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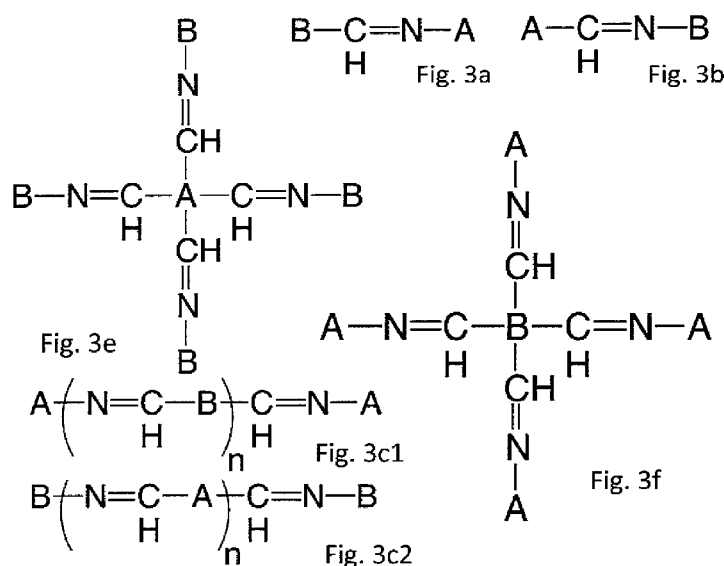
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(54) Title: HOLE TRANSPORT AZOMETHINE MOLECULE



(57) Abstract: The present invention is in the field of an azomethine molecule having hole conducting characteristics and applicable as a hole transporter, in a photovoltaic device, the device further comprising a light absorbing material, such as a perovskite based device, and a solar cell comprising said molecule as a hole transporter or said device.

FIELD OF THE INVENTION

The present invention is in the field of a azomethine molecule having photovoltaic characteristics and applicable as a hole transporter, in a photovoltaic device, the device further comprising a light absorbing material, such as a perovskite based device, and a solar cell comprising said molecule as a hole transporter or said device.

BACKGROUND OF THE INVENTION

The present invention is in the field of cost effective solar cells. These cells can be processed from a liquid solution comprising a photovoltaic material, hence the possibility of a simple roll-to-roll printing process, potentially leading to inexpensive, large scale production. In addition, these cells could be beneficial for applications where mechanical flexibility and disposability are important. Current flexible solar cell efficiencies have a low power conversion efficiency (PCE) of 8-10%), compared to inorganic based cells, and practical devices are essentially non-existent. On top of that, costs of organic materials used therein are very high, at least partly due to process costs.

In solar cells perovskites may be used. Perovskites have a general formula of ABC_3 . A may be an alkaline earth element, a rare earth element, or an organic molecule, such as an amine, such as formamidinium, an ammonium, such as methylammonium. B may be a 3d, 4d, and 5d transition metal element, such as Pb, Sn, Ti. C may be a halide, such as Cl^- , Br^- , I^- , and F^- , and oxygen. A perovskite solar cell is a type of solar cell which includes a perovskite light absorber.

Perovskite absorber materials are cheap to produce and simple to manufacture. Solar cell efficiencies of devices using these materials have recently increased by a factor.

It is noted that architectures of perovskite solar cells may vary.

It is noted that perovskite materials can also act as highly efficient, ambipolar charge-conductor. After light absorption and the subsequent charge-generation, both negative and positive charge carrier are transported through the

perovskite to charge selective contacts (typically anode and cathode).

Power conversion efficiency (PCE) with a thin layer of perovskite on e.g. mesoporous TiO_2 as electron-collector was in the order of 5%, which is considerably less than e.g. silicon based solar cells. Recently it was shown that efficiencies of almost 10% were achievable using a TiO_2 architecture. New techniques achieved more than 20% efficiency. It was also shown to fabricate perovskite solar cells in what is considered a typical 'organic solar cell' architecture, i.e. an 'inverted' configuration having a hole transporter below and the electron collector above.

In an alternative approach of using solar energy photolysis of water using perovskite solar cells was shown. Thereto two perovskite solar cells were connected.

There are still some limitations to be overcome. For instance the power-conversion efficiency of a solar cell is usually determined by characterizing its current-voltage (JV) behaviour under simulated solar illumination. In contrast to other solar cells it has been observed that the JV-curves of perovskite solar cells show a hysteretic behaviour: there is a discrepancy between the scan from forward-bias to short-circuit (FB-SC) and the scan from short-circuit to forward bias (SC-FB). Another issue is the UV-instability of the perovskite systems. And also the systems are prone to deterioration due to water.

Another class of solar cells, briefly described above already, relates to hybrid cells. Hybrid solar cells are supposed to combine advantages of both organic and inorganic semiconductors, wherein one may act as hole transporter and the other as electron transporter. Hybrid photovoltaics typically have organic materials that consist of e.g. conjugated polymers that absorb light as the donor and transport holes. Inorganic materials in hybrid cells are used as the acceptor and electron transporter in the structure. The hybrid photovoltaic devices have various advantages.

As indicated above, the efficiency of perovskite-based solar cells has increased rapidly in the last five years making this one of the most promising photovoltaic technologies and al-

most being competitive with current silicon-based technologies. Although the perovskite material itself is relatively inexpensive, the best devices prepared to date use an expensive organic hole-conducting material, called spiro-OMeTAD (~\$700/gram, see
5 Solaronix: spiro-OMeTAD). This material is expensive to produce because the synthesis requires expensive monomers, transition metal catalysts, inert reaction conditions and extensive product purification.

Many research groups around the world are currently
10 publishing new materials to replace Spiro-OMeTAD. However, these materials are generally synthesized in transition metal catalysed reactions, requiring stringent reaction conditions and significant product workup.

Many molecules that are in principle suited for photo-
15 voltaic application, can not be produced or only with difficulty into bulk photovoltaic devices, such as into a film.

Some documents recite perovskite type photovoltaic materials.

Takeo et al. in "Microstructures and photovoltaic properties of perovskite-type $\text{CH}_3\text{NH}_3\text{PbI}_3$ compounds", Applied Physics Express, Jap. Soc. Applied Physics, Vol. 7, No. 12 (November 25, 2014), p. 121601-1-4, recites in table III various PV cells. These however have a relatively low efficiency η of 3-7% and therefore do not offer a promising starting point for further
25 developments, especially as prior art devices have already achieved much higher efficiencies of about 12%.

The use of azomethines in organic photovoltaics is for instance shown by Petrus et al. in "Small-molecule azomethines: organic photovoltaics via Schiff base condensation chemistry",
30 J. Mater. Chem. A, 2014, 2, p. 9474-9477. They report use of azomethines as electron transport molecules (donor) in bulk heterojunction systems. Despite some characteristics being promising, such as a HOMO energy level of about -5.3 eV, which is comparable to the -5.6 eV of the above spiro-OMeTAD, the efficiencies reported are still considered poor (table 2, 0.6-1.2 %). The article also recites the use of relative large amounts PCBM in
35 combination with the azomethine. PCBM's are relatively expensive and are therefore not preferred. In addition polymer type azomethines also perform poorly (e.g. 0.2%). Such would be a demoti-

vator to use the azomethines. In addition, apparently the HOMO energy is at best one characteristic that may need to be taken into account. Other items could be transport mobility, LUMO energy, presence of unreacted functional groups, protonation of a bond, such as an azomethine bond, and a morphology of a layer.

Doping of layers may be considered. For instance Kaya et al. in Synthetic Metals 156 (2006), p. 1123-1132 recites an oligomer-metal complex compound comprising 2-[(4-morpholin-4-yl-phenyl)imino]methylphenol (2-MPIMP) obtained by an oxidative polycondensation reaction using various oxidants. Iodine (I₂) was claimed to be used as doping agent in order to increase a conductivity, which is considered different from hole/electron mobilities; in addition iodine has a tendency to sublime out of a material, which makes it unsuited. The compounds and structures do not relate to small molecules, but to oligomers or polymers, the materials are not well defined as a consequence, e.g. in terms of molecular mass, and the conductivities indicate that effectively the materials are insulators (see fig. 9, at the best giving a value of 10⁻⁶ S/cm) making them not very suited for PV-cells and also requiring doping.

