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(54) **Title:** FULLERENE DERIVATIVES IN A PHOTORESPONSIVE DEVICE

(57) **Abstract:** A compound of formula (I): $[(Fu)_r\text{-}L]_s\text{-}(NFA)_t$, Fu is a fullerene; NFA is a non-fullerene acceptor; L is a linker group; r, s and t are each at least 1; and NFA is a non-fullerene acceptor. The NFA contains electron-accepting groups, electron-donating groups and, optionally, bridging groups therebetween. At least one bridging group or electron-donating group of the NFA is bound to at least one group of formula (Fu)r-L-.

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FULLERENE DERIVATIVES IN A PHOTORESPONSIVE DEVICE

BACKGROUND

Embodiments of the present disclosure relate to electron-accepting compounds and more specifically compounds suitable for use as an electron-accepting material in a photoresponsive device.

An organic photodetector may contain a photactive layer of a blend of an electron-donating material and an electron-accepting material between an anode and a cathode. Known electron-accepting materials include fullerenes and non-fullerene acceptors (NFAs).

Yu et al, "Realizing Broadband NIR Photodetection and Ultrahigh Responsivity with Ternary Blend Organic Photodetector" Nanomaterials (Basel) 2022, 12(8), 1378 discloses an organic photodetector containing ternary blend of a donor polymer "PM6", a non-fullerene acceptor "BTP-eC9" and fullerene $PC_{71}BM$.

Wu et al, "Fullerene–non-fullerene hybrid acceptors for enhanced light absorption and electrical properties in organic solar cells", Materials Today: Energy Volume 20, June 2021, 100651 discloses fullerene-non-fullerene hybrid acceptors "IP" and "PIP" for use in organic solar cell containing non-fullerene acceptor IDITC and fullerene PC61BM bound to an electron-accepting unit of the IDITC.

Zhou et al, "Hybrid Nonfused-Ring Electron Acceptors with Fullerene Pendant for High-Efficiency Organic Solar Cells", *ACS Appl. Mater. Interfaces* 2021, 13, 1, 1603–1611 discloses a compound for use in solar cells in which a fullerene is bound to a central benzene ring of a non-fullerene acceptor.

SUMMARY

The present disclosure provides a compound of formula (I):

$$[(Fu)_r\text{-}L]_s\text{-}(NFA)_t$$

(I)

wherein

Fu is a fullerene;

NFA is a non-fullerene acceptor;

L is a linker group;

r is at least 1;

s is at least 1;

t is at least 1 and

NFA is a compound of formula (II) or (III):

$$A^2 - (B^1)x^1 - (D^1)y^1 - (B^1)x^2 - A^3$$

(II)

$$A^2 - (B^2)z^1 - (D^2)y^2 - (B^3)x^3 - A^1 - (B^3)x^4 - (D^3)y^3 - (B^2)z^2 - A^3$$

(III)

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

A^2 and A^3 independently in each occurrence is a monovalent electron-accepting group;

D^1, D^2 and D^3 independently in each occurrence is an electron-donating group;

B^1, B^2, and B^3 independently in each occurrence is a bridging group;

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

x^3 and x^4 are each independently 0, 1, 2 or 3;

y^1, y^2 and y^3 are each independently at least 1;

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

wherein at least one occurrence of at least one of B^1 and D^1 of formula (II) or at least one occurrence of at least one of B^2, B^3, D^2 and D^3 of formula (III) is bound to at least one group of formula (Fu)r-L-.

The present disclosure provides a composition comprising an electron-donating material and an electron-accepting material wherein the electron accepting material is a compound as described herein.

The present disclosure provides an organic electronic device comprising an active layer comprising a compound or composition as described herein.

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 the light source.

The present disclosure provides a formulation comprising a compound or composition as described herein dissolved or dispersed in one or more solvents.

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;

Figure 2 is the absorption spectrum of Intermediate Compound 1, containing a benzocyclobutene group bound to a bridging unit, in dichlorobenzene solution; and

Figure 3 is the is the absorption spectrum of Comparative Compound 1 in dichlorobenzene solution.

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 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.

The compound of formula (I) is:

$$[(Fu)_r\text{-}L]_s\text{-}(NFA)_t$$

(I)

Fu is a fullerene.

NFA is a non-fullerene acceptor of formula (II) or (III).

L is a linker group.

r is at least 1.

s is at least 1.

t is at least 1.

In some embodiments, s and t are each 1.

In some embodiments, t is 1 and s is greater than 1, preferably 2, 3 or 4.

In some embodiments, s is 1 and t is greater than 1, optionally 2, 3 or 4.

The, or each, group (Fu)r-L- is covalently bound directly to an electron-donating unit or a bridging unit of NFA, suitably to an aromatic carbon atom of an electron-donating unit or a bridging unit of NFA. By binding the fullerene to an electron-donating unit or a bridging unit, substituents of an electron-accepting unit of the NFA can be selected so as to tune the electron-accepting properties of the compound of formula (I).

In some embodiments, the compound of formula (I) has an absorption peak greater than 900 nm, optionally greater than 1100 nm, optionally greater than 1250 nm. The absorption peak is suitably less than 1500 nm.

Unless stated otherwise, absorption spectra of materials as described herein are measured using a Cary 5000 UV-VIS-NIR Spectrometer. Measurements were taken from 175 nm 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 solution sample. Absorption intensity is plotted vs. incident wavelength to generate an absorption spectrum. A method for measuring absorption may comprise measuring a 15 mg / ml solution in a quartz cuvette and comparing to a cuvette containing the solvent only.

Unless stated otherwise, absorption data as provided herein is as measured in toluene solution.

NFA

The non-fullerene acceptor of formula (I) has either formula (I) or (II):

$$A^2 – (B^1)x^1 – (D^1)y^1 – (B^1)x^2 – A^3$$

(II)

$$A^2 – (B^2)z^1 – (D^2)y^2 – (B^3)x^3 – A^1 – (B^3)x^4 – (D^3)y^3 – (B^2)z^2 – A^3$$

(III)

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

A^2 and A^3 independently in each occurrence is a monovalent electron-accepting group;

D^1, D^2 and D^3 independently in each occurrence is an electron-donating group;

B^1, B^2, and B^3 independently in each occurrence is a bridging group;

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

x^3 and x^4 are each independently 0, 1, 2 or 3, preferably 0 or 1, more preferably 0;

y^1, y^2 and y^3 are each independently at least 1, preferably 1, 2 or 3; and

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

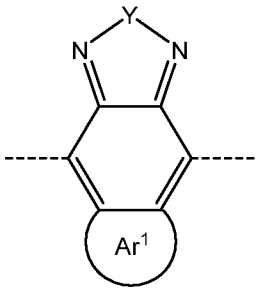
Each of the electron-accepting groups A^1, A^2 and A^3 has a lowest unoccupied molecular orbital (LUMO) level that is deeper (i.e., further from vacuum) than the LUMO of any of the electron-donating groups D^1, D^2 or D^3 of the compound of formula (I), preferably at

least 1 eV deeper. The LUMO levels of electron-accepting groups and electron-donating groups may be as determined by modelling the LUMO level of these groups, in which each bond to adjacent group is replaced with a bond to a hydrogen atom. Modelling may be performed using Gaussian09 software available from Gaussian using Gaussian09 with B3LYP (functional) and LACVP* (Basis set).

Acceptor Unit A^1

A^1 is preferably a fused heteroaromatic group comprising at least two fused rings, preferably at least three fused rings.

In some embodiments, A^1 of formula (II) is a group of formula (VIII):



(VIII)

wherein:

Ar^1 is an aromatic or heteroaromatic group; and

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

In the case where A^1 is a group of formula (II), Ar^1 may be a monocyclic or polycyclic heteroaromatic group which is unsubstituted or substituted with one or more R^2 groups wherein R^2 in each occurrence is independently a substituent.

Preferred R^2 groups are selected from

F;

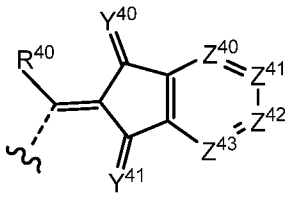
CN;

NO_2;

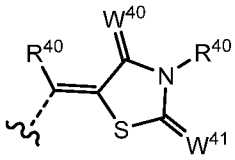
C_{1-20} alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, NR^7 wherein R^7 is a C_{1-12} hydrocarbyl, COO or CO and one or more H atoms of the alkyl may be replaced with F;

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

a group selected from



or



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

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

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

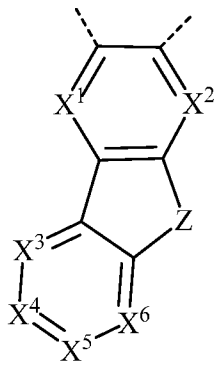
By "non-terminal C atom" of an alkyl group as used anywhere herein means a C atom other than the C atom of the methyl group at the end of an n-alkyl chain or the C atoms of the methyl groups at the ends of a branched alkyl chain.

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

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

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

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



(V)

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

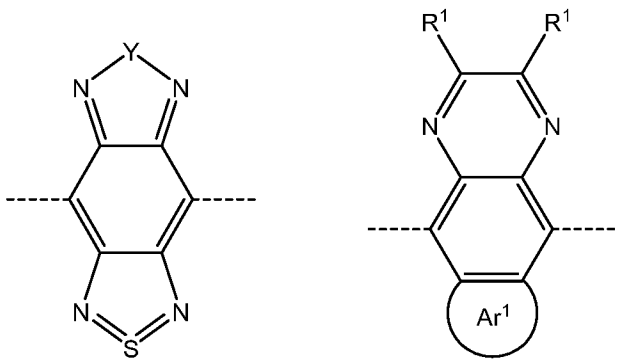
X^3, X^4, X^5 and X^6 are each independently selected from N and CR^3 with the proviso that at least one of X^3, X^4, X^5 and X^6 is CR^3.

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

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

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

A^1 groups of formula (VIII) are preferably selected from groups of formulae (VIIIa) and (VIIIb):



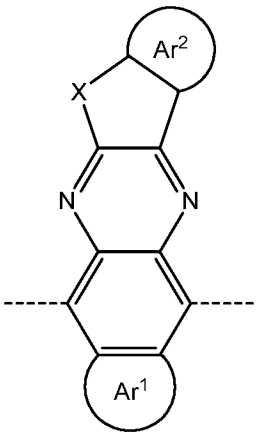
(VIIIa) (VIIIb)

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

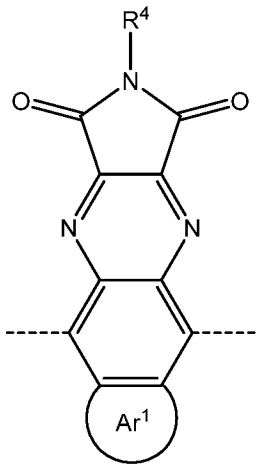
Preferably, when the two R^1 groups are not linked each R^1 is independently selected from H; F; CN; NO_2; C_{1-20} alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, NR^7, CO, COO, NR^4, PR^4, or $Si(R^3)_2$ wherein R^3 and R^4 are as described above

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

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



(VIIIb-1)

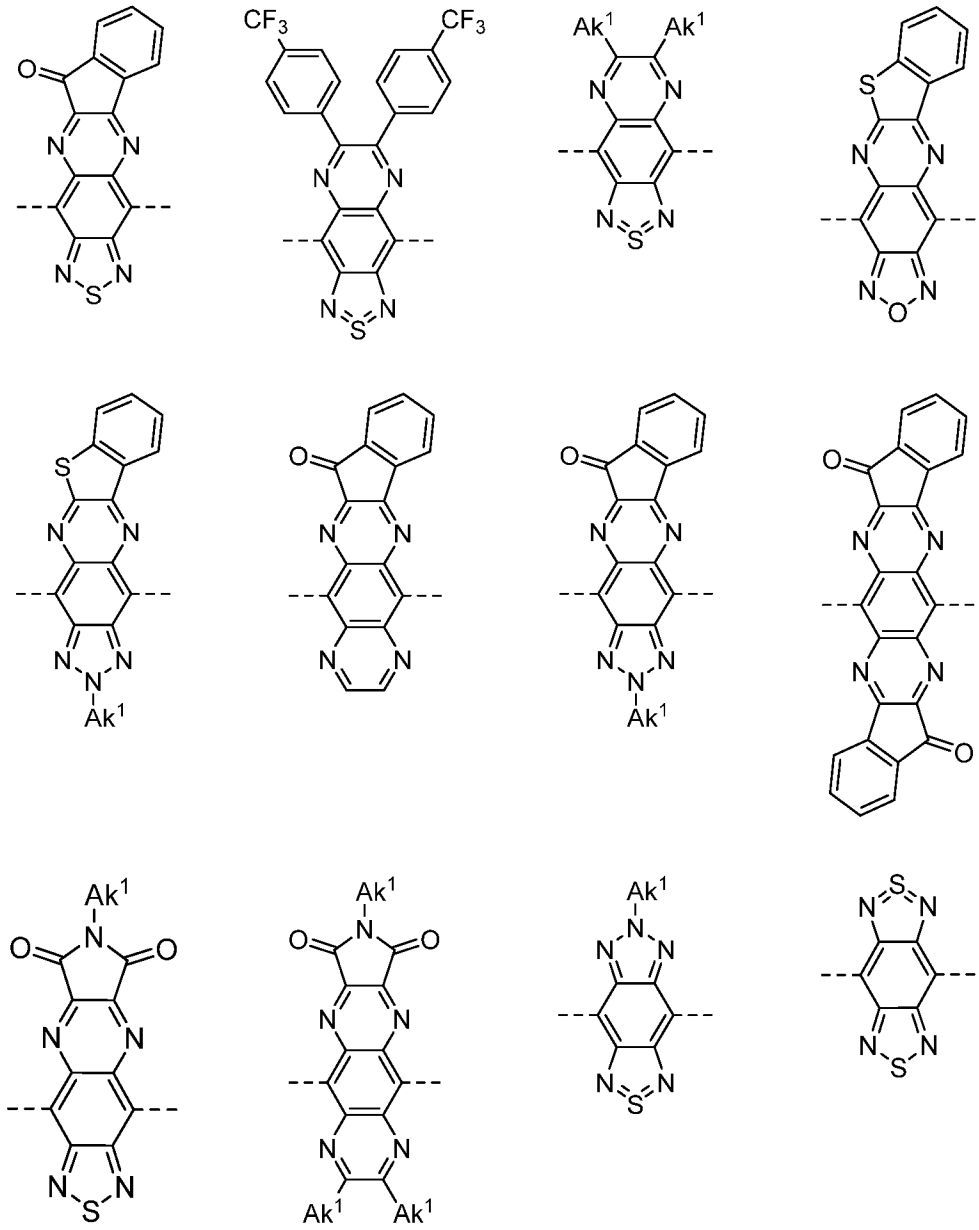


(VIIIb-2)

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

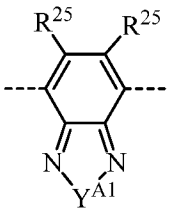
X is selected from O, S, SO_2, NR^4, PR^4, $C(R^3)_2$, $Si(R^3)_2$ C=O, C=S and $C=C(R^5)_2$ wherein R^3, R^4 and R^5 are as described above.

