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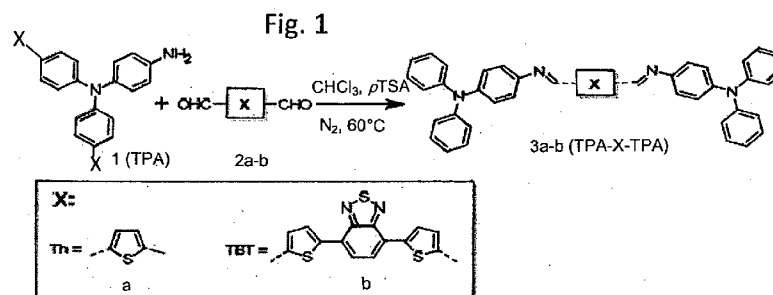
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(54) Title: SMALL AZOMETHINE MOLECULES AND THEIR USE IN PHOTOVOLTAIC DEVICES



(57) Abstract: The present invention is in the field of a small azomethine molecule having photovoltaic characteristics, a method of synthesizing said molecule, use of said molecule in a photovoltaic device, a solar cell comprising said molecule, and a film comprising said molecule. The present molecules may find application in the field of organic solar cells.

## SMALL AZOMETHINE MOLECULES AND THEIR USE IN PHOTOVOLTAIC DEVICES

## FIELD OF THE INVENTION

The present invention is in the field of a small azomethine molecule having photovoltaic characteristics, a method of synthesizing said molecule, use of said molecule in a photovoltaic device, a solar cell comprising said molecule, and a film comprising said molecule.

## BACKGROUND OF THE INVENTION

The present invention is in the field of organic solar cells. These organic solar cells may lead to a substantial price reduction compared to e.g. silicon based 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 organic solar cell efficiencies are low (photon to current 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 are very high, at least partly due to process costs.

Organic solar cells and polymer solar cells are typically built from thin films of organic (semi)conductors including polymers and block copolymers, such as poly(3-hexylthiophene-2,5-diyl). In addition small-molecule compounds like copper phthalocyanine (a blue or green organic pigment) and carbon fullerenes and fullerene derivatives such as PCBM are added.

A(n organic) solar typically comprises two materials, one which acts as an electron donor and the other as an acceptor. It is considered that a photon is converted into an electron hole pair, by the photovoltaic material. The device converts the electron hole pair into an electrical current. At present highly efficient transparent solar cells have a limited power efficiency with a transparency to the human eye greater than 65% (under laboratory conditions). In principle lightweight and flexible cells could be produced in bulk at a low production cost, and could be used to create power generating windows.

Drawbacks of prior art materials, and especially synthesis thereof, is that stringent reaction conditions are required, making the materials difficult to obtain, expensive (transition metal) catalysts and typically also starting products are involved in the reaction, and extensive and therefore costly product purification/work-up is required. Typical product costs are as a consequence in the order of €1000/g (or €10<sup>6</sup>/kg). Some alternative molecules, having e.g. photovoltaic properties, may be obtained in more efficient and cheaper ways, but these materials typically suffer from low performance characteristics.

Many (organic) molecules that are in principle suited for photovoltaic application, can not be produced or only with difficulty into bulk photovoltaic devices, such as into a film.

Organic bulk heterojunction photovoltaics are a relative new class of solar cells, which have been widely studied the last decade, however has not been commercialized on a large scale so far. Conjugated azomethines (polymers) as electron donating materials in photovoltaics have been published, however efficiencies have been low (<0.31%).

Some documents on conjugated azomethines only mention their potential as photovoltaic materials, but to it has not been shown that these could be used in practice as photovoltaic materials. Typically the azomethines relate to polyazomethines, which are not well-defined molecules.

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1213, Berlin et al. in Mol. Crystals and Liquid Crystals, Vol. 118 (1-4) (1985), p. 413-416, Pastour et al. in Compt. Rend., Vol. 260(11) (1965), p. 3110/3112, Vaysse et al. in Compt. Rend., Vol. 259(16) (1964), p. 2657-2659, EP 2 537 075 A1, CN 101 962 823 A, CN 102 304 226 A, CN 101 885 821 A, CN 102 585 218 A, Petrus et al. in Polymer Chemistry, Vol. 4, No. 15 (2013-01-01), p. 4182, Hindson et al. in J. Materials Chemistry, Vol. 20, No. 5 (2010-01-01), p. 937, all recite various azomethine molecules, and Kwon et al. in New Journal of Chemistry, Vol. 34, No. 4 (2010-01-01), p. 744 recites styryl (vinyl) equivalents. Only the last three documents mentioned relate to solar cells or the like; however these relate to polymers, i.e. having large molecular masses typically much larger than 10.00 Da; the oligomers mentioned may be smaller (e.g. 1000 Da) but the polymers that are formed are much larger. Hence these documents are not very relevant in terms of size of the molecules and potential application thereof.