The present invention therefore relates to use of an azomethine comprising molecule having photovoltaic characteristics as a hole transport layer in a photovoltaic device, and a solar cell comprising said hole transport layer, which solve one or more of the above problems and drawbacks of the prior art, providing reliable results, without jeopardizing functionality and advantages.

SUMMARY OF THE INVENTION

The present invention relates to a photovoltaic device comprising a hole transporting molecule and optionally at least one hole mobility improver in a hole transport layer, and further a light absorbing material layer, wherein the hole transporting molecule comprises an azomethine molecule according to figure 3, and a solar cell comprising said device according to claim 14.

The present inventors have developed azomethine-based hole-transport materials as a cheap alternative, because they are found to be easily synthesized in a one-step condensation reaction (upon losing water as only by-product a conjugated

chemical bond is formed), do not require expensive catalysts and do not require extensive workup. The estimated price of the present material is some 5\$/gram. So far azomethines have not been used as charge transport layer, such as in perovskite-based photovoltaics.

The azomethine molecules have hole transport capabilities, but these are typically insufficient for the intended application in a photovoltaic device. In order to apply the azomethines in a PV-device at least one hole mobility improver is therefore preferably provided to the hole transport layer. The hole mobility improver is typically of p-type. A typical amount of the first hole mobility improver is 0.1-100 mole %, relative to the azomethine molecule, preferably 0.5-50 mole %, more preferably 1-30 mole %, even more preferably 2-20 mole %, such as 3-5 mole%. The hole mobility improver may be considered as a dopant to the hole transport material; it is noted that the concentration of the hole mobility improver is typically much higher than e.g. dopants in semiconductor devices.

The hole mobility improver is typically capable of oxidizing the hole transport material, and/or promote oxidative reaction thereof; in this respect the hole mobility improver may be considered as an oxidant. In principle any such oxidant could be applied in the present invention. Likewise so-called ionic liquids may be used.

Hole mobility improvers may be selected from earth alkali metal, monovalent salts, hydrogen salts (or acids), N,N-dimethyl-pyrrolidinium, and N-methyl-N-propylpyrrolidinium salts of bis(tris-fluoromethylsulfonyl)imide (TFSI), such as LiTFSI, AgTFSI, HTFSI, and N,N-dimethyl-pyrrolidinium iodide.

In order to improve the conductivity and the hole mobility the hole transport materials are p-type doped. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and monovalent salt equivalents thereof (e.g. Ag+) are attractive additives; also other additives like N(PhBr)₃SbCl₆, F4TCNQ and cobalt dopants can be used.

Also other additives for passivating a surface can be used. Generally these additives are combined with the first and/or second hole mobility improver, typically in a concentration of 10-1000 mole%, such as 100 mole%. In an example 4-tert-

butylpyridine (TBP) is used; also pyridine and iodopentafluorobenzene (IPFB) have shown to improve the device performance, like pyridine, 2,6-lutidine, and 4-methylpyridine.

A series of small-molecule azomethines has been synthesized for further investigation. The synthesis typically results in small-molecules with a very narrow molecular mass distribution, and typically mostly one specific type of molecule is formed in an amount of >90%, such as >95% or even >99%; i.e. conversion and selectivity are high. Perovskite based solar cells using these azomethines or likewise a (co-)polymer comprising said molecule as hole transport layer, in combination with the hole mobility improver, have been prepared and measured, showing record efficiencies of around 11% (for sake of comparison, under the same processing conditions Spiro-OMeTAD shows efficiencies up to 12%). Such came as a surprise; first that the azomethines function well as hole transporter in view of the typical prior art use as electron transporter; second in that the efficiencies as a hole transporter, in combination with further features as the perovskite, are much higher than as electron transporter (about 1-2%); third in that the azomethines need not be mixed with further materials, such as PCBM; and further that apparently morphologies of various layers are fine and match well mutually. Further optimisation will increase the efficiency and reduce hysteresis.

The present azomethine molecules as hole transport material can relate to both small molecules and polymers comprising said azomethine molecules, but preferably well-defined small-molecules.

The present azomethine molecules are considered to relate to small, well-defined molecules having well defined properties, such as relatively excellent photovoltaic properties, a molecular mass of 300-3000, preferably 400-1500, more preferably 500-1000, such as 600-750, good film forming properties, low costs, etc. With reference to claim 1 and fig. 3, the present molecules comprise two entities, one aromatic entity A, and one aromatic (optionally heterocycle) bridging entity (B), and a connecting C=N moiety. The present aromatic entity A is non-heterocyclic, i.e. only comprising carbon atoms in the aromatic ring. The C=N moiety may be connected with the nitrogen thereof

to entity A or to entity B, and likewise with the carbon thereof to entity B or entity A. Entity B is connected to at least one entity A, or to more than one A entities, such as in a tree like structure, in a chain like structure, and combinations thereof.

5 The aromatic entity A preferably has a molecular mass of 64-1250, preferably 64-700, such as 64-500, whereas, independently, the aromatic (optionally heterocycle) bridging entity B preferably has a molecular mass of 65-1500, preferably 65-1000, such as 64-750. The aromatic entity A preferably has 1-4
10 aromatic ring structures, more preferably 1-3, such as 2, whereas, independently, the aromatic (optionally heterocycle) bridging entity B preferably has 1-8 aromatic ring structures, more preferably 1-5, such as 2-4.

For better understanding the background and synthesis
15 of the present molecules the Dutch Patent application NL2012451, filed on 17 March 2014, is referred to, which reference and the contents thereof are incorporated by reference.

The present azomethine molecules and polymeric equivalents thereof find application as a hole transport material in
20 the present photovoltaic device.

Thereby the present invention provides a solution to one or more of the above mentioned problems and drawbacks.

Advantages of the present description are detailed throughout the description.

25 DETAILED DESCRIPTION OF THE INVENTION

The present invention relates in a first aspect to a photovoltaic device according to claim 1.

The present molecules have excellent properties. For instance a glass transition temperature (T_g) of about 100 °C is
30 obtained, melting points of about 200 °C, a thermal decomposition temperature (T_d , 5%) of about 400 °C, and a crystallization temperature T_c of about 150 °C. Such makes the present molecules particularly suited for applications such as hybrid photovoltaic devices that function reliable under ambient conditions.

35 Further optical properties are also excellent. The molecules exhibit absorbance of light over a range of about 280 nm- about 600 nm, with a λ_{max} of about 500 nm, and an onset wavelength λ_{onset} of about 600 nm. The band-gap is in the order of 2.0 eV. These absorbance properties can be improved for the present mol-

ecules. Further, a maximum ϵ_{abs} of 30,000-60,000 ($\text{M}^{-1}\text{cm}^{-1}$) is found.

Electrical properties are also fine. For instance an E_{oxi} of about 1 V (versus Ag/Ag^+), a voltage below vacuum (HOMO) of about -5.0- -6.0 eV, and a LUMO of about -3 eV.

The molecules provide a good solubility and good film forming properties.

In an example of the present azomethine molecule the molecule has an $(\text{A-B})_n\text{-A}$ structure (fig. 3c) or $(\text{B-A})_n\text{-B}$ structure, wherein $n \in [1-5]$, preferably $n \in [2-3]$, or wherein the molecule has an $\text{A}_m\text{-B}$ structure (fig. 3d), wherein $m \in [1-5]$, preferably $m \in [2-3]$, or wherein the molecule has a $\text{B}_r\text{-A}$ structure (fig. 3e), wherein $r \in [1-5]$, preferably $r \in [2-3]$, or combinations thereof. A-B-A, A-B, B-A-B, A_3B , B_3A , A-B-A-B and A-B-A-B-A type molecules are preferred.

