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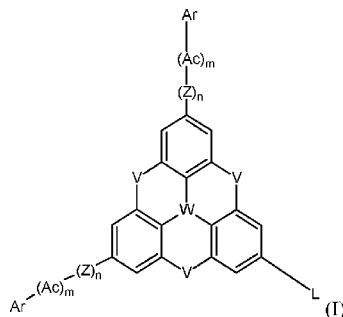
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(54) Title: HOLE TRANSPORTING AND LIGHT ABSORBING MATERIAL FOR SOLID STATE SOLAR CELLS



(57) Abstract: The present invention relates to a compound of formula (I) based on quinoxilino acridine and used as hole transporting and light absorbing material in a photovoltaic device, in particular in a solid state solar cell. (I)



## **Hole Transporting and Light Absorbing Material for Solid State Solar Cells**

### **Technical Field**

The present invention relates to hole transporting and light absorbing material, to hole transporting and light absorbing material for solid state photovoltaic devices, in particular solid state solar cells, and for thin-film photovoltaic devices and organic-inorganic perovskite films or layer photovoltaic devices, to a solid-state heterojunction and flat junction, to a solid state solar cell and to a method for preparing said solid state solar cell.

### **Prior Art and the Problem Underlying the Invention**

The conversion of solar energy to electrical current using thin film third generation photovoltaics (PV) is being widely explored for the last two decades. The sandwich/monolithic-type PV devices, consisting of a mesoporous photoanode with an organic/inorganic light harvester, redox electrolyte/solid-state hole conductor, and counter electrode, have gained significant interest due to the ease of fabrication, flexibility in the selection of materials and cost effective production. Recently, the organometallic halide perovskite based on tin ( $\text{CsSnX}_3$ ) or lead ( $\text{CH}_3\text{NH}_3\text{PbX}_3$ ) (Eggar, L. et al.; J. Am. Chem. Soc. 2012, 134, 17396-17399), have been introduced as light harvester to replace traditional metal-organic complex or organic molecules. The lead perovskite shows a power conversion efficiency (PCE) of 6.54% in liquid electrolyte based devices, while 12.3% in solid state devices (Noh, J. H. et al.; Nano Lett. 2013). Unpublished European patent application EP 12179323.6 disclosed a solid-state solar cell comprising one or more organic-inorganic perovskite layers and showing remarkable conversion efficiencies even though in absence of organic hole transporting material.

In these solid state photovoltaic devices, the perovskite pigment is usually applied from a solution of two precursors of the perovskite pigment,  $\text{PbX}_2$  ( $\text{X} = \text{I}, \text{Br}$  or  $\text{Cl}$ ) and  $\text{CH}_3\text{NH}_3\text{I}$ , in a common solvent. The optimal protocol for the deposition of  $\text{CH}_3\text{NH}_3\text{PbX}_3$  on  $\text{TiO}_2$  is achieved by the spin-coating of the precursor ( $\text{CH}_3\text{NH}_3\text{X}$  and  $\text{PbX}_2$ ,  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) solution on the mesoporous  $\text{TiO}_2$  film, followed by low temperature annealing step which results in a crystalline  $\text{CH}_3\text{NH}_3\text{PbX}_3$  (Noh et al.). From experience, the morphology of the perovskite crystals formed during this kind of solution processing cannot be well controlled and is one

of the reasons for the poor reproducibility of photovoltaic cell performance. Unpublished European patent application EP 13166720.6 disclosed an efficient and reproducible method for the application of the light harvester layer of perovskite on the nanoporous layer of the current collector. The two precursors of the organic-inorganic perovskite being in solution are separately applied on the nanoporous layer of the current collector in a two-step deposition, namely a first step for forming a film on the nanoporous layer with the first precursor and a second step for applying a film of the second precursor, to obtain a layer comprising the organic-inorganic perovskite pigment. Recently, solid-state solar cells being prepared according to this method and comprising the hybrid organic-inorganic perovskite  $\text{CH}_3\text{NH}_3\text{PbX}_3$ , X being  $\text{Cl}^-$ ,  $\text{Br}^-$  or  $\text{I}^-$ , in combination with spiro-MeOTAD (2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine) -9,9'-spirobifluorene) as organic hole transporting material (HTM) achieve power conversion efficiency (PCE) of 15% under full illumination.

However the use of spiro-MeOTAD as hole transporting material may trigger instability in such solid-state solar cells. Because Spiro-MeOTAD has two oxidation potentials being very close, this hole transporting material in the oxidized form is able to form a dication, which in turn can dismutate and might cause device instability. The use of other HTMs such as polytriarylamine (PTAA) and poly(3-hexylthiophen) (P3HT) in combination with perovskite pigment has resulted in photovoltaic device showing a PCE up to 12%.

US 2009/0295275 discloses compounds based on quinoxilino acridine, which are used as hole transporter material in organic electroluminescent devices and which, for most of them are colorless or emitting in the blue.

The present invention addresses the disadvantage of organic hole transporting material, which provides instability to the device, when said hole transporter material is in oxidized form, as it is the case of spiro-MeOTAD.

The present invention also pursues to provide new hole transporting material, which provides a higher PCE to the solid-state photovoltaic devices comprising perovskite as sensitizer or light absorbing material.

The present invention addresses the disadvantage of the perovskite pigment, which cannot absorb the complete incident light, in particular in the visible part of the light spectrum and

to absorb the remnant light passing through the layer comprising the perovskite pigment to increase the photoconversion and photocurrent generation of the whole device and therefore the efficiency and the performance of the photovoltaic device.

The invention pursues to provide an efficient solar cell, which can be rapidly prepared in an efficient way, using readily available or low cost materials such as conductive material, using a short manufacturing procedure based on industrially known manufacturing step, keeping the material costs and the material impact on the environment very low.

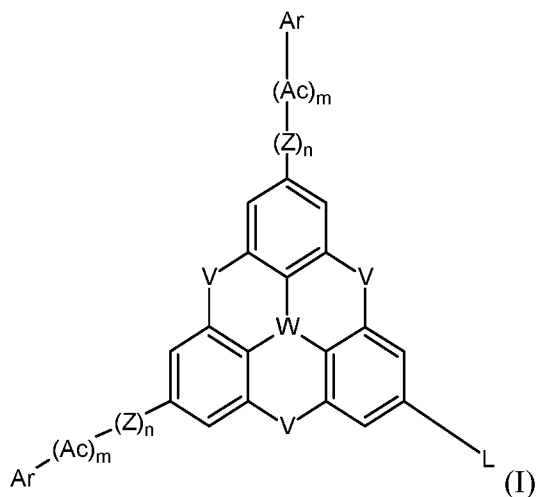
The present invention addresses the problems depicted above.

### **Summary of the Invention**

Remarkably, in some aspects, the present inventors have found that a compound based on quinolizino acridine operates as a hole transporting material and as a light harvester or a light absorbing material and improves the PCE of solid photovoltaic devices comprising perovskite pigment as sensitizer. Said compound may absorb light to the near IR regions of the light spectrum, namely from 400 nm to 920 nm. In a solid state photovoltaic device, said compound also absorbs the remanent light passing through a sensitizer layer and in particular a particular a sensitizer layer comprising perovskite pigment.

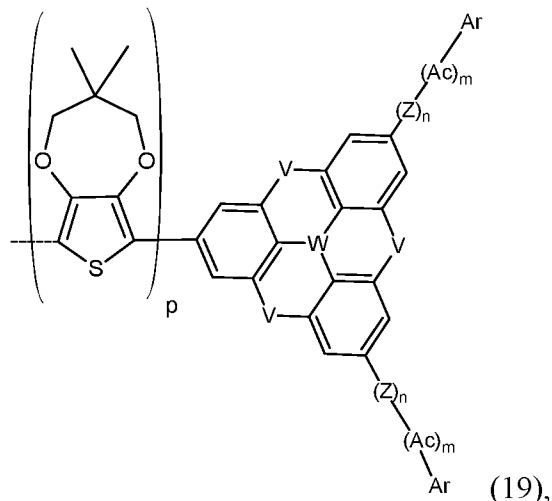
The specific configuration of the structure of the compound based on quinolizino acridine being the donor moiety separated from the acceptor moieties provides a fine tuning of the free charges extracted from the sensitizer layer, in particular from the perovskite layer. Although their large size, said compounds are good soluble in organic solvent, which greatly facilitates their purification and processing and their application or deposition on the sensitizer layer in the solid photovoltaic device.

In an aspect, the present invention provides compound of formula (I):

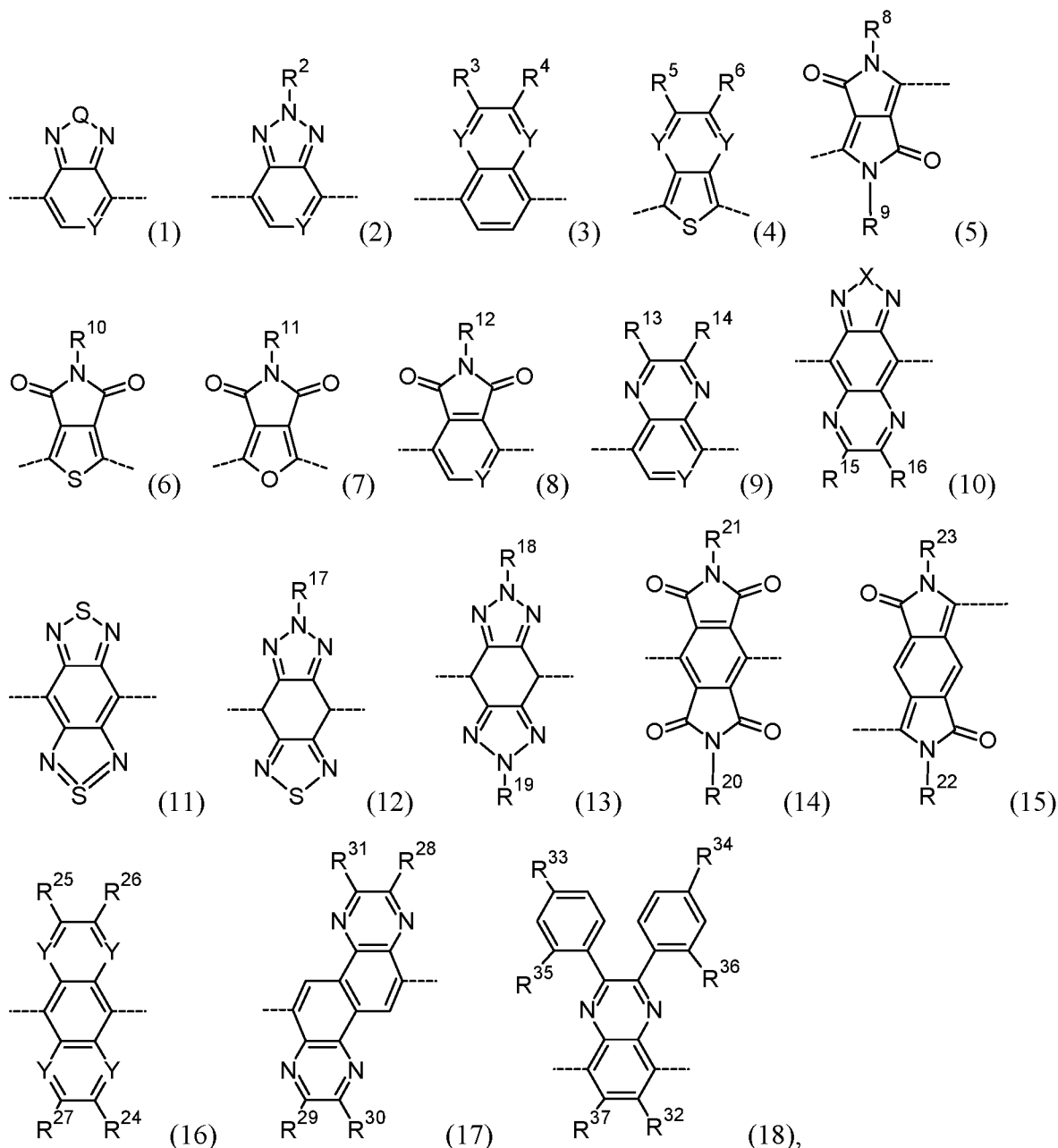


wherein

- W is a nitrogen (N) or phosphorus (P) atom;
- V is, on each occurrence, identically or differently selected from C(R<sup>1</sup>)<sub>2</sub>, C=O or O, R<sup>1</sup> being selected from C1-C12 alkyl;
- L is selected from moiety of formula  $\text{---(Z)}_n\text{---(Ac)}_m\text{---Ar}$  as defined below or from moiety of formula (19)



- p being 0, 1 or 2 and moiety of formula  $\text{---(Z)}_n\text{---(Ac)}_m\text{---Ar}$  being as defined below;
- Z is a heteroaromatic ring system, on each occurrence, identically or differently selected from C4-C20 heteroaryl, C4-C20 heteroaryloxy group, wherein the heteroatoms are selected from O, S, Se, Si and wherein said heteroaryl, aryloxy group, heteroaryloxy group are substituted by C1-C20 alkyl, C1-C20 heteroalkyl, C2-C20 alkenyl or C2-C20 alkynyl, wherein said alkyl, alkenyl, and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, and n is 0, 1, 2, or 3;
  - Ac is an acceptor group, on each occurrence, identically or differently selected from a moiety according to any one of the formulae (1) to (18),



- wherein

-  $R^2$  to  $R^{37}$  are substituents independently selected from H, ether group, C1-C16 alkyl, C1-C16 alkoxy group, C1-C16 thioalkyl, C1-C16 alkoxyalkyl, C4-C16 aryl, C1-C16 arylalkyl or C4-C16 heteroaryl, C4-C16 heteroarylalkyl, the heteroatoms being selected from O, S, or N,

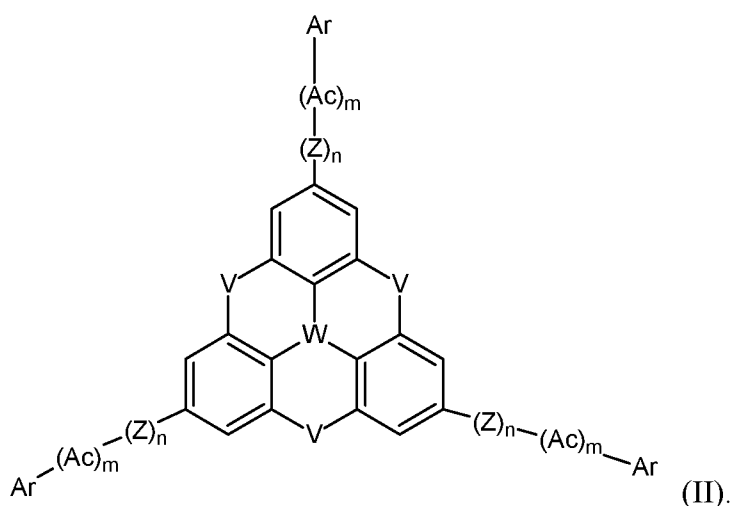
- Q is selected from S, O, Se, Si or N and when Q is N, said nitrogen atom is substituted by substituent as defined for  $R^2$  to  $R^{32}$ ,

- Y is, on each occurrence, identically or differently selected from N or C, being unsubstituted or substituted by halogen selected from F, Cl, I, and Br, and

- m is 0 or 1;

- -Ar is a successive bound heteroaromatic rings system comprising from 2 to 10 heteroaromatic rings, said heteroaromatic rings being, on each occurrence, identically selected from C4-C20 heteroaryl and C4-C20 heteroaryloxy group, wherein the heteroatoms are selected from O, S, Se, Si and wherein said heteroaryl and heteroaryloxy groups are unsubstituted or substituted by C1-C20 alkyl, C1-C20 heteroalkyl, C2-C20 alkenyl or C2-C20 alkynyl, wherein said alkyl, alkenyl, and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, -COOH, =O (keto), C4-C16 cyanoalkenyl carboxylic acid.

