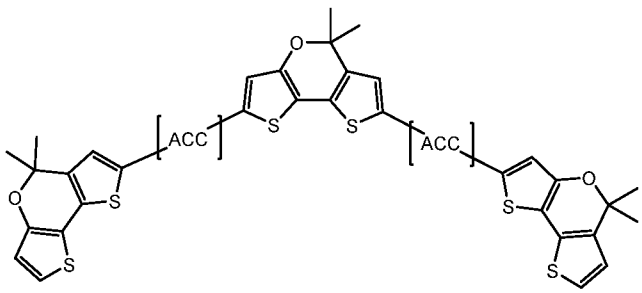
Rho  ICF  IC2F 

Model Compound	Ar^1	Ar^2	X	HOMO (eV)	LUMO (eV)	Eg (eV)	Abs (nm)
2A (Comparative)	-	-	**H**	–4.63	–1.98	2.64	469
2B (Exemplary)			**Rho**	–5.24	–3.19	2.05	605
2C (Exemplary)			**I2F**	–5.0	–3.29	1.72	723
2D (Exemplary)			**IC2F**	–5.29	–3.77	1.52	816
2E (Comparative)	–		**H**	–4.45	–2.81	1.70	734
2F (Exemplary)			**Rho**	–4.86	–3.25	1.61	772
2G (Exemplary)			**I2F**	–4.72	–3.32	1.40	888
2H (Exemplary)			**IC2F**	–4.87	–3.59	1.29	964
2I (Comparative)			**H**	–4.32	–3.37	0.95	1304
2J (Exemplary)			**Rho**	–4.53	–3.712	0.81	1534
2K (Exemplary)			**I2F**	–4.42	–3.75	0.67	1842
2L (Exemplary)			**IC2F**	–4.58	–3.99	0.59	2101

2M (Comparative)			**H**	−4.31	−3.16	1.16	1071
2N (Exemplary)			**Rho**	−4.77	−3.74	1.03	1204
2O (Exemplary)			**I2F**	−4.52	−3.75	0.78	1600
2P (Exemplary)			**IC2F**	−4.75	−4.12	0.63	1968

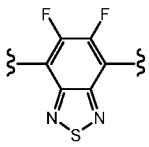
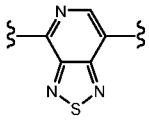
Modelling Example 3

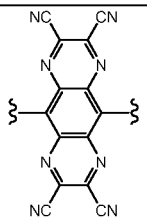
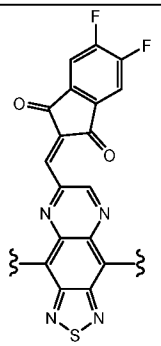
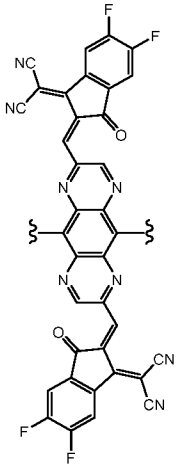
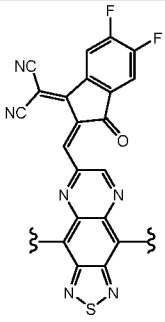
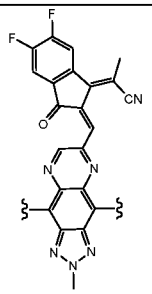
The effect of the electron-accepting unit of formula (I) on the LUMO and band gap of model compounds of General Formula 3, in which ACC is the electron-accepting unit, is shown in Table 3.

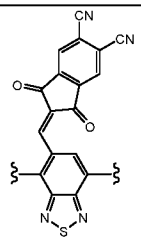
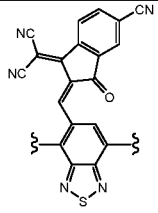
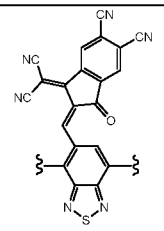


General Formula 3

Table 3

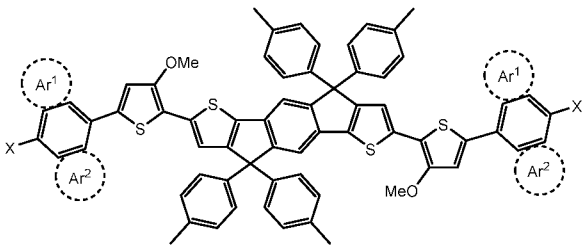
Model Compound	**ACC**	**HOMO (eV)**	**LUMO (eV)**	**E_g (eV)**	**Abs (nm)**
3A (Comparative)		-4.65	-2.92	1.73	716
3B (Comparative)		-4.60	-3.06	1.54	803

3C (Comparative)		–5.10	–4.40	0.70	1779
3D (Exemplary)		–4.42	–3.75	0.67	1842
3E (Exemplary)		–4.75	–4.12	0.63	1968
3F (Exemplary)		–4.58	–3.99	0.59	2101
3G (Exemplary)		-4.46	-3.66	0.80	1552

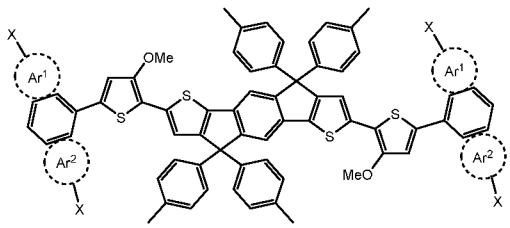
3H (Exemplary)		-4.92	-3.73	1.19	1044
3I (Exemplary)		-4.93	-3.78	1.15	1078
3J (Exemplary)		-5.07	-4.02	1.04	1190

Modelling Example 4

The effect of the position of the electron-accepting unit of formula (I) on the LUMO and band gap of model compounds of General Formula 4-I and General Formula 4-II, is shown in Table 4.