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

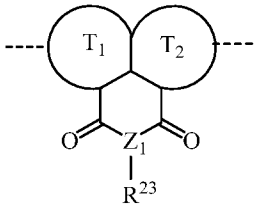


wherein Ak^1 is a C_{1-20} alkyl group

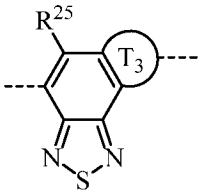
Divalent electron-accepting groups other than formula (VIII) are optionally selected from formulae (IVa)-(IVk)



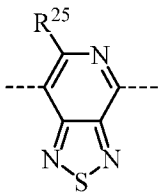
(IVa)



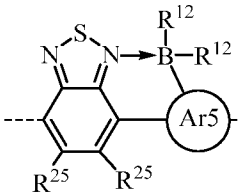
(IVb)



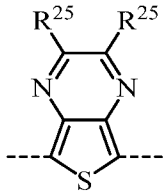
(IVc)



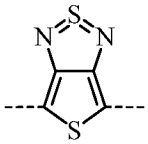
(IVd)



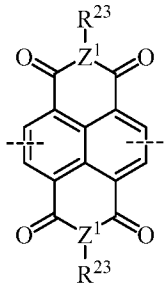
(IVe)



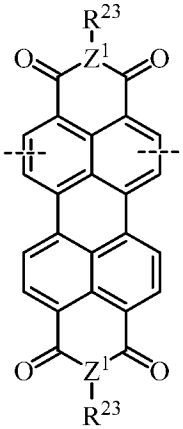
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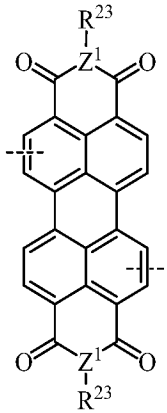
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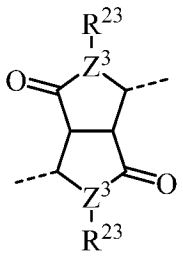
(IVh)



(IVi)



(IVj)

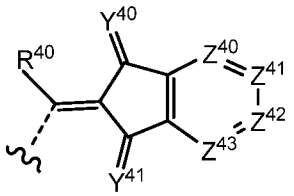


(IVk)

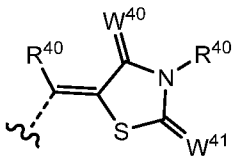
Y^{A1} is O or S, preferably S.

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

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



or



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

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

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

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

Z^1 is N or P.

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

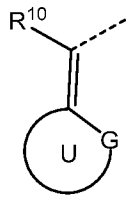
R^{12} in each occurrence is a substituent, preferably a C_{1-20} hydrocarbyl group.

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

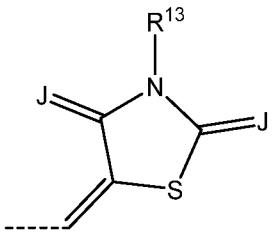
Electron-Accepting Groups A^2, A^3

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

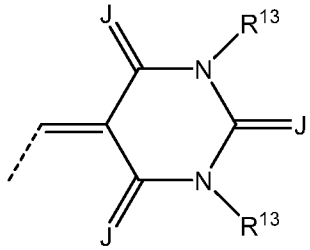
Exemplary monovalent acceptor units include, without limitation, units of formulae (IXa)-(IXq)



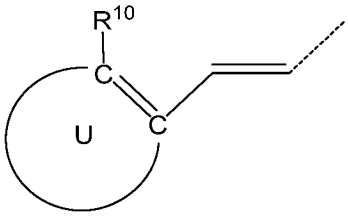
(IXa)



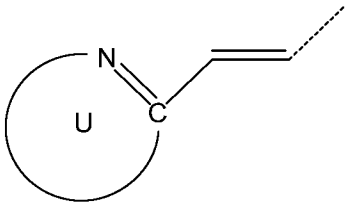
(IXb)



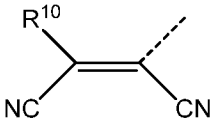
(IXc)



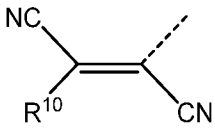
(IXd)



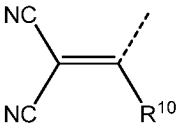
(IXe)



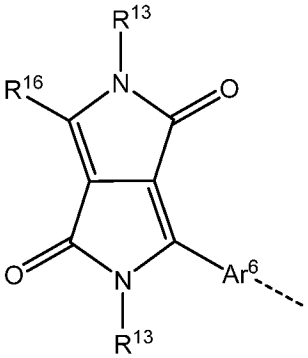
(IXf)



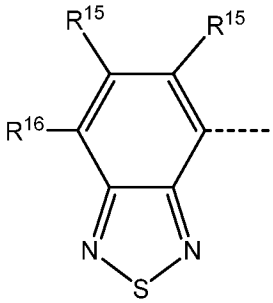
(IXg)



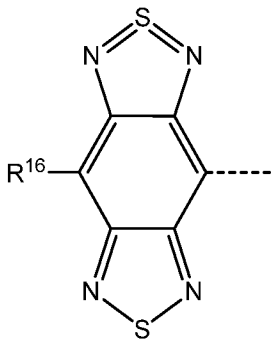
(IXh)



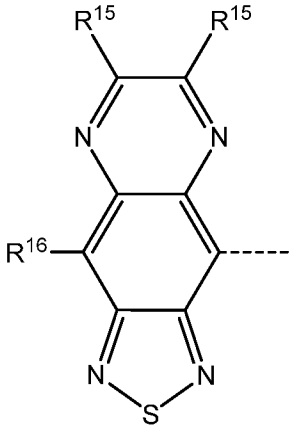
(IXi)



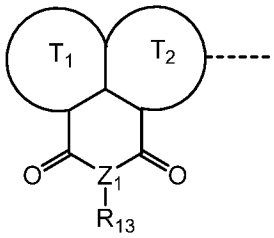
(IXj)



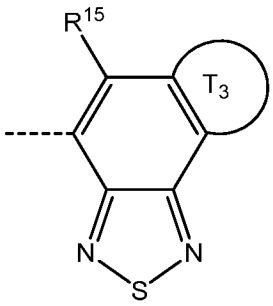
(IXk)



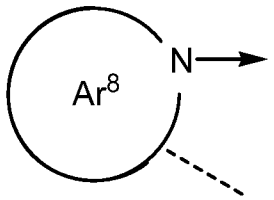
(IXl)



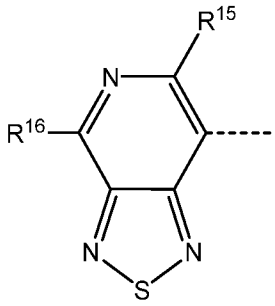
(IXm)



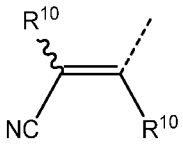
(IXn)



(IXo)



(IXp)



(IXq)

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

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

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

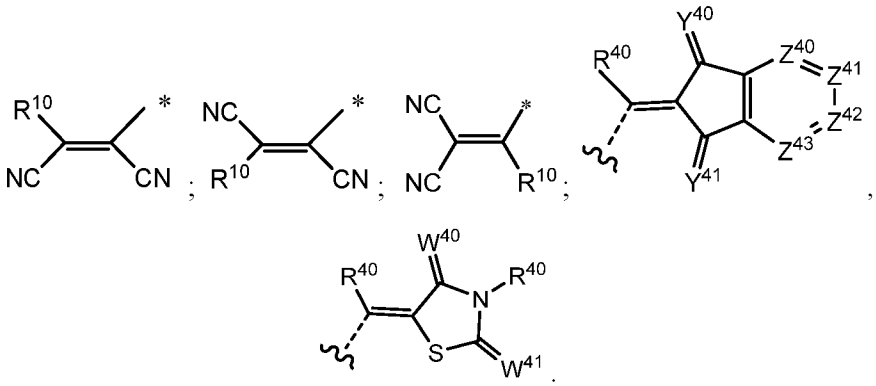
Preferably, R^{10} is H.

J is C=O or C=S, NR^{11} or $CR^{12}R^{13}$ wherein R^{11} is CN or $COOR^{40}$ and R^{40} is H or a substituent and R^{12} and R^{13} are each independently CN, CF_3 or $COOR^{40}$, preferably C=O.

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

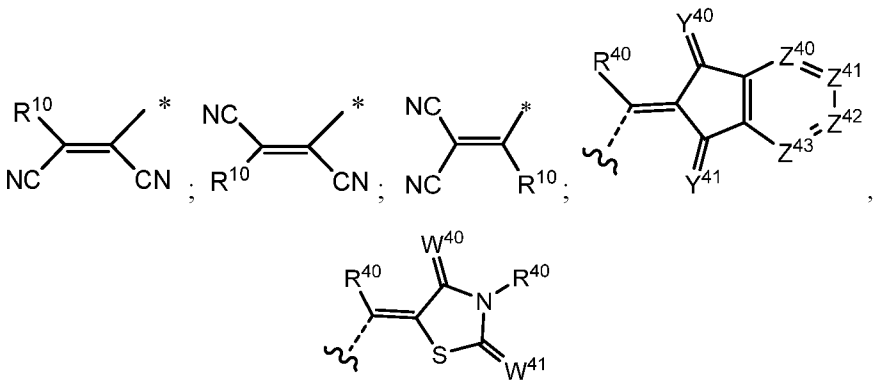
R^{13} in each occurrence is a substituent, optionally C_{1-12} alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, NR^7, COO or CO and one or more H atoms of the alkyl may be replaced with F.

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



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

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



and

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

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

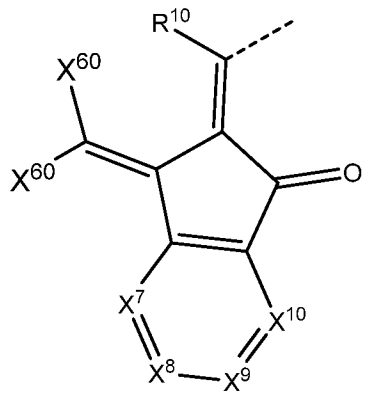
Substituents of Ar^3 and Ar^6, where present, are optionally selected from C_{1-12} alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, NR^7, COO or CO and one or more H atoms of the alkyl may be replaced with F.

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

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

Preferred groups A^2 and A^3 are groups having a non-aromatic carbon-carbon bond which is bound directly to D1 or D2 or, if present to B^2.

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



(IXa-1)

wherein:

R^{10} is as described above;

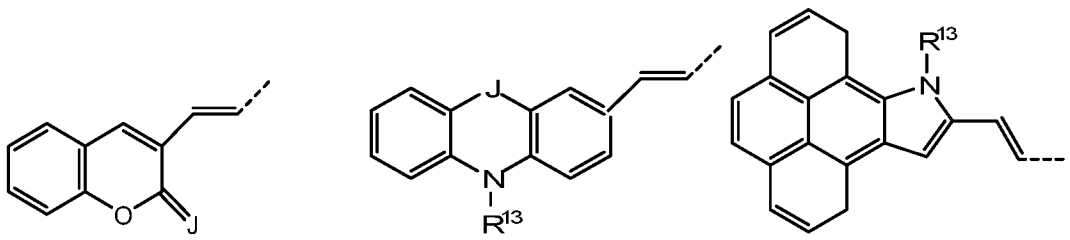
each X^7-X^{10} is independently CR^{12} or N wherein R^{12} in each occurrence is H or a substituent selected from C_{1-20} hydrocarbyl and an electron withdrawing group. Preferably, the electron withdrawing group is F, Cl, Br or CN, more preferably F, Cl or CN; and

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

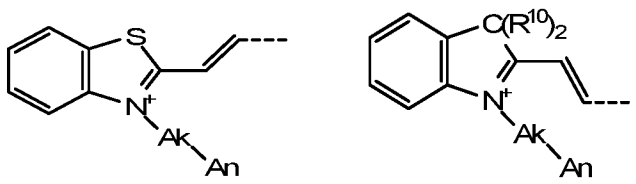
The C_{1-20} hydrocarbyl group R^{12} may be selected from C_{1-20} alkyl; unsubstituted phenyl; and phenyl substituted with one or more C_{1-12} alkyl groups.

In a particularly preferred embodiment, each of X^7-X^{10} is CR^{12} and each R^{12} is independently selected from H or an electron-withdrawing group, preferably H, F or CN. According to his embodiment, R^{12} of X^8 and X^9 is an electron-withdrawing group, preferably F or CN.