According to an embodiment, the invention provides more specifically a compound of formula (II):



In an aspect, the invention provides a photovoltaic solid state device comprising a compound of the invention of formula (I), or in particular of formula (II).

In an aspect, the invention specifically provides a photovoltaic solid state device comprising a compound of the invention of formula (I), or in particular of formula (II) and further comprising an organic-inorganic perovskite as sensitizer, said perovskite being under the form of layer.

In another aspect, the invention provides use of a compound of the invention as a hole transporting and light absorbing material in photovoltaic solid state device.

Further aspects and preferred embodiments of the invention are detailed herein below and in the appended claims. Further features and advantages of the invention will become apparent

to the skilled person from the description of the preferred embodiments given below.

### **Brief Description of the Drawings**

**Figure 1A** shows schematic diagram for the synthesis of compound of formula (49). **Figure 1B** shows, on the left, the schematic architecture of a photovoltaic device of the invention, in particular a solid solar cell comprising the following layers from the side of the light exposure: FTO glass being coated by a compact  $\text{TiO}_2$  layer, on which mesoporous  $\text{TiO}_2$  is provided with the sensitizer, an organic-inorganic perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , on which the HTM (hole transporting material) being compound of formula (49), also named Fused-F, is spin-coated, and a metal layer being Au is provided on HTM, and, on the right, said **Figure 1B** shows the corresponding energy level diagram of the photovoltaic device.

**Figure 2A** shows UV-Visible absorption (continuous line) and fluorescence (dashed line) spectra of compound of formula (49)(Fused-F) in chloroform. **Figure 2B** shows UV-Visible absorption spectra of Fused-F (compound of formula (49)) coated on mesoporous  $\text{TiO}_2$  (line with triangles) and  $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$  (line with round dots) films.  $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$  (line with squares) film without HTM is shown for comparison.

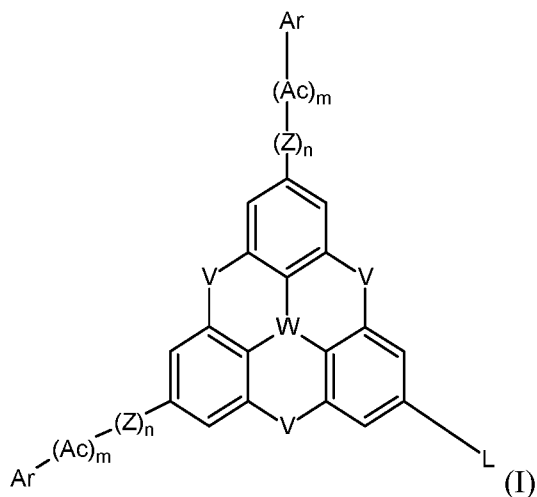
**Figure 3A** shows the Current-Voltage characteristics of the photovoltaic device with (round) and without (square) Fused-F(compound of formula (49)) measured in the dark (unfilled) and under  $100 \text{ mW.cm}^{-2}$  photon flux (AM 1.5G) (filled). **Figure 3B** shows the incident photo-to-electron conversion efficiency spectra of the photovoltaic device with (round) and without (square) Fused-F (compound of formula (49)).

**Figure 4A** shows schematic diagram for the synthesis of compound of formula (51), also named FA-CN-Final. **Figure 4B** shows UV-Visible absorption (continuous line) and fluorescence (dashed line) spectra of compound of formula (51)(FA-CN-Final) in chloroform.

### **Detailed Description of the Preferred Embodiments**

The present invention concerns a compound based on quinolizino acridine of formula (I).

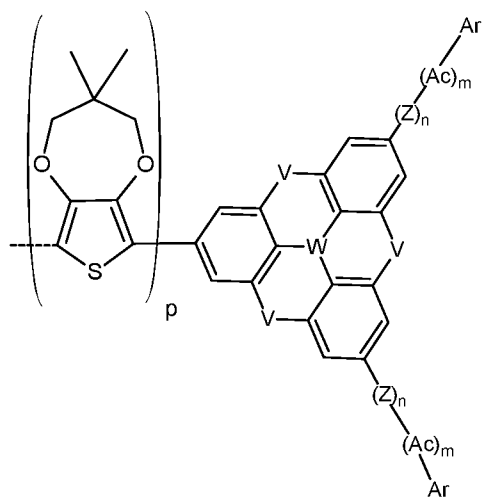




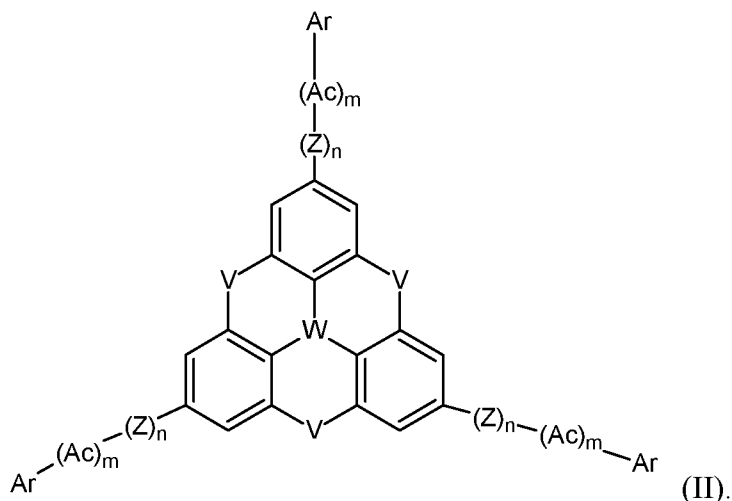
wherein

- W is a nitrogen (N) or phosphorus (P) atom;
- V is, on each occurrence, identically or differently selected from  $C(R^1)_2$ ,  $C=O$  or  $O$ ,  $R^1$  being selected from C1-C12 alkyl and C1 alkyl;
- m is an integer selected from 0 or 1; and
- n is an integer selected from 0, 1, 2, or 3.

L is a linked moiety selected from moiety of formula  $\text{---}(Z)_n\text{---}(\text{Ac})_m\text{---Ar}$  as defined below or from moiety of formula (19)



The compound of formula (I) may be a monomer, when L is a moiety of formula  $\text{---}(Z)_n\text{---}(\text{Ac})_m\text{---Ar}$ , or a dimer, when L is a moiety of formula (19). Said monomer is represented by a compound of formula (II)



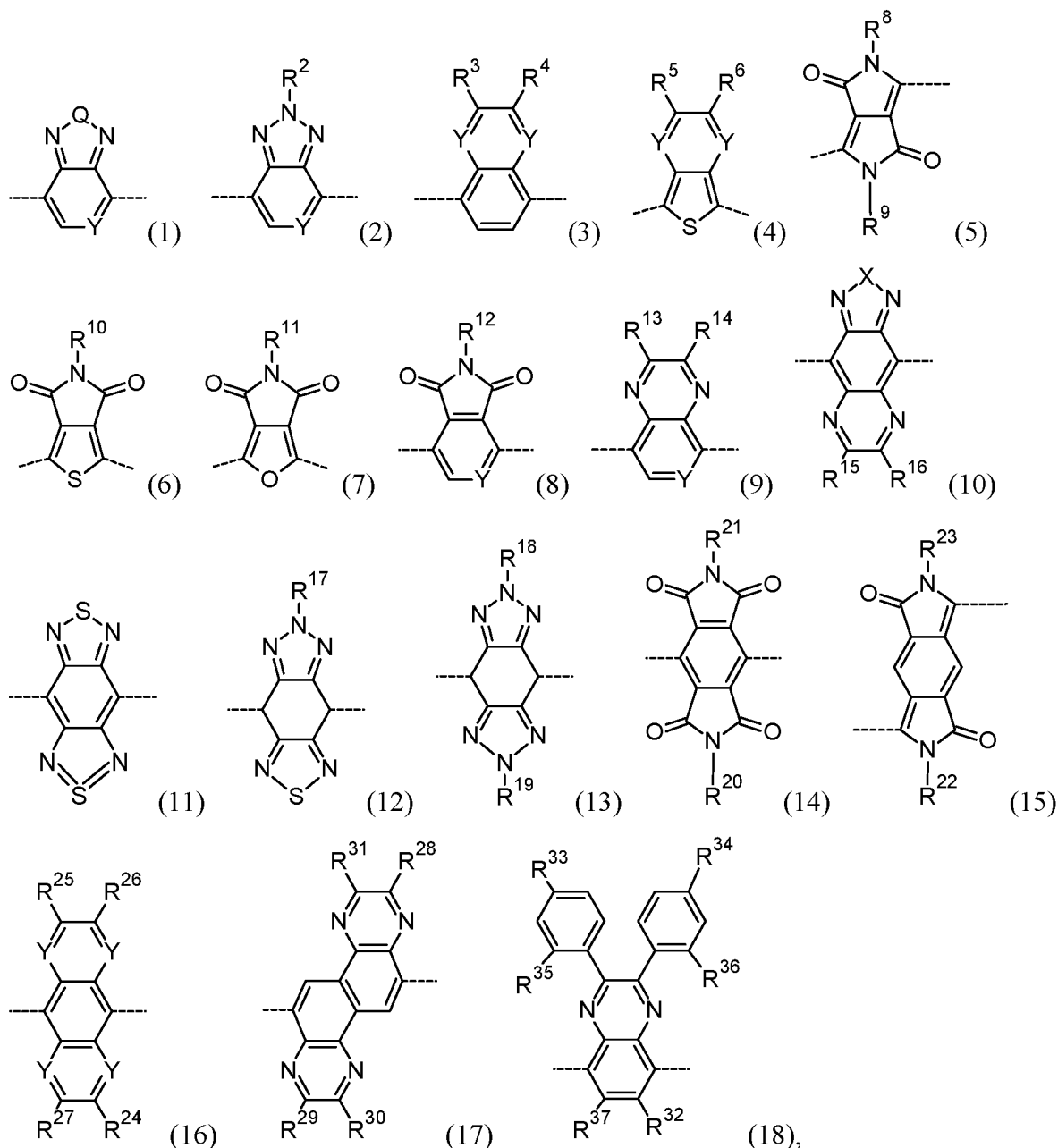
In the compound of the invention of formula (I) and/or of formula (II), W is preferably a nitrogen (N) atom.

In the compound of the invention of formula (I) and/or of formula (II), V is at least preferably, on each occurrence, identically selected from  $C(R^1)_2$ ,  $C=O$  or  $O$ ,  $R^1$  being selected from C1-C12 alkyl and C1 alkyl. V is identical on each occurrence and represents selected from  $C(R^1)_2$ ,  $R^1$  being selected from C1-C12 alkyl, C4-C12 alkyl, C6-C10 alkyl and C1 alkyl, preferably C1 alkyl.

In the compound of formula (I), when L is selected from moiety of formula  $----- (Z)_n - (Ac)_m - Ar$ , said moiety is identical to one or two of the two other moieties  $----- (Z)_n - (Ac)_m - Ar$  substituted the quinolizinoacridine core of the compound of formula (I). In the compound of formula (I) and/or in the compound of formula (II), said moieties of formula  $----- (Z)_n - (Ac)_m - Ar$  may be identical or different on each occurrence.

In the compound of formula (I), when L is selected from moiety of formula (19), p may be 0, 1, or 2, preferably 0 and the moiety of formula  $----- (Z)_n - (Ac)_m - Ar$  may be identical or different on each occurrence on the quinolizinoacridine core of moiety of formula (19) and/or on the quinolizinoacridine core of moiety of formula (I).

Ac is an acceptor group, on each occurrence, identically or differently selected from a moiety according to any one of the formulae (1) to (18),



- wherein

- $R^2$  to  $R^{37}$  are substituents independently selected from H, ether group, C1-C16 alkyl, C1-C16 alkoxy group, C1-C16 thioalkyl, C1-C16 alkoxyalkyl, C4-C16 aryl, C1-C16 arylalkyl or C4-C16 heteroaryl, C4-C16 heteroarylalkyl, the heteroatoms being selected from O, S, or N,
- Q is selected from S, O, Se, Si or N and when Q is N, said nitrogen atom is substituted by substituent as defined for  $R^2$  to  $R^{37}$ ,
- Y is, on each occurrence, identically or differently selected from N or C, being unsubstituted or substituted by halogen selected from F, Cl, I, and Br, preferably F or Cl.

Preferably alkyl, alkoxy, thioalkyl, alkoxyalkyl, arylalkyl and heteroaryl of substituents  $R^2$ - $R^{37}$  are selected from hydrocarbon containing from 1 to 16 carbons, 1 to 12 carbons or 1 to 8 carbons. Substituents from  $R^2$ - $R^{37}$  substituting the same moiety of same formula may be identical to the other substituent substituting the same moiety of same formula or different. For example,  $R^3$  and  $R^4$  substituting the moiety of formula (3) may be identical or different.

According to a further embodiment, the acceptor group Ac is selected from a moiety according to any one of the formulae (1) to (4) and (10) to (13) as defined above. Ac is preferably selected from a moiety according to any one of the formulae (1), (10) and (11) as defined above or most preferably is moiety of formula (1).

According to an embodiment, the acceptor group Ac is selected from a moiety according to any one of the formulae (1) to (18) as defined above, wherein Q is selected from S, O, Se, Si, or from S, O, or Se.

According to further embodiment, the acceptor group Ac is selected from a moiety according to any one of the formulae (1) to (18) as defined above, wherein Y is C atom, preferably said C atom being further substituted by halogen.