The present invention therefore relates to an improved small azomethine molecule having photovoltaic characteristics, a method of synthesizing said molecule, use of said molecule in a photovoltaic device, a solar cell comprising said molecule, and a film comprising said molecule, 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 use of azomethine molecules according to claim 1, specific azomethine molecules of claim 6, a method of producing said molecule according to claim 7, a photovoltaic device comprising said molecule according to claim 8, a solar cell comprising said molecule according to claim 13, a film comprising said molecule according to claim 14 and a sensor according to claim 15.

The present 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, even more preferably 600-900, such as 700-750, good

film forming properties, low costs, etc. With reference to claim 1 and fig. 5, the present molecules comprise two entities, one aromatic entity A, and one aromatic 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, or is heterocyclic. 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.

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

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.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates in a first aspect to a photovoltaic use of an azomethine molecule according to claim 1.

The azomethine molecules have excellent properties. For instance a glass transition temperature ( $T_g$ ) of about 100 °C is 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 organic photovoltaic devices that function reliable under ambient conditions.

Further, optical properties are also excellent. The molecules exhibit absorbance of light over a range of about 280 nm-about 600 nm, with a  $\lambda_{max}$  of about 500 nm, and an onset

wavelength  $\lambda_{\text{onset}}$  of about 600 nm. The band-gap is in the order of 2.0 eV. These absorbance properties can be improved for the present molecules. Further, a maximum  $\epsilon_{\text{abs}}$  of 30,000-60,000 ( $\text{M}^{-1}\text{cm}^{-1}$ ) is found.

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

The photovoltaic performance is unexpectedly high, even for non-optimized molecules. It is a factor (5-10) times better than comparable prior art molecules. The  $V_{\text{oc}}$  is for instance about 0.5 V, the current density  $J_{\text{sc}}$  from 1-2  $\text{mA}/\text{cm}^2$ , the FF is about 0.3 and the photo-current efficiency is about 0.3%.

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

By providing a hole transport layer, in combination with a layer comprising the present molecule, photovoltaic performance can be improved. For instance, poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) (PEDOT-PSS) improves the performance to about a  $V_{\text{oc}}$  of about 0.5 V,  $J_{\text{sc}}$  to about 2.5  $\text{mA}/\text{cm}^2$ , the fill factor (FF) to about 0.35 and the photo-current efficiency to about 0.35%, whereas a  $\text{MoO}_x$  layer improves the performance to about a  $V_{\text{oc}}$  of about 0.7 V,  $J_{\text{sc}}$  to about 2.5  $\text{mA}/\text{cm}^2$ , the FF to about 0.30 and the photo-current efficiency to about 0.45%. After annealing (of e.g. a  $\text{MoO}_x$  based device at 70 °C for about 30 min.) the above values improve to a  $V_{\text{oc}}$  of about 0.8 V,  $J_{\text{sc}}$  to about 2.7  $\text{mA}/\text{cm}^2$ , the FF to about 0.35 and the photo-current efficiency to about 0.75%.

The photovoltaic performance can be improved even further by providing an improvement molecule, such as a fullerene, such as [60]PCBM, and [70]PCBM. The above values improve to a  $V_{\text{oc}}$  of about 0.8 V,  $J_{\text{sc}}$  to about 5  $\text{mA}/\text{cm}^2$ , the FF to about 0.35 and the photo-current efficiency to about 1.25%. Therewith, and/or in combination with the above measures, also wavelength absorption properties improve; e.g. an onset wavelength  $\lambda_{\text{onset}}$  to about 750 nm.

In an example of the present use of the azomethine molecule the molecule has an  $(\text{A-B})_n\text{-A}$  structure (fig. 5c) or  $(\text{B-A})_n\text{-B}$  structure, wherein  $n \in [1-5]$ , preferably  $n \in [2-3]$ , or

wherein the molecule has an  $A_m-B$  structure (fig. 5d), wherein  $m \in [1-5]$ , preferably  $m \in [2-3]$ , or wherein the molecule has an  $B_r-A$  structure (fig. 5e), 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 use of the azomethine molecule the aromatic heterocyclic 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 heterocyclic entity B at least two, and preferably at least two different, heteroatoms are present, one of which preferably is S.

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

In an example of the present use in the 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.

In an example of the present use in the azomethine molecule the R is independently selected from H, -CN, OAlk, Alk, and combinations thereof, and Alk is selected from alkanes, such as  $C_1-C_{18}$ , preferably  $C_1-C_{12}$ , such as Me, Et, and combinations thereof.

In a second aspect the present invention relates to azomethine molecules, wherein 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-benzothiadiaazole (TBT), and combinations thereof. The R is independently selected from H, -CN, OAlk, Alk, and combinations thereof, and Alk is selected from alkanes, such as C<sub>1</sub>-C<sub>18</sub>, preferably C<sub>1</sub>-C<sub>12</sub>, such as Me, Et, and combinations thereof. In an example the azomethine molecule comprises at least one 4-aminotriphenylamine (TPA) according to figure 4.

In a third aspect the present invention relates to a cheap, simple and reliable method of producing a photovoltaic molecule according to the invention. Therein at least one aromatic entity A, which in this case may or may not be a heterocyclic aromatic entity, and at least one aromatic heterocyclic bridging entity (B) are condensed, i.e. form a connection under release of a water molecule. The azomethine product formed can be separated or applied directly. Such is surprising, especially in view of cumbersome prior art methods in this respect, requiring advanced processing. If required, the condensate may be washed, such as with water.