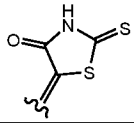


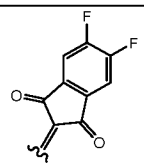
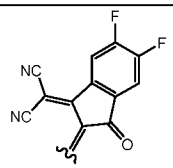
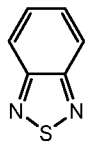
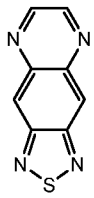
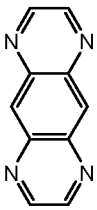
General Formula 4-I



General Formula 4-II

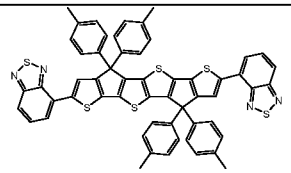
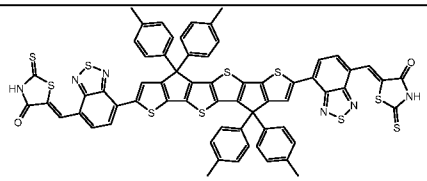
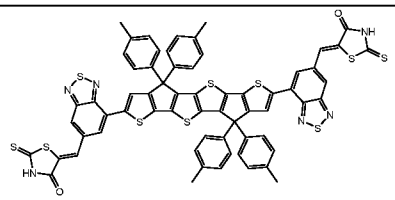
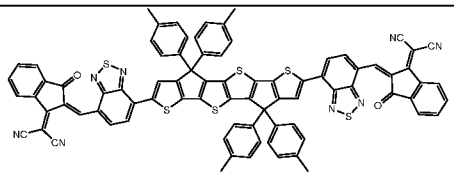
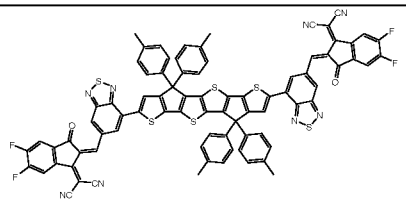
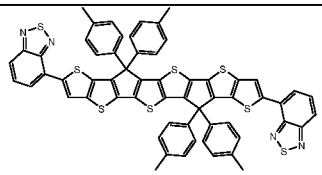
Table 4

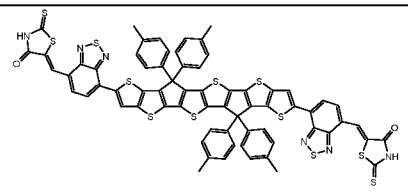
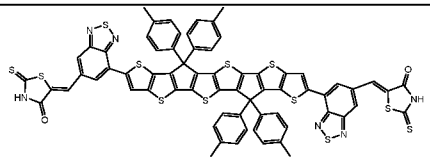
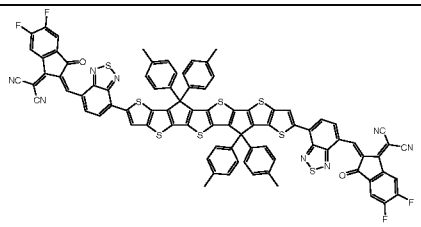
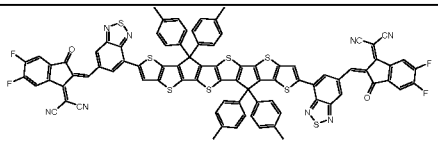
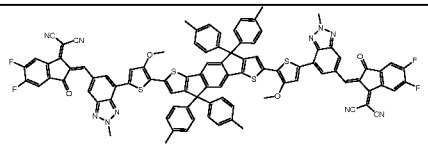
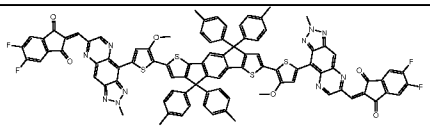
Model Compound	General Formula	Ar	X	HOMO (eV)	LUMO (eV)	E_g (eV)	Abs (nm)
4A (Comparative)	4-I			-4.67	-2.79	1.88	661
4B	4-II			-4.69	-3.27	1.43	869