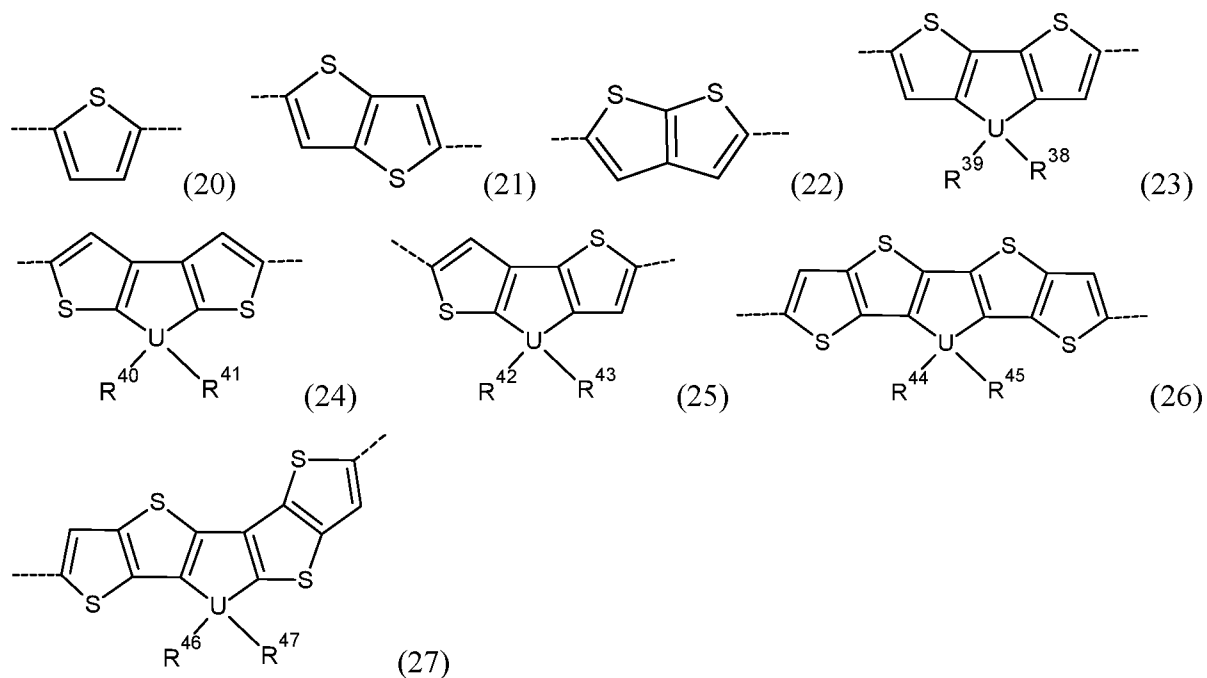
In another embodiment, the acceptor group Ac is selected from a moiety according to any one of the moiety of formula (1), wherein Q is S and Y is C atom.

Z is a heteroaromatic ring system, on each occurrence, identically or differently selected from C4-C20 heteroaryl, C4-C20 aryloxy group, C4-C20 heteroaryloxy group, wherein the heteroatoms are selected from O, S, Se, Si and wherein said heteroaryl, aryloxy group, heteroaryloxy group are substituted by C1-C20 alkyl, C1-C20 heteroalkyl, C2-C20 alkenyl or C2-C20 alkynyl, wherein said alkyl, alkenyl, and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic.

Z is a heteroaromatic ring system, on each occurrence, identically or differently selected from C4-C20 heteroaryl and C4-C20 heteroaryloxy group, wherein the heteroatoms are selected from O, S, Se, Si and wherein said heteroaryl and heteroaryloxy group are substituted by C1-C20 alkyl, C1-C20 heteroalkyl, C2-C20 alkenyl or C2-C20 alkynyl, wherein said alkyl, alkenyl, and alkynyl, if they comprise 3 or more carbons, may be linear,

branched or cyclic.

According to another embodiment, the heteroaromatic ring system Z of the compound of formula (I) and/or the compound of formula (II) is selected from a moiety according to any one of the formulae (20) to (27)



- wherein  $R^{39}$  to  $R^{47}$  are substituents independently selected from H, C1-C16 alkyl, C1-C16 alkoxy group, C1-C16 thioalkyl, C1-C16 alkoxyalkyl and if they comprise 3 or more carbons, they may be linear or branched and U is selected from S, Si or C.

In a further embodiment, Z is selected from a moiety according to any one of the formulae (20), (23) to (26).

In the compound of formula (I) and/or of formula (II), Ar is an aromatic ring system or a heteroaromatic ring system, on each occurrence, identically or differently selected from C4-C20 aryl, C4-C20 heteroaryl, C4-C20 aryloxy group, C4-C20 heteroaryloxy group, wherein the heteroatoms are selected from O, S, Se, Si and wherein said aryl, heteroaryl, aryloxy group, heteroaryloxy group are unsubstituted or substituted by C1-C20 alkyl, C1-C20 heteroalkyl, C2-C20 alkenyl or C2-C20 alkynyl, wherein said alkyl, alkenyl, and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, -COOH, =O (keto), C4-C16 cyanoalkenyl carboxylic acid.

In another embodiment, Ar is a heteroaromatic ring system, on each occurrence, identically

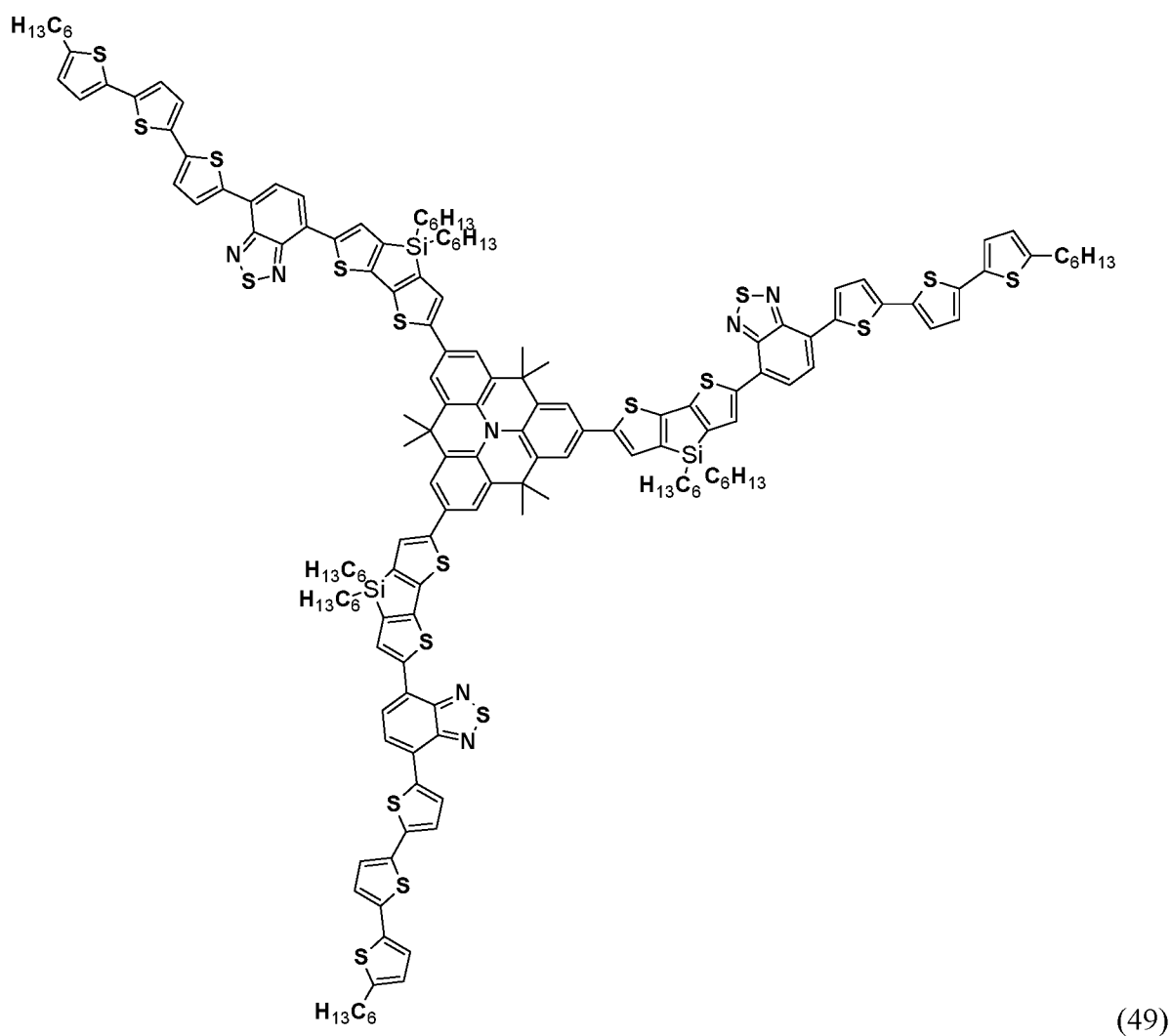
or differently selected from C4-C20 heteroaryl, C4-C20 aryloxy group, C4-C20 heteroaryloxy group, wherein the heteroatoms are selected from O, S, Se or Si, preferably S and wherein said heteroaryl, aryloxy group, heteroaryloxy group are unsubstituted or substituted by C1-C20 alkyl, C1-C20 heteroalkyl, C2-C20 alkenyl or C2-C20 alkynyl, wherein said alkyl, alkenyl, and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, -COOH, =O (keto), C4-C16 cyanoalkenyl carboxylic acid. Thus Ar as being a heteroaromatic ring system is or represents one heteroaromatic ring system (one unit) or a successive bound heteroaromatic rings system (several units) comprising from 2 to 10 heteroaromatic rings, preferably 3 heteroaromatic rings, said heteroaromatic rings being, on each occurrence, identically selected from C4-C20 heteroaryl and C4-C20 heteroaryloxy group, wherein the heteroatoms are selected from O, S, Se, Si and wherein said heteroaryl and heteroaryloxy groups are unsubstituted or substituted by C1-C20 alkyl, C1-C20 heteroalkyl, C2-C20 alkenyl or C2-C20 alkynyl, wherein said alkyl, alkenyl, and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, -COOH, =O (keto), C4-C16 cyanoalkenyl carboxylic acid.

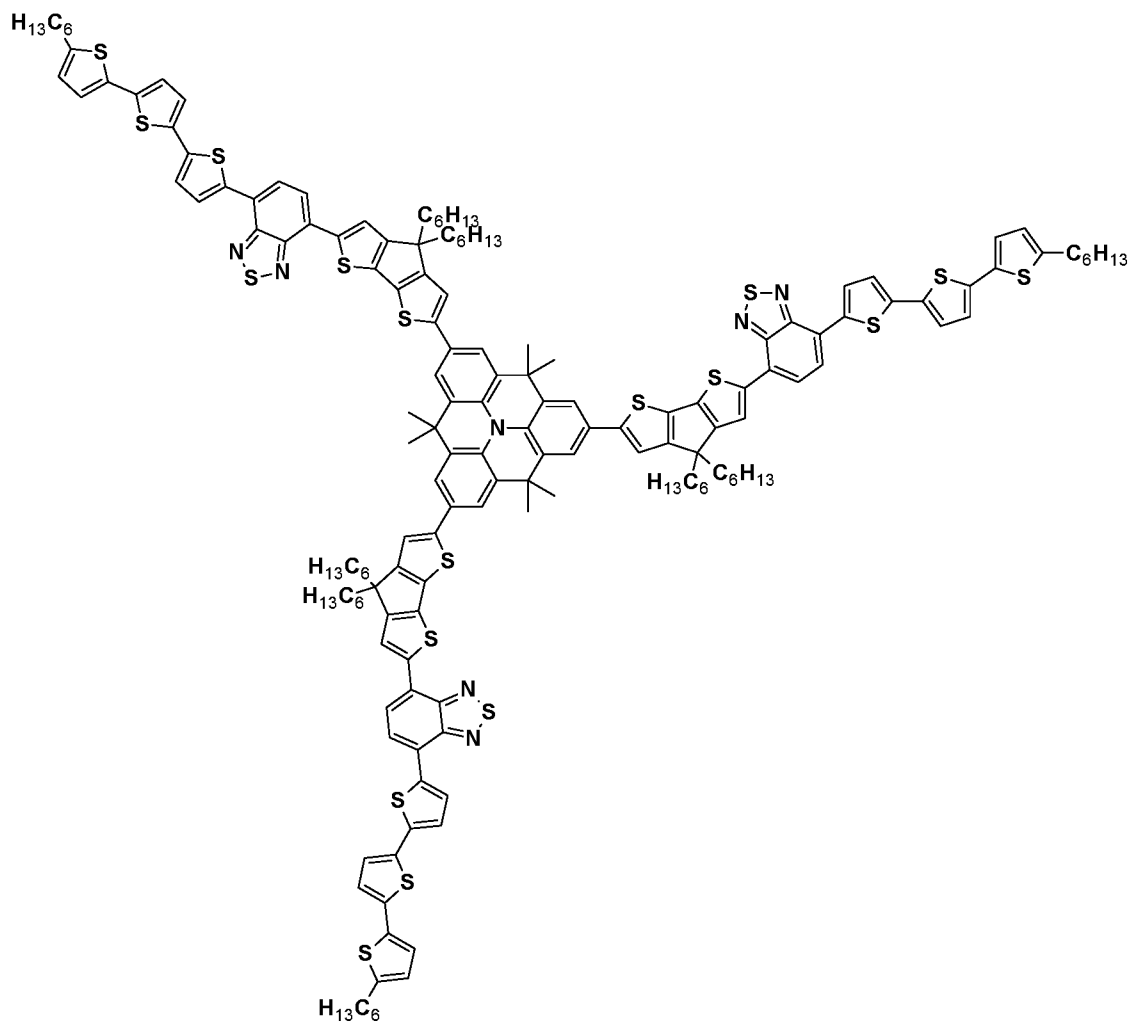
For the meaning of the present application, Ar may represent one heteroaromatic ring system comprising one heteroaromatic ring or a successive bound heteroaromatic rings system comprising from 2 to 10 heteroaromatic rings, preferably 3 heteroaromatic rings, wherein the heteroaromatic rings or the last heteroaromatic rings of the successive bound heteroaromatic rings system may be further unsubstituted or substituted as defined above. For the meaning of the present application, the term “bound” in the successive bound heteroaromatic rings system does not mean “fused”. Thus the successive heteroaromatic rings in the system are not fused but bound to each other.