The method of preparing the small molecule azomethines is extremely simple, no special equipment or trained people are necessary to perform the synthesis. Duplicating this work will be very easy and by using different monomers new small molecules can easily be made. Because no inert reaction conditions or extensive product purification are required, the synthesis is easy and scale-up is relatively easy. The present method relates to a simple reaction, requires no expensive catalyst, no water absorbing material, does not use scarcely available resources (such as transition metals), relates to an easy synthesis with high yield, high selectivity and high purity. The obtained product can be upgraded if required without difficulty. Water is produced as primary by-product. The starting molecules, such as 4-aminotriphenylamine (TPA) and thiophene (Th), are readily available. The present method provides bipolar A-B-A molecules.

The present small molecule azomethines (TPA-X-TPA, or

indicated as A-B-A) were prepared in a simple condensation reaction by capping in an example different dialdehydes, such as 2,5-thiophenedicarbaldehyde (Th, mol. weight 140.2), 2,3-dihydrothieno[3,4-b][1,4]dioxine-5,7-dicarbaldehyde (EDOT, 5 mol. weight 198.2), 2,2'-bithiazole-5,5'-dicarbaldehyde (BTz, mol. weight 113.14) or 4,7-bis(5-formylthiophen-2-yl)-2,1,3-benzothiadiazole (TBT), respectively, with 4-aminotriphenylamine (TPA). The reaction can be supported by addition of p-toluene sulfonic acid or by applying heat (reflux). It is noted that the above Th, EDOT and TPA monomers, respectively, are 10 commercially available and relatively cheap.

Azomethines were chosen because it has been found that their synthesis has several advantages over traditional conjugated organic materials. Small molecules were synthesized 15 because it was found that they have an increased solubility compared to polymers. Inventors found that especially the limited solubility of the analogue polymers made the processing of the molecules obtained more difficult. Besides that, it was found that small molecules also have the advantage of a well-defined and well controllable molecular structure (such as A-B-A), definite molecular weight (only one type of molecule being formed), high yields, good selectivity, and small batch-to-batch variations ( $\pm 2\%$ ) compared to polymers. 20

So far inventors have not performed extensive experiments to improve characteristics yet, such as in view of the 25 absorption/band gap, which is rather limited. By using different monomers molecules with a smaller band gap are synthesized, having higher currents and efficiencies. Also a larger phase separation is obtained, which is beneficial for the present device performance; in an example thereof an alkyl side 30 chain is introduced on the monomers.

In an example the present method further comprises one or more steps selected from before spin coating the condensate, adding an electron acceptor, thereby forming a solution, wherein the solution is spin coated on a substrate, removing the solvent, and annealing the condensate. Thereby the 35 present product can be applied directly, e.g. to a substrate, without a further intermediate step, which is a big advantage.

In an example of the present method annealing is per-

formed at a temperature of 50-150 °C, such as 70-100 °C, for a period of time of 10-60 min., such as 20-30 min. Within a relative short period of time at a relatively modest temperature the photovoltaic characteristics of the present coating can be improved significantly.

In a fourth aspect the present invention relates to a photovoltaic device according to claim 8, comprising the azomethine molecule.

Bulk heterojunction photovoltaic devices prepared from the present small molecules with PCBM showed an enhanced efficiency when MoO<sub>x</sub>, such as MoO<sub>3</sub>, was used instead of PEDOT-PSS as hole transporting layer. Annealing of the device resulted in another increase in the efficiency. Using [70]PCBM as acceptor efficiencies up to 1.2% were achieved. (see experiments for details).

It is noted that in the prior art some analogues of the present molecules have been investigated. For TPA-Th-TPA and TPA-TBT-TPA vinyl analogues have been published (having a PCE of 0.23% and 0.26%, respectively). For TPA-TBT-TPA also the fully aromatic analogue has been published, which showed a slightly higher efficiency of 1.3% compared to 1.15% for the vinyl analogues. The present azomethines outperform these materials by a factor of at least 5, without even being optimized.

Albeit the present conversion efficiencies are somewhat limited (state of the art conjugated polymers reach efficiencies up to 10%), 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, which is considered to provide market breakthrough opportunities.

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

Also a spin coat of the active layer directly from the reaction mixture results directly into a working device. As a further advantage thereof no workup is required for preparing the devices.

In an example the present photovoltaic device com-

prises a substrate, an anode layer, a bulk hetero-junction layer comprising a photovoltaic molecule as disclosed in any of claims 1-6, and one or more of electron acceptor molecules, such as a copper phthalocyanine, a carbon fullerene, and fullerene derivative, such as [60]PCBM, [70]PCBM, and a cathode layer. In principle the above sequence of layers is considered a minimal set of layers in view of performance, Further (intermediate and protecting) layers may be added, e.g. in order to improve performance.

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 anode layer is selected from tin doped indium oxide (ITO), graphene, and fluorine doped tin oxide (FTO), preferably ITO.