(Exemplary)			Rho				
4C (Comparative)	4-I		 I2F	-4.65	-2.845	1.80	688
4D (Exemplary)	4-II			-4.57	-3.37	1.20	1033
4E (Comparative)	4-I		 IC2F	-4.83	-3.334	1.50	829
4F (Exemplary)	4-II			-4.78	-3.86	0.93	1335
4G (Comparative)	4-I		Rho	-4.79	-3.28	1.51	823
4H (Exemplary)	4-II			-4.60	-3.16	1.43	864
4I (Comparative)	4-I		I2F	-4.79	-3.29	1.50	827
4J (Exemplary)	4-II			-4.45	-3.24	1.21	1029
4K (Comparative)	4-I		IC2F	-4.97	-3.58	1.39	895
4L (Exemplary)	4-II			-4.57	-3.65	0.92	1355
4M (Comparative)	4-I		Rho	-4.81	-3.75	1.06	1169
4N (Exemplary)	4-II			-4.67	-3.61	1.06	1170
4O (Comparative)	4-I		I2F	-4.79	-3.62	1.17	1060
4P (Exemplary)	4-II			-4.58	-3.56	1.02	1219
4Q (Comparative)	4-I		IC2F	-5.0	-3.88	1.12	1109
4R (Exemplary)	4-II			-4.64	-3.79	0.85	1460
4S (Comparative)	4-I		Rho	-4.73	-3.54	1.19	1039
4T (Exemplary)	4-II			-4.73	-3.74	0.99	1250
4U (Comparative)	4-I		I2F	-4.67	-3.378	1.29	959
4V (Exemplary)	4-II			-4.69	-3.78	0.91	1357
4W (Comparative)	4-I		IC2F	-4.87	-3.645	1.22	1017
4X (Exemplary)	4-II			-4.867	-4.03	0.83	1490

Modelling Example 5

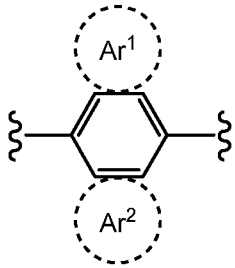
The effect of the position of the electron-accepting unit of formula (I) on the LUMO and band gap of model compounds, is shown in Table 5.

Name	Structure	HOMO (eV)	LUMO (eV)	E_g (eV)	Abs (nm)
5A (Comparative)		–4.67	–2.59	2.08	596
5B (Comparative)		-5.05	-3.35	1.70	731
5C (Exemplary)		–4.90	–3.21	1.69	734
5C (Comparative)		-5.09	-3.47	1.61	768
5D (Exemplary)		–4.92	–3.53	1.39	892
5E (Comparative)		-4.57	-2.59	1.98	627

5F (Comparative)		-4.91	-3.32	1.58	784
5G (Exemplary)		-4.77	-3.22	1.55	800
5H (Comparative)		-5.06	-3.62	1.45	857
5I (Exemplary)		-4.78	-3.54	1.24	1000
5J (Exemplary)		-4.43	-3.36	1.07	1155
5K (Exemplary)		-4.42	-3.24	1.18	1054

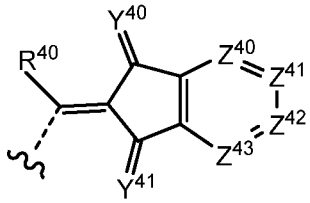
Claims

1. A material comprising an electron-accepting unit of formula (I):

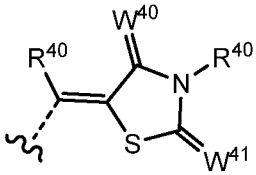


(I)

wherein Ar^1 is a 5- or 6-membered aromatic or heteroaromatic ring or is absent; Ar^2 is a 5- or 6-membered aromatic or heteroaromatic ring or is absent; and wherein the electron-accepting unit of formula (I) is substituted with at least one group of formula (Xa) or (Xb):



(Xa)



(Xb)

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;

Y^{40} and Y^{41} are each independently O, S, NX^{70} wherein X^{70} is CN or $COOR^{40}$; or $CX^{60}X^{61}$ wherein X^{60} or X^{61} is independently CN, CF_3 or $COOR^{40}$;

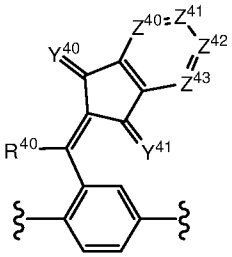
W^{40} and W^{41} are each independently O, S, NX^{70} wherein X^{70} is CN or $COOR^{40}$; or $CX^{60}X^{61}$ wherein X^{60} or X^{61} is independently CN, CF_3 or $COOR^{40}$; and

R^{40} in each occurrence is H or a substituent;

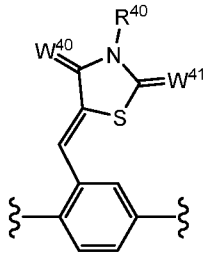
and wherein the material further comprises an electron-donating unit D comprising a fused or unfused furan or thiophene.

2. The material according to claim 1 wherein each (Xa) or (Xb) is an electron-withdrawing group.

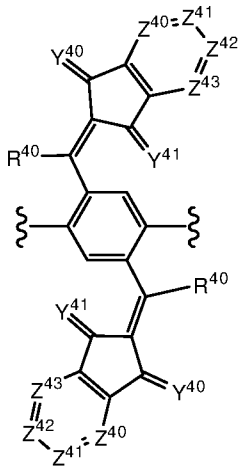
3. The material according to claim 1 or 2 wherein the material has formula (I-1) – (I-11):



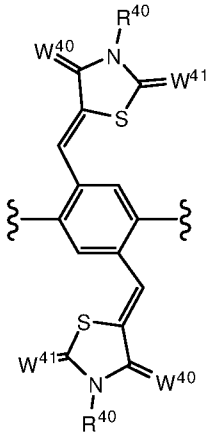
(I-1)