The moiety Ar may represent one heteroaromatic ring (one unit) or successive bound heteroaromatic rings (several units), from 2 to 10 heteroaromatic ring, preferably 3 heteroaromatic rings, wherein said one heteroaromatic ring or the last heteroaromatic ring, if Ar is a successive bound heteroaromatic rings system, is substituted by C1-C20 alkyl, C1-C20 heteroalkyl, C2-C20 alkenyl or C2-C20 alkynyl, wherein said alkyl, alkenyl, and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, -COOH, =O (keto), C4-C16 cyanoalkenyl carboxylic acid. Said last ring may be substituted by an anchoring group independently selected from -COOH, PO<sub>3</sub>H<sub>2</sub>, -PO<sub>4</sub>H<sub>2</sub>, -P(R<sup>48</sup>)O<sub>2</sub>H, -SO<sub>3</sub>H<sub>2</sub>, -SO<sub>4</sub>H<sub>2</sub>, -CONHOH, 1,2-hydroxybenzene, 1-hydroxy-2-carboxybenzene,

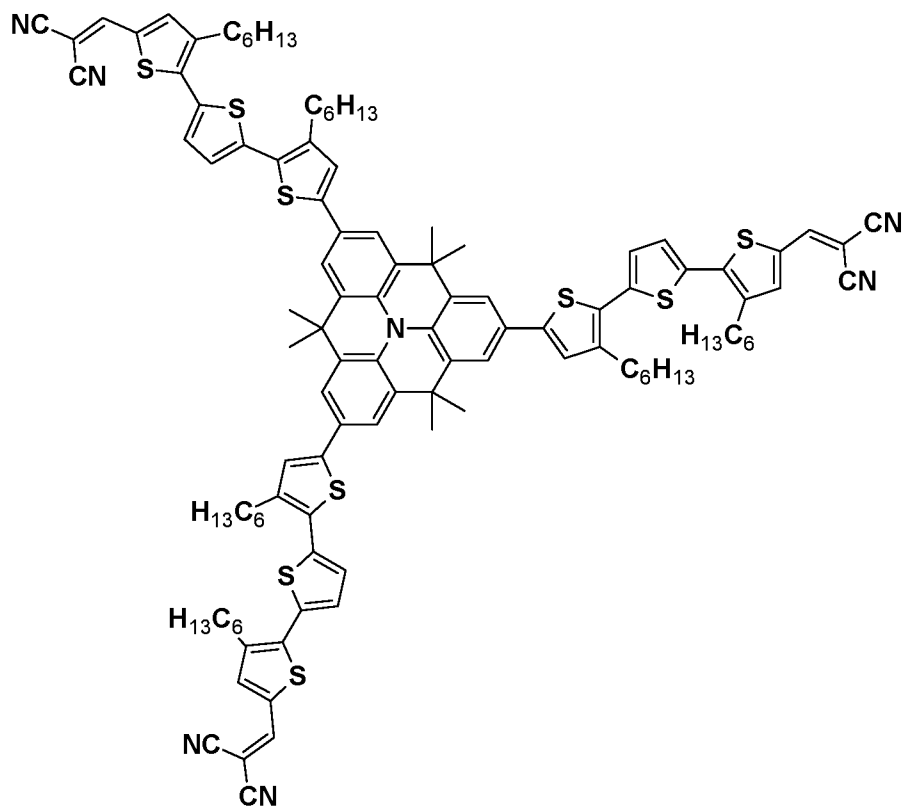
acetylacetonate, deprotonated forms of the aforementioned, organic and /or inorganic salts of said deprotonated forms, and chelating groups with  $\pi$ -conducting character.  $R^{48}$  may be a hydrocarbon comprising from 1 to 50 carbons and 0-25 heteroatoms selected from O, N, or S, said hydrocarbon being covalently bound to the P atom of said phosphinic acid group by a carbon atom.  $R^{48}$  may be substituted or unsubstituted, linear, branched or cyclic C1-C20 alkyl, C2-C20 alkenyl, C2-C20 alkynyl, and C4-C20 aryl.

According to a further embodiment, the compound of formula (I) and/or the formula (II) is selected from a compound according to any one of formulae (49) to (52), preferably a compound according to any one of the formulae (49) and (50):





(50)



(51)



The invention also provides in another aspect a photovoltaic solid state device comprising a compound of formula (I) and/or formula (II).

The photovoltaic solid state device is selected from a solar cell, a heterojunction, an optoelectronic device, a light emitting device. Preferably the solar cell of the invention is a solid state solar cell. Preferably the heterojunction is a solid heterojunction.

According to an embodiment, the photovoltaic device of the invention comprises a conducting support layer, a surface-increasing scaffold structure, a sensitizer or sensitizer layer, a hole transporting layer and a counter electrode and/or metal layer.

In an embodiment, the hole transporting layer of the photovoltaic device is a compound of formula (I) and/or of formula (II).

According to an embodiment, the conducting support layer, the scaffold structure, the perovskite layer and the counter electrode are present in this order from one side to the other of the solar cell of the invention. A protective layer may or may not be present, for example at appropriate positions between the above layers, as disclosed elsewhere in this specification.

According to another embodiment, the photovoltaic device comprises a hole collector layer, a conductive layer, an electron blocking layer, a sensitizer layer and a current collector layer, wherein the hole collector layer is coated by the conductive layer; wherein the electron blocking layer is between the conductive layer and the sensitizer layer, which is in contact with the current collector layer being a metal or a conductor.

According to a further embodiment, the conductive material is selected from one or more conductive polymers or one or more hole transporting materials, which may be selected from poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate):grapheme nanocomposite (PEDOT:PSS:graphene), poly(N-vinylcarbazole) (PVK) and sulfonated poly(diphenylamine) (SPDPA), preferably from PEDOT:PSS, PEDOT:PSS:graphene and PVK, more preferably from PEDOT:PSS. Conductive polymers may also be selected from polymers comprising polyaniline, polypyrrole, polythiophene, polybenzene,

polyethylenedioxythiophene, polypropylenedioxy-thiophene, polyacetylene, and combinations of two or more of the aforementioned, for example. The conductive polymer of the invention is preferably selected from the above polymer in a watery dispersion.

For the purpose of the present specification, the expression "in electric contact with" means that electrons or holes can get from one layer to the other layer with which it is in electric contact, at least in one direction. In particular, considering the electron flow in the operating device exposed to electromagnetic radiation, layers through which electrons and/or holes are flowing are considered to be in electric contact. The expression "in electric contact with" does not necessarily mean, and preferably does not mean, that electrons and/or holes can freely move in any direction between the layers.

The conducting support layer is preferably substantially transparent. "Transparent" means transparent to at least a part, preferably a major part of the visible light. Preferably, the conducting support layer is substantially transparent to all wavelengths or types of visible light. Furthermore, the conducting support layer may be transparent to non-visible light, such as UV and IR radiation, for example.

According to an embodiment, the conducting support layer provides the support layer of the solar cell of the invention. Preferably, the solar cell is built on said support layer. According to another embodiment, the support of the solar cell is provided on the side of the counter electrode. In this case, the conductive support layer does not necessarily provide the support of the device, but may simply be or comprise a current collector, for example a metal foil.

The conducting support layer preferably functions and/or comprises a current collector, collecting the current obtained from the solar cell. The conducting support layer may comprise a material selected from indium doped tin oxide (ITO), fluorine doped tin oxide (FTO), ZnO-Ga<sub>2</sub>O<sub>3</sub>, ZnO-Al<sub>2</sub>O<sub>3</sub>, tin-oxide, antimony doped tin oxide (ATO), SrGeO<sub>3</sub> and zinc oxide, preferably coated on a transparent substrate, such as plastic or glass. In this case, the plastic or glass provides the support structure of the layer and the cited conducting material provides the conductivity. Such support layers are generally known as conductive glass and conductive plastic, respectively, which are thus preferred conducting support layers in accordance with the invention. According to an embodiment, the conducting support layer comprises a conducting transparent layer, which may be selected from

conducting glass and from conducting plastic.

According to an embodiment of the invention, a surface-increasing scaffold structure is provided on said conducting support structure or on a protective layer that may be provided on said scaffold structure.

According to an embodiment of the solar cell and the heterojunction of the invention, the surface-increasing scaffold structure is nanostructured and/or nanoporous. The scaffold structure is thus preferably structured on a nanoscale. The structures of said scaffold structure increase the effective surface compared to the surface of the conductive support.

According to an embodiment, said scaffold structure is made from and/or comprises a metal oxide. For example, the material of the scaffold structure is selected from semiconducting materials, such as Si, TiO<sub>2</sub>, SnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, ZnO, WO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, CdS, ZnS, PbS, Bi<sub>2</sub>S<sub>3</sub>, CdSe, CdTe, SrTiO<sub>3</sub>, GaP, InP, GaAs, CuInS<sub>2</sub>, CuInSe<sub>2</sub>, and combinations thereof, for example. Preferred semiconductor materials are Si, TiO<sub>2</sub>, SnO<sub>2</sub>, ZnO, WO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub> and SrTiO<sub>3</sub>, for example. According to an embodiment, the surface-increasing scaffold structure is nanostructured and/or nanoporous.

The invention does not intend to exclude the possibility that there are one or more intermediate layers between the scaffold structure and the conductive support. Such intermediate layers, if present, would preferably be conducting and/or semiconducting.

According to an embodiment, the sensitizer layer of the photovoltaic device comprising at least one pigment being selecting from organic, inorganic, organometallic and organic-inorganic pigments or a combination thereof. The sensitizer is preferably a light absorbing compound or material. Preferably, the sensitizer is a pigment, and most preferably the sensitizer is an organic-inorganic pigments.

The sensitizer layer may comprise one or more pigments of the group consisting of organometallic sensitizing compounds (telocyanine derived compounds, porphyrine derived compounds), metal free organic sensitizing compounds (diketopyrrolopyrrole (DPP) based sensitizer), inorganic sensitizing compounds such as quantum dots, Sb<sub>2</sub>S<sub>3</sub> (Antimonysulfide, for example in the form of thin films), aggregates of organic pigments, nanocomposites, in

particular organic-inorganic perovskites, and combinations of the aforementioned. For the purpose of the invention, it is in principle possible to use any type of dyes or sensitizer, including combinations of different types of dyes or different dyes of the same type.

According to one embodiment, the photovoltaic device of the invention comprising a compound of formula (I) and/or of formula (II) further comprises an organic-inorganic perovskite as sensitizer, said perovskite being under the form of layer.

According to an embodiment, the sensitizer layer of the photovoltaic device of the invention is coated by a layer comprising the compound of formula (I) and/or of formula (II). Preferably said sensitizer layer comprises an organic-inorganic perovskite.

According to an embodiment, the sensitizer or the sensitizer layer comprises, consists of or is made of an organic-inorganic perovskite. Said organic-inorganic perovskite is provided under a film of one perovskite pigment or mixed perovskite pigments or perovskite pigments mixed with further dyes or sensitizers.

According to a further embodiment, the sensitizer layer comprises a further pigment in addition to the organic-inorganic perovskite pigment, said further pigment selected from organic pigment, organometallic pigment or inorganic pigment.

Organometallic sensitizers are disclosed, for example, in EP0613466, EP0758337, EP 0983282, EP 1622178, WO2006/038823, WO2009/107100, WO2010/055471 and WO2011/039715. Exemplary organic dyes are those disclosed in WO2009/098643, EP1990373, WO2007/100033 for example. An organic dye was also used in European patent application no. EP11161954.0. and in PCT/IB2011/054628. Metal free organic sensitizers such as DPP based compounds are disclosed, for example, in PCT/IB2013/056648 and in European patent application no. EP12182817.2.

The term "perovskite", for the purpose of this specification, refers to the "perovskite structure" and not specifically to the perovskite material,  $\text{CaTiO}_3$ . For the purpose of this specification, "perovskite" encompasses and preferably relates to any material that has the same type of crystal structure as calcium titanium oxide and of materials in which the bivalent cation is replaced by two separate monovalent cations. The perovskite structure has

the general stoichiometry  $AMX_3$ , where “A” and “M” are cations and “X” is an anion. The “A” and “M” cations can have a variety of charges and in the original Perovskite mineral ( $CaTiO_3$ ), the A cation is divalent and the M cation is tetravalent. For the purpose of this invention, the perovskite formulae includes structures having three (3) or four (4) anions, which may be the same or different, and/or one or two (2) organic cations, and/or metal atoms carrying two or three positive charges, in accordance with the formulae presented elsewhere in this specification.

According to an embodiment, the photovoltaic device of the invention comprises one or more layer of an organic-inorganic perovskite.

According to an embodiment, the sensitizer layer comprises, consists essentially of or consists of a nanocomposite material or an organic-inorganic pigments. According to a preferred embodiment, the sensitizer layer comprises, consists essentially of or consists of an organic-inorganic perovskite.

According to a further embodiment, the organic-inorganic perovskite layer material of the photovoltaic device of the invention further comprises a perovskite-structure of any one of formulae (I), (II), (III), (IV), (V) and/or (VI) below:

$AA'MX_4$	(I)
$AMX_3$	(II)
$AA'N_{2/3}X_4$	(III)
$AN_{2/3}X_3$	(IV)
$BN_{2/3}X_4$	(V)
$BMX_4$	(VI)

wherein,

- A and A' are organic, monovalent cations that are independently selected from primary, secondary, tertiary or quaternary organic ammonium compounds, including N-containing heterorings and ring systems, A and A' having independently from 1 to 60 carbons and 1 to 20 heteroatoms;
- B is an organic, bivalent cation selected from primary, secondary, tertiary or quaternary organic ammonium compounds having from 1 to 60 carbons and 2-20 heteroatoms and having two positively charged nitrogen atoms;
- M is a divalent metal cation selected from the group consisting of  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,

$\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ge}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Eu}^{2+}$ , or  $\text{Yb}^{2+}$ ;

- N is selected from the group of  $\text{Bi}^{3+}$  and  $\text{Sb}^{3+}$ ; and,
- X is independently selected from  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NCS}^-$ ,  $\text{CN}^-$ , and  $\text{NCO}^-$ .

In particular, the three or four X may be the same or different. For example, in  $\text{AMX}_3$  (formula II) may be expressed as formula (II') below:



wherein  $\text{X}^i$ ,  $\text{X}^{ii}$ ,  $\text{X}^{iii}$  are independently selected from  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NCS}^-$ ,  $\text{CN}^-$ , and  $\text{NCO}^-$ , preferably from halides ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ), and A and M are as defined elsewhere in this specification.  $\text{X}^i$ ,  $\text{X}^{ii}$ ,  $\text{X}^{iii}$  may thus be the same or different in this case. The same principle applies to the perovskites of formulae (I) and (III)-(VI) and the more specific embodiments of formulae (VIII) to (XIV) below. In case of  $\text{AA}'\text{MX}_4$  (formula I), for example, formula (I') applies:



wherein  $\text{X}^i$ ,  $\text{X}^{ii}$ ,  $\text{X}^{iii}$  are independently selected from  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NCS}^-$ ,  $\text{CN}^-$ , and  $\text{NCO}^-$ , preferably from halides ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ).

Preferably, if  $\text{X}^i$ ,  $\text{X}^{ii}$ ,  $\text{X}^{iii}$  in formulae (II) and (IV) or  $\text{X}^i$ ,  $\text{X}^{ii}$ ,  $\text{X}^{iii}$ ,  $\text{X}^{iv}$  in formulae (I), (III), (V) or (VI) comprise different anions X, there are not more than two different anions. For example,  $\text{X}^i$  and  $\text{X}^{ii}$  being the same with  $\text{X}^{iii}$  being an anion that is different from  $\text{X}^i$  and  $\text{X}^{ii}$ .

According to a preferred embodiment, the perovskite material has the structure selected from one or more of formulae (I) to (III), preferably (II) or (II').

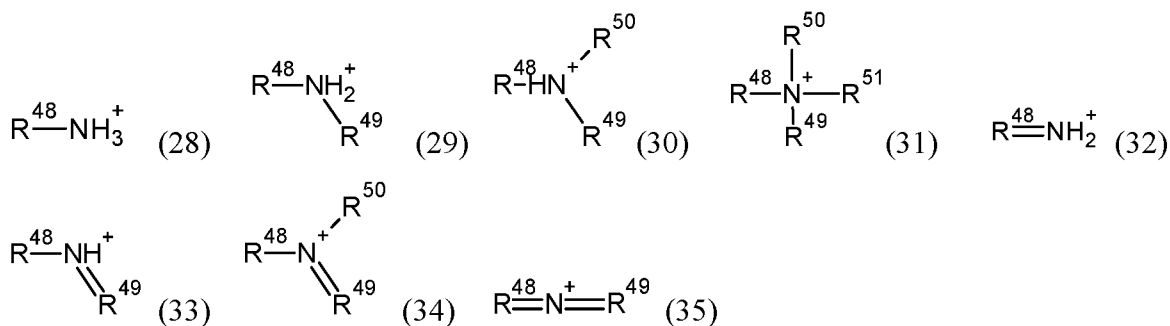
According to a preferred embodiment, said organic-inorganic perovskite layer comprises a perovskite-structure of any one of the formulae (VIII) to (XIV):



wherein A, A', B and X are as defined elsewhere in this specification. Preferably, X is preferably selected from Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>, most preferably X is I<sup>-</sup>.