In an example of the present photovoltaic device the cathode layer is optically transparent and selected from Al, Cu, Mg, Ba, ZnO, and Ca, preferably Al.

In an example the present photovoltaic device comprises a hole transport layer, wherein the hole transport layer is preferably selected from PEDOT-PSS, MoO<sub>x</sub>, NiO, V<sub>2</sub>O<sub>5</sub>, and combinations thereof.

In an example the present photovoltaic device comprises an electron transport layer, wherein the electron transport layer is preferably selected from LiF.

In an example the present photovoltaic device has a sequence of layers comprising one or more of an 20-200 nm anode layer, such as ITO, a 3-100 nm hole transport layer, such as MoO<sub>x</sub>, an 20-200 nm photovoltaic layer, such as an azomethine as disclosed in any of claims 1-6 and [70]PCBM, an 0.5-50 nm electron transport layer, such as LiF, and a 20-200 nm cathode layer, such as Al.

In a fifth aspect the present invention relates to a solar cell according to claim 13.

In a sixth aspect the present invention relates to a film according to claim 14. In an example the film may be applied as a coating for steel. Together with steel the coating may relate to an inverted organic solar cell.

In a seventh aspect the present invention relates to a sensor, such as for detecting an intensity and/or frequency of light, comprising a film according to the invention, or a photovoltaic molecule as disclosed in the invention.

5 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.

10 In a study inventors have synthesized two 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  
15 possess good charge transport properties. Besides that, both materials are readily available from commercial sources. 4,7-Bis(5-formylthiophen-2-yl)-2,1,3-benzothiadiazole (TBT, 2b) was used because it is found to have a large overlap with the solar spectrum, high mobilities and good film-forming abilities.  
20 The reaction was performed in chloroform and p-toluene sulfonic acid was used as a catalyst. The products (3a-b) were precipitated, and treated with diluted triethylamine to neutralize the azomethine bond. The small molecules were obtained in good yields (>80%) and characterized using  $^1\text{H}$  and  $^{13}\text{C}$  NMR,  
25 FTIR, and mass spectrometry where possible. The thermal properties of the new molecules were assessed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Both small molecules show excellent thermal stabilities with degradation temperatures ( $T_d^{5\%}$ ) above 350 °C. Comparing  
30 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 that both TPA-Th-TPA and TPA-TBT-TPA exhibit a glass transition temperature ( $T_g$ ) at 86 and  
35 114 °C, respectively. TPA-Th-TPA also showed a cold crystallization exotherm during the second heating at 143 °C. Both 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 rec-

orded in solution and in the solid state (Figure 2a) 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 both TPA-X-TPA small molecules. The push-pull character of TPA-TBT-TPA results in a large redshift (95 nm) of the absorption onset as compared to TPA-Th-TPA. In addition, TPA-TBT-TPA exhibits an extra absorption maximum at 400 nm, which was also observed in its vinyl analogue. The molecular extinction coefficients at the most red-shifted absorption maxima were calculated to be on the order of  $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . TPA-TBT-TPA displays the highest molar extinction coefficient (Table 1). 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.

Comparing the absorption maxima with those of their vinyl analogues, a redshift for TPA-Th-TPA was observed (21 nm), while TPA-TBT-TPA shows a 22 nm blue shift. Halochromatic behaviour was observed when the azomethine solutions were acidified. Photoluminescence spectra were measured both in the solid state and in solution. The photoluminescence is found to be very weak, which indicates fast non-radiative decay channels.

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 ( $>1.2 \text{ V}$ ) 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 highest occupied molecular orbital (HOMO) energy levels of the small molecules were determined by measuring the oxidation onset of the first oxidation and were found to be around  $-5.3 \text{ eV}$  below vacuum. The electron-donating triphenylamine moiety of the molecule is dominating the contributions to the HOMO energy level, explaining the similar HOMO energy levels (Table 1). The relatively deep HOMO energy levels are expected to result in a fairly high  $V_{oc}$  and good ox-

idative stability. The lowest unoccupied molecular orbital (LUMO) energy levels were estimated by combining the optical band-gap with the obtained HOMO energy level. The LUMO energy level, which is considered to be dominated by contributions from the electron accepting part of the molecules, was significantly lower for TPA-TBT-TPA as compared to TPA-Th-TPA (Table 1). 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.

PEDOT:PSS, which is most commonly used as the anode layer in OPVs, is acidic and could potentially protonate the azomethine functionality of the present small molecule azomethines. Density functional theory (DFT) calculations were carried out to study the effect of protonation of the azomethine linker. The calculations indicate that protonation breaks the symmetry and enforces localisation of the HOMO, and a lowering of the HOMO energy by approximately ~2 eV (Figure 2) while the LUMO level shows a downward shift in energy by more than 3 eV.