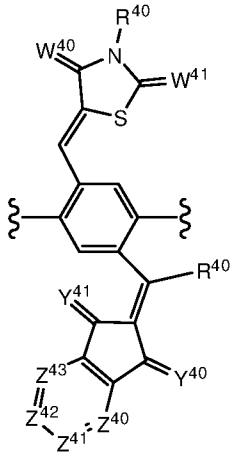
(I-2)



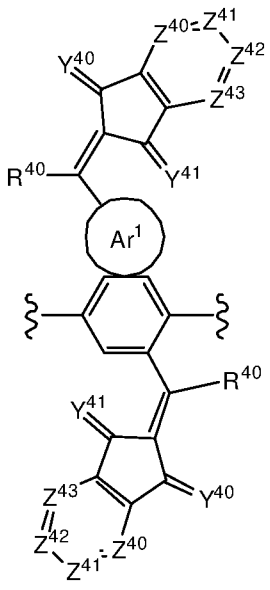
(I-3)



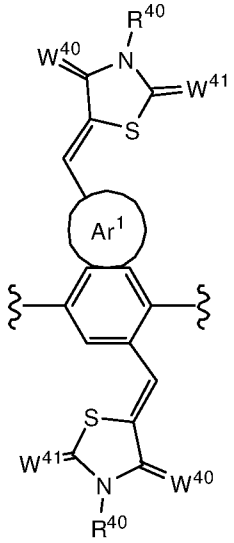
(I-4)



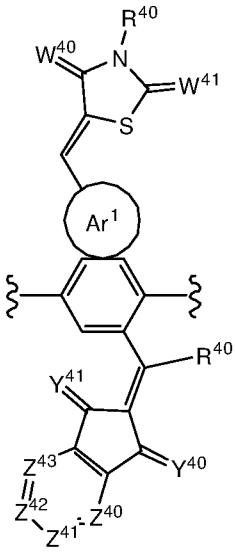
(I-5)



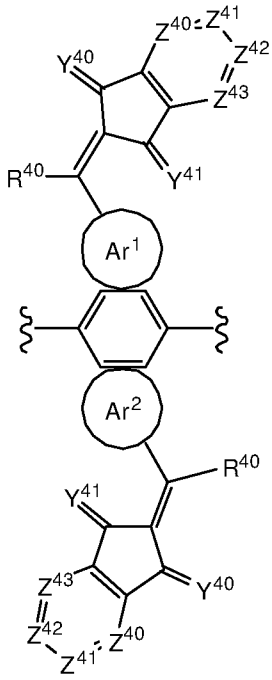
(I-6)



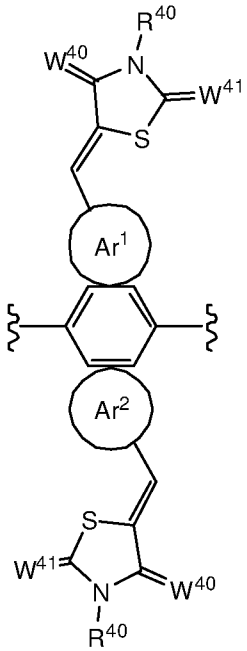
(I-7)



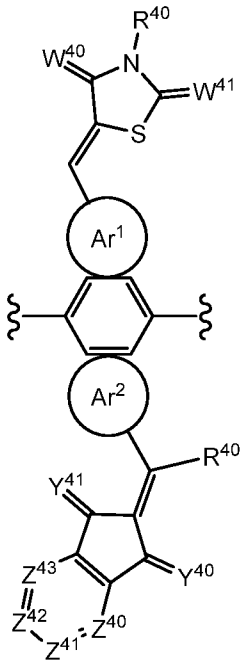
(I-8)



(I-9)



(I-10)

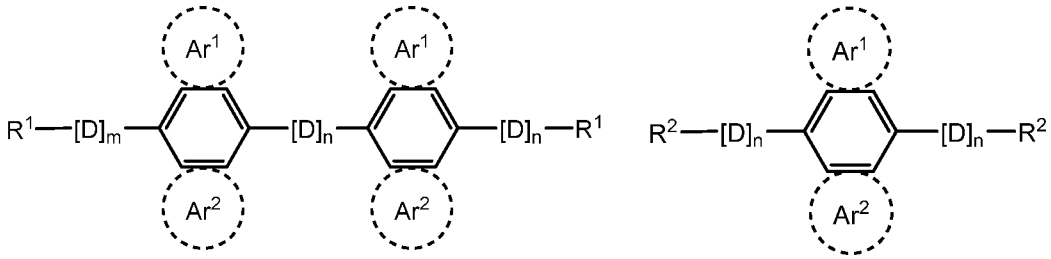


(I-11)

4. The material according to any preceding claim wherein Ar^1 and Ar^2, where present are independently a 5- or 6-membered heteroaromatic ring containing at least one N atom.