According to a preferred embodiment, said organic-inorganic perovskite layer comprises a perovskite-structure of the formulae (VIII) to (XII), more preferably (VIII) and/or (IX) above.

According to an embodiment, A and A' are monovalent cations selected independently from any one of the compounds of formulae (28) to (35) below:



wherein,

any one of R<sup>48</sup>, R<sup>49</sup>, R<sup>50</sup> and R<sup>51</sup> is independently selected from C1-C15 organic substituents comprising from 0 to 15 heteroatoms.

According to an embodiment of said C1-C15 organic substituent any one, several or all hydrogens in said substituent may be replaced by halogen and said organic substituent may comprise up to fifteen (15) N, S or O heteroatoms, and wherein, in any one of the compounds (29) to (35), the two or more of substituents present (R<sup>48</sup>, R<sup>49</sup>, R<sup>50</sup> and R<sup>51</sup>, as applicable) may be covalently connected to each other to form a substituted or unsubstituted ring or ring system. Preferably, in a chain of atoms of said C1-C15 organic substituent, any heteroatom is connected to at least one carbon atom. Preferably, neighboring heteroatoms are absent and/or heteroatom-heteroatom bonds are absent in said C1-C15 organic substituent comprising from 0 to 15 heteroatoms. The heteroatoms may be selected from N, S, and/or O.

According to an embodiment any one of R<sup>48</sup>, R<sup>49</sup>, R<sup>50</sup> and R<sup>51</sup> is independently selected from C1 to C15 aliphatic and C4 to C15 aromatic or heteroaromatic substituents, wherein any one, several or all hydrogens in said substituent may be replaced by halogen and wherein, in any one of the compounds (29) to (35), the two or more of the substituents present may be





in addition to and/or independently of said 2 to 7 heteroatoms.

Preferably, if the number of carbons in G is impair, the number of heteroatoms is smaller than the number of carbons. Preferably, in the ring structure of formula (37), the number of ring heteroatoms is smaller than the number of carbon atoms. According to an embodiment, G is an aliphatic, aromatic or heteroaromatic linker structure having from 1 to 10 carbons.

Preferably, the dotted line in substituents (38) to (43) represents a carbon-nitrogen bond, connecting the nitrogen atom shown in the substituent to a carbon atom of the linker.

According to an embodiment, in the compound of formula (36), G is an organic linker structure having 1 to 8 carbons and from 0 to 4 N, S and/or O heteroatoms or having 1 to 6 carbons and from 0 to 3 N, S and/or O heteroatoms, wherein any one, several or all hydrogens in said G may be replaced by halogen. Preferably, L is an aliphatic, aromatic or heteroaromatic linker structure having 1 to 8 carbons, wherein any one, several or all hydrogens in said G may be replaced by halogen. According to an embodiment, in the compound of formula (36), said linker G is free of any O or S heteroatoms. According to an embodiment, G is free of N, O and/or S heteroatoms.

According to an embodiment, any one of  $R^{48}$ ,  $R^{49}$ ,  $R^{50}$  and  $R^{51}$  is independently selected from C1 to C10 alkyl, C2 to C10 alkenyl, C2 to C10 alkynyl, C4 to C10 heteroaryl and C6 to C10 aryl, wherein said alkyl, alkenyl, and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, wherein said heteroaryl and aryl may be substituted or unsubstituted, and wherein several or all hydrogens in  $R^1$ - $R^4$  may be replaced by halogen.

According to an embodiment, any one of  $R^{48}$ ,  $R^{49}$ ,  $R^{50}$  and  $R^{51}$  is independently selected from C1 to C8 alkyl, C2 to C8 alkenyl, C2 to C8 alkynyl, C4 to C8 heteroaryl and C6 to C8 aryl, wherein said alkyl, alkenyl, and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, wherein said heteroaryl and aryl may be substituted or unsubstituted, and wherein several or all hydrogens in  $R^1$ - $R^4$  may be replaced by halogen.

According to an embodiment, any one of  $R^{48}$ ,  $R^{49}$ ,  $R^{50}$  and  $R^{51}$  is independently selected from C1 to C6 alkyl, C2 to C6 alkenyl, C2 to C6 alkynyl, C4 to C6 heteroaryl and C6 aryl, wherein said alkyl, alkenyl, and alkynyl, if they comprise 3 or more carbons, may be linear,

branched or cyclic, wherein said heteroaryl and aryl may be substituted or unsubstituted, and wherein several or all hydrogens in  $R^1$ - $R^4$  may be replaced by halogen.

According to an embodiment, any one of  $R^{48}$ ,  $R^{49}$ ,  $R^{50}$  and  $R^{51}$  is independently selected from C1 to C4 alkyl, C2 to C4 alkenyl and C2 to C4 alkynyl, wherein said alkyl, alkenyl and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, and wherein several or all hydrogens in  $R^1$ - $R^4$  may be replaced by halogen.

According to an embodiment, any one of  $R^{48}$ ,  $R^{49}$ ,  $R^{50}$  and  $R^{51}$  is independently selected from C1 to C3, preferably C1 to C2 alkyl, C2 to C3, preferably C2 alkenyl and C2 to C3, preferably C2 alkynyl, wherein said alkyl, alkenyl and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, and wherein several or all hydrogens in  $R^1$ - $R^4$  may be replaced by halogen.

According to an embodiment, any one of  $R^{48}$ ,  $R^{49}$ ,  $R^{50}$  and  $R^{51}$  is independently selected from C1 to C4, more preferably C1 to C3 and even more preferably C1 to C2 alkyl. Most preferably, any one of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are methyl. Again, said alkyl may be completely or partially halogenated.

According to an embodiment, A, A' and B are monovalent (A, A') and bivalent (B) cations, respectively, selected from substituted and unsubstituted C5 to C6 rings comprising one, two or more nitrogen heteroatoms, wherein one (for A and A') or two (for B) of said nitrogen atoms is/are positively charged. Substituents of such rings may be selected from halogen and from C1 to C4 alkyls, C2 to C4 alkenyls and C2 to C4 alkynyls as defined above, preferably from C1 to C3 alkyls, C3 alkenyls and C3 alkynyls as defined above. Said ring may comprise further heteroatoms, which may be selected from O, N and S. Bivalent organic cations B comprising two positively charged ring N-atoms are exemplified, for example, by the compound of formula (37) above. Such rings may be aromatic or aliphatic.

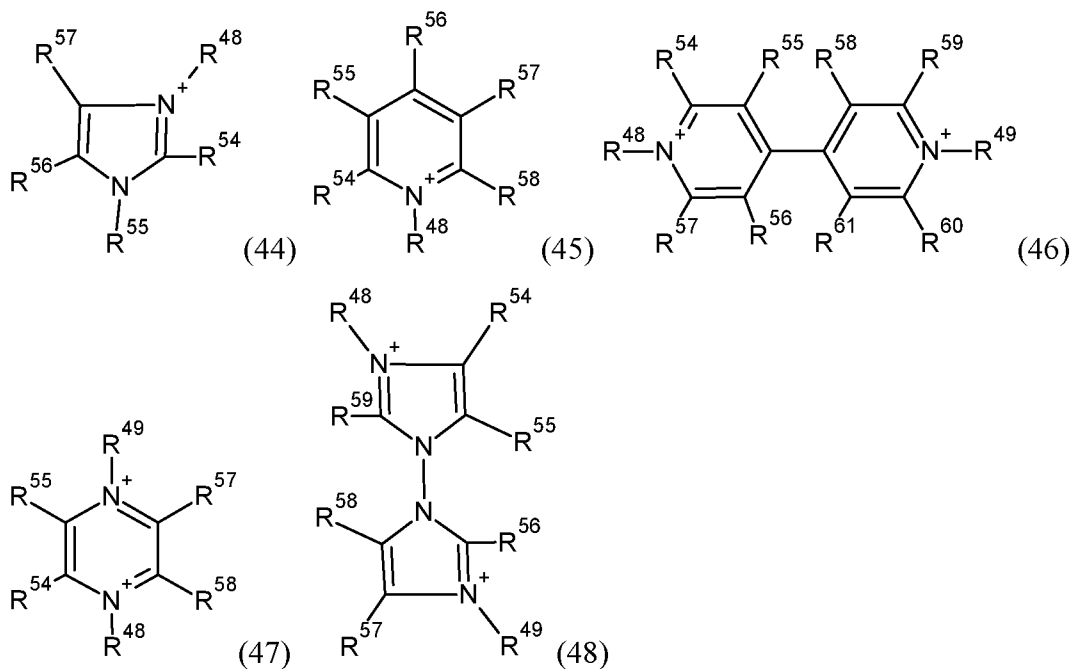
A, A' and B may also comprise a ring system comprising two or more rings, at least one of which being from substituted and unsubstituted C5 to C6 ring as defined as above. The elliptically drawn circle in the compound of formulae (10) may also represent a ring system comprising, for example, two or more rings, but preferably two rings. Also if A and/or A' comprises two rings, further ring heteroatoms may be present, which are preferably not

charged, for example.

According to an embodiment, however, the organic cations A, A' and B comprise one (for A, A'), two (for B) or more nitrogen atom(s) but are free of any O or S or any other heteroatom, with the exception of halogens, which may substitute one or more hydrogen atoms in cation A and/or B.

A and A' preferably comprise one positively charged nitrogen atom. B preferably comprises two positively charged nitrogen atoms.

A, A' and B may be selected from the exemplary rings or ring systems of formulae (44) and (45) (for A) and from (46) to (48) (for B) below:



in which R<sup>48</sup> and R<sup>49</sup> are, independently, as defined above, and R<sup>54</sup>, R<sup>55</sup>, R<sup>56</sup>, R<sup>57</sup>, R<sup>58</sup>, R<sup>59</sup> and R<sup>60</sup> are independently selected from H, halogen and substituents as defined above for R<sup>48</sup> to R<sup>51</sup>. Preferably, R<sup>54</sup>, R<sup>55</sup>, R<sup>56</sup>, R<sup>57</sup>, R<sup>58</sup>, R<sup>59</sup> and R<sup>60</sup> are selected from H and halogen, most preferably H.

In the organic cations A, A' and B, hydrogen atoms may be substituted by halogens, such as F, Cl, I, and Br, preferably F or Cl. Such a substitution is expected to reduce the hygroscopic properties of the perovskite layer or layers and may thus provide a useful option for the purpose of the present specification.

According to a preferred embodiment, A and A' are independently selected from organic cations of formula (28). Preferably, R<sup>48</sup> in the cation of formula (28) is selected from C1 to C8 organic substituents comprising, from 0 to 4 N, S and/or O heteroatom. More preferably, R<sup>1</sup> is selected from C1 to C4, preferably C1 to C3 and most preferably C1 to C2 aliphatic substituents.

According to a preferred embodiment, the metal M is selected from Sn<sup>2+</sup> and Pb<sup>2+</sup>, preferably Pb<sup>2+</sup>. According to a preferred embodiment, N is Sb<sup>3+</sup>.

According to a preferred embodiment, the three or four X are independently selected from Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>.

According to a preferred embodiment, the organic-inorganic perovskite material has the formula of formulae (XV) to (XIX) below:

AMl <sub>3</sub>	(XV)
AMl <sub>2</sub> Br	(XVI)
AMl <sub>2</sub> Cl	(XVII)
AMBr <sub>3</sub>	(XVIII)
AMCl <sub>3</sub>	(XIX)

wherein A and M are as defined elsewhere in this specification, including the preferred embodiments of A and M, such as those defined below. Preferably, M is selected from Sn<sup>2+</sup> and Pb<sup>2+</sup>. Preferably, A is selected from organic cations of formula (28). Preferably, R<sup>48</sup> in the cation of formula (28) is selected from C1 to C8 organic substituents comprising, from 0 to 4 N, S and/or O heteroatom. More preferably, R<sup>48</sup> is selected from C1 to C4, preferably C1 to C3 and most preferably C1 to C2 aliphatic substituents.

According to a preferred embodiment, the organic-inorganic perovskite is a compound of formula (VII) (AMXiXiiXiii), wherein A is a monovalent cation of formula (1) as defined above, M is Sn<sup>2+</sup> or Pb<sup>2+</sup>, and Xi, Xii, Xiii are independently selected from Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>. Preferably, R<sup>1</sup> in the cation of formula (1) is selected from C1 to C4, preferably C1 to C3 and most preferably C1 to C2 aliphatic substituents. Preferably, Xi –Xiii are identical.

In the moieties of formula (1) to (48), the connection of any moiety to quinoxilino acridine

core, a preceding moiety or a following moiety (for example, if one or the other of the integer m, n is different from 0) is illustrated by way of a dashed line representing the bond indicating the connection between said moieties.

In a further aspect, the invention provides a use of a compound of formula (I) and/or of formula (II) as a hole transporting and light absorbing material in photovoltaic solid state device.

The present invention will now be illustrated by way of examples. These examples do not limit the scope of this invention, which is defined by the appended claims.

### **Examples**

#### **Example 1 Synthesis of compound of formula (49) (Fused F)**

*Tris[[4-[3,3'-dihexylsilylene-2,2'-bithiophene]-7-[5''-n-hexyl-(2,2';5',2''-terthiophene)-5-yl]-benzo[c]-[1,2,5]thiadiazole]-2,6,10-yl]-4,4,8,8,12,12-Hexamethyl-4H,8H,12Hbenzo[1,9]quinolizino [3,4,5,6,7,-defg]acridine*

The scheme of synthesis of compound of formula (49), a low band gap highly absorbing HTM is shown in Figure 1A.

Under nitrogen atmosphere and at -78 °C, *n*-BuLi (0.21 ml, 1.6 M in hexane) was added drop-wise to a anhydrous THF solution containing 2,6,10-tribromo-4,4,8,8,12,12-Hexamethyl-4H,8H,12Hbenzo[1,9]quinolizino[3,4,5,6,7,-defg]acridine (**v**) (0.06 g, 0.1 mmol). After 1 hour stirring at -78 °C, 0.33 ml of trimethyltin chloride (1.0 M in THF solution) was added slowly to the reaction solution at -78 °C. The temperature of the solution was warmed to room temperature and the reaction was stirred for overnight. Then, the reaction was quenched with brine. The solution was extracted with dichloromethane, dried with MgSO<sub>4</sub>. 2,6,10-trimethylstannyl-4,4,8,8,12,12-Hexamethyl-4H,8H,12Hbenzo[1,9]quinolizino[3,4,5,-6,7,-defg]acridine (**vi**) was obtained without any purification. 4-[5-Bromo-3,3'-dihexylsilylene-2,2'-bithiophene]-7-[5''-n-hexyl-(2,2';5',2''-terthiophene)-5-yl]- benzo[c]-[1,2,5] thiadiazole (**iv**) (0.36 g, 0.4 mmol), 2,6,10-trimethylstannyl-4,4,8,8,12,12-Hexamethyl-4H,8H,12H-benzo[1,9]quinolizino[3,4,5,6,7,-defg]acridine (**vi**) (0.085 g, 0.1 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.012 g, 0.01 mmol), and anhydrous toluene (50 ml) were added to a 125 mL flame-dried 2-neck round-bottom flask with a

condenser under a nitrogen atmosphere. The reaction mixture was heated to reflux for 2 days. The reaction mixture was then cooled to room temperature. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed in *vacuo*. The orange product was purified by column chromatography.