As protonation could limit the device performance, inventors compared the photovoltaic device characteristics of a device (ITO/PEDOT:PSS/TPA-TBT-TPA:[60]PCBM/LiF/Al) with a device where the acidic PEDOT:PSS was replaced by neutral molybdenum oxide ( $\text{MoO}_x$ ). Replacing PEDOT:PSS with  $\text{MoO}_x$  increases the efficiency from 0.35% to 0.42%, and an increase in voltage from 0.45 V to 0.68 V. Also a lower work function of  $\text{MoO}_x$  (between 5.3 and 5.7 eV while PEDOT:PSS is approximately 5.0 eV) was found. Annealing at 70 °C for 30 minutes further improved the device performance up to 0.65%; annealing at a temperature of 100 °C or higher destroyed the exemplary devices. The use of [70]PCBM resulted in an additional increase in efficiency, resulting in higher currents. The influence of the hole-blocking layer, annealing temperature and time, and type of fullerene were investigated for TPA-TBT-TPA and the optimal conditions were also used to prepare the TPA-Th-TPA devices (Table 2, Figure 3a). As expected from the absorption spectra, TPA-TBT-TPA, which has the smallest band-gap and thus the best overlap with the solar spectrum, shows a higher current. However, TPA-Th-TPA shows the best power conversion efficiency (PCE). The high open circuit voltages up to 0.83 V are in

agreement with the fairly low-lying HOMO energy levels. All devices show a strong voltage dependence, i.e. significantly higher currents were obtained under reverse bias. This indicates a low charge carrier mobility and/or a poor morphology. The poor fill factors also hint towards unbalanced charge transport, which is likely attributed to the limited mobility of azomethines when processed under these conditions. The vinyl analogues of TPA-Th-TPA and TPA-TBT-TPA show PCEs of 0.34% and 0.26%, respectively after optimization, which is significantly lower than 1.21% and 1.15% found for the present azomethine.

The external quantum efficiency (EQE) spectra of the devices coincide with the peaks in the absorption spectra of the small molecules (Figure 3b). Using [70]PCBM instead of [60]PCBM resulted in slight broadening of the absorption spectrum and an overall increase of the EQE to 30%. The absorption maximum around 310 nm was not observed in the EQE spectrum.

The film morphology of the small-molecule:[70]PCBM active layers was investigated using transmission electron microscopy (TEM). Both active layers show an amorphous film with PCBM islands on the order of 2-3 nm. These domains are relatively small; the use of a different solvent or a co-solvent might induce a stronger phase separation, which is expected to improve the device performance.

Condensation chemistry is found to be very convenient for the synthesis of conjugated small-molecule azomethines. Besides the molecular components and a suitable solvent no other reagents or catalysts are required and water is the only side product. To demonstrate the simplicity and ease of this chemistry, inventors prepared a device by spin-coating the reaction mixture without any form of workup or purification. For this 2,5-thiophenedicarboxaldehyde (2a, Th) and two equivalents of 4-aminotriphenylamine (1, TPA) were stirred overnight in dry chloroform at 60 °C. The next day the resulting deep orange solution was diluted to the required concentration and [70]PCBM was added prior to spin-coating the active layer. The device showed a PCE of 0.60%, demonstrating that "one-pot" synthesized azomethines can be used as donor material in organic photovoltaic devices (Table 2). The EQE spectrum of the

"one-pot" synthesized TPA-Th-TPA device coincides with that of the devices prepared using the conventional method, indicating that in both cases charge transfer from TPA-Th-TPA was obtained.

5 In conclusion, two conjugated small-molecule azomethines were synthesized via simple and cheap condensation chemistry. The small molecules both exhibit reversible oxidation behaviour, a fairly deep lying HOMO energy level, and a band-gap between 1.9 to 2.2 eV. Photovoltaic devices based on MoO<sub>x</sub> as the hole-transporting layer performed better when compared to PEDOT:PSS, which is mainly attributed to an increased voltage. Both small molecules showed efficiencies around 1.2% with [70]PCBM as the electron acceptor. TPA-Th-TPA performed slightly better (PCE of 1.21% with a J<sub>sc</sub> of 3.7 mA cm<sup>-2</sup>, V<sub>oc</sub> of 10 0.83 V, and FF of 39%) after post annealing. Both azomethine-based devices outperform their vinyl analogues, indicating that azomethines are promising candidates for organic photovoltaic applications. Inventors also demonstrated that this chemistry enables the fabrication of OPV devices directly from the reaction mixture without any product workup. These devices 20 showed a PCE of 0.6%. Because azomethine chemistry is easy, clean and proceeds under near ambient conditions we believe that this approach has the ability to reduce materials and production costs of organic photovoltaic devices.

25 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. 30

#### FIGURES

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

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

Fig. 2 shows UV-Vis absorption spectrum and computational study of the small molecules. 2a, Normalized UV-Vis absorption spectrum of TPA-X-TPA small molecules in

the solid state. 2b and 2c, DFT-calculated (CAM-B3LYP/6-31G\*) Kohn-Sham HOMO level for the TPA-Th-TPA molecule: 2b, Shows the small molecule in the neutral state where the HOMO is delocalized over the entire molecule. 2c, Protonation of the azomethine nitrogen-atom interrupts conjugation and enforces localization of the HOMO to the non-protonated part of the molecule.