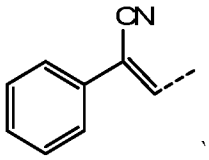
Exemplary groups of formula (IXd) include:



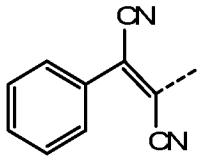
Exemplary groups of formula (IXe) include:



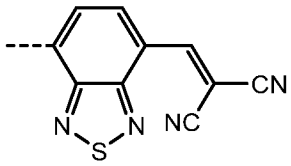
An exemplary group of formula (IXq) is:



An exemplary group of formula (IXg) is:

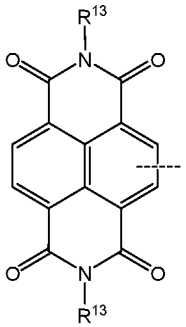


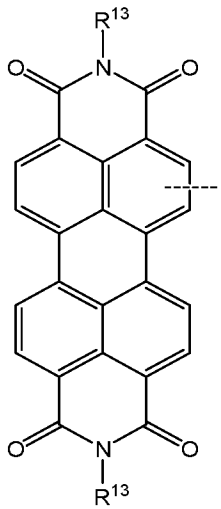
An exemplary group of formula (IXj) is:



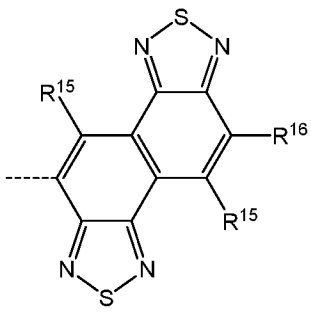
wherein Ak is a C_{1-12} alkylene chain in which one or more C atoms may be replaced with O, S, NR^7, CO or COO; An is an anion, optionally $-SO_3^-$; and each benzene ring is independently unsubstituted or substituted with one or more substituents selected from substituents described with reference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

Exemplary groups of formula (IXm) are:





An exemplary group of formula (IXn) is:

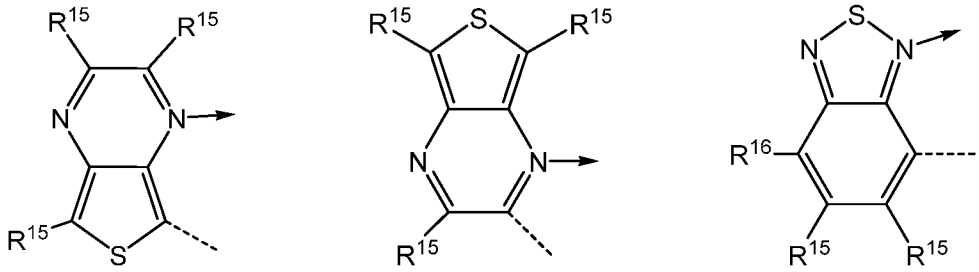


Groups of formula (IXo) are bound directly to a bridging group B^2 substituted with a -$B(R^{14})_2$ wherein R^{14} in each occurrence is a substituent, optionally a C_{1-20} hydrocarbyl group; → is a bond to the boron atom -$B(R^{14})_2$ of R^3 or R^6; and --- is the bond to B^2.

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

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

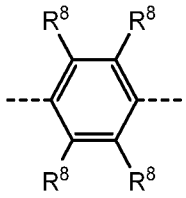
Optionally groups of formula (IXo) are selected from:



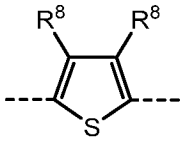
Bridging units

Bridging units B^1, B^2 and B^3 are preferably each selected from vinylene, arylene, heteroarylene, arylenevinylene and heteroarylenevinylene wherein the arylene and heteroarylene groups are monocyclic or bicyclic groups, each of which may be unsubstituted or substituted with one or more substituents.

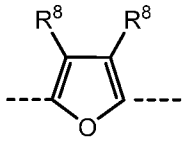
Optionally, B^1, B^2 and B^3 are selected from units of formulae (VIa) – (VIn):



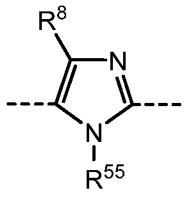
(VIa)



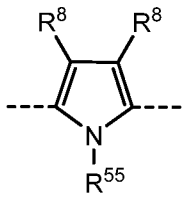
(VIb)



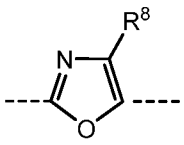
(VIc)



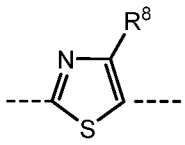
(VId)



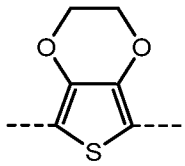
(VIe)



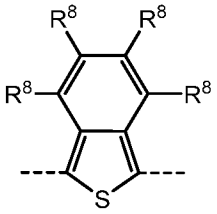
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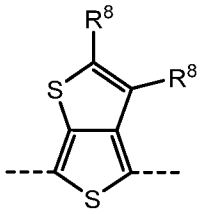
(VIg)



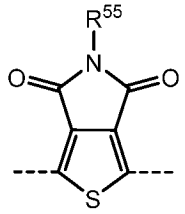
(VIh)



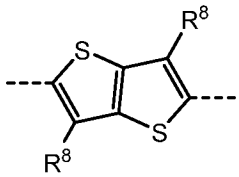
(VIi)



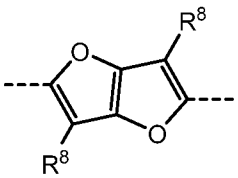
(VIj)



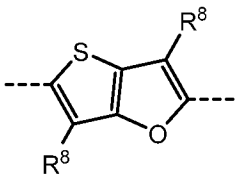
(VIk)



(VIl)



(VIm)



(VIn)

R^8 in each occurrence is independently H or a substituent, preferably H, a group of formula (Fu)r-L- as described with reference to Formula (I), or a substituent selected from F; CN; NO_2; C_{1-20} alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, NR^7, COO or CO and one or more H atoms of the alkyl may be replaced with F; phenyl which is unsubstituted or substituted with one or more substituents; and $-B(R^{14})_2$

wherein R^{14} in each occurrence is a substituent, optionally a C_{1-20} hydrocarbyl group. R^8 groups of formulae (VIa), (VIb) and (VIc) may be linked to form a bicyclic ring, for example thienopyrazine.

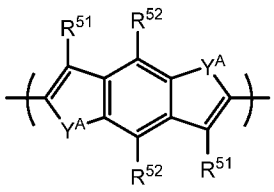
In a particularly preferred embodiment for compounds of formula (III), x^3 and x^4 are 0 (B^3 is not present) and z^1 and z^2 are each 1 (B^2 is present).

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

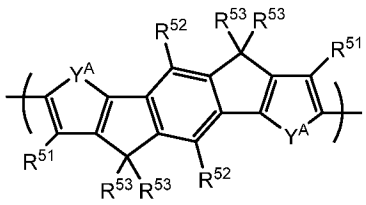
Electron-Donating Groups D^1, D^2 and D^3

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

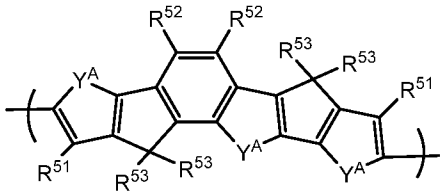
Exemplary electron-donating groups D^1, D^2 and D^3 include groups of formulae (VIIa)-(VIIm):



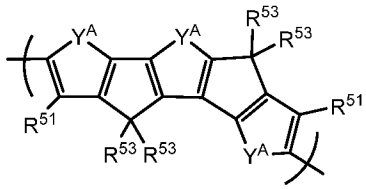
(VIIa)



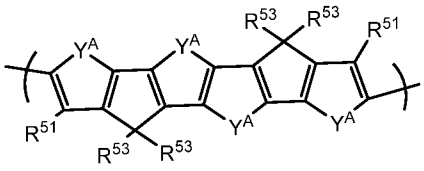
(VIIb)



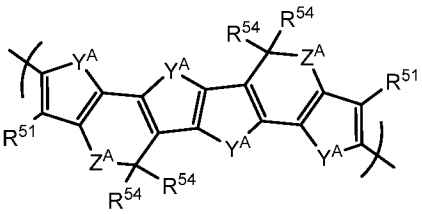
(VIIc)



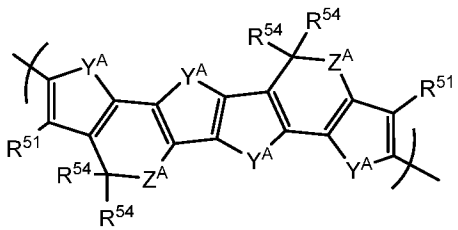
(VIId)



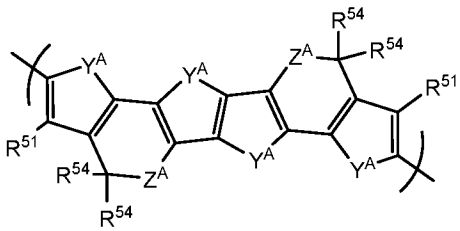
(VIIe)



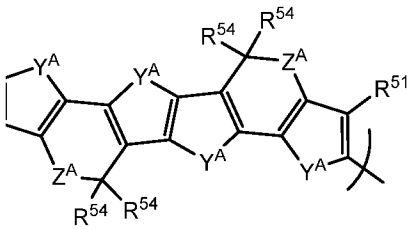
(VIIf)



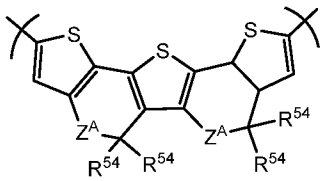
(VIIg)



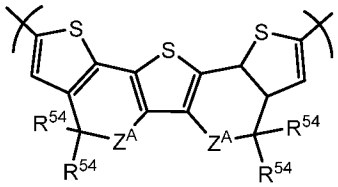
(VIIh)



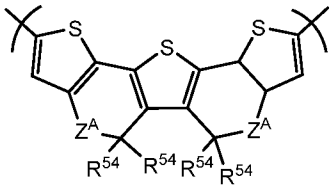
(VIIi)



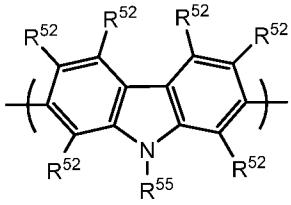
(VIIj)



(VIIk)



(VIIl)



(VIIm)

wherein Y^A in each occurrence is independently O, S or NR^{55}, Y^{A1} in each occurrence is independently O or S; Z^A in each occurrence is O, CO, S, NR^{55} or $C(R^{54})_2$; R^{51}, R^{52} R^{54} and R^{55} independently in each occurrence is H or a substituent; and R^{53} independently in each occurrence is a substituent.

Optionally, R^{51} and R^{52} independently in each occurrence are selected from H; F; C_{1-20} alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, NR^7, COO or CO and one or more H atoms of the alkyl may be replaced with F; an aromatic or heteroaromatic group Ar^3 which is unsubstituted or substituted with one or more substituents; and a group of formula (Fu)r-L- as described with reference to Formula (I).

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

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

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

H;

F;

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

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

a group of formula (Fu)r-L- as described with reference to Formula (I).

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

Preferably, each R^{51} is H or a group of formula (Fu)r-L-.

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

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

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

In some embodiments, at least one of y^1 and y^2 is greater than 1. In these embodiments, the chain of D^1 and / or D^2 groups, respectively, may be linked in any orientation

Electron-donating material

A photoactive layer as described herein comprises an electron-donating material. The photoactive layer may be a bulk heterojunction layer comprising an electron-donating material and a compound of formula (I) as described herein. The photoactive layer may comprise two or more sub-layers including an electron-donating sub-layer comprising or consisting of an electron-donating material and an electron-accepting sub-layer comprising or consisting of a compound of formula (I).

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

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

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

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

Further preferably the electron-donating polymer is a conjugated organic polymer with a low bandgap, typically between 2.5 eV and 1.5 eV, preferably between 2.3 eV and 1.8 eV.

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

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

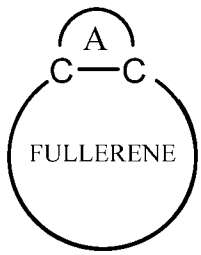
A particularly preferred donor polymer comprises donor unit (VIIa) provided as a repeat unit of the polymer, most preferably with an electron-accepting repeat unit, for example

divalent electron-accepting units A^1 as described herein provided as polymeric repeat units.

Fullerene

The, or each, fullerene of the compound of formula (I) may be selected from, without limitation, C_{60}, C_{70}, C_{76}, C_{78} and C_{84} fullerenes or a derivative thereof, including, without limitation, PCBM-type fullerene derivatives including phenyl-C_{61}-butyric acid methyl ester (C_{60}PCBM), TCBM-type fullerene derivatives (e.g. tolyl-C_{61}-butyric acid methyl ester (C_{60}TCBM)), and ThCBM-type fullerene derivatives (e.g. thienyl-C_{61}-butyric acid methyl ester (C_{60}ThCBM).

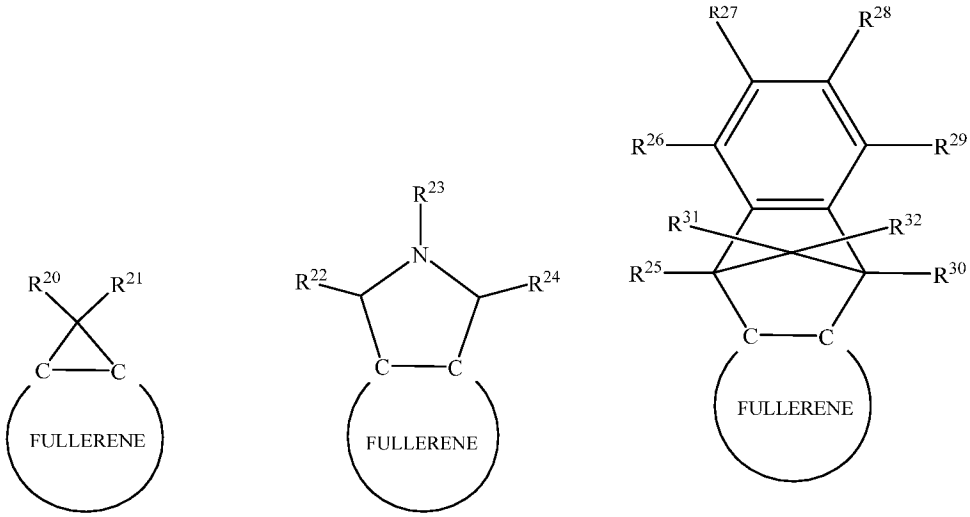
Fullerene derivatives may have formula (V):



(V)

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

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



(Va) (Vb) (Vc)

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

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

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

Linking group

The linker group may be selected from an optionally substituted arylene or heteroarylene, preferably phenylene, or a C_{1-20} alkylene wherein one or more non-adjacent C atoms may be replaced with a optionally substituted phenylene, O, S, CO, COO, $CONR^4$, NR^4, PR^4, or $Si(R^3)_2$ and wherein R^3 and R^4 are as described herein and wherein optional substituents of arylene or heteroarylene groups may be selected from F; Cl; NO_2; CN; and C_{1-20} alkyl

wherein one or more non-adjacent C atoms may be replaced with O, S, NR^4, CO or COO and one or more H atoms may be replaced with F.

In some embodiments, the, or each, linking group L is formed by reaction of a fullerene substituted with a group L^1 comprising a first reactive group and a non-fullerene acceptor substituted with one or more groups L^2 comprising a second reactive group wherein the first and second reactive groups react to form the linking group L from L^1 and L^2.

The first and second reactive groups may be any groups known to the skilled person which react to form a covalent bond. This includes first and second reactive groups as follows:

- A nucleophile, for example an alcohol, and a leaving group such as a halide or a pseudohalide such as a sulfonic acid ester, which react to form a linking group L comprising an ether group.
- A carboxylic acid or derivative such as an ester, amide, acid chloride or anhydride and an alcohol, thiol or amine which react to form a linking group L comprising a carboxylic ester, thioester or amide group.
- Linkages formed by click chemistry reactions such as an azide-alkyne cycloaddition.