In an example of the present azomethine molecule the aromatic (optionally heterocycle) bridging entity comprises one or more of S, N, P, Si, Se and O, preferably one or more of S, Se and Si, such as a pyrrolidine, a pyrrole, a tetrahydrofuran, a furan, a thiolane, a thiophene, a phospholane, a phosphole, a sililane, a silole, an azole, such as an imidazolidine, a pyrazolidine, an imidazole, a pyrazole, an (is)oxazolidine, an (is)oxazole, a (iso)thiasolidine, an (iso)thiazole, a dioxolane, a dithiolane, a piperidine, a pyridine, an oxane, a pyran, a thiane, a thiopyran, a salinane, a saline, a phosphinane, a phosphinine, a piperazine, a diazine, a morpholine, an oxazine, a thiomorpholine, a thiazine, a dioxane, a dioxine, a dithiane, a dithiine, a triazine, a trioxane, an azepane, an azepine, an oxepane, an oxepine, a thiepane, a thiepine, a homopiperazine, a diazepine and a thiazepine. The aromatic ring preferably has 5-6 ring members, such as 5-6 ring members. It is further preferred that in the at least one aromatic (optionally heterocycle) entity B at least two, and preferably at least two different, heteroatoms are present, one of which preferably is S.

In an example the present azomethine molecule comprises at least one 4-aminotriphenylamine (TPA) according to figure 2. This TPA is readily available.

In an example of the present azomethine molecule the bridging entity is selected from 2,5-thiophenedicarbaldehyde

(Th), 2,3-dihydrothieno[3,4-b][1,4]dioxine-5,7-dicarbaldehyde (EDOT), 2,2'-bithiazole-5,5'-dicarbaldehyde (BTz), 4,7-bis(5-formylthiophen-2-yl)-2,1,3-benzothiadiazole (TBT), and combinations thereof.

5 In an example of the present azomethine molecule the R is independently selected from H, -CN, OAlk, Alk, and combinations thereof, and Alk is selected from alkanes, such as C₁-C₁₈, preferably C₁-C₁₂, such as Me, Et, and combinations thereof.

10 It is noted that the present azomethine can be obtained by a cheap, simple and reliable method, as detailed in the above NL2012451 application.

15 In an example the method further comprises one or more steps selected from before spin coating the condensate, thereby forming a solution, wherein the solution is spin coated on a substrate, removing the solvent, and annealing the condensate. Thereby the present product can be applied directly, e.g. to a substrate, without a further intermediate step, which is a big advantage.

20 Albeit the present conversion efficiencies are somewhat limited (state of the art materials reach efficiencies up to 15%), initial experiments directed to product development and improvement are so promising that these efficiencies are expected to be in reach. At that point the present molecules, films, fibres and device, can be obtained at much lower costs, 25 which is considered to provide market break through opportunities.

The device preparation has not been optimized yet. Optimizing the layer thickness, dopants and solvent/co-solvent will further increase the efficiency.

30 Generally, a p-type dopant is added to the hole transporting material before spin coating. An oxidant, for example lithium bis-trifluoromethanesulfonimide (LiTFSI). Also an additive, like 4-tert-butylpyridine (TBP), is added, in order to passivate the surface.

35 In an example of the present photovoltaic device the hole transport layer comprises a second hole transport improver in an amount of 0.1-15 mole % relative to the azomethine molecule, preferably 0.5-10 mole %, such as 1-5 mole%. Generally it is combined with one of the first hole mobility improver. Exam-

ples of second hole transport improver materials are tris(2-(1H-pyrazol-1-yl)pyridine) cobalt(III) bis-(hexafluorophosphate) (FK102), Tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III)Tris(bis (trifluoromethylsulfonyl)imide)) (FK209),
5 SnCl_4 , LiClO_4 , 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ), $\text{N}(\text{PhBr})_3\text{SbCl}_6$, NOBF_4 (exposing to vapour), WO_3 (evaporating a thin layer on top), and combinations thereof. Likewise further hole transport improvers may be added; typically 2-5 improvers are added, independently of
10 one and another, in similar concentrations as above.

It is noted that at least one first hole mobility improver may be selected, optionally in combination with at least one second hole mobility improver, and so on.

In an example the present photovoltaic device comprises
15 a stack, the stack comprising a substrate, a first optically transparent electrode layer, a second electrode layer, and between the electrode layers, (i) a perovskite layer as light absorbing layer, (ii) the present hole transport layer, and (iii) an intermediate layer. In principle the above sequence of layers
20 is considered an almost minimal set of layers in view of performance, Further (intermediate and protecting) layers may be added, e.g. in order to improve performance.

Two stacks of layers are considered specifically, relating to a so-called inverted and standard perovskite devices
25 (see fig. 4a-b). The substrate 11 therein is typically glass. In the inverted device the anode 21 is an optically transparent electrode, such as FTO, in contact with the substrate. In contact with the anode and the perovskite 31 is the present hole transport layer 41. A metal layer 22 (such as Al) acts as second
30 electrode. Typically an intermediate layer 51, such as a fullerene, is present between the cathode and perovskite. The perovskite may be $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbBr}_3$, a mixed halide, such as $\text{CH}_3\text{NH}_3\text{PbX}^{1}_{3-x}\text{X}^2_x$, (X^1 and X^2 being independently selected from halides), such as $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$, and an inorganic perovskite, such
35 as CsSnX_3 , or mixed inorganic perovskite, such as $\text{CsSnX}^{1}_{3-x}\text{X}^2_x$ (X , X^1 and X^2 being independently selected from halides), such as iodides. In the standard perovskite device the cathode 21, such as FTO is on the substrate 11, such as glass. A metal layer (such as Au) acts as second electrode 22. In contact with the cathode

and perovskite layer 31 is an intermediate layer 51, such as TiO_2 . In contact with the anode 22 and the perovskite 31 is the present hole transport layer 41.

The present perovskites, having the general formula of ABC_3 , preferably relate to A being an alkaline earth element, a rare earth element, such as Na, K, Li, Ca, Mg, Ce, or an organic molecule, such as an amine, such as formamidinium, and an ammonium, such as methylammonium CH_3NH_3 , and ethylammonium $\text{C}_2\text{H}_5\text{NH}_3$, to B being a 3d, 4d, and 5d transition metal element, such as Pb, Sn, Bi, Mn, Ni, Co, Fe, and Ti, C being a halide, such as Cl^- , Br^- , I^- , and F^- , and oxygen, as well as mixed minerals thereof. Examples are lead halogenides, such as $\text{CH}_3\text{NH}_3\text{PbI}_3$, tin halogenides, such as $\text{CH}_3\text{NH}_3\text{SnI}_3$, titanates such as CaTiO_3 . The band gap of the perovskite is preferably from 1.4-2.5 eV, such as 1.5-2.3 eV.

Note that the first electrode and second electrode in the above two stacks of layers change function, from anode to cathode, and vice versa. Also the nature of the intermediate layer changes. On the other hand the functions of the perovskite layer and hole transport layer remain the same.

In an example of the present photovoltaic device the substrate is selected from glass, silicon, steel, aluminium, silicon oxide, polymers, and combinations thereof, preferably glass.

In an example of the present photovoltaic device the first electrode layer is selected from optically transparent and electrically conducting materials, such as tin doped indium oxide (ITO), graphene, and fluorine doped tin oxide (FTO), preferably ITO.

In an example of the present photovoltaic device the second electrode layer is selected from metals, such as Al, Cu, Mg, Ba, ZnO, Au, Ag, and Ca, preferably Au or Al, respectively. Au has better properties in view of hole transport, whereas Al has better properties in view of electron transport.

In an example of the present photovoltaic device the perovskite is highly crystalline, such as > 90% crystalline, preferably > 95% crystalline, more preferably > 99% crystalline, such as may be confirmed by X-ray diffraction experiments.