Fig. 3 shows a device performance of small molecule BHJ solar cells. 3a, Current-voltage (J-V) characteristics and 3b, EQE spectra of small molecule bulk heterojunction solar cells based on TPA-X-TPA:[70]PCBM using MoO<sub>x</sub> as hole blocking layer after annealing.

Fig. 4 shows a TPA molecule with an optional group R. Fig. 5a-e show basic configurations of the small azomethine molecules.

#### 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 <sup>a</sup> |                                                                  | UV-vis film <sup>b</sup> |                                  | E <sub>g</sub><br>(eV) <sup>c</sup> | E <sub>exi.onset</sub><br>(V) | HOMO<br>(eV) <sup>d</sup> | LUMO<br>(eV) <sup>e</sup> |
|-------------|------------------------------|------------------------------------------------------------------|--------------------------|----------------------------------|-------------------------------------|-------------------------------|---------------------------|---------------------------|
|             | $\lambda_{\max}$ (nm)        | $\epsilon$ (M <sup>1</sup><br>cm <sup>-1</sup> 10 <sup>4</sup> ) | $\lambda_{\max}$ (nm)    | $\lambda_{\text{onset}}$<br>(nm) |                                     |                               |                           |                           |
| TPA-Th-TPA  | 306, 467                     | 3.6                                                              | 314, 463                 | 565                              | 2.19                                | 0.85                          | -5.32                     | -3.13                     |
| TPA-TBT-TPA | 306, 389, 520                | 5.6                                                              | 310, 400, 538            | 660                              | 1.88                                | 0.79                          | -5.26                     | -3.36                     |

<sup>a</sup> Measured in a quartz cuvette in dichloromethane.

<sup>b</sup> Spin cast on a quartz substrate from chloroform.

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

<sup>d</sup> Determined by cyclic voltammetry, with Fc/Fc<sup>+</sup> at 4.8 eV below vacuum.

<sup>e</sup> Estimated by subtracting the band-gaps from the HOMO energy levels.

Table 2. Summary of the characteristics of photovoltaic devices with ITO/MoO<sub>x</sub>/TPA-XTPA:[70]PCBM (1:2)/LiF/Al configuration after annealing at 70 °C.

| Compound                          | $J_{sc}(\text{mAcm}^{-2})^a$ | $V_{oc}(\text{V})$ | FF(%) | PCE(%) |
|-----------------------------------|------------------------------|--------------------|-------|--------|
| TPA-Th-TPAb                       | 3.73                         | 0.83               | 39    | 1.21   |
| TPA-TBT-TPAc                      | 4.50                         | 0.75               | 34    | 1.15   |
| TPA-Th-TPA (one-pot) <sup>b</sup> | 2.60                         | 0.75               | 31    | 0.60   |

5 <sup>a</sup>  $J_{sc}$  was calculated by integrating the EQE spectrum with the AM1.5G spectrum under bias.

<sup>b</sup>After annealing for 30 minutes.

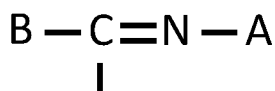
<sup>c</sup>After annealing for 5 minutes.

CLAIMS

1. Use of an azomethine molecule according to figure 5 in a photovoltaic application, the molecule comprising at least one aromatic entity (A) comprising

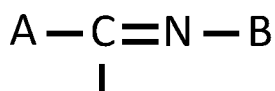
(Ai) at least one nitrogen atom directly attached to the aromatic entity (fig. 5a), or

(Fig. 5a)



(Aii) at least one carbon atom directly attached to the aromatic entity (fig. 5b),

(fig. 5b)



at least one aromatic heterocyclic 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 heterocyclic entity and to the nitrogen atom (fig. 5a), or

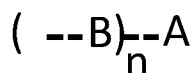
(Bii) (in case of Aii) at least one nitrogen atom directly attached the aromatic heterocyclic entity and to the carbon atom (fig. 5b), and

the molecule has a molecular mass of 300-3000,

wherein the molecule has an (A-B)<sub>n</sub>-A structure (fig.

5c),

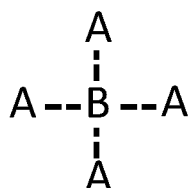
fig. 5c



or (B-A)<sub>n</sub>-B structure, wherein n∈[1-5],

or wherein the molecule has an A<sub>m</sub>-B structure (fig. 5d),

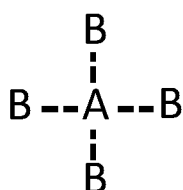
(fig. 5d)



wherein m∈[1-5],

or wherein the molecule has an B<sub>r</sub>-A structure (fig. 5e),

(fig. 5e)

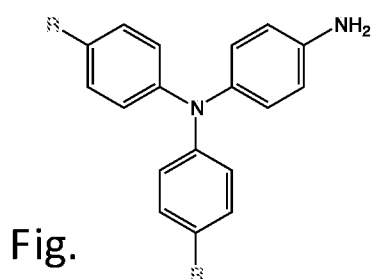


wherein  $r \in [1-5]$ , or combinations thereof.

2. Use of an azomethine according to any of the preceding claims, wherein the molecule has a molecular mass of 300-900.

3. Use of an azomethine according to any of the preceding claims, wherein the aromatic heterocyclic bridging entity comprises one or more of S, N, P, Si, Se and O.