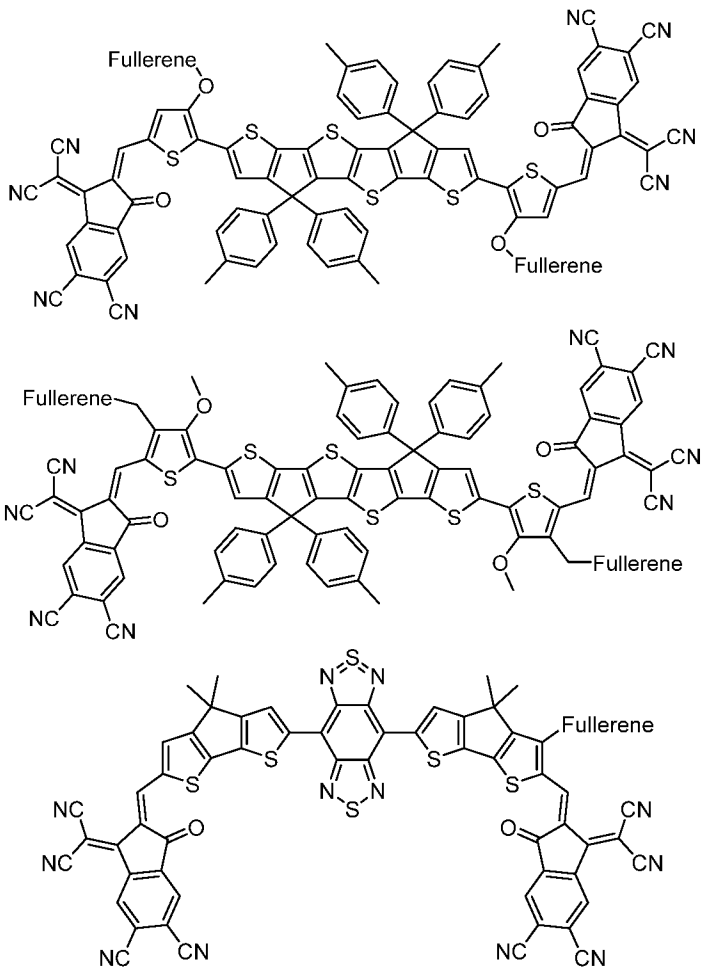
In some embodiments, a carbon-carbon double bond of the fullerene may be reacted with a compound substituted with a NFA to form a cycloadduct of the fullerene substituted with the NFA. In these embodiments, it will be understood that the group L formed by reaction of the fullerene with the substituent of the NFA is fused to the fullerene. Methods of forming such a cycloadduct include:

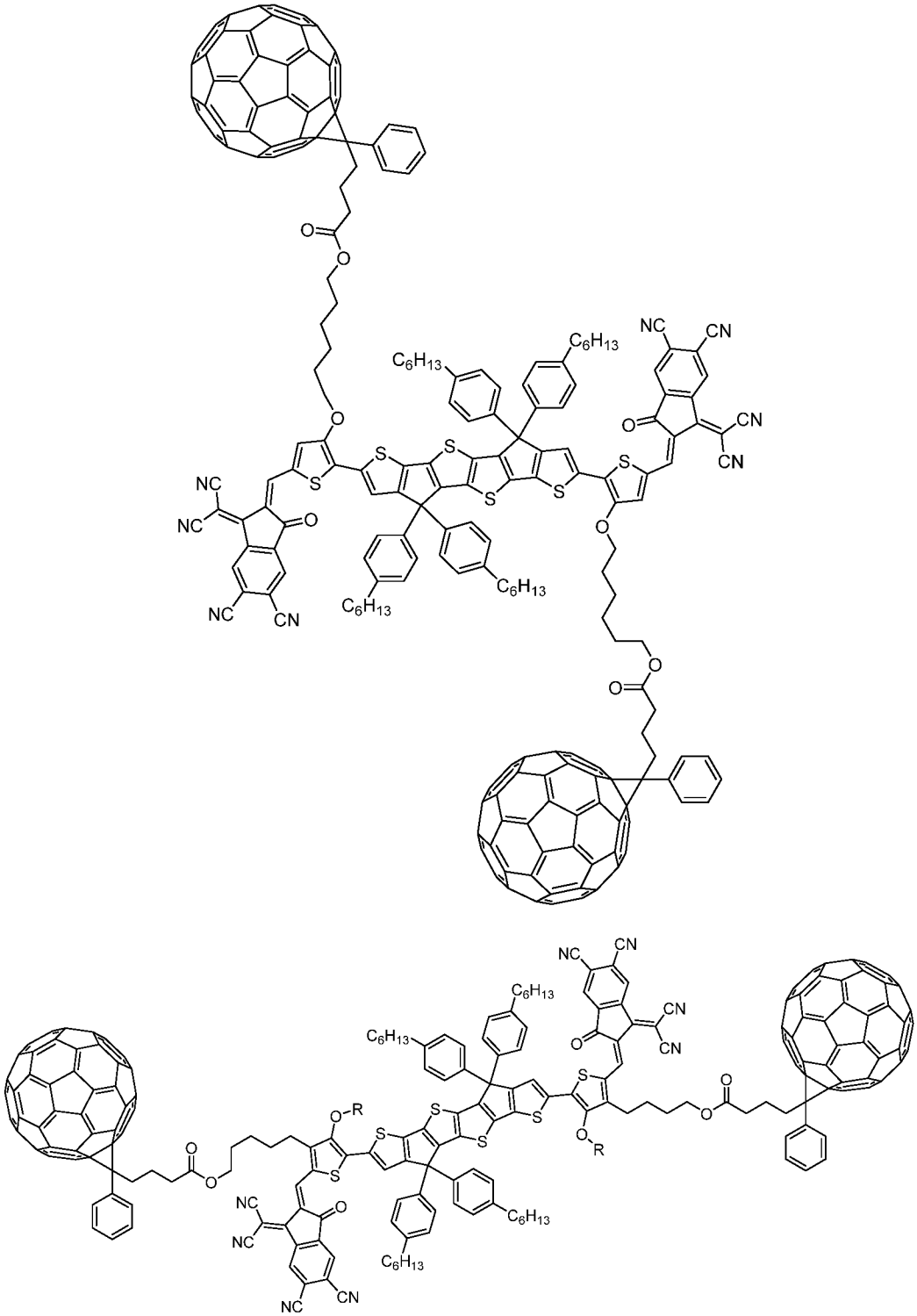
- Reaction of a fullerene with a NFA substituted with a substituent containing a group of formula $-C(R^{11})_2$ wherein R^{11} in each occurence is a halogen or pseudohalogen leaving group, preferably Br. This cycloaddition may be as described in, for example, Si, W., Zhang, X., Lu, S. *et al.* "Manganese powder promoted highly efficient and selective synthesis of fullerene mono- and biscycloadducts at room temperature" Sci Rep 5, 13920.
- Reaction of a fullerene compound with a NFA substituted with a group of formula $-O(C=O)-CR^{11}-(C=O)O-$ wherein R^{11} is as defined above, preferably a bromo-

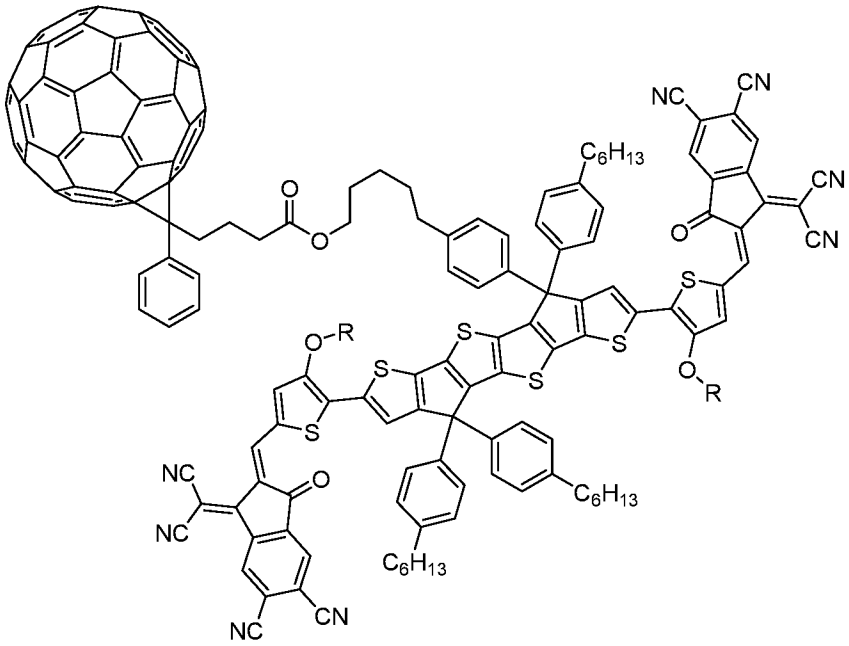
malonate group (Bingel reaction), for example as disclosed in Castro et al, New thiophene-based C_{60} fullerene derivatives as efficient electron transporting materials for perovskite solar cells , *New J. Chem.*, 2018, 42, 14551-14558.

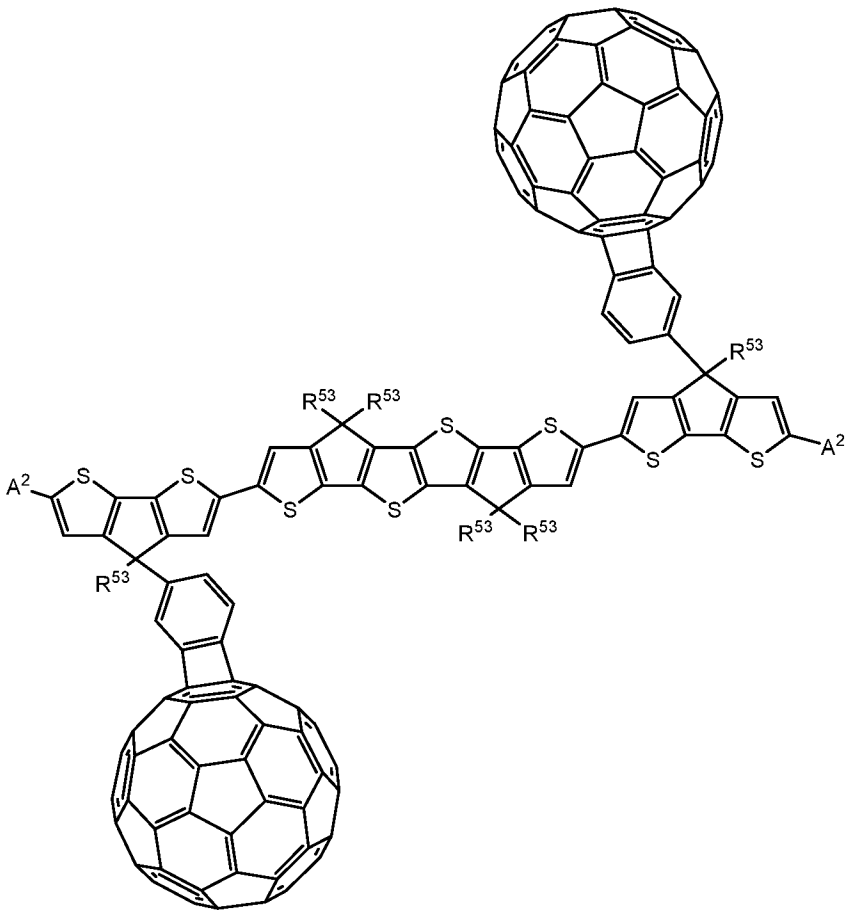
- Reaction of a fullerene compound with a NFA substituted with an azomethine group (Prato reaction), for example as disclosed in Calderon Cerquera et al, "Synthesis, characterization and photophysics of novel BODIPY linked to dumbbell systems based on Fullerene[60]pyrrolidine and Fullerene[60]isoxazoline" *Dyes and Pigments*, Vol., 184, 2021, 108752.
- Reaction of a fullerene compound with a NFA substituted with a non-aromatic carbon-carbon double-bond or benzocyclobutene.

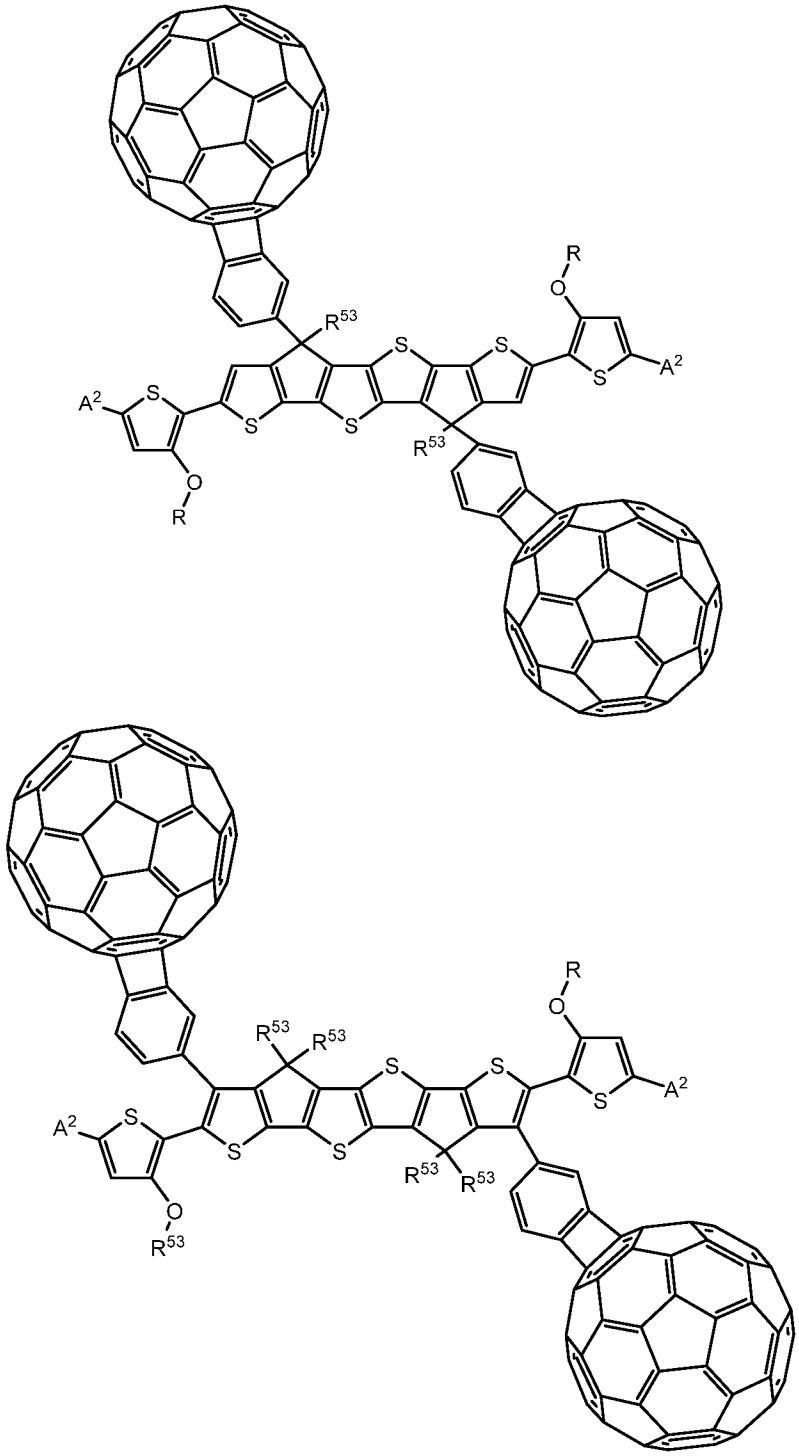
Exemplary compounds of formula (I) include, without limitation:

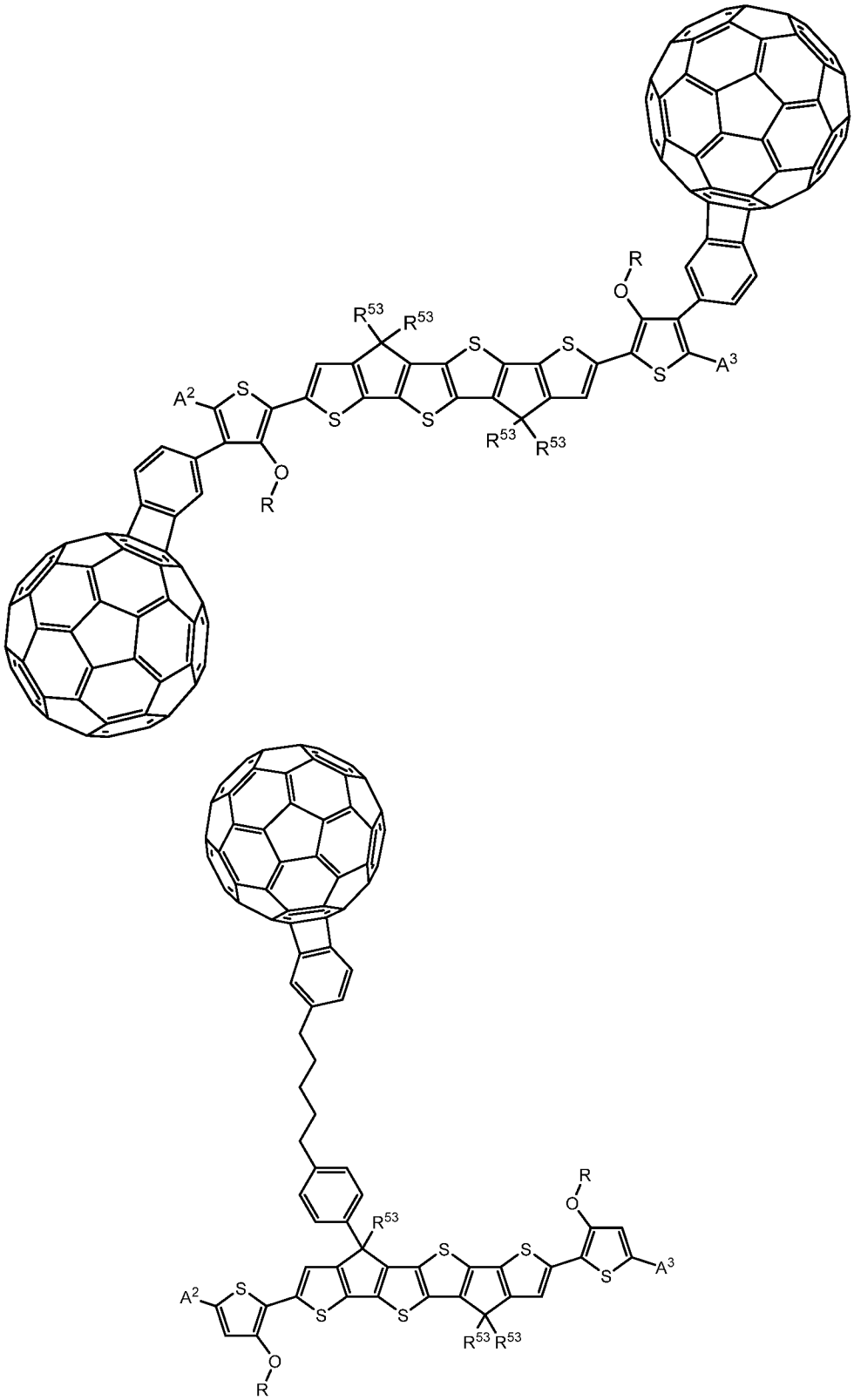


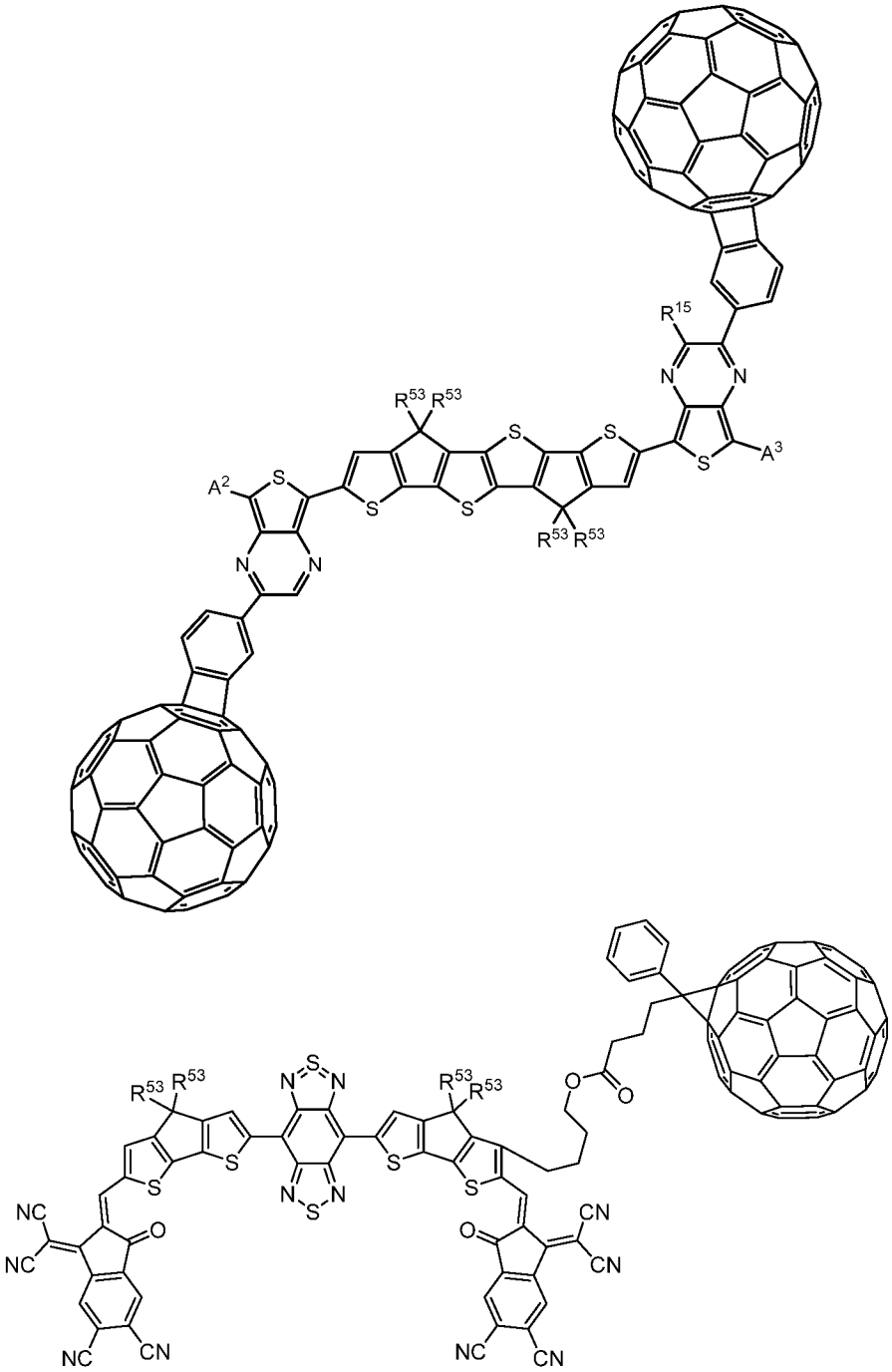


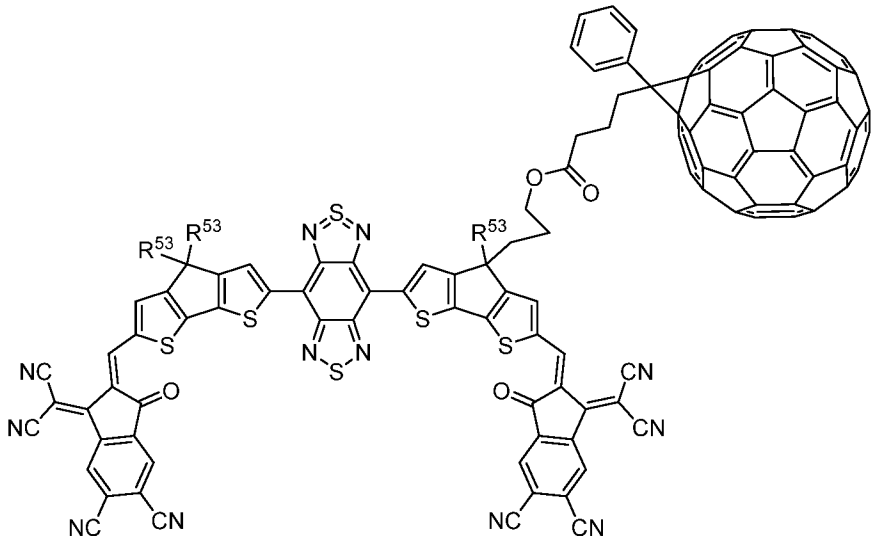












wherein R^{53} is a substituent not containing a fullerene as described above and R is C_{1-12} alkyl.

Organic Electronic Device

A compound of formula (I) may be provided as an active layer of an organic electronic device. In a preferred embodiment, a photoactive layer of an organic photoresponsive device, more preferably an organic photodetector, comprises a compound of formula (I) as described herein.

In some embodiments, the photoactive layer is a bulk heterojunction layer comprising a composition as described herein.

In some embodiments, the photoactive layer comprises two or more sub-layers including an electron-accepting sublayer comprising or consisting of a compound as described herein and an electron-donating sublayer comprising or consisting of an electron-donating material.

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

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

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

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

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

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

The apparatus to measure HOMO or LUMO energy levels by SWV may comprise a cell containing 0.1 M tertiary butyl ammonium hexafluorophosphate in acetonitrile; a 3 mm diameter glassy carbon working electrode; a platinum counter electrode and a leak free Ag/AgCl reference electrode.

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

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

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

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

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

Figure 1 illustrates an organic photoresponsive device according to some embodiments of the present disclosure. The organic photoresponsive device comprises a cathode 103, an anode 107 and a bulk heterojunction layer 105 disposed between the anode and the cathode. The organic photoresponsive device may be supported on a substrate 101, optionally a glass or plastic substrate.

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

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

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

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

Figure 1 illustrated herein comprises a bulk heterojunction photoactive layer 105. In other embodiments, photoactive layer 105 comprises two or more sub-layers including an electron-accepting sublayer comprising or consisting of a compound as described herein and an electron-donating sublayer comprising or consisting of an electron-donating material.

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

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

Formulations

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

Preferably, the photoactive layer comprising the compound of formula (I) or (II) is formed by depositing a formulation comprising or consisting of the electron-accepting material(s) and, in the case of a the bulk heterojunction layer, the electron-donating materials 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 or naphthalene substituted with one or more substituents selected from fluorine, chlorine, C_{1-10} alkyl and C_{1-10} alkoxy wherein two or more substituents may be linked to form a ring which may be unsubstituted or substituted with one or more C_{1-6} alkyl groups,

optionally toluene, xylenes, trimethylbenzenes, tetramethylbenzenes, anisole, indane and its alkyl-substituted derivatives, and tetralin and its alkyl-substituted derivatives.

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

The formulation may comprise further components in addition to the electron-accepting material, the electron-donating material (in the case of a bulk heterojunction layer) 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 900 nm or at least 1000 nm, optionally in the range of 900-1500 nm.

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

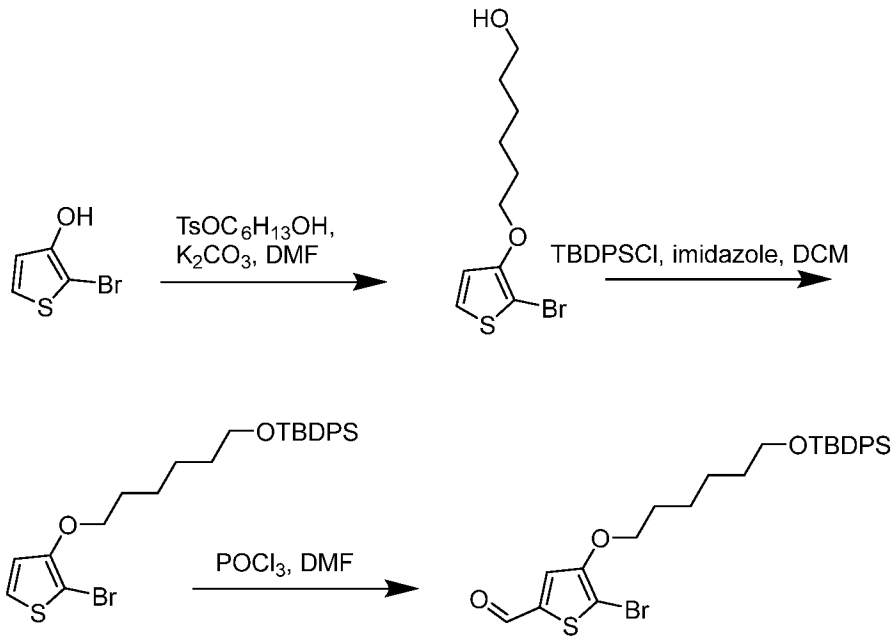
In some embodiments, the light from the light source may or may not be changed before reaching the OPD. For example, the light may be reflected, filtered, down-converted or up-converted before it reaches the OPD.