Yield: 60 %. Mp: 97 °C. MS:  $m/z$  2840 [M<sup>+</sup>]. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.18 (s, 3H), 8.01 (d,  $J$  = 3.9 Hz, 3H), 7.81 (s, 6H), 7.66 (s, 6H), 7.35 (s, 3H), 7.22 (d,  $J$  = 3.6 Hz, 3H), 7.16 (d,  $J$  = 3.6 Hz, 3H), 7.02 (d,  $J$  = 3.6 Hz, 3H), 6.99 (d,  $J$  = 3.3 Hz, 3H) 6.69 (d,  $J$  = 3.9 Hz, 3H), 2.80 (t, 6H), 1.78 (s, 18H), 1.68 – 1.30 (m, 72H), 1.07 (m, 12H), 0.89 (m, 27H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  152.55, 152.49, 151.33, 147.61, 146.44, 145.84, 144.28, 142.50, 140.26, 138.46, 140.26, 138.46, 138.21, 137.33, 135.45, 134.52, 130.96, 130.57, 129.68, 126.44, 126.36, 125.43, 124.71, 124.58, 124.07, 121.29, 35.94, 33.18, 31.71, 31.25, 30.40, 29.90, 28.97, 24.47, 22.86, 22.78, 14.48, 14.20, 12.28.

#### Example 2. Photovoltaic characterization of compound of formula (49) (Fused-F)

A 450 W xenon lamp (Oriel) with a Schott K133 Tempax sunlight filter was used as the light source. The current-voltage characteristics were measured by applying an external potential bias to the device, and recorded the generated photocurrent with a Keithley model 2400 digital source meter. IPCE spectra were measured by an array of white light emitting diodes. The excitation beam passed through a Genimi-180 double monochromator (Jobin Yvon Ltd) and chopped at approximately 2 Hz before it illuminated the device. The spectra were recorded using a Model SR830 DSP Lock-In Amplifier. In both cases, the device was measured by using a black mask with an area of 0.2025 cm<sup>2</sup>.

The UV-Visible absorption and emission spectra of compound of formula (49) (Fused-F) in solution are shown in Figure 2A. In contrast to the most efficient HTMs spiro-MeOTAD and PTAA, which exhibit absorptions mainly in the UV region, said compound of formula (49) shows intensive charge-transfer absorption bands in the visible region with peak at 421 nm (molar extinction coefficients  $\epsilon$  = 108000 L mol<sup>-1</sup> cm<sup>-1</sup>) and 580 nm ( $\epsilon$  = 135000 L mol<sup>-1</sup> cm<sup>-1</sup>). The visible light harvesting ability of the compound of formula (49) serves the purpose of absorbing the remaining light passed through the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> layer. The fluorescence spectrum shows a maximum at 746 nm, with a large Stokes shift of more than 150 nm. To further investigate the contribution of light absorption from compound of formula (49), the UV-vis spectra of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films with and without compound of formula (49) were recorded for comparison. As seen in Figure 2B, with the presence of compound of formula (49), there is a significant enhancement in absorption in the whole

visible region for the perovskite film, confirming its additional contribution for light harvesting. It absorbs the photons after passing through the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  layer, and contributes for the photocurrent generation of the device.

Example 3. Characterization of solar cell comprising organic-inorganic perovskite  $\text{CH}_3\text{NH}_3\text{PbI}$  and compound of formula (49) (Fused-F) as HTM

*Solar Cell Fabrication*

$\text{CH}_3\text{NH}_3\text{PbI}$  was synthesized as reported in Etgar et al. ((2012), *J. Am. Chem. Soc.* **134**, 17396–17399). The compact  $\text{TiO}_2$  layer was deposited on the etched fluorine-doped tin oxide conductive glass (NSG 10) by spray pyrolysis at  $450^\circ\text{C}$ , using titanium diisopropoxide bis(acetylacetonate) solution as precursor and  $\text{O}_2$  as carrier gas. The substrate was then dipped into a 20 mM  $\text{TiCl}_4$  aqueous solution for 30 min at  $70^\circ\text{C}$ , and sintered at  $500^\circ\text{C}$  for 30 min. The mesoporous  $\text{TiO}_2$  film was spin-coated on the top at 5000 rpm for 30 s by using Dyesol 18NRT  $\text{TiO}_2$  paste, following by sintering at  $500^\circ\text{C}$  for 30 min in air. The 1.3 M  $\text{PbI}_2$  in DMF solution was dropped on the  $\text{TiO}_2$  surface, and spin-coated at 6500 rpm for 30 s in the dry air box. The film was annealed at  $70^\circ\text{C}$  for 30 min. After cooling down, the film was dipped into  $\text{CH}_3\text{NH}_3\text{I}$  solution (10 mg / mL in 2-propanol) for 25 s, and dried at  $70^\circ\text{C}$  for 15 min. The 12 mM Fused-F in chlorobenzene was spin-coated on the top of the perovskite layer with the spin speed of 3000 rpm. Finally, 60 nm of Au was deposited by thermal evaporation on the top of the HTM as the back contact.

Figure 1B shows the device architecture where fluorine-doped tin oxide glass substrate coated with a thin compact  $\text{TiO}_2$  as a hole blocking layer. A mesoporous  $\text{TiO}_2$  layer of about 250 nm as scaffold as well as electron collector was deposited. Lead iodide ( $\text{PbI}_2$ ) was deposited onto the mesoporous  $\text{TiO}_2$  surface by spin-coating, followed by immersion into a solution of methylammonium iodide ( $\text{CH}_3\text{NH}_3\text{I}$ ) to form perovskite. The Fused-F HTM is then introduced by spin-coating from the chlorobenzene solution. No additives are used, such as lithium bis(trifluoromethyl sulfonyl)imide (LiTFSI), 4-tert-butylpyridine (TBP) and the dopants, which were normally used together with spiro-MeOTAD and semiconducting polymers to get higher efficiencies. We measured cyclic voltammetry of the Fused-F, and found that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels are -5.23 eV and -3.66 eV, respectively. Under illumination, free charge carriers generated in the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  layer, and can be extracted by both

electron transfer to TiO<sub>2</sub> and hole transfer to Fused-F due to their appropriate energy levels to avoid unfavorable recombination.

Surface morphology and film thickness were examined using a high-resolution scanning electron microscope (SEM). The ~100 nm film of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> nanocrystals is uniformly distributed over the surface of titanium dioxide photoanode. Further CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> nanocrystals are uniformly covered with fused-F. In addition to the infiltration into the perovskite layer, the fused-F forms an overlayer.

The current-voltage (*J-V*) characteristics of TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/Fused-F/Au solar cell measured under dark and simulated AM 1.5 G (100 mW cm<sup>-2</sup>) irradiation is shown in Figure 3A, and the corresponding photovoltaic parameters are summarized in Table 1. For comparison, a reference cell without a HTM was fabricated.

**Table 1** Photovoltaic parameters derived from *J-V* measurements of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> based devices with and without Fused-F (compound of formula (49))

	$J_{sc}$ [mA cm <sup>-2</sup> ]	$V_{oc}$ [mV]	<i>FF</i>	<b>PCE</b> [%]
<b>Compound (49) (Fused-F)</b>	17.9	1036	0.68	12.8
<b>No HTM</b>	14.0	790	0.69	7.6

The device with Fused-F shows a short-circuit current density ( $J_{sc}$ ) of 17.9 mA/cm<sup>2</sup>, an open-circuit voltage ( $V_{oc}$ ) of 1036 mV and a fill factor (*FF*) of 0.68, leading to a PCE of 12.8%. Under the same conditions, the device without HTM shows both lower  $J_{sc}$  and  $V_{oc}$ , finally giving a PCE of 7.6%. The high  $J_{sc}$  with the presence of Fused-F is due to the effective charge extraction, as well as the improved light harvesting. The incident photo-to-current conversion efficiency (IPCE) spectra for the cells are given in Figure 3B. The presence of Fused-F showed improvement of the photocurrent in the whole visible region between 400 to 800 nm, further confirming the efficient charge extraction.

In summary, the novel hole transporting and light absorbing material of the invention, a compound of formula (I) and/or formula (II), more specifically compound of formula (49) shows suitable HOMO levels to extract efficiently holes from perovskite and contributes in enhancing light harvesting efficiency. The Fused-F (compound of formula (49)) is a hybrid molecule that has donor and acceptor functionalities to induce charge transfer-transitions



with the molecule. The highest occupied molecular orbitals energy levels were modulated incorporating thiophene groups and the solubility is due to presence of long alkyl groups.

Example 5. Synthesis of compound of formula (51) (FA-CN-Final)

*2,6,10-tris-(3,3'',3''',4'-tetraoctyl[2,2':5',2'':5'',2'''-quaterthiophen]-5'''-methylenemalononitrile-5-yl)-4,4,8,8,12,12-Hexamethyl-4H,8H,12H-benzof[1,9]quinolizino[3,4,5,6,7,-defg]acridine*

The scheme of synthesis of compound of formula (51) is shown in Figure 4A. Compound 3 (0.15 g, 0.088 mmol) and malononitrile (58 mg, 0.88 mmol) was dissolved in dry CHCl<sub>3</sub> and then a few drops of triethylamine was stirred for 1 h, under nitrogen at room temperature. The solution was extracted with dichloromethane and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo. The product was purified by column chromatography. Yield: 80 %. MS: *m/z* 1836 [M<sup>+</sup>]. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.70 (s, 3H), 7.61 (s, 6H), 7.55 (s, 3H), 7.37 (d, *J* = 3.6 Hz, 3H), 7.20 (d, *J* = 3.9 Hz, 3H), 7.18 (s, 3H), 2.86 (m, 12H), 1.69 (m, 12H), 1.43 – 1.25 (m, 36H), 0.91 (m, 18H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 149.94, 144.08, 143.29, 141.92, 140.69, 140.17, 133.23, 132.18, 131.22, 130.62, 128.95, 128.37, 121.28, 114.56, 113.62, 35.94, 33.42, 31.77, 30.77, 30.26, 30.07, 29.55, 22.80, 14.30.

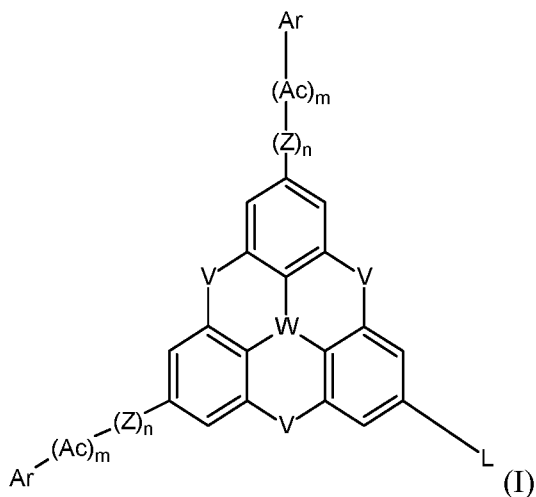
Example 6. Photovoltaic characterization of compound of formula (51) (FA-CN-Final)

The characterization is performed as described for Example 2.

The UV-Visible absorption and emission spectra of compound of formula (51) (FA-CN-Final) in solution are shown in Figure 4B.

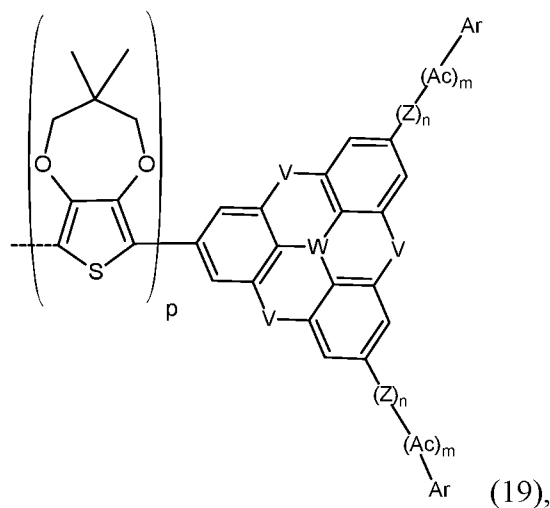
**Claims**

1. A compound of formula (I):



wherein

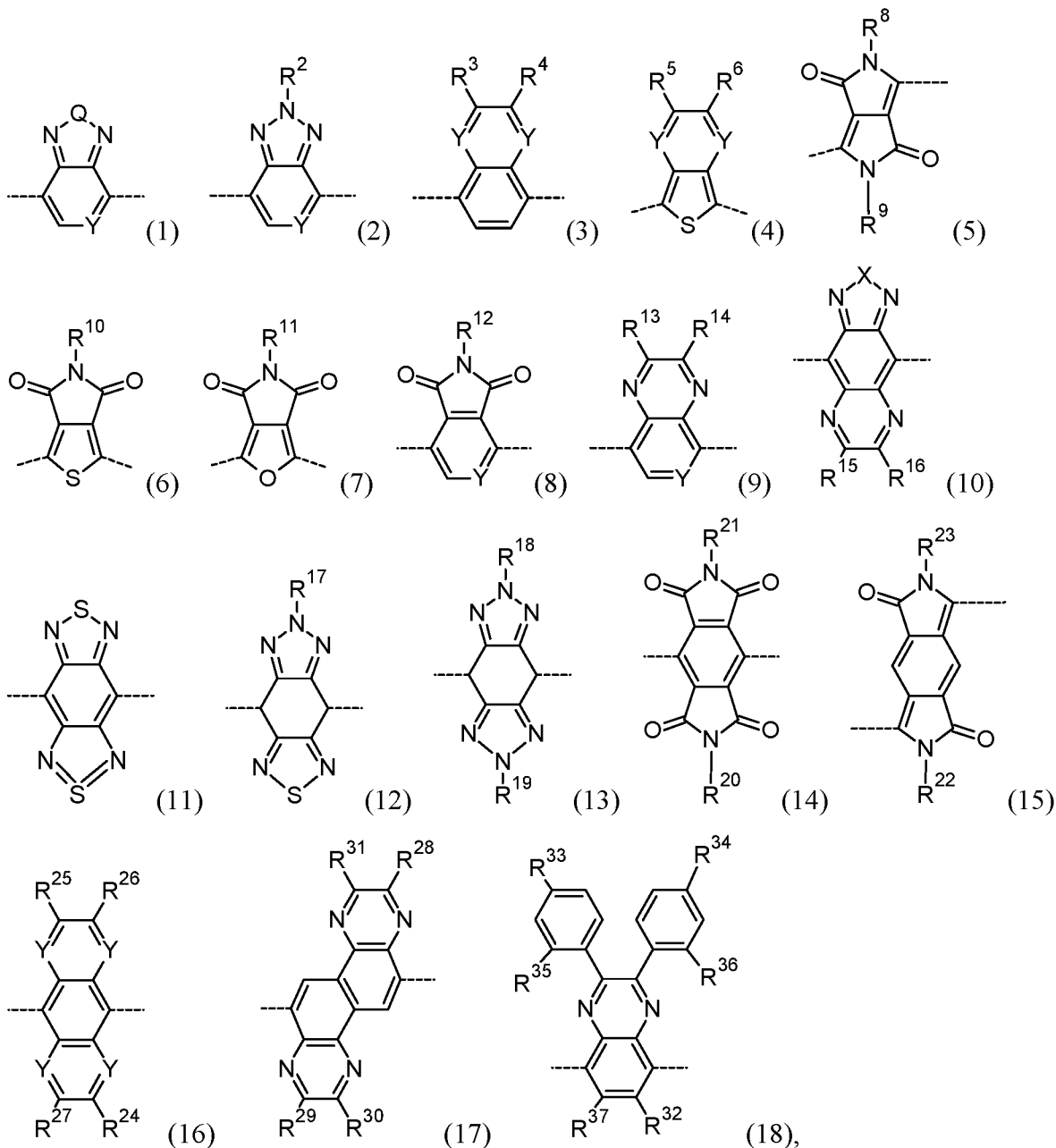
- W is a nitrogen (N) or phosphorus (P) atom;
- V is, on each occurrence, identically or differently selected from  $C(R^1)_2$ , C=O or O,  $R^1$  being selected from C1-C12 alkyl;
- L is selected from moiety of formula  $-----(Z)_n---(Ac)_m---Ar$  as defined below or from moiety of formula (19)



p being 0, 1 or 2 and moiety of formula  $-----(Z)_n---(Ac)_m---Ar$  being as defined below;