4. Use of an azomethine according to any of the preceding claims, comprising at least one 4-aminotriphenyl-amine- $R_2$  (TPA) according to figure 4,



and

wherein the bridging entity 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.

5. Use of an azomethine according to claim 4, wherein R is independently selected from H, -CN, OAlk, Alk, and combinations thereof, and wherein Alk is selected from alkanes, and combinations thereof.

6. Photovoltaic azomethine as disclosed in any of claims 2-5.

7. Method of producing a photovoltaic molecule as disclosed in any of claims 1-6 comprising the steps of

- (i) condensing under suitable conditions at least one (hetero)aromatic entity (A) comprising
  - (Ai) at least one primary amine directly attached to the aromatic entity, or
  - (Aii) at least one aldehyde directly attached to the aromatic entity, and
  - at least one aromatic heterocyclic bridging entity

(B), the bridging and aromatic entity being capable of forming at least one N=C bond (azomethine), the bridging entity comprising

(Bi) (in case of Ai) at least one aldehyde directly attached to the aromatic heterocyclic entity, or

(Bii) (in case of Aii) at least one primary amine directly attached to the aromatic heterocyclic entity,

(ii) separating or directly applying the condensate,

before spin coating the condensate, adding an electron acceptor, thereby forming a solution,

wherein the solution is spin coated on a substrate, removing the solvent,

(iii) optionally washing the separated condensate, and annealing the condensate, wherein annealing is performed

at a temperature of 50-150 °C, for a period of time of 10-60 min.

8. Photovoltaic device comprising a photovoltaic molecule as disclosed in any of claims 1-6.

9. Photovoltaic device according to claim 8, comprising

a substrate,

an anode layer,

a bulk hetero junction layer comprising a photovoltaic molecule as disclosed in any of claims 1-6, and one or more of electron acceptor molecules, such as a copper phthalocyanine, a carbon fullerene, and fullerene derivative, such as [60]PCBM, [70]PCBM, and

a cathode layer.

10. Photovoltaic device according to any of claim 8-9,

wherein the substrate is selected from glass, silicon, steel, aluminium, silicon oxide, polymers, and combinations thereof, and/or

wherein the anode layer is selected from tin doped indium oxide (ITO), graphene, and fluorine doped tin oxide (FTO), and/or

wherein the cathode layer is optically transparent and selected from Al, Cu, Mg, Ba, ZnO, and Ca.

11. Photovoltaic device according to any of claims 8-

10, further comprising a hole transport layer, wherein the hole transport layer is preferably selected from PEDOT-PSS, MoO<sub>x</sub>, NiO, V<sub>2</sub>O<sub>5</sub>, and combinations thereof, an electron transport layer.

5           12. Photovoltaic device according to any of claims 8-11, having a sequence of layers comprising one or more of  
a 20-200 nm anode layer,  
a 3-100 nm hole transport layer,  
a 20-200 nm photovoltaic layer, comprising an azome-  
10 thine as disclosed in any of claims 1-6 and [70]PCBM,  
an 0.5-50 nm electron transport layer, and  
a 20-200 nm cathode layer.

13. Solar cell comprising a photovoltaic molecule as disclosed in any of claims 1-6 and/or a photovoltaic device  
15 according to any of claims 8-12.

14. Film comprising a photovoltaic molecule as disclosed in any of claims 1-6.

15. Sensor, such as for detecting an intensity and/or frequency of light, comprising a film according to claim 14,  
20 or a photovoltaic molecule as disclosed in any of claims 1-6.

## AMENDED CLAIMS

received by the International Bureau on 15 July 2015 (15.07.2015).

1. Use of a conjugated azomethine molecule having a definite molecular weight according to figure 5 in a photo-voltaic film application as an electron donor, the molecule comprising

5 at least one aromatic entity (A) comprising

(Ai) at least one nitrogen atom directly attached to the aromatic entity (fig. 5a), or



|

10 (Aii) at least one carbon atom directly attached to the aromatic entity (fig. 5b),



|

15 at least one aromatic heterocyclic 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 heterocyclic entity and to the nitrogen atom (fig. 5a), or

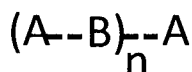
20 (Bii) (in case of Aii) at least one nitrogen atom directly attached the aromatic heterocyclic entity and to the carbon atom (fig. 5b), and

the molecule has a molecular mass of 300-3000,

wherein the molecule has an (A-B)<sub>n</sub>-A structure (fig.

25 5c),

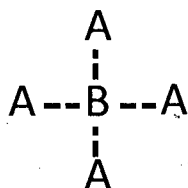
fig. 5c



or (B-A)<sub>n</sub>-B structure, wherein n<sub>e</sub>[1-5],

or wherein the molecule has an A<sub>m</sub>-B structure (fig. 5d),

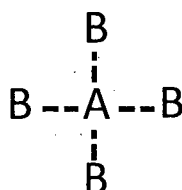
30 (fig. 5d)



wherein m<sub>e</sub>[1-5],

35 or wherein the molecule has an B<sub>r</sub>-A structure (fig. 5e),

(fig. 5e)



wherein  $r \in [1-5]$ , or combinations thereof,  
 wherein the aromatic entity A has a molecular mass of 64-1250  
 and has 1-4 aromatic ring structures,  
 5 wherein the aromatic heterocycle bridging entity B has a molecular mass of 65-1500 and independently has 1-4 aromatic ring structures, and  
 wherein the aromatic heterocyclic bridging entity comprises one or more of S, N, P, Si, Se and O.