In an example the present photovoltaic device comprises an intermediate layer, typically for electron transport, which

layer is preferably selected from fullerenes and TiO_2 , respectively. The layer may have a thickness of 10-500 nm, preferably 20-300 nm, more preferably 50-200 nm, such as 100-150 nm.

In an example the present photovoltaic device has a sequence of layers comprising one or more of an 20-1000 nm thick first electrode layer, preferably 100-750 nm, more preferably 200-500 nm, such as 300-400 nm, such as ITO, a 10-1000 nm thick light absorbing layer, preferably 20-800 nm, more preferably 50-500 nm, such as 200-400 nm, an 10-300 nm thick hole transport layer, preferably 20-200 nm, such as 50-100 nm, such as an azomethine according to the invention and an 10-500 nm thick electron transport layer, preferably 20-400 nm, such as 50-300 nm, and a 20-200 nm thick second electrode layer, preferably 30-100 nm, such as 50-75 nm, such as Au. The hole transport layer is preferably not too thin, as holes in the layer may occur and coverage of in particular the perovskite layer may be insufficient. The hole transport layer is preferably not too thick, as it may act as a semi-insulator. In general the hole transport layer can be somewhat thinner than comparable materials.

A further intermediate layer between e.g. hole transport layer and second electrode may be present.

In a second aspect the present invention relates to a solar cell according to claim 11.

The one or more of the above examples and embodiments may be combined, falling within the scope of the invention.

EXAMPLES

The below relates to examples, which are not limiting in nature.

In a study inventors have synthesized three azomethine-based small molecules via a simple condensation reaction (Figure 1). 4-Aminotriphenylamine (TPA, 1) was reacted with two conjugated dialdehydes. 2,5-Thiophenedicarbaldehyde (Th, 2a) was used since thiophenes have been studied extensively and possess good charge transport properties. Besides that, both materials are readily available from commercial sources. 2,3-dihydrothieno[3,4-b][1,4]dioxine-5,7-dicarbaldehyde (EDOT, 2b) was used because it is found to have high mobilities and good film-forming abilities. Also 4-amino-4',4''-dimethoxytriphenylamine (TPA(OMe)₂, 1b) was reacted with 2,3-

dihydrothieno[3,4-b][1,4]dioxine-5,7-dicarbaldehyde (EDOT, 2b) because the alkoxy groups are considered to improve the interfaces with the perovskite and are considered to align better with the perovskite. The reaction was performed in chloroform and p-toluenesulfonic acid was used as a catalyst. The products (3a-c) were precipitated, and treated with diluted triethylamine to neutralize the azomethine bond. The small molecules were obtained in good yields (>80%) and characterized using ^1H and ^{13}C NMR, FTIR, and mass spectrometry where possible. The thermal properties of the new molecules were assessed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All small molecules show excellent thermal stabilities with degradation temperatures ($T_d^{5\%}$) above 350 °C. Comparing TPA-Th-TPA to its vinyl analogue, inventors found that the degradation temperature is approximately 40 °C higher, confirming the superior thermal stability of the present azomethines. DSC experiments showed a glass transition temperature (T_g) in the range of 86 to 113 °C. The azomethine based small-molecule TPA(OMe)₂-EDOT-TPA(OMe)₂ shows a higher T_g compared to its fully conjugated analogue (H101, T_g = 73 °C), which is considered to be a more thermal stable hole transporting layer. TPA-Th-TPA and TPA-EDOT-TPA also showed a cold crystallization exotherm during the second heating at 143 °C and 171 °C, respectively. All small molecules melt above 200 °C and form isotropic melts, as was confirmed by hot-stage optical microscopy.

Absorption spectra of the small molecules were recorded in solution and in the solid state and the data are summarized in Table 1. The absorption peak around 310 nm can be ascribed to the triphenylamine moiety and is found for all small molecules. The absorption spectra of the small molecules in the solid state show no large shifts as compared to the solution spectra (Table 1). The band-gap of the small molecules could be estimated from the onset of the absorption spectra, which is around 600 nm for all small molecules, resulting in band gaps in the range of 2.0 to 2.2 eV.

The electrochemical properties of the small molecules in solution were investigated using cyclic voltammetry. Contrary to prior art azomethines inventors found that oxidation is reversible. However, when applying a higher potential (>1.2 V) the

small molecules are oxidized to their 2^+ form, and this second oxidation appears to be irreversible. It is well-known from literature that oxidation of triphenylamines results in the formation of a cationic radical, which can dimerise via the para-position. The oxidation potential was found between 0.1 and 0.5 V (vs Fc/Fc $^+$). The methoxy functionalized small-molecule shows the lowest oxidation potential, which is ascribed to the electron donating methoxy groups. The highest occupied molecular orbital (HOMO) energy levels of the small molecules were estimated by using the oxidation onset of the first oxidation and were found in the range of -5.2- -5.5 eV below vacuum. The relatively deep HOMO energy levels are expected to give a good energy alignment with the perovskite. The lowest unoccupied molecular orbital (LUMO) energy levels were estimated by combining the optical band-gap with the obtained HOMO energy level. The azomethine moiety was found to slightly deepen the HOMO energy level compared to the vinyl and fully aromatic analogues, which are about 0.1-0.3 eV higher.

Planar perovskite based photovoltaics with the azomethine as hole transporting layer show power conversion efficiencies (PCE) exceeding 10% (Table 2). This efficiency is only slightly lower compared state of the art materials, whereas optimisation of the chemical structure and processing conditions is found to further increase the PCE. As azomethines can be prepared in a simple and clean condensation reaction under near ambient conditions we believe this approach offers a cost effective route towards hole transporting materials.

Device fabrication

As a substrate FTO glass was etched with zinc powder and HCl (2M) and cleaned afterwards. A compact 50 nm layer of TiO $_2$ was deposited by spin-coating a titanium isopropyl solution. It was heated to 500 °C for 45 minutes. After cooling down the substrate were transferred to a nitrogen filled glove-box. A solution of 1M PbI $_2$ and 1M methylammoniumiodide was spin coated dynamically (at 5000 rpm, total 15 sec) onto the substrate. After 5 seconds 100 μ L of chlorobenzene was added on top of the spinning substrate. Thereafter the substrate was placed on a hot-plate at 100 °C for 10 minutes. After cooling to ambient temper-

ature the present hole transporter was spin-coated on top. In an example TPA(OMe)₂-EDOT-TPA(OMe)₂ (10 mg mL⁻¹), and Spiro-OMeTAD (75 mg mL⁻¹) were dissolved in chlorobenzene. Lithium bis(tris-fluoromethylsulfonyl)imide (Li-TFSI; 10 μL mL⁻¹ of a 170 mg mL⁻¹ acetonitrile solution) and *Tert*-butylpyridine (TBP; 30 μL mL⁻¹) were added to the hole transport material solutions. As a Co-dopant tris(2-(1H-pyrazol-1-yl)pyridine) cobalt(III) bis(hexafluorophosphate) (FK102) was pre-dissolved in acetonitrile and added to the hole transport material solution at a ratio of 0-15 mole%. The thickness of the hole transport layer was found to be 20nm for TPA(OMe)₂-EDOT-TPA(OMe)₂ and ~250nm for Spiro-OMeTAD. Thereafter a top electrode was deposited by thermal evaporation of gold under vacuum (at 10⁻⁶ mbar), with a thickness of 40 nm.

In conclusion, three conjugated small-molecule azomethines were synthesized via simple and cheap condensation chemistry. The small molecules exhibit reversible oxidation behaviour, a fairly deep lying HOMO energy level, and a band-gap between 1.9 to 2.2 eV. Inventors demonstrated that this chemistry enables the fabrication of hole transport materials for perovskite-based photovoltaics. Because azomethine chemistry is easy, clean and proceeds under near ambient conditions inventors consider that this approach has the ability to reduce materials and production costs of organic photovoltaic devices.