- Z is a heteroaromatic ring system, on each occurrence, identically or differently selected from C4-C20 heteroaryl and C4-C20 heteroaryloxy group, wherein the heteroatoms are selected from O, S, Se, Si and wherein said heteroaryl and heteroaryloxy group are substituted by C1-C20 alkyl, C1-C20 heteroalkyl, C2-C20 alkenyl or C2-C20 alkynyl, wherein said alkyl, alkenyl, and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, and n is 0, 1, 2, or 3;

- Ac is an acceptor group, on each occurrence, identically or differently selected from a moiety according to any one of the formulae (1) to (18),



- wherein

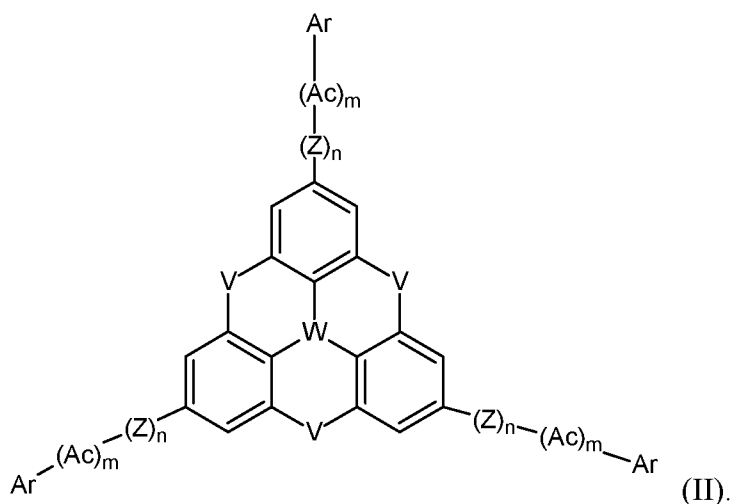
- $R^2$  to  $R^{37}$  are substituents independently selected from H, ether group, C1-C16 alkyl, C1-C16 alkoxy group, C1-C16 thioalkyl, C1-C16 alkoxyalkyl, C4-C16 aryl, C1-C16 arylalkyl or C4-C16 heteroaryl, C4-C16 heteroarylalkyl, the heteroatoms being selected from O, S, or N,
- Q is selected from S, O, Se, Si or N and when Q is N, said nitrogen atom is substituted by substituent as defined for  $R^2$  to  $R^{37}$ ,
- Y is, on each occurrence, identically or differently selected from N or C, being unsubstituted or substituted by halogen selected from F, Cl, I, and Br,

and

- m is 0 or 1;

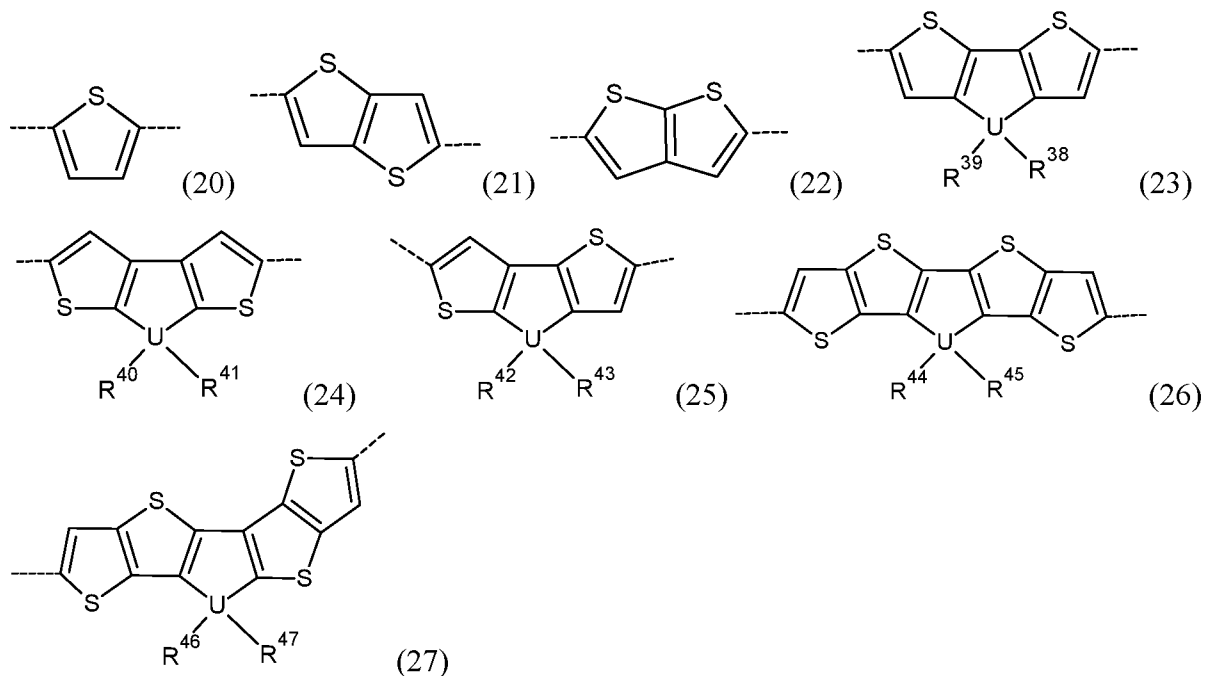
- -Ar is a successive bound heteroaromatic rings system comprising from 2 to 10 heteroaromatic rings, said heteroaromatic rings being, on each occurrence, identically selected from C4-C20 heteroaryl and C4-C20 heteroaryloxy group, wherein the heteroatoms are selected from O, S, Se, Si and wherein said heteroaryl and heteroaryloxy groups are unsubstituted or substituted by C1-C20 alkyl, C1-C20 heteroalkyl, C2-C20 alkenyl or C2-C20 alkynyl, wherein said alkyl, alkenyl, and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, -COOH, =O (keto), C4-C16 cyanoalkenyl carboxylic acid.

2. The compound of claim 1, wherein L is moiety of formula  $\text{---}(Z)_n\text{---}(\text{Ac})_m\text{---Ar}$  and is a compound of formula (II):



3. The compound according to any one of the preceding claims, wherein Ac is selected from a moiety according to any one of the formulae (1) to (4) and (10) to (13).
4. The compound according to any one of the preceding claims, wherein Ac is selected from a moiety according to any one of the formulae (1), (10) and (11).
5. The compound according to any one of the preceding claims, wherein Q of any one of the formulae (1) to (18) is selected from S, O or Se.
6. The compound according to any one the preceding claims, wherein Y of any one of the formulae (1) to (18) is C.

7. The compound according to any one of the preceding claims, wherein Z is selected from a moiety according to any one of the formulae (20) to (27)



- wherein

- $R^{39}$  to  $R^{47}$  are substituents independently selected from H, C1-C16 alkyl, C1-C16 alkoxy group, C1-C16 thioalkyl, C1-C16 alkoxyalkyl and if they comprise 3 or more carbons, they may be linear or branched;
- U is selected from S, Si or C,

8. The compound according to claim 7, wherein Z is selected from a moiety of any one of the formulae (20), (23) to (26).

9. A photovoltaic solid state device comprising a compound according to any one of claims 1 to 8.

10. The device of claim 9 further comprising an organic-inorganic perovskite as sensitizer, said perovskite being under the form of layer.

11. The device according to claim 10, wherein the organic-inorganic perovskite layer material comprises a perovskite-structure of any one of formulae (I), (II), (III), (IV), (V) and/or (VI) below:



(I)

AMX <sub>3</sub>	(II)
AA'N <sub>2/3</sub> X <sub>4</sub>	(III)
AN <sub>2/3</sub> X <sub>3</sub>	(IV)
BN <sub>2/3</sub> X <sub>4</sub>	(V)
BMX <sub>4</sub>	(VI)

wherein,

- A and A' are organic, monovalent cations that are independently selected from primary, secondary, tertiary or quaternary organic ammonium compounds, including N-containing heterorings and ring systems, A and A' having independently from 1 to 60 carbons and 1 to 20 heteroatoms;
- B is an organic, bivalent cation selected from primary, secondary, tertiary or quaternary organic ammonium compounds having from 1 to 60 carbons and 2-20 heteroatoms and having two positively charged nitrogen atoms;
- M is a divalent metal cation selected from the group consisting of Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Cr<sup>2+</sup>, Pd<sup>2+</sup>, Cd<sup>2+</sup>, Ge<sup>2+</sup>, Sn<sup>2+</sup>, Pb<sup>2+</sup>, Eu<sup>2+</sup>, or Yb<sup>2+</sup>;
- N is selected from the group of Bi<sup>3+</sup> and Sb<sup>3+</sup>; and,
- X is independently selected from Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NCS<sup>-</sup>, CN<sup>-</sup>, and NCO<sup>-</sup>.

**12.** The device according to any one of claims 10 to 11, wherein the sensitizer layer made of organic-inorganic perovskite is coated by a layer comprising the compound according to any one of claims 1-8.

**13.** The device according to any one of claims 9 to 12, wherein said device is selected from a solar cell, a heterojunction, an optoelectronic device and a light emitting device.

**14.** The device according to any one of claims 9 to 12, wherein the solar cell is a solid state solar cell.

**15.** Use of a compound according to any one of claims 1-8 as a hole transporting and light absorbing material in photovoltaic solid state device.