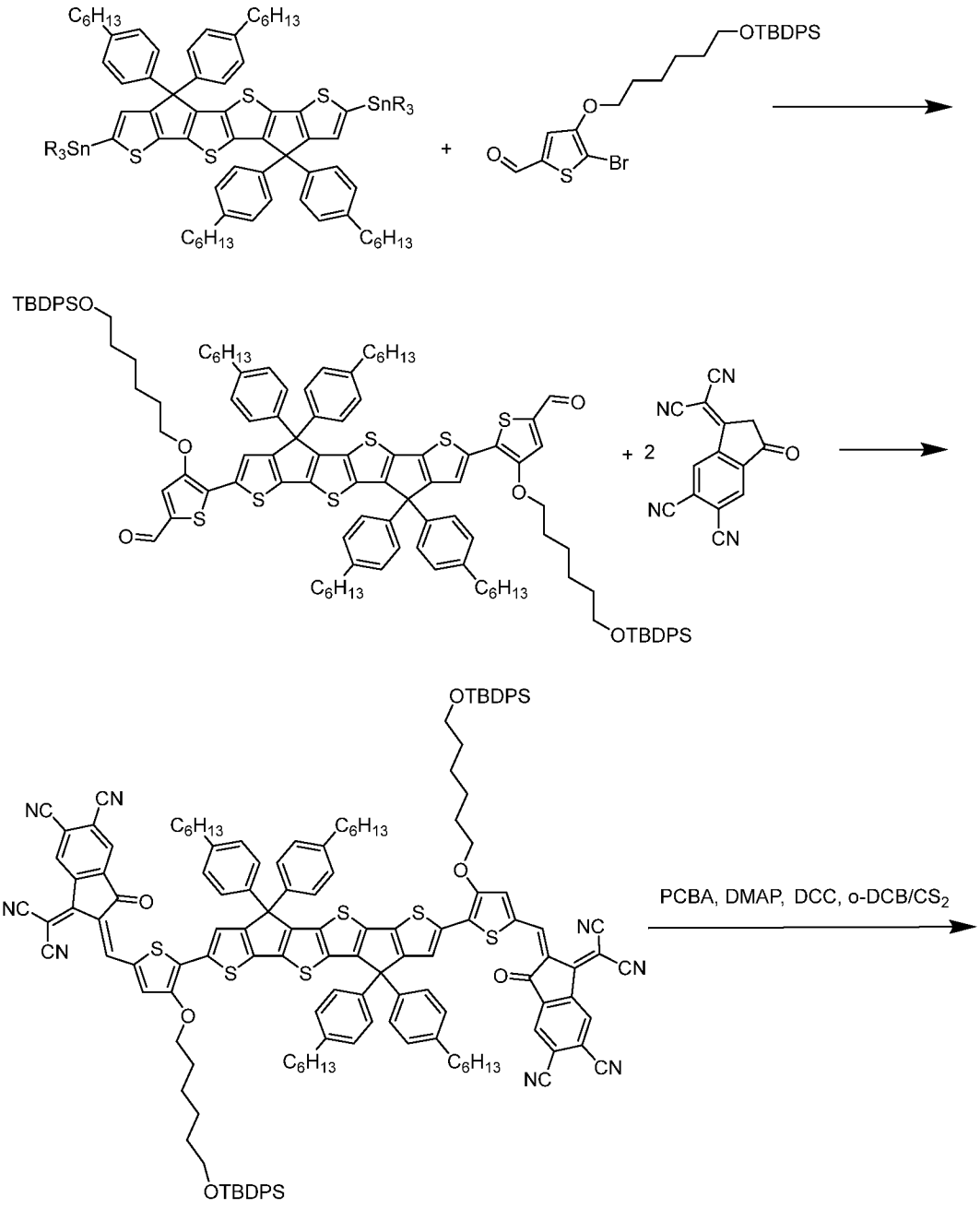
The organic photoresponsive device as described herein may be an organic photovoltaic device or an organic photodetector. An organic photodetector as described herein may be used in a wide range of applications including, without limitation, detecting the presence and / or brightness of ambient light and in a sensor comprising the organic photodetector and a light source. The photodetector may be configured such that light emitted from the light source is incident on the photodetector and changes in wavelength and/or brightness of the light may be detected, e.g., due to absorption by, reflection by and/or emission of light from an object, e.g. a target material in a sample disposed in a light path between the light source and the organic photodetector. The sample may be a non-biological sample, e.g. a water sample, or a biological sample taken from a human or animal subject. The sensor may be, without limitation, a gas sensor, a biosensor, an X-ray imaging device, an image sensor such as a camera image sensor, a motion sensor (for example for use in security applications) a proximity sensor or a fingerprint sensor. A 1D or 2D photosensor array may comprise a plurality of photodetectors as described herein in an image sensor. The photodetector may be configured to detect light emitted from a target analyte which emits light upon irradiation by the light source or which is bound to a luminescent tag which emits light upon irradiation by the light source. The photodetector may be configured to detect a wavelength of light emitted by the target analyte or a luminescent tag bound thereto.

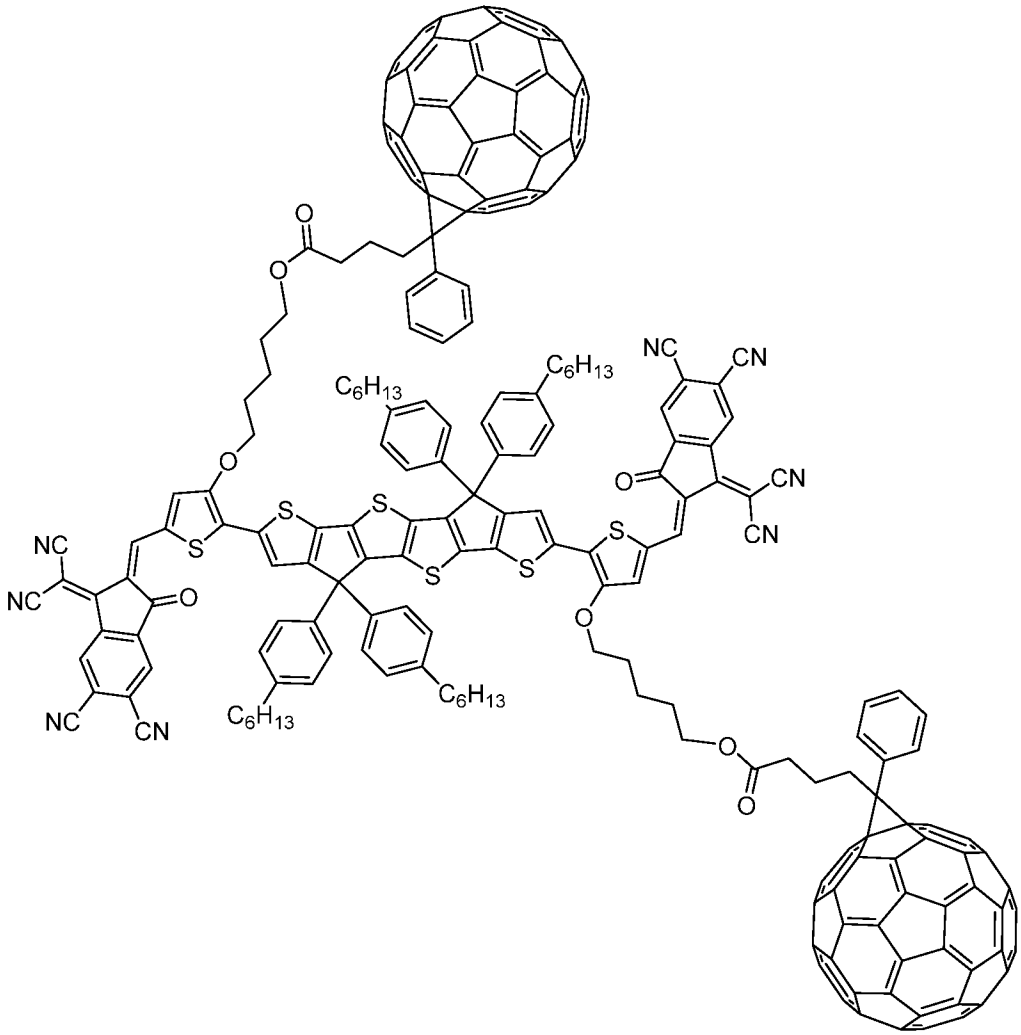
Examples

Compound Example 1

Compound Example 1 may be formed according to the following reaction scheme:


OH
Br
S
TsOC6H13OH,
K2CO3, DMF
HO
O
Br
S
TBDPSCl, imidazole, DCM
OTBDPS
O
Br
S
POCl3, DMF
OTBDPS
O
O
Br
S