Characterization of the Electrical Transport in Conjugated Azomethine-based Materials for Optoelectronic Applications

Azomethine-based low molar mass molecules show good performance as hole-transporting material in perovskite photovoltaic devices. A single molecule conductance of a 3-ring, conjugated azomethine using a mechanically controlled break junction (MCBJ) is found to be fine. The azomethine model compound exhibits transport properties comparable to vinyl-based analogues. These findings are supported with density functional calculations. Its simple preparation in combination with the good transport properties makes azomethine-based molecules a very attractive class of materials for a wide variety of organic semi-conductor applications.

To comment on measured conductance value of (thiophene-2,5-diylbis(N-phenylmethanimine, (TYPI) inventors compared it

with the single molecule conductance of the well-studied oligo(p-phenylene vinylene) trimer (OPV3). This molecule has approximately the same length (1.92 nm compared to 1.85 nm of TYPI) and same basic electronic structure, which consist of three conjugated rings connected with sp² hybridized linkers. The conductance of OPV3 with thiol anchoring groups lies between 1•10⁻⁴ G₀ and 2•10⁻⁴ G₀ for MCBJ setups. Comparing the conductance values of both TYPI and OPV3 shows that a thiophene ring with azomethine linkers has a comparable charge transport efficiency as a benzene ring with vinyl linking. It is found that the HOMO's of all molecules have a pi character and closely resemble each other, both in shape and in energy. They extend from one sulphur atom to the other and hybridize well with the gold atoms, as can be seen by the finite density around the gold-sulphur bond and their extension throughout the entire gold electrodes. The similar electronic structure is further supported by the transmission calculations, which show similar broadening of the HOMO's indicating comparable hybridization of the molecules with the gold electrodes. Furthermore, the HOMO-LUMO gap is of comparable size, 3.2 eV for TYPI, 3.4 eV for OPV3 and 3.4 eV for OPA3.

The transmission of the three molecules is shown in Figure 3d, where peaks in the transmission originate from resonant charge transport through molecular orbitals. Based on its energy, the over-lapping peaks just below -5.5 eV can be identified, as the HOMO's of TYPI, OPV3 and OPA3. Focusing on the transmission in the region around the Fermi energy, which calculations predict to be around -4.8 eV, inventors see that for all molecules transport is dominated by the HOMO. This is expected for thiol anchoring groups. Moreover, in the same energy range, the transmissions follow each other closely which is considered a result of the similar energy of the HOMO's and their broadening. This supports the conclusion drawn from the measurements, which is that the thiophene core with azomethine linker units has a comparable conductance to the benzene core with vinyl linking units.

Synthesis of thiophene-2,5-diylbis(N-phenylmethanimine, TYPI)

2,5-Thiophenedicarboxaldehyde was purified by vacuum sublima-

tion, prior to use.

4-aminobenzenethiol (339 mg, 2.7 mmol) and 2,5-thiophenedicarboxaldehyde (173 mg, 1.2 mmol) were placed in a dry round-bottom flask with reflux condenser under argon atmosphere. Dry chloroform (20 mL) was added, followed by a crystal of p-toluenesulfonic acid as a catalyst while stirring. The mixture turned yellow and was heated to reflux. A precipitate was formed overnight. After 3 days the reaction mixture was poured in methanol and filtered off. The product was washed with methanol, isopropanol, isopropanol:triethylamine (98:2) and again isopropanol and dried in vacuo. Yield 0.40 g (87%, 1.1 mmol). λ_{max} (CHCl₃) = 398 nm; ¹H-NMR (CDCl₃, 400MHz) δ 8.56 (s, 2H); 7.48 (s, 2H); 7.30 (d, J = 8.4Hz, 4H); 7.15 (d, J = 8.4Hz, 4H); 3.50 (s, 2H) ppm; FTIR: 3037, 2570, 1902, 1604, 1575, 1480, 1404, 1195, 828 cm⁻¹; MS m/z (relative intensity): 355.0 (24), 353.9 (M⁺, 99), 321.0 (75), 217.9 (22), 136.0 (59), 109.0 (100), 108.0 (32), 77.1 (23), 69.0 (37), 65.1 (85), 45.1 (27).

The invention is further detailed by the accompanying figures, which are exemplary and explanatory of nature and are not limiting the scope of the invention. To the person skilled in the art it may be clear that many variants, being obvious or not, may be conceivable falling within the scope of protection, defined by the present claims.

FIGURES

The invention although described in detailed explanatory context may be best understood in conjunction with the accompanying figures.

Fig. 1 shows a synthesis route and molecular structures of the present small-molecule azomethines.

Fig. 2 shows a TPA molecule with an optional group R.

Fig. 3a-e show basic configurations of the present azomethine molecules.

Fig. 4a-b relate to a so-called inverted perovskite device and standard perovskite device, respectively.

DETAILED DESCRIPTION OF THE FIGURES

The figures have been detailed throughout the description.

TABLES

Table 1. Summary of the optoelectronic properties of TPA-X-TPA

small molecules

Compound	UV-vis solution ^a		UV-vis film ^b		λ_{onset} (nm)	E_g (eV) ^c	$E_{\text{oxi, onset}}$ (V)	HOMO (eV) ^d	LUMO (eV) ^e
	$\lambda_{\text{max 1}}$	$\lambda_{\text{max 2}}$	$\lambda_{\text{max 1}}$	$\lambda_{\text{max 2}}$					
	(nm)	(nm)	(nm)	(nm)					
TPA-Th-TPA	306	467	314	463	565	2.19	0.45	5.55	3.36
TPA-EDOT-TPA	305	476	308	472	575	2.16	0.37	5.48	3.32
TPA(OMe) ₂ -EDOT-TPA(OMe) ₂	306	495	306	505	625	1.98	0.17	5.28	3.28

^a Measured in a quartz cuvette in dichloromethane.

^b Spin cast on a quartz substrate from chloroform.

^c Estimated from the onset of the absorption spectrum of the film, $1240/\lambda_{\text{onset}}$.

^d Determined by cyclic voltammetry, with Fc/Fc⁺ at 5.1 eV below vacuum.