5. The material according to any preceding claim wherein the material is a non-polymeric compound.

6. The material according to claim 5 wherein the material has formula (Ia) or (Ib):

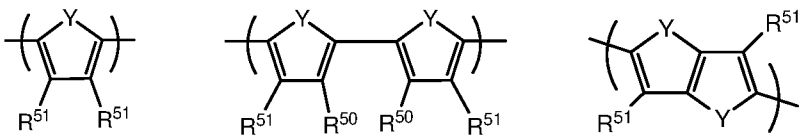


(Ia) (Ib)

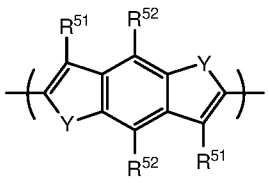
wherein n is at least 1; m is 0, 1, 2 or 3; D in each occurrence is independently an electron-donating unit comprising a fused or unfused thiophene or furan which may be unsubstituted or substituted with one or more substituents; and R^1 and R^2 independently in each occurrence is H or a substituent.

7. The material according to any one of claims 1 to 4 wherein the material is a polymer; the unit of formula (I) is an electron-accepting repeat unit of formula (I); and the electron-donating unit D is an electron-donating repeat unit.

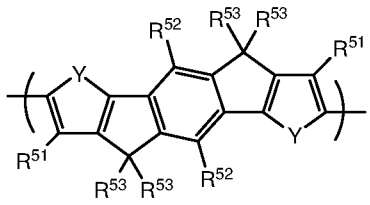
8. The material according to any one of the preceding claims wherein D is selected from formulae (IIa) – (IIm):



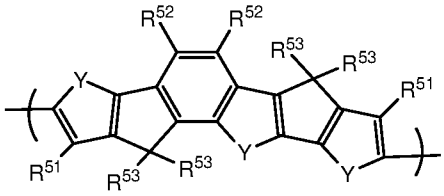
(IIa) (IIb) (IIc)



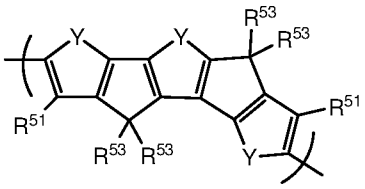
(IId)



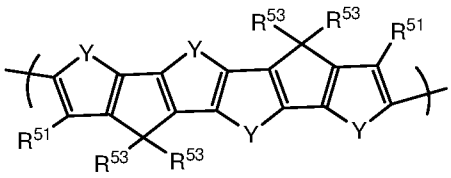
(IIe)



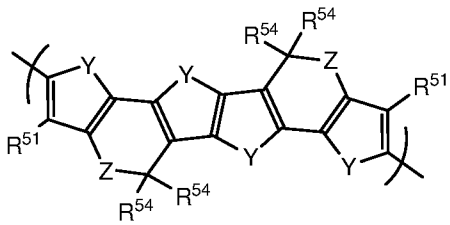
(IIf)



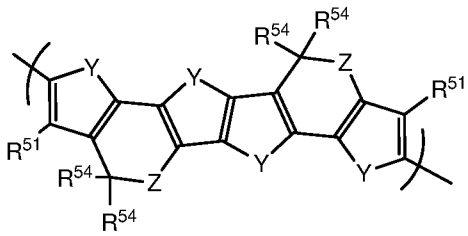
(IIg)



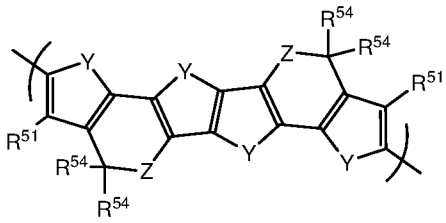
(IIh)



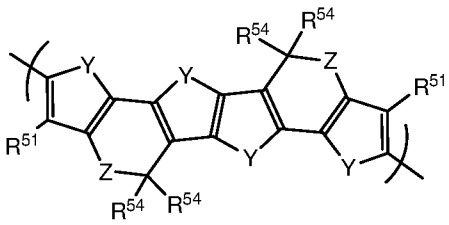
(IIi)

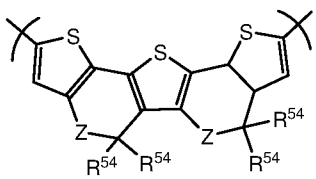


(IIj)



(IIk)

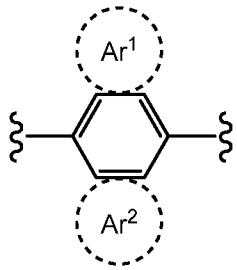




(III) (IIm)

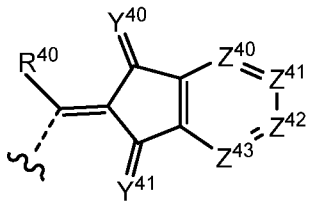
wherein Y in each occurrence is independently O or S, Z in each occurrence is independently O, S, NR^{55} or $C(R^{54})_2$; R^{50}, R^{51}, R^{52} R^{54} and R^{55} independently in each occurrence is H or a substituent wherein R^{50} groups may be linked to form a ring; and R^{53} independently in each occurrence is a substituent.