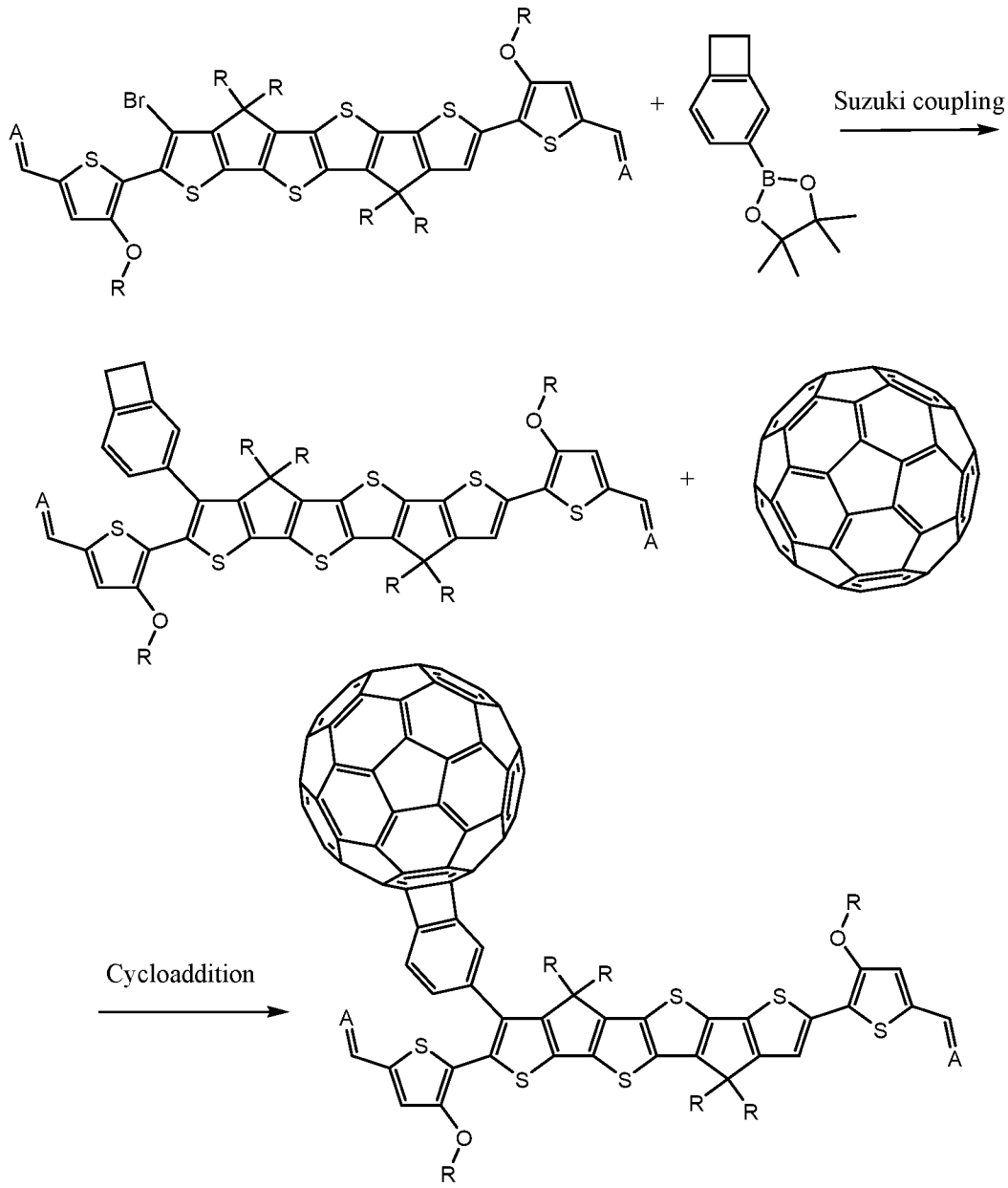

C6H13
C6H13
SnR3
R3Sn
OTBDPS
O
Br
TBDPSO
CN
NC
+ 2
PCBA, DMAP, DCC, o-DCB/CS2



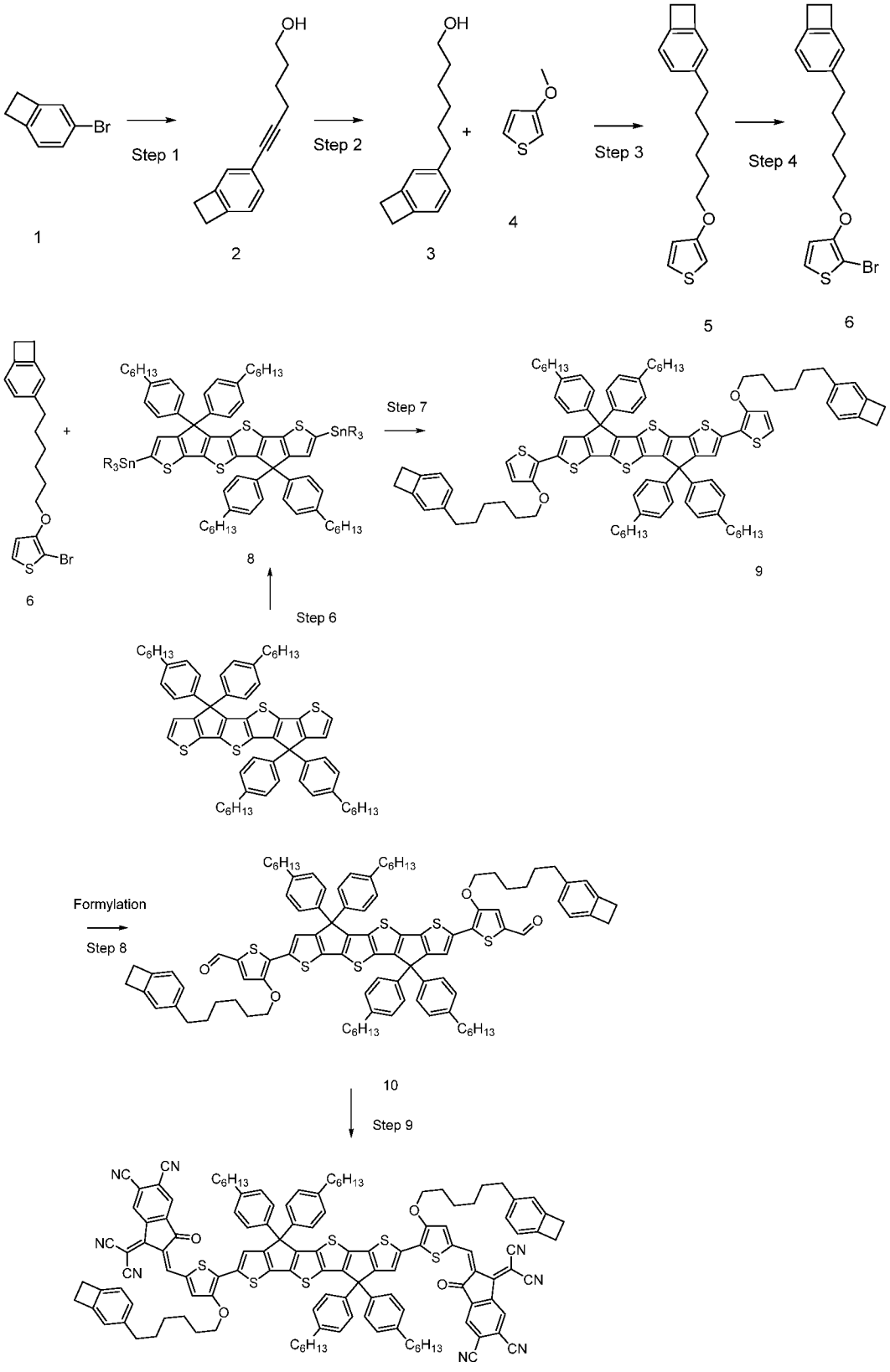
Compound Example 2

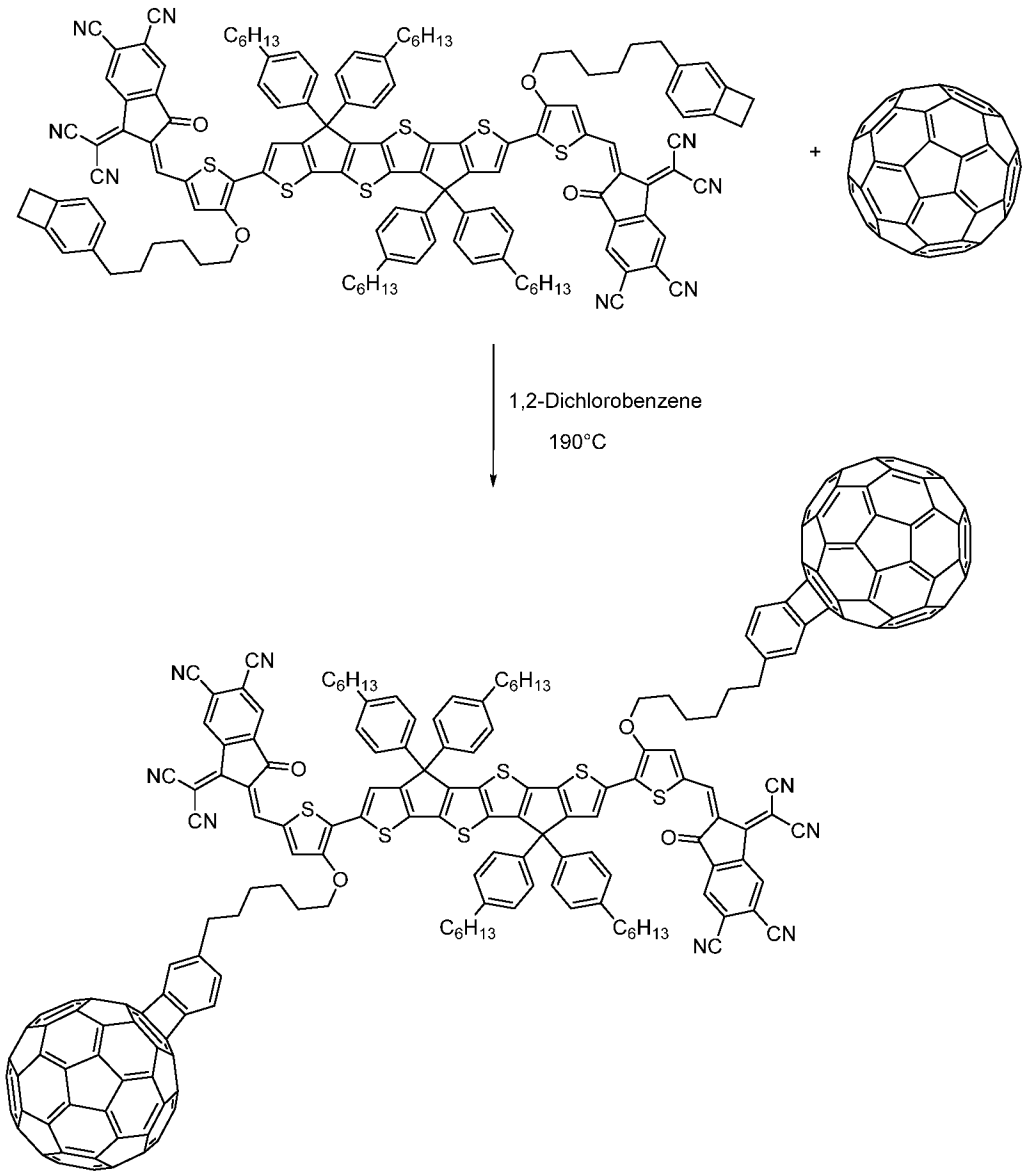
Compound Example 2 may be formed according to the following reaction scheme:

5



Compound Example 3

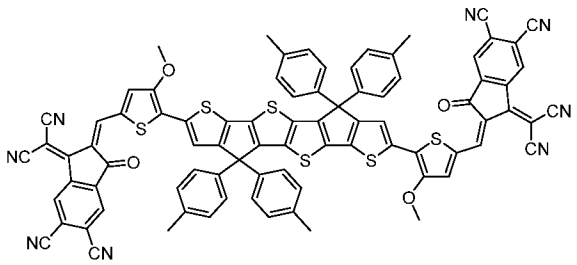
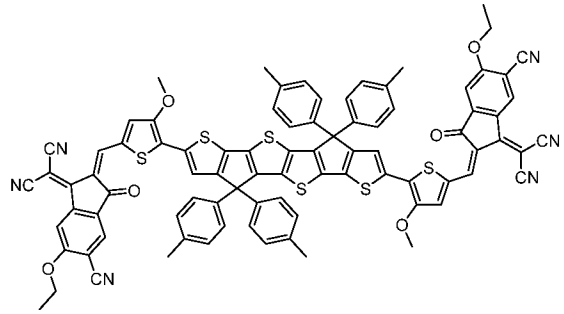

Br
Step 1
OH
Step 2
OH
+
O
S
Step 3
Step 4
1
2
3
4
5
6
+
Br
6
C_6H_{13}
SnR_3
R_3Sn
8
Step 7
9
Step 6
Formylation
Step 8
10
Step 9
NC
CN
O



Modelling

The HOMO and LUMO energy levels of two NFAs having electron-accepting units A2 and A3 of formula (IXa-1) were modelled.

Table 1

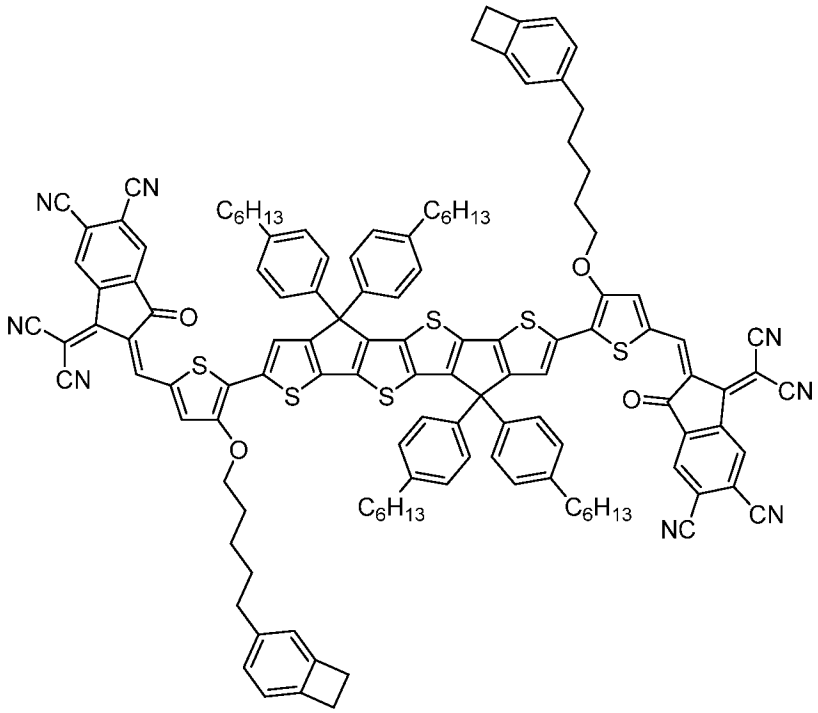
Structure/ID	HOMO /eV	LUMO /eV	Eg /nm	S1f	Eopt / nm
	-5.28	-3.84	864	2.95	923
	-5.05	-3.52	816	3.12	878

With reference to Table 1, replacement of an electron-withdrawing group of Model Compound 1 with an alkoxy group results in a significant shallowing of the LUMO level and an increase in the compound's band gap. By binding the fullerene to a NFA through a donor or bridge unit of the NFA rather than through an electron-accepting unit, such an increase in band gap necessitated by the presence of a linking group, such as an alkoxy group, on the electron accepting unit might be avoided.

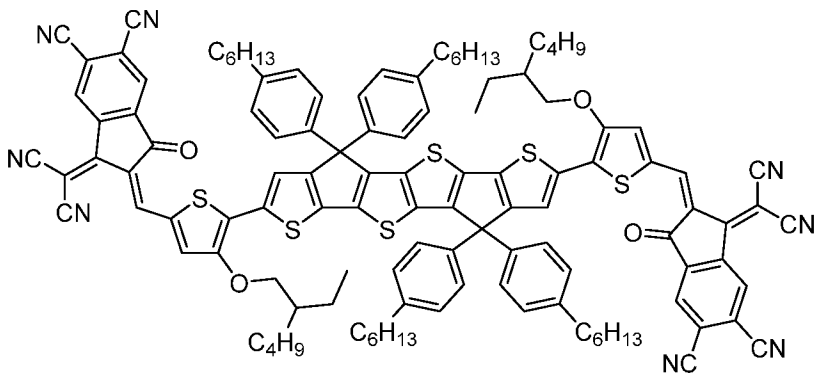
SWV measurements

The HOMO and LUMO levels of films of Intermediate Compound 1 and Comparative Compound 1, illustrated below, were measured. Results are set out in Table 2.

Intermediate Compound 1 is the product of step 9 in formation of Compound Example 3.



Intermediate Compound 1



Comparative Compound 1

Table 2

Name	HOMO [eV]	LUMO [eV]
Comparative Compound 1	5.26	4.23

Intermediate Compound 1	5.28	4.04

HOMO levels of Comparative Compound 1 and Intermediate Compound 1 are similar showing that attachment of a reactive group to the thiophene bridge unit of Comparative Compound 1 and spaced apart from the bridge unit results in little or no change to the HOMO level of the compound, unlike attachment through the electron-accepting group as shown in the modelling data of Table 1.

Absorption spectra

Absorption spectra of Intermediate Compound 1 (Figure 2) and Comparative Compound 1 (Figure 3) were measured in dichlorobenzene solution.

The spectra are very similar, indicating that attachment of the benzocyclobutene group to the bridging unit of Comparative Compound 1 has little or no effect on the absorption of this compound.

CLAIMS

1. A compound of formula (I):

$$[(Fu)_r\text{-}L]_s\text{-}(NFA)_t$$

(I)

wherein

Fu is a fullerene;

NFA is a non-fullerene acceptor;

L is a linker group;

r is at least 1;

s is at least 1;

t is at least 1 and

NFA is a compound of formula (II) or (III):

$$A^2 - (B^1)x^1 - (D^1)y^1 - (B^1)x^2 - A^3$$

(II)

$$A^2 - (B^2)z^1 - (D^2)y^2 - (B^3)x^3 - A^1 - (B^3)x^4 - (D^3)y^3 - (B^2)z^2 - A^3$$

(III)

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

A^2 and A^3 independently in each occurrence is a monovalent electron-accepting group;

D^1, D^2 and D^3 independently in each occurrence is an electron-donating group;

B^1, B^2, and B^3 independently in each occurrence is a bridging group;

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

x^3 and x^4 are each independently 0, 1, 2 or 3;

y^1, y^2 and y^3 are each independently at least 1;

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

wherein at least one occurrence of at least one of B^1 and D^1 of formula (II) or at least one occurrence of at least one of B^2, B^3, D^2 and D^3 of formula (III) is bound to at least one group of formula (Fu)r-L-.

2. The compound of formula (I) according to claim 1 wherein A^2 and A^3 are not substituted with a fullerene.

3. The compound according to claim 1 or 2 wherein the linker group L is fused to the fullerene.

4. The compound according to claim 1 or 2 wherein the linker group L is an optionally substituted phenylene, or a C_{1-20} alkylene wherein one or more non-adjacent C atoms may be replaced with a phenylene, O, S, CO, COO, $CONR^4$, NR^4, PR^4, or $Si(R^3)_2$ and wherein R^3 and R^4 are each independently H or a substituent.

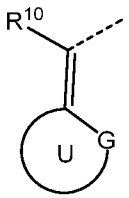
5. The compound according to any one of the preceding claims wherein $(Fu)_r$-L- is bound to at least one of D^1, D^2 and D^3.

6. The compound according to any one of the preceding claims wherein $(Fu)_r$-L- is bound to at least one bridging group B^1, B^2 and B^3.