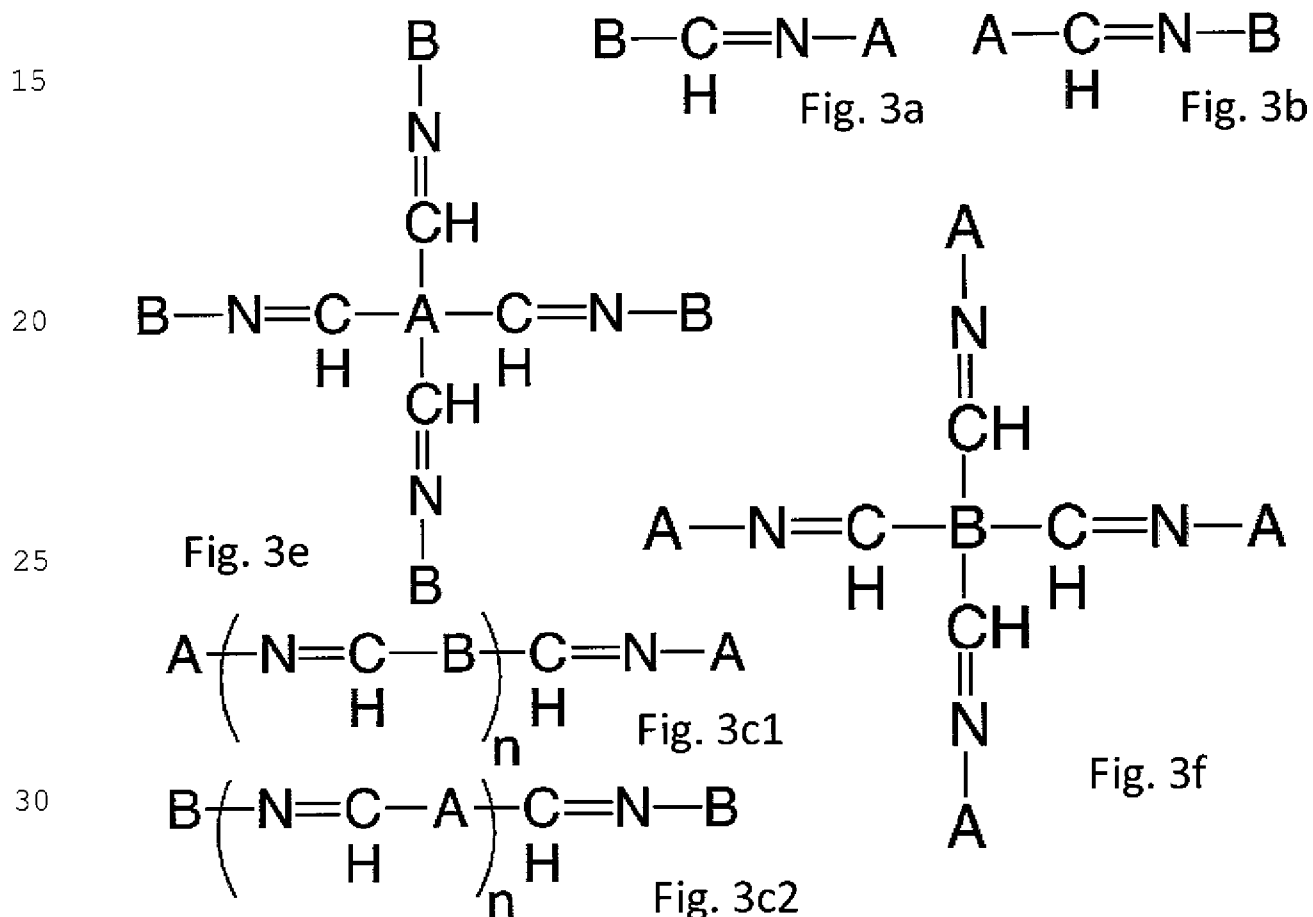
^e Estimated by subtracting the band-gaps from the HOMO energy levels.

Table 2: J-V characteristics of the photovoltaic devices with different HTMs.

HTM	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE (%)
TPA-Th-TPA	12.6	1.00	56	7.1
TPA-EDOT-TPA	16.9	0.90	61	9.4
TPA(OMe) ₂ -EDOT-TPA(OMe) ₂	18.6	0.95	61	11.0
Spiro-OMeTAD	17.9	1.00	66	11.9

CLAIMS

1. Photovoltaic device comprising
 a substrate,
 a first optically transparent electrode layer, acting
 as an anode or cathode,
 5 a second electrode layer, acting as a cathode or anode,
 and between the electrode layers
 (i) a perovskite layer as light absorbing layer,
 (ii) a hole transport layer, the hole transport layer being in
 contact with the anode layer and the perovskite layer, and
 10 (iii) an intermediate layer, the intermediate layer being in
 contact with the cathode layer and the perovskite layer,
 wherein the hole transport layer comprises an azomethine mole-
 cule according to figure 3



the azomethine molecule comprising
 at least one aromatic entity (A) comprising

35 (Ai) at least one nitrogen atom directly attached to
 the aromatic entity (fig. 3a), or

(Aii) at least one carbon atom directly attached to the aromatic entity (fig. 3b),

at least one aromatic bridging entity (B), the bridging and aromatic entity having a connecting N=C bond (azomethine), the

5 bridging entity comprising

(Bi) (in case of Ai) at least one carbon atom directly attached to the aromatic entity and to the nitrogen atom (fig. 3a), or

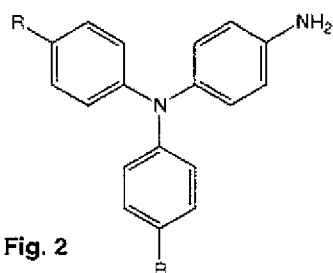
10 (Bii) (in case of Aii) at least one nitrogen atom directly attached the aromatic entity and to the carbon atom (fig. 3b),

2. Photovoltaic device according to claim 1, comprising at least one hole mobility improver in the hole transport layer, wherein a first hole mobility improver is present in an amount
15 of 0.1-100 mole %, relative to the azomethine molecule.

3. Photovoltaic device according to any of the preceding claims, wherein the molecule has an (A-B)_n-A structure (fig. 3c1) or (B-A)_n-B structure (fig. 3c2), wherein n∈[1-5], or wherein the molecule has an A_m-B structure (fig. 3d), wherein m∈[1-5],
20 or wherein the molecule has a B_r-A structure (fig. 3e), wherein r∈[1-5], or combinations thereof.

4. Photovoltaic device according to any of the preceding claims, wherein the aromatic bridging entity comprises one or more of S, N, P, Si, Se and O.

25 5. Photovoltaic device according to any of the preceding claims, comprising at least one 4-aminotriphenyl-amine-X₂ (TPA) according to figure 2,



and wherein the bridging entity R is selected from 2,5-thiophenedi-carbaldehyde (Th), 2,3-dihydrothieno[3,4-
35 b][1,4]dioxine-5,7-dicarbaldehyde (EDOT), 2,2'-bithiazole-5,5'-dicarbaldehyde (BTz), 4,7-bis(5-formylthiophen-2-yl)-2,1,3-benzothiadiazole (TBT), and combinations thereof.

6. Photovoltaic device according to claim 5, wherein R

of fig. 2 is independently selected from H, -CN, OAlk, Alk, and combinations thereof, and

wherein Alk is selected from alkanes, and combinations thereof.

5 7. Photovoltaic device according to any of claims 1-6, wherein the hole transport layer comprises a second hole transport improver in an amount of 0.001-20 mole % relative to the azomethine molecule.

8. Photovoltaic device according to any of claims 1-7, wherein the substrate is selected from glass, silicon, steel, 10 aluminium, silicon oxide, polymers, and combinations thereof, and/or wherein the first electrode layer is selected from tin doped indium oxide (ITO), graphene, fluorine doped tin oxide (FTO), and/or wherein the second electrode layer is selected from met- 15 als, such as Al, Cu, Mg, Ba, ZnO, Au, Ag, and Ca, and/or wherein the intermediate layer is selected from TiO₂, and fullerenes.

9. Photovoltaic device according to any of the preceding claims, wherein the first electrode comprises a crystalline 20 material.

10. Photovoltaic device according to any of the preceding claims, wherein the perovskite is highly crystalline.

11. Photovoltaic device according to any of the preceding claims, wherein between perovskite layer and intermediate 25 layer a second intermediate layer is provided, which second intermediate layer is crystalline at a boundary with the first intermediate layer, is amorphous at a boundary with the perovskite layer, and has a continuous or step-wise increasing amorphousness from the first intermediate layer towards the perovskite 30 layer.