9. A polymer comprising a repeat unit of formula (I):

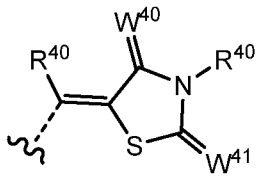


(I)

wherein Ar^1 is a 5- or 6-membered aromatic or heteroaromatic ring or is absent; Ar^2 is a 5- or 6-membered aromatic or heteroaromatic ring or is absent; and wherein the repeat unit of formula (I) is substituted with at least one group of formula (Xa) or (Xb):



(Xa)



(Xb)

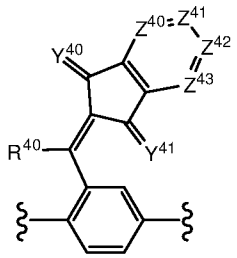
Z^{40}, Z^{41}, Z^{42} and Z^{43} are each independently CR^{13} or N wherein R^{13} in each occurrence is H or a substituent;

Y^{40} and Y^{41} are each independently O, S, NX^{70} wherein X^{70} is CN or $COOR^{40}$; or $CX^{60}X^{61}$ wherein X^{60} or X^{61} is independently CN, CF_3 or $COOR^{40}$;

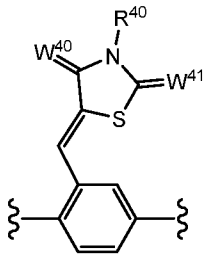
W^{40} and W^{41} are each independently O, S, NX^{70} wherein X^{70} is CN or $COOR^{40}$; or $CX^{60}X^{61}$ wherein X^{60} or X^{61} is independently CN, CF_3 or $COOR^{40}$; and

R^{40} in each occurrence is H or a substituent;

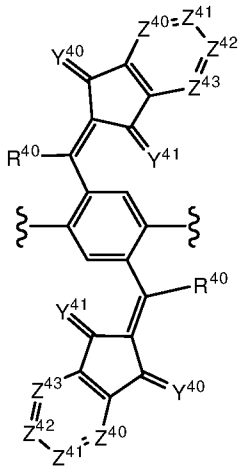
10. A polymer according to claim 9 where the repeat unit of formula (I) has formula (I-1) to (1-11):



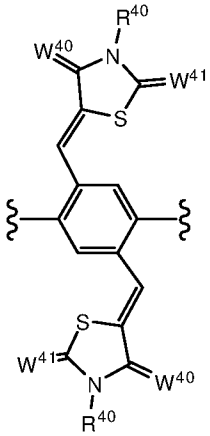
(I-1)



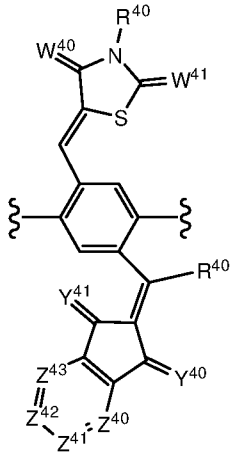
(I-2)



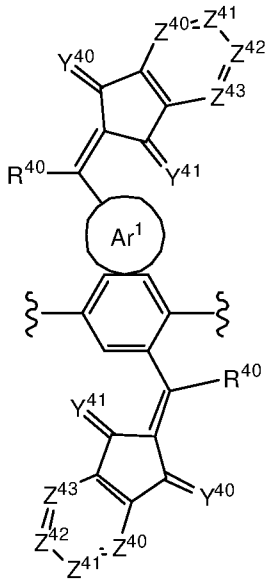
(I-3)



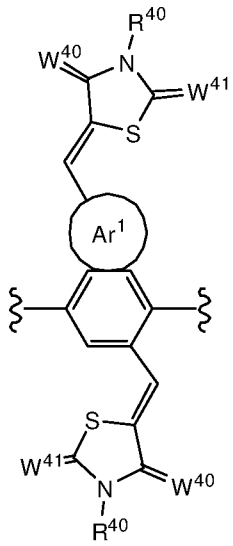
(I-4)



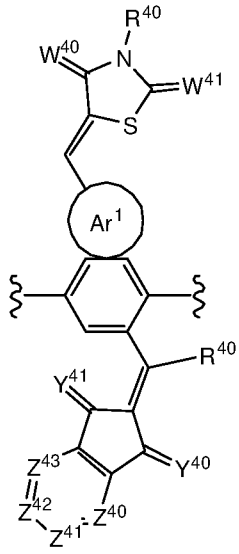
(I-5)



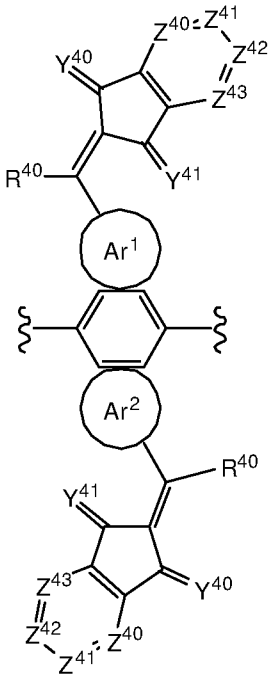
(I-6)



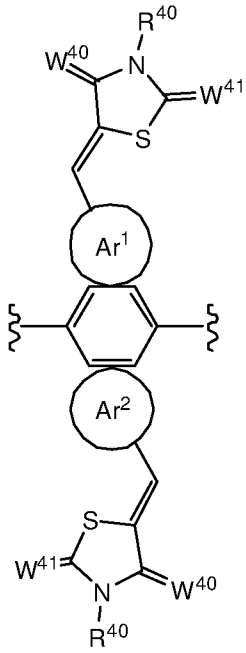
(I-7)