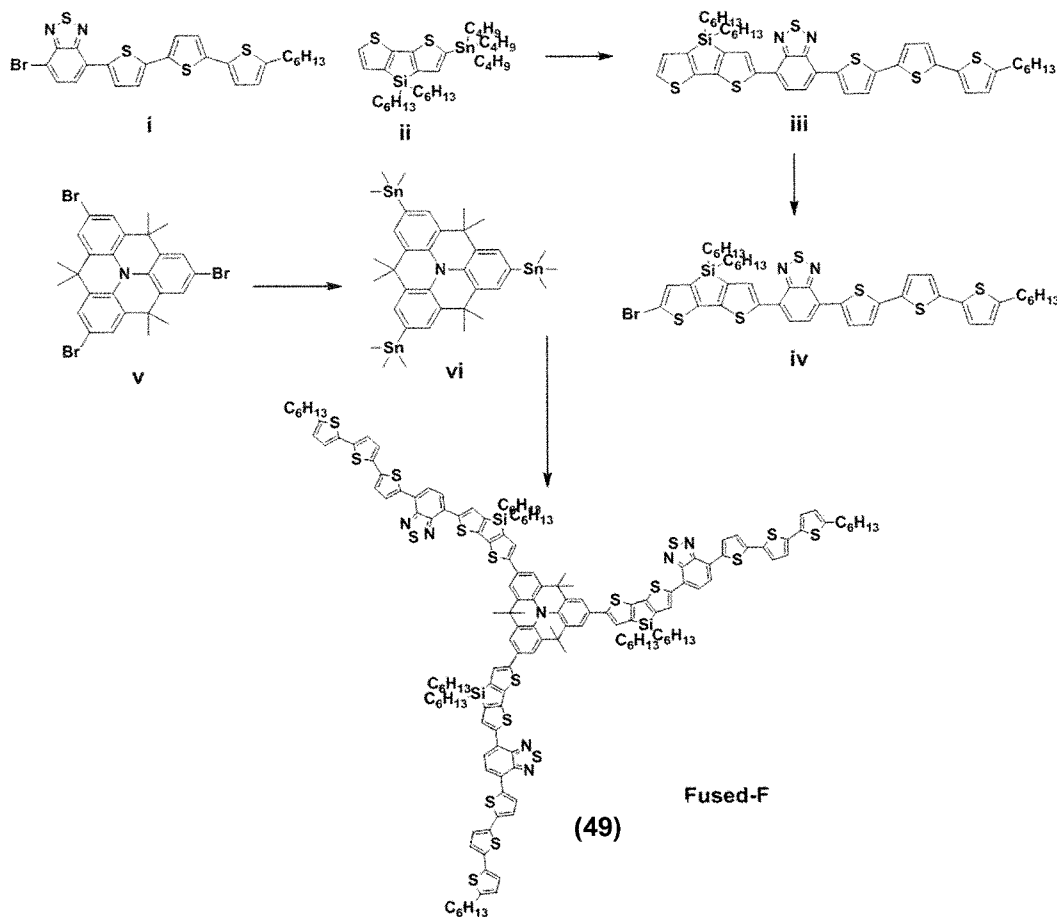


Figure 1A

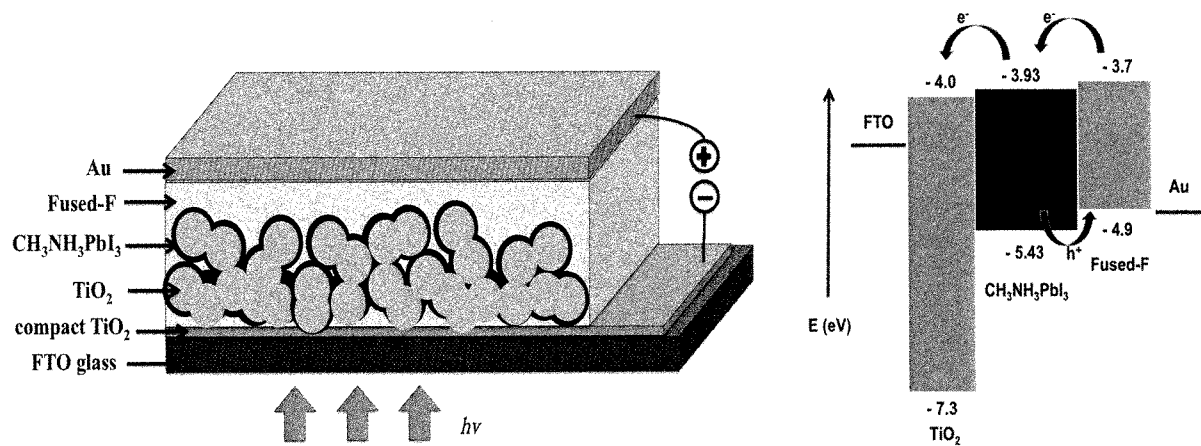


Figure 1B

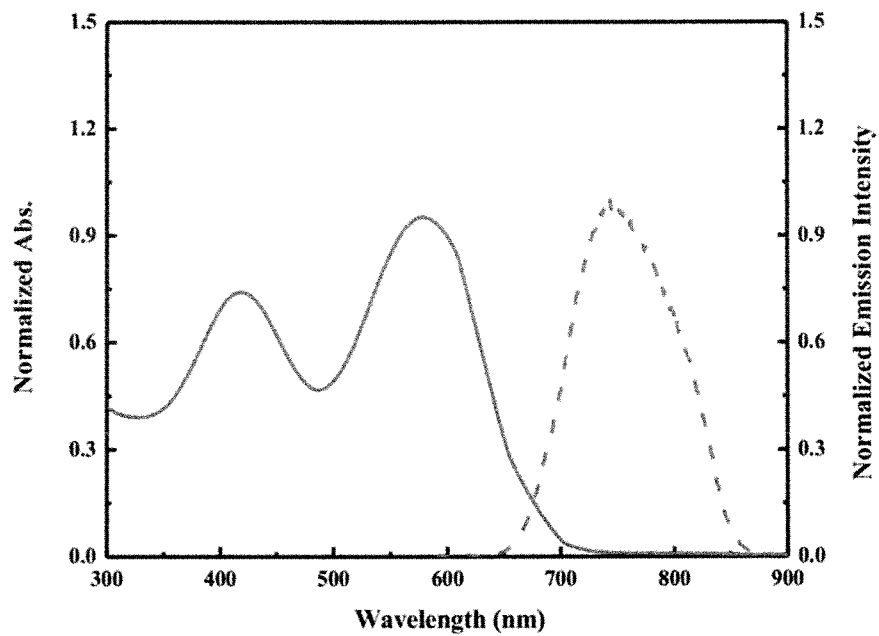


Figure 2A

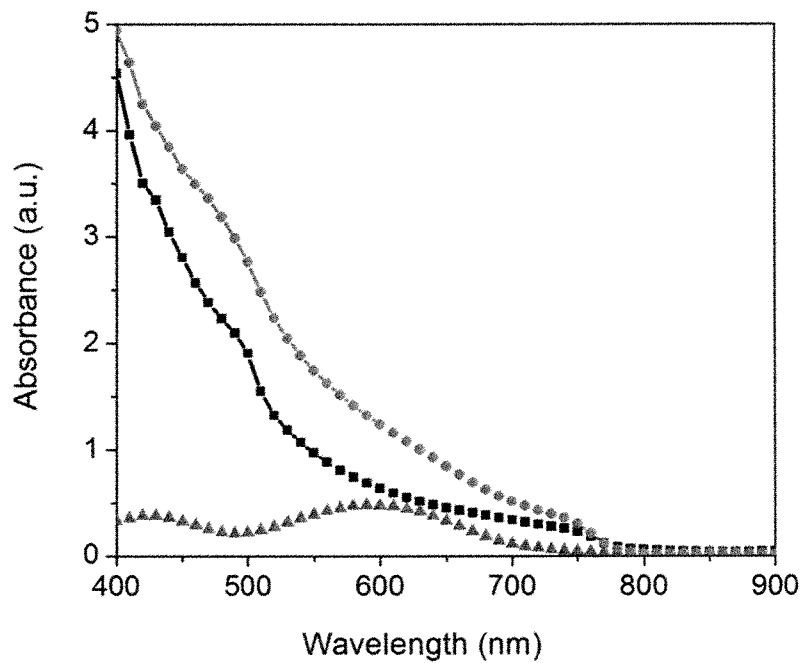


Figure 2B



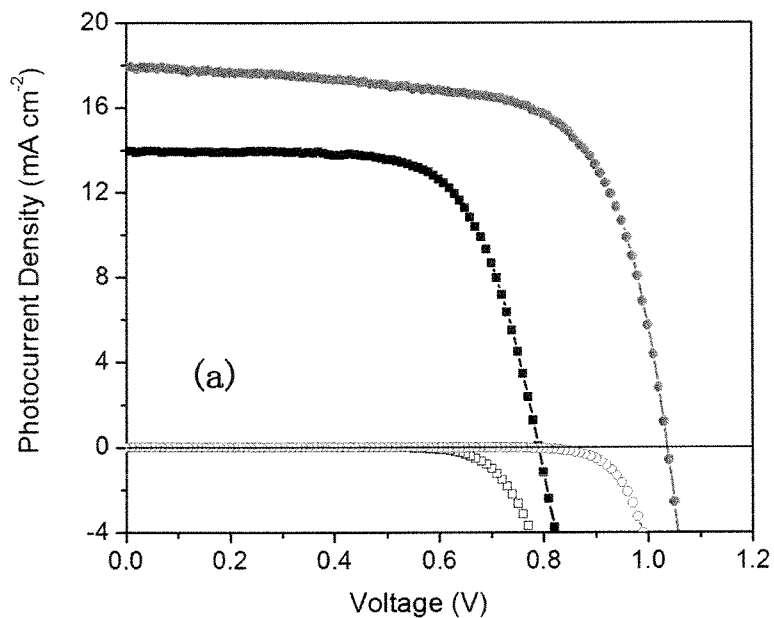


Figure 3A

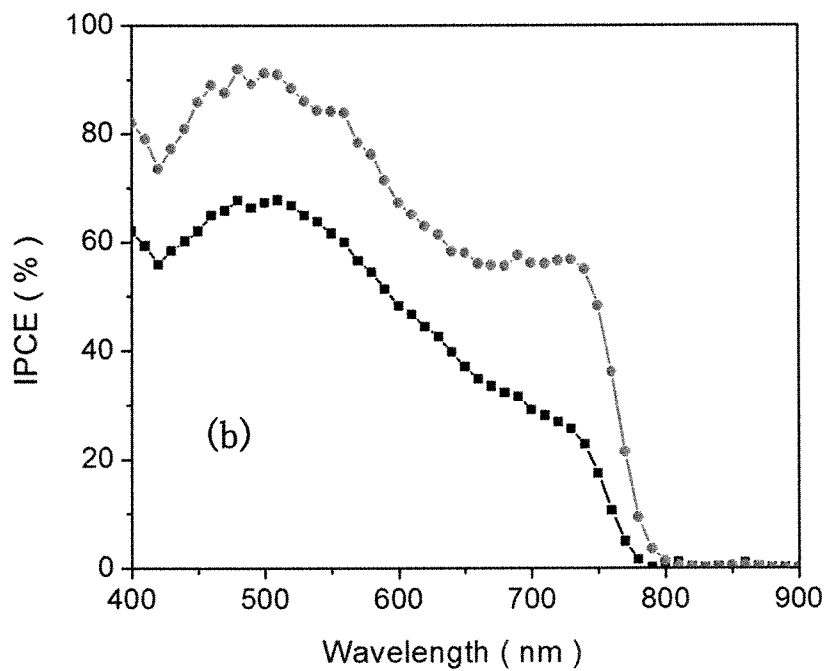


Figure 3B

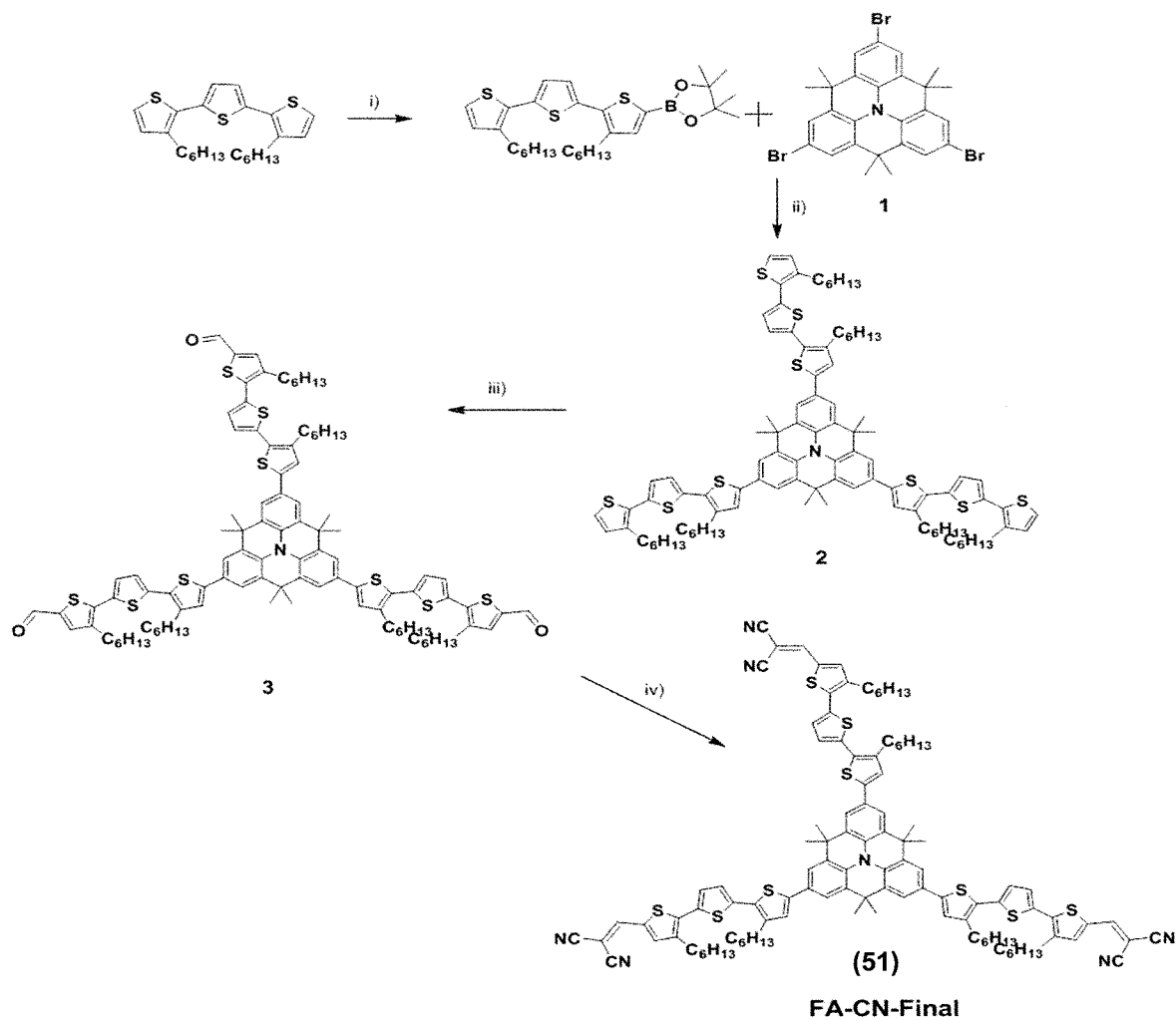


Figure 4A

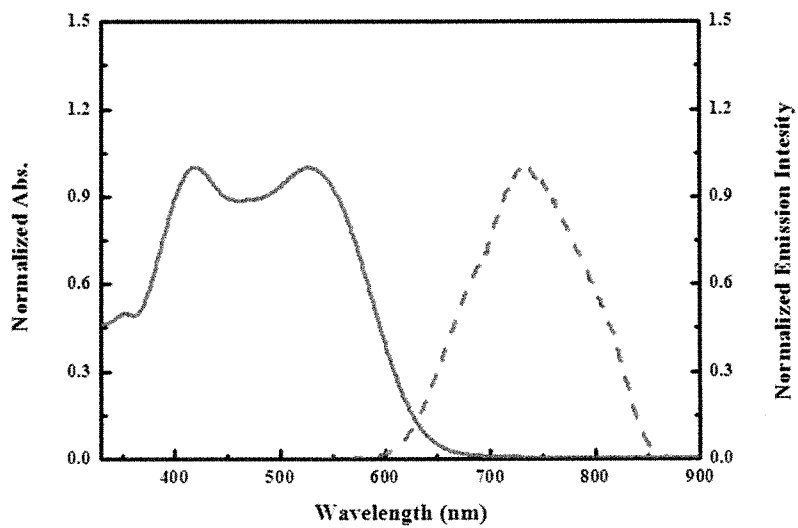


Figure 4B

# INTERNATIONAL SEARCH REPORT

International application No PCT/IB2015/050245
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**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. C09B57/00 C09K11/06 H01L51/00 H05B33/14  
 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)  
 C09B C09K H01L H05B

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, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 248 869 A2 (MERCK PATENT GMBH [DE]) 10 November 2010 (2010-11-10) page 7; compounds 3,4,5 page 8; compounds 13,14 page 10; compound 24 page 13; compound 36 examples & US 2009/295275 A1 (PARHAM AMIR [DE] ET AL) 3 December 2009 (2009-12-03) cited in the application -----	1-9, 13-15
A	EP 2 182 040 A2 (GRACEL DISPLAY INC [KR]) 5 May 2010 (2010-05-05) page 84; compounds 1498-1506 ----- -/--	1-9, 13-15

Further documents are listed in the continuation of Box C.       See patent family annex.

\* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&amp;" document member of the same patent family</p>
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Date of the actual completion of the international search  <b>7 April 2015</b>	Date of mailing of the international search report  <b>15/04/2015</b>
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  <b>Ketterer, Michael</b>
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## INTERNATIONAL SEARCH REPORT

 International application No  
 PCT/IB2015/050245

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2011/107186 A2 (MERCK PATENT GMBH [DE]; BROCKE CONSTANZE [DE]; PFLUMM CHRISTOF [DE]; P) 9 September 2011 (2011-09-09) page 112; compound PA3Cbz -----	1-9, 13-15
A	KR 101 172 374 B1 (UNIV SUNGKYUNKWAN RES & BUS [KR]) 8 August 2012 (2012-08-08) abstract page 10; table 1 CH3NH3I + PbI2 proposed -----	10-12
A	WO 2009/098643 A2 (ECOLE POLYTECH [CH]; XU MINGFEI [CN]; QIN HAO [CN]; GAO FEIFEI [CN]; W) 13 August 2009 (2009-08-13) cited in the application claims -----	1,2,7,9, 13-15
A	EP 1 990 373 A1 (NIPPON KAYAKU KK [JP]) 12 November 2008 (2008-11-12) cited in the application claims; compounds -----	1,2,7,9, 13-15
A	DE 198 08 088 A1 (SYNTEC GES FUER CHEMIE UND TEC [DE]) 26 August 1999 (1999-08-26) the whole document -----	1,9, 13-15

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/IB2015/050245
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
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