12. Photovoltaic device according to any of claims 1-11, further comprising an electron transport layer.

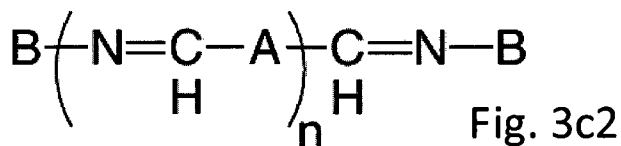
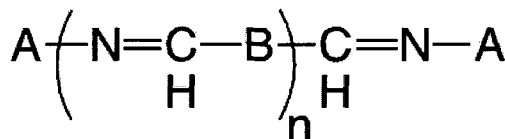
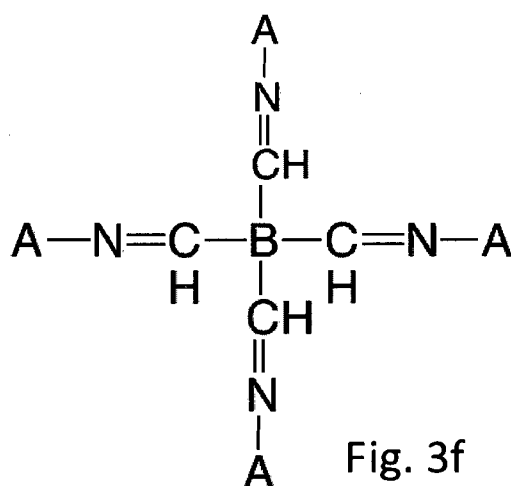
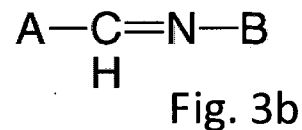
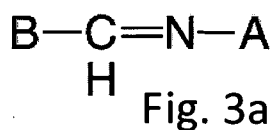
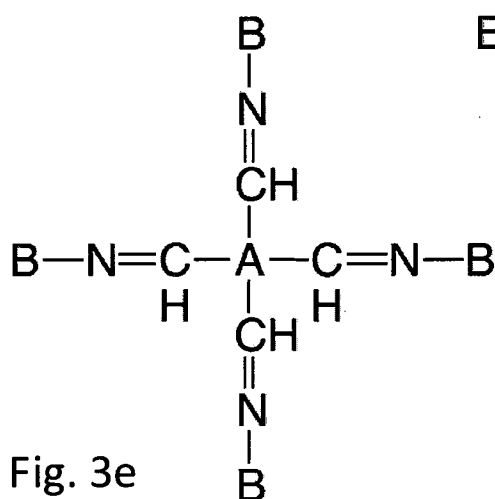
13. Photovoltaic device according to any of claims 1-12, comprising a sequence of layers comprising one or more of 35 a 20-1000 nm first electrode layer, such as ITO, a 10-1000 nm light absorbing layer, a 10-300 nm hole transport layer, an 10-500 nm electron transport layer, and a 20-200 nm second electrode layer.

14. Solar cell comprising a photovoltaic device according to any of claims 1-13.

AMENDED CLAIMS

received by the International Bureau on 23 June 2016 (23.06.2016)

1. Photovoltaic device comprising
 a substrate (11),
 a first optically transparent electrode layer (21),
 acting as an anode or cathode,
 5 a second electrode layer (22), acting as a cathode or
 anode,
 and between the electrode layers
 (i) a perovskite layer (31) as light absorbing layer,
 (ii) a hole transport layer (41), the hole transport layer
 10 being in contact with the anode layer and the perovskite
 layer, and
 (iii) an intermediate layer (51), the intermediate layer
 being in contact with the cathode layer and the perovskite
 layer, **characterized in that**
 15 the hole transport layer comprises an azomethine molecule ac-
 cording to figure 3



the azomethine molecule comprising
 at least one aromatic entity (A) comprising

(Ai) at least one nitrogen atom directly attached to the aromatic entity (A) (fig. 3a), or

(Aii) at least one carbon atom directly attached to the aromatic entity (A) (fig. 3b),

at least one aromatic bridging entity (B), the bridging and aromatic entity having a connecting N=C bond (azomethine), the bridging entity comprising

(Bi) (in case of Ai) at least one carbon atom directly attached to the aromatic entity (B) and to the nitrogen atom (fig. 3a), or

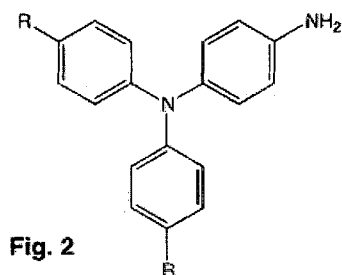
(Bii) (in case of Aii) at least one nitrogen atom directly attached the aromatic entity (B) and to the carbon atom (fig. 3b),

2. Photovoltaic device according to claim 1, comprising at least one hole mobility improver in the hole transport layer, wherein a first hole mobility improver is present in an amount of 0.1-100 mole %, relative to the azomethine molecule.

3. Photovoltaic device according to any of the preceding claims, wherein the molecule has an (A-B)_n-A structure (fig. 3c1) or (B-A)_n-B structure (fig. 3c2), wherein n ∈ [1-5], or wherein the molecule has an A_m-B structure (fig. 3d), wherein m ∈ [1-5], or wherein the molecule has a B_r-A structure (fig. 3e), wherein r ∈ [1-5], or combinations thereof.

4. Photovoltaic device according to any of the preceding claims, wherein the aromatic bridging entity comprises one or more of S, N, P, Si, Se and O.

5. Photovoltaic device according to any of the preceding claims, comprising at least one 4-aminotriphenyl-amine-R₂ (TPA) according to figure 2,



and wherein the bridging entity R is selected from 2,5-thiophenedi-carbaldehyde (Th), 2,3-dihydrothieno[3,4-b][1,4]dioxine-5,7-dicarbaldehyde (EDOT), 2,2'-bithiazole-5,5'-dicarbaldehyde (BTz), 4,7-bis(5-formylthiophen-2-yl)-

2,1,3-benzothiadiazole (TBT), and combinations thereof.

6. Photovoltaic device according to claim 5, wherein R of fig. 2 is independently selected from H, -CN, OAlk, Alk, and combinations thereof, and

5 wherein Alk is selected from alkanes, and combinations thereof.

7. Photovoltaic device according to any of claims 1-6, wherein the hole transport layer (41) comprises a second hole transport improver in an amount of 0.001-20 mole % relative to the azomethine molecule.

8. Photovoltaic device according to any of claims 1-7,

15 wherein the substrate (11) is selected from glass, silicon, steel, aluminium, silicon oxide, polymers, and combinations thereof, and/or wherein the first electrode layer is selected from tin doped indium oxide (ITO), graphene, fluorine doped tin oxide (FTO),

and/or wherein the second electrode layer (22) is selected from metals, such as Al, Cu, Mg, Ba, ZnO, Au, Ag, and Ca, and/or wherein the intermediate layer (51) is selected from TiO₂, and fullerenes.

9. Photovoltaic device according to any of the preceding claims, wherein the first electrode (11) comprises a crystalline material.

25 10. Photovoltaic device according to any of the preceding claims, wherein the perovskite is highly crystalline.

11. Photovoltaic device according to any of the preceding claims, wherein between perovskite layer (31) and intermediate layer (51) a second intermediate layer is provided, which second intermediate layer is crystalline at a boundary with the first intermediate layer, is amorphous at a boundary with the perovskite layer, and has a continuous or step-wise increasing amorphousness from the first intermediate layer towards the perovskite layer.

35 12. Photovoltaic device according to any of claims 1-11, further comprising an electron transport layer.

13. Photovoltaic device according to any of claims 1-12, comprising a sequence of layers comprising one or more of a 20-1000 nm first electrode layer(11), such as ITO,

a 10-1000 nm light absorbing layer (31),
a 10-300 nm hole transport layer(41),
an 10-500 nm electron transport layer (51), and
a 20-200 nm second electrode layer (22).

5 14. Solar cell comprising a photovoltaic device according to any of claims 1-13.