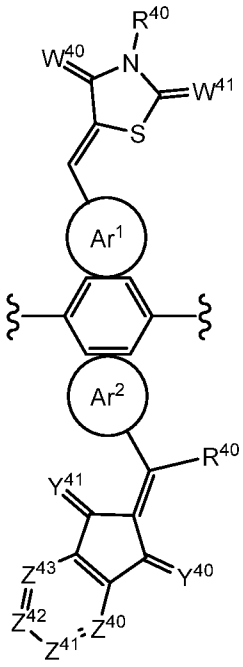
(I-8)



(I-9)



(I-10)



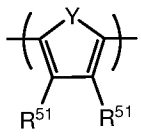
(I-11)

11. A polymer according to claim 9 or 10, wherein the polymer comprises an electron-donating repeat unit.

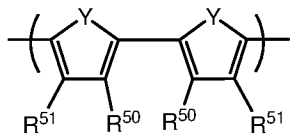
12. A polymer according to claim 11 wherein the polymer comprises an electron-donating repeat unit D.

13. A polymer according to claims 11 or 12 wherein the electron-donating repeat unit D comprises a fused or unfused furan or thiophene.

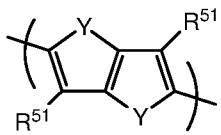
14. A polymer according to claim 13 wherein the electron-donating repeat unit D is selected from formulae (IIa) – (IIm):



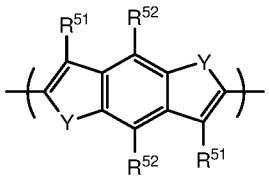
(IIa)



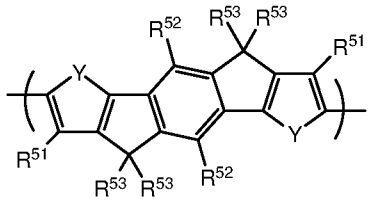
(IIb)



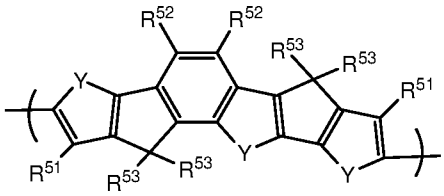
(IIc)



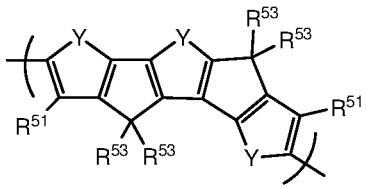
(IId)



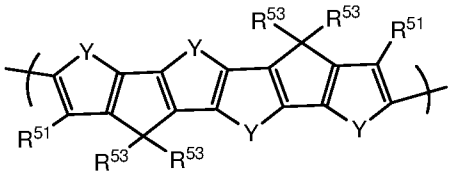
(IIe)



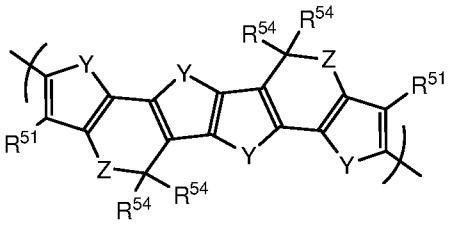
(IIf)



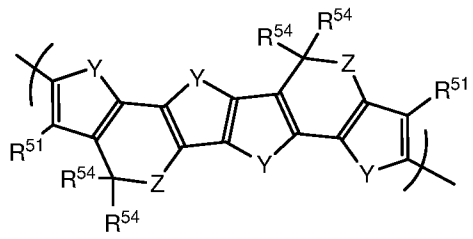
(IIg)



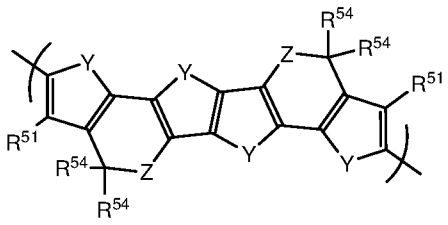
(IIh)



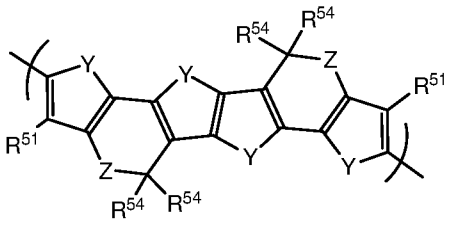
(IIi)



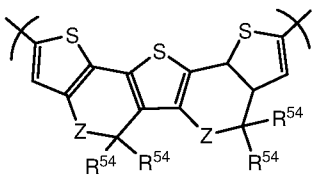
(IIj)



(IIk)



(III)



(IIm)

wherein Y in each occurrence is independently O or S, Z in each occurrence is independently O, S, NR^{55} or $C(R^{54})_2$; R^{50}, R^{51}, R^{52} R^{54} and R^{55} independently in each occurrence is H or a substituent wherein R^{50} groups may be linked to form a ring; and R^{53} independently in each occurrence is a substituent.