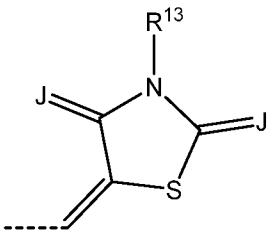
7. The compound according to any one of the preceding claims wherein at least one of A^2 and A^3 comprises a non-aromatic carbon-carbon double bond and a carbon

atom of the carbon-carbon double bond is bound directly to D^1, D^2 or D^3, or if present, to B^1 or B^2.

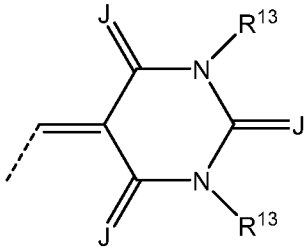
8. The compound according to any one of the preceding claims wherein A^2 and A^3 are each independently selected from groups of formulae (IIIa)-(IIIq)



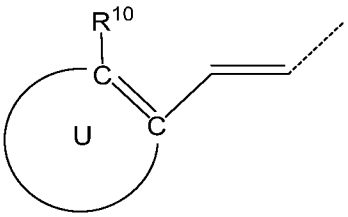
(IIIa)



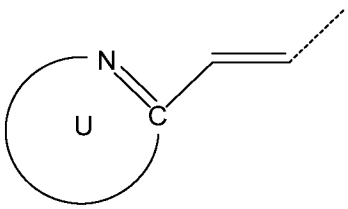
(IIIb)



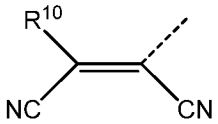
(IIIc)



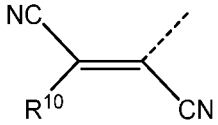
(IIId)



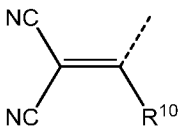
(IIIe)



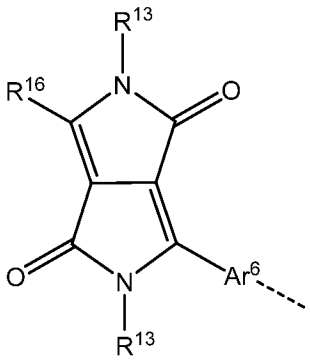
(IIIf)



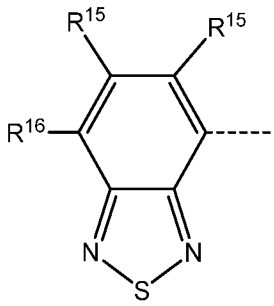
(IIIg)



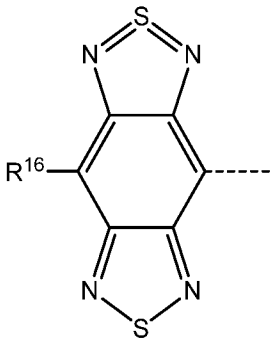
(IIIh)



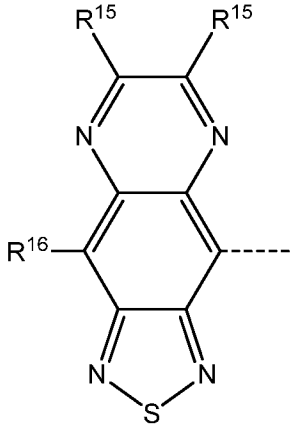
(IIIi)



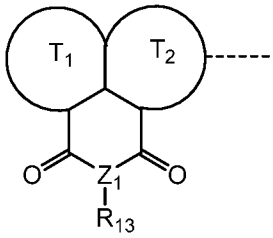
(IIIj)



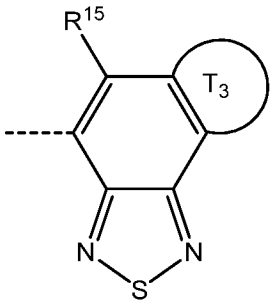
(IIIk)



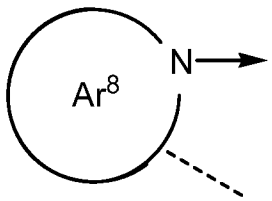
(IIIl)



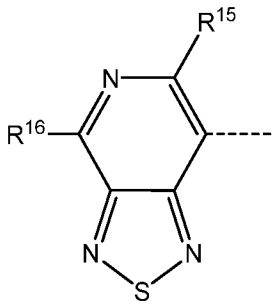
(IIIm)



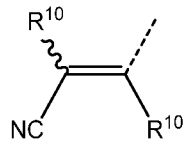
(IIIn)



(IIIo)



(IIIp)



(IIIq)

wherein:

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

R^{10} is H or a substituent;

J is C=O, C=S, NR^{11} or $CR^{12}R^{13}$ wherein R^{11} is CN or $COOR^{40}$ and R^{40} is H or a substituent and R^{12} and R^{13} are each independently CN, CF_3 or $COOR^{40}$;

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

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

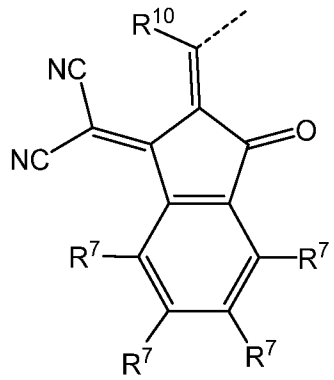
R^{16} is a substituent;

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

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

Ar^8 is a fused heteroaromatic group which is unsubstituted or substituted with one or more substituents and which is bound to an aromatic C atom of B^1 or B^2 and to a boron substituent of B^1 or B^2.

9. The compound according to claim 8 wherein at least one of A^2 and A^3 is a group of formula (IIIa-1):



(IIIa-1)

wherein:

R^{10} in each occurrence is H or a substituent;

---- represents a linking position to EDG; and

R^7 in each occurrence is H or a substituent with the proviso that at least one R^7 is an electron withdrawing group.

10. A compound according to claim 9 wherein the electron withdrawing group is F, Cl or CN.

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

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

13. An organic electronic device according to claim 12 wherein the organic electronic device is an organic photoresponsive device comprising a photoactive layer comprising a compound or composition according to any one of claims 1-11 disposed between the anode and cathode.

14. The organic electronic device according to claim 13 wherein the photoactive layer is a bulk heterojunction layer comprising a composition according to claim 11.

15. An organic electronic device according to claim 13 or 14 wherein the organic photoresponsive device is an organic photodetector.

16. A photosensor comprising a light source and an organic photodetector according to claim 15 wherein the photosensor is configured to detect light emitted from the light source.

17. The photosensor according to claim 16, wherein the light source emits light having a peak wavelength of greater than 900 nm.

18. A formulation comprising a compound or composition according to any one of claims 1 to 11 dissolved or dispersed in one or more solvents.

19. A method of forming an organic electronic device according to any one of claims 12-14 wherein formation of the active layer comprises deposition of a formulation according to claim 18 onto a surface and evaporation of the one or more solvents.

FIGURE 1

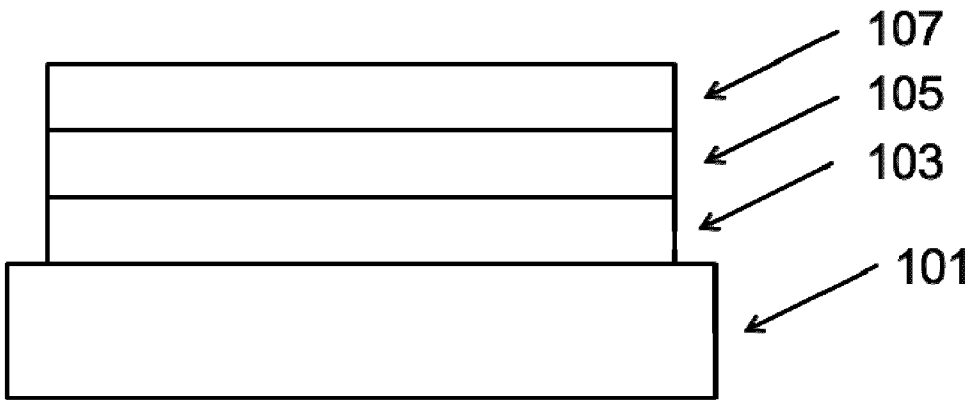


FIGURE 2

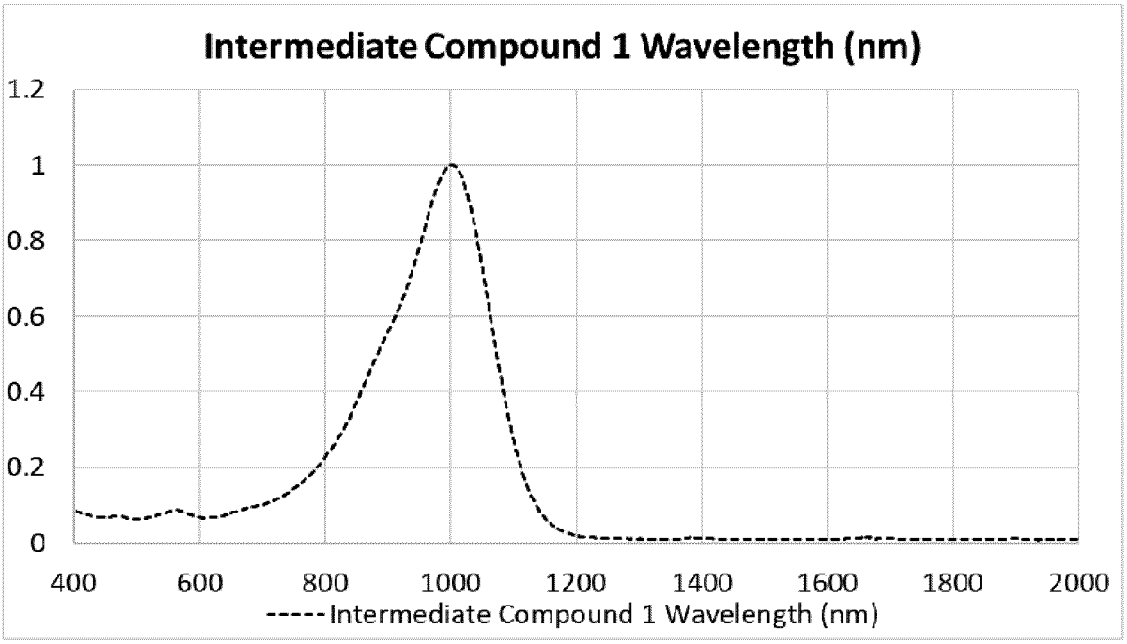
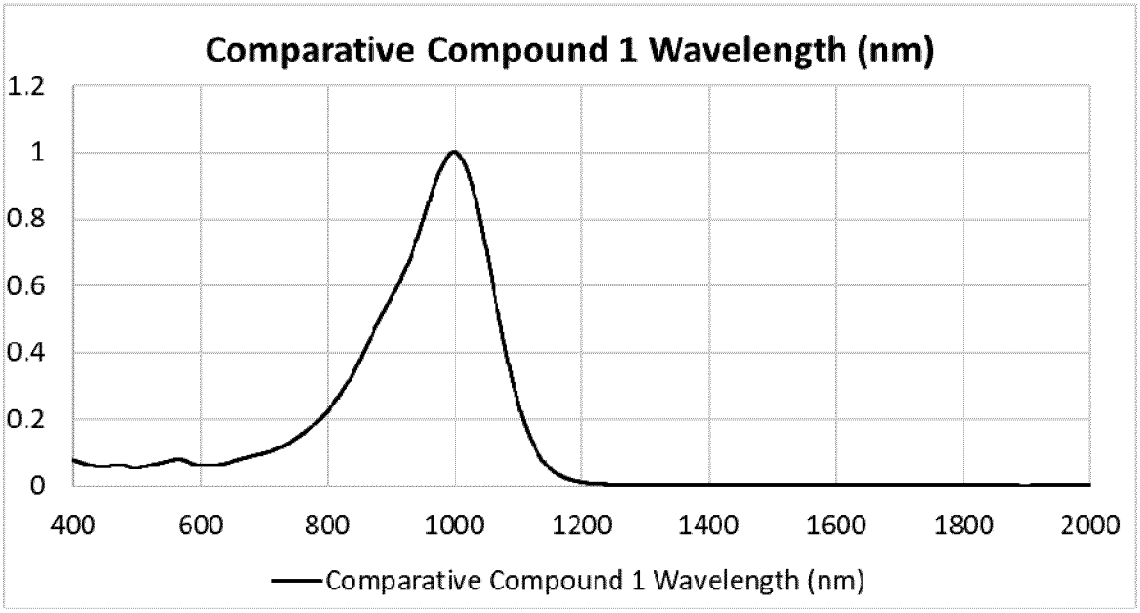


FIGURE 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/083080

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D495/22 C07D513/22 H10K85/20
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 H10K

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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZHOU YUANYUAN ET AL: "Hybrid Nonfused-Ring Electron Acceptors with Fullerene Pendant for High-Efficiency Organic Solar Cells", APPLIED MATERIALS & INTERFACES, vol. 13, no. 1, 29 December 2020 (2020-12-29), pages 1603-1611, XP093136156, US ISSN: 1944-8244, DOI: 10.1021/acsami.0c19632 cited in the application page 1604 ----- -/--	1-19

[x] Further documents are listed in the continuation of Box C.
[ ] 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
9 April 2024	02/05/2024

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	Fazzi, Raffaella

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

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/083080

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WU Z. ET AL: "Fullerene-non-fullerene hybrid acceptors for enhanced light absorption and electrical properties in organic solar cells", MATERIALS TODAY ENERGY, vol. 20, June 2021 (2021-06), page 100651, XP093136153, ISSN: 2468-6069, DOI: 10.1016/j.mtener.2021.100651 cited in the application page 3	1-19
A	CALDERON-CERQUERA KYANGZI ET AL: "Synthesis, characterization and photophysics of novel BODIPY linked to dumbbell systems based on Fullerene[60]pyrrolidine and Fullerene[60]isoxazoline", DYES AND PIGMENTS, ELSEVIER APPLIED SCIENCE PUBLISHERS BARKING, GB, vol. 184, 15 August 2020 (2020-08-15), XP086300677, ISSN: 0143-7208, DOI: 10.1016/J.DYEPIG.2020.108752 [retrieved on 2020-08-15] the whole document	1-19

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2023/083080

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

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

1. [X] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
cf. item III

2. [X] Claims Nos.: 1-19(partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

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

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

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

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

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

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

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

Remark on Protest

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

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

[ ] No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.1

cf. item III

Continuation of Box II.2

Claims Nos.: 1-19(partially)

cf. item III

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.3), should the problems which led to the Article 17(2) PCT declaration be overcome.