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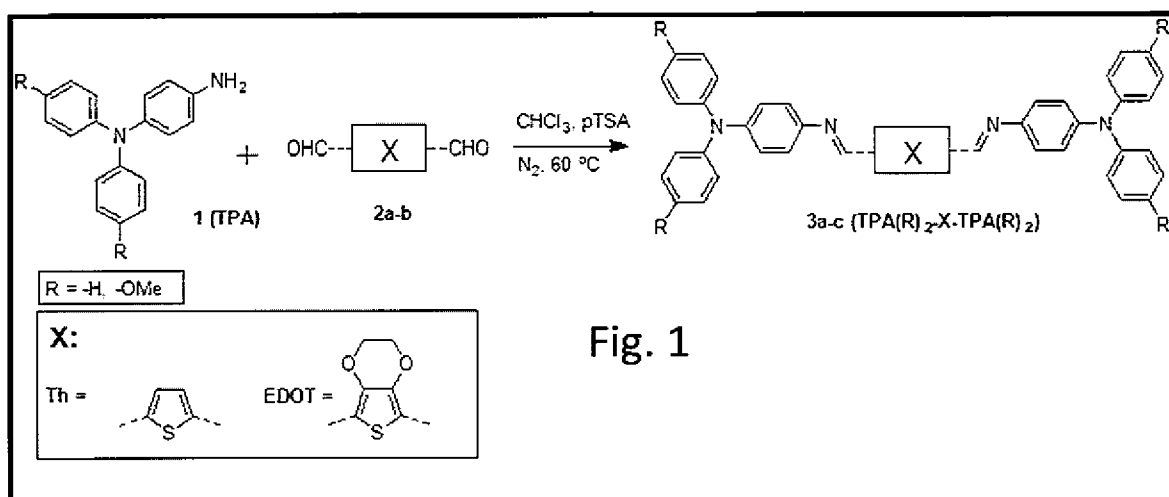
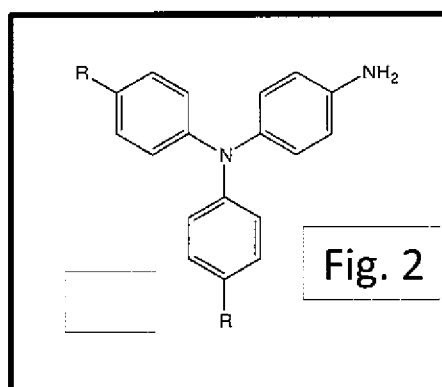
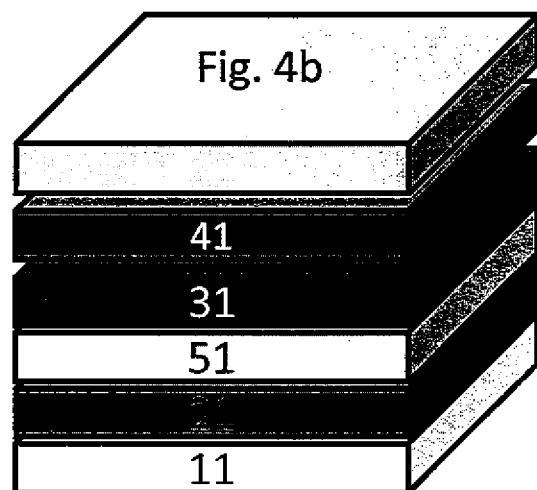
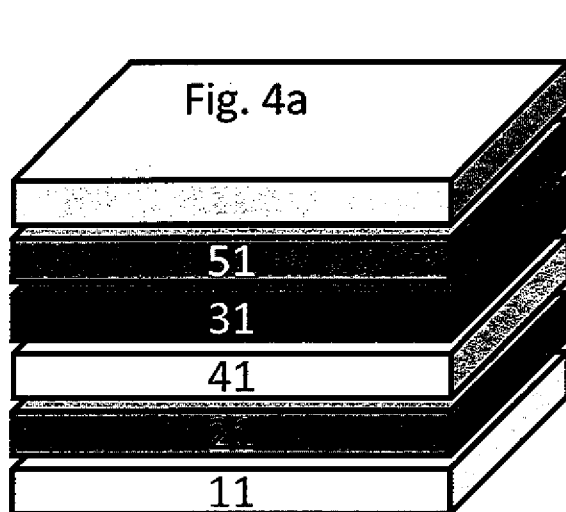
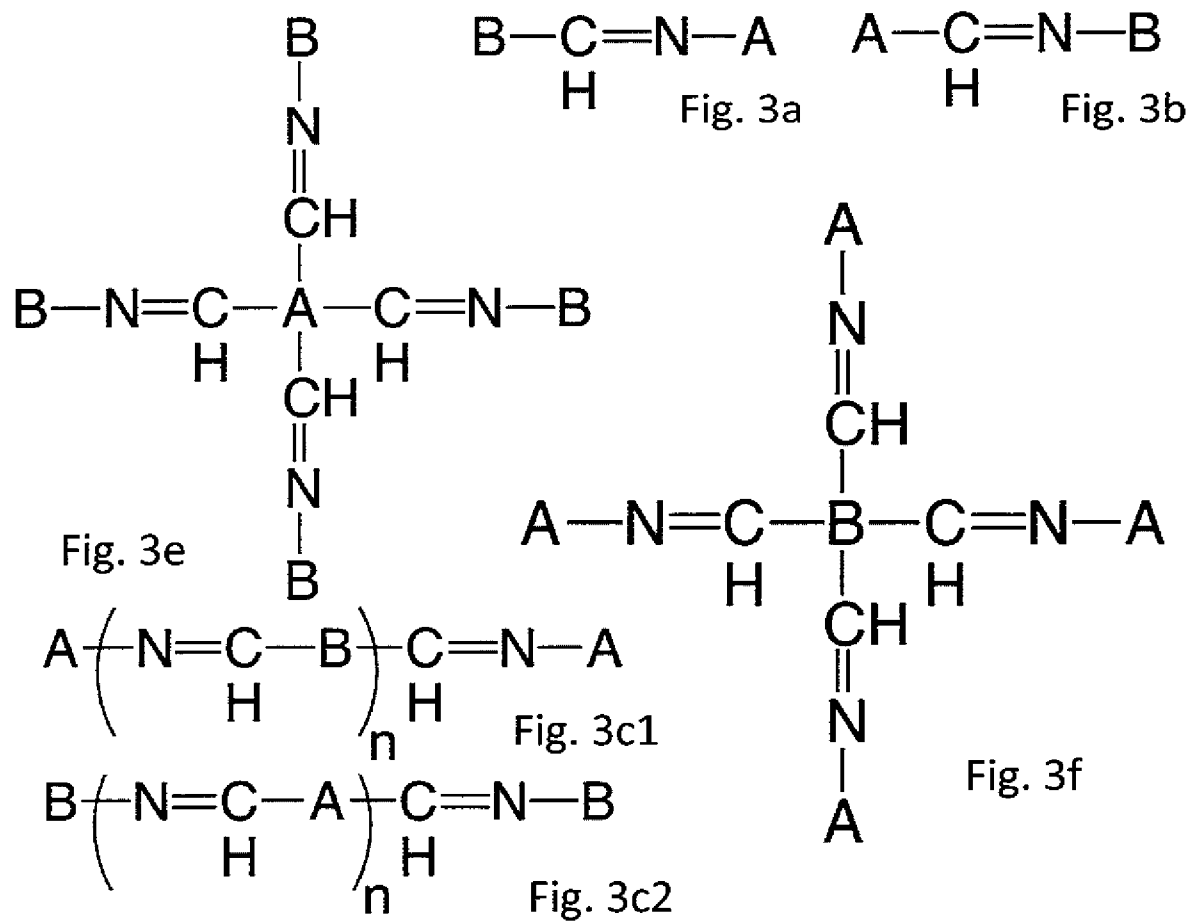


Fig. 1



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INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2016/050007

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L51/46
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)
H01L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
T	TAKEO OKU ET AL: "Microstructures and photovoltaic properties of perovskite-type CH₃NH₃PbI₃ compounds", APPLIED PHYSICS EXPRESS, JAPAN SOCIETY OF APPLIED PHYSICS; JP, JP, vol. 7, no. 12, 25 November 2014 (2014-11-25), pages 121601-1, XP001594231, ISSN: 1882-0778, DOI: 10.7567/APEX.7.121601 [retrieved on 2014-11-25] pages 121601-1; figures 1, 7a ----- -/--	1



Further documents are listed in the continuation of Box C.



See patent family annex.

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

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Date of the actual completion of the international search

30 May 2016

Date of mailing of the international search report

07/06/2016

Name and mailing address of the ISA/

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Authorized officer

Beierlein, Udo

INTERNATIONAL SEARCH REPORT

International application No

PCT/NL2016/050007

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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