15. A composition comprising an electron donor and an electron acceptor wherein at least one of the electron donor and electron acceptor is a material or polymer according to any one of the preceding claims.

16. The composition according to claim 15 wherein the electron acceptor is the material according to any one of claims 1 to 6.

17. The composition according to claim 16 wherein the electron acceptor is a non-polymeric compound according to claim 5 or 6.

18. The composition according to claim 15 wherein the electron donor is the polymer according to claim 9 to 14.

19. An organic electronic device comprising an active layer comprising a material or polymer 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 any one of claims 15 to 18.

21. An organic electronic device according to claim 19 wherein the organic photoresponsive device is an organic photodetector.

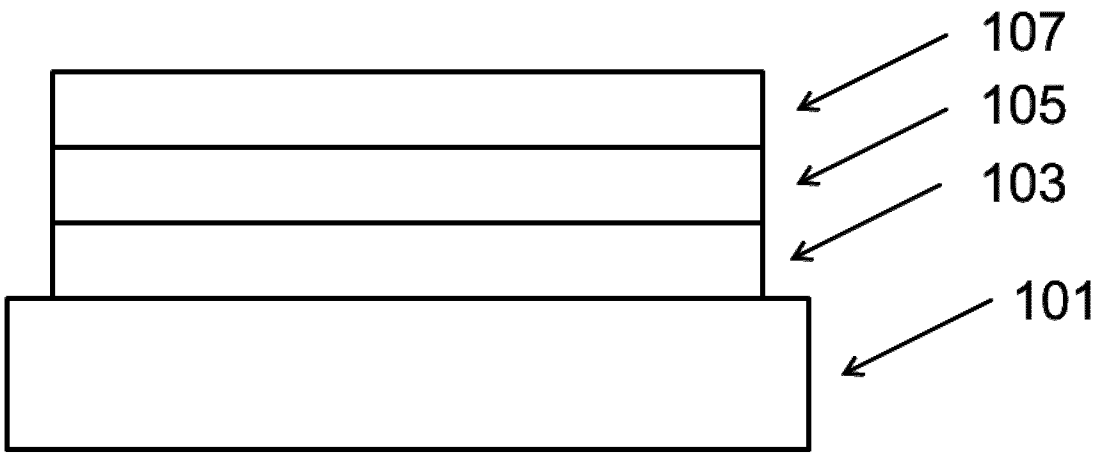
22. A photosensor comprising a light source and an organic photodetector according to claim 21, wherein the photosensor is configured to detect light emitted from a light source.

23. A photosensor according to claim 22, wherein the light source emits light having a peak wavelength of greater than 750 nm.

24. A formulation comprising a material, polymer 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 to 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



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2021/072089

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D495/04 C07D495/14 C07D495/22 C07D519/00 C08G61/12
H01L51/00
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D H01L C08G

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 2018 0104398 A (LG CHEMICAL LTD.) 21 September 2018 (2018-09-21) claims; examples	1,2,4-6, 8,15-17, 19
X	WO 2019/091995 A1 (MERCK PATENT GMBH) 16 May 2019 (2019-05-16) cited in the application page 158, compounds S2-1 and S2-2	1,2,4-6, 15-17, 19-21
X	CN 108 218 887 A (UNIVERSITY OF SOUTH CHINA TECH) 29 June 2018 (2018-06-29) cited in the application claims; examples	1,2,4-6, 8,15-17, 19,24,25

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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 September 2021	07/10/2021

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

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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	CN 108 912 125 A (UNIVERSITY OF NANJING POSTS AND TELECOMMUNICATIONS) 30 November 2018 (2018-11-30) cited in the application claims; examples	1,2,4-6, 15-17, 19,24,25
X	CN 106 065 020 A (UNIVERSITY OF NANCHANG HANGKONG) 2 November 2016 (2016-11-02) cited in the application page 2; claims	1,2,4-6, 8,15-17, 19,24,25
X	WO 2007/081091 A1 (KOREA RESEARCH INSTITUTE OF BIOSCIENCE AND BIOTECHNOLOGY) 19 July 2007 (2007-07-19) Table 2, compounds 57-61, 66, Table 5, compounds 91, 92	1-3,5
Y	WO 2020/109823 A1 (SUMITOMO CHEMICAL CO.LTD.) 4 June 2020 (2020-06-04) claims; examples	7,9-14, 22,23
A	C.B. NIELSEN ET.AL.: "Electron deficient Truxenone derivatives and their use in organic photovoltaics.", JOURNAL OF MATERIALS CHEMISTRY A, vol. 2, no. 31, 16 June 2014 (2014-06-16), pages 12348-12354, XP002804234, DOI: 10.1039/C4TA01653J figures	1-25
Y	US 2020/194684 A1 (KAMTEKER) 18 June 2020 (2020-06-18) claims; examples	7,9-14, 22,23
Y	US 2018/006228 A1 (LEE ET. AL.) 4 January 2018 (2018-01-04) claims; examples	7,9-14, 22,23

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2021/072089

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		WO 2019091995 A1	16-05-2019
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		EP 3888150 A1	06-10-2021
		WO 2020109823 A1	04-06-2020
US 2020194684 A1	18-06-2020	GB 2579806 A	08-07-2020
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		US 2018006228 A1	04-01-2018