10 2. Use of an azomethine according to any of the preceding claims, wherein the molecule has a molecular mass of 300-750.

3. Use of an azomethine according to any of the preceding claims, wherein B is selected from a furan, a thiophene, a phosphole, a silole, an azole, such as an imidazolidine, an imidazole, a pyrazole, an (is)oxazolidine, an (is)oxazole, a (iso)thiasolidine, an (iso)thiazole, a pyridine, an oxane, a pyran, a thiane, a thiopyran, a phosphinine, a diazine, an oxazine, a thiazine, a dithiane, a triazine, a thiopine, a diazepine, and a thiazepine, and combinations thereof.

4. Use of an azomethine according to any of the preceding claims, wherein the molecule has an  $(A-B)_n-A$  structure (fig. 5c) or  $(B-A)_n-B$  structure, wherein  $n \in [1-3]$ , or wherein the molecule has an  $A_m-B$  structure (fig. 5d), wherein  $m \in [1-3]$ , or wherein the molecule has an  $B_r-A$  structure (fig. 5e), wherein  $r \in [1-3]$ , or combinations thereof, preferably A-B-A, A-B, B-A-B,  $A_3B$ ,  $B_3A$ , A-B-A-B and A-B-A-B-A type molecules.

5. Use of an azomethine according to any of the preceding claims, comprising at least one 4-aminotriphenylamine- $R_2$  (TPA) according to figure 4,

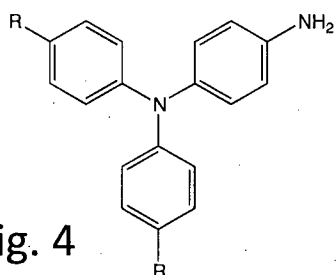


Fig. 4

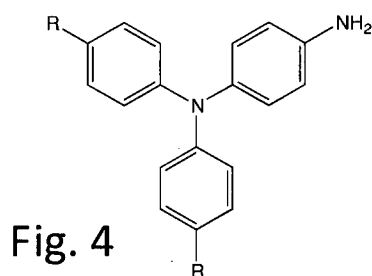
and

wherein the bridging entity 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,

wherein R is independently selected from H, -CN, OAlk, Alk, and combinations thereof, and wherein Alk is selected from alkanes, and combinations thereof.

6. Photovoltaic conjugated azomethine having a definite molecular weight as disclosed in any of claims 1-5, comprising at least one 4-aminotriphenyl-amine-R<sub>2</sub> (TPA) according to figure 4,



and wherein 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,

wherein R is independently selected from H, -CN, OAlk, Alk, and combinations thereof, and wherein Alk is selected from alkanes, and combinations thereof.

7. Method of producing a conjugated photovoltaic azomethine molecule as disclosed in any of claims 1-6 comprising the steps of

- (i) condensing under suitable conditions at least one (hetero)aromatic entity (A) comprising
  - (Ai) at least one primary amine directly attached to the aromatic entity, or
  - (Aii) at least one aldehyde directly attached to the aromatic entity, and
- at least one aromatic heterocyclic bridging entity (B), the bridging and aromatic entity being

capable of forming at least one N=C bond (azomethine), the bridging entity comprising

(Bi) (in case of Ai) at least one aldehyde directly attached to the aromatic heterocyclic entity, or

(Bii) (in case of Aii) at least one primary amine directly attached to the aromatic heterocyclic entity,

(ii) directly applying the condensate into a film onto a substrate, such as by spin coating,

before applying the condensate, adding an electron acceptor, thereby forming a solution,

wherein the solution is applied as a film on a substrate,

removing the solvent,

(iii) optionally washing the separated condensate, and

annealing the condensate, wherein annealing is performed at a temperature of 50-150 °C, for a period of time of 10-60 min.

8. Photovoltaic device comprising a photovoltaic film as disclosed in any of claims 1-6.

9. Photovoltaic device according to claim 8, comprising

a substrate,

an anode layer,

a bulk hetero junction layer comprising a photovoltaic molecule as electron donor as disclosed in any of claims 1-6, and one or more of electron acceptor molecules, such as a copper phthalocyanine, a carbon fullerene, and fullerene derivative, such as [60]PCBM, [70]PCBM, and

a cathode layer.

10. Photovoltaic device according to any of claim 8-9,

wherein the substrate is selected from glass, silicon, steel, aluminium, silicon oxide, polymers, and combinations thereof, and/or

wherein the anode layer is selected from tin doped indium oxide (ITO), graphene, and fluorine doped tin oxide (FTO), and/or

wherein the cathode layer is optically transparent and selected from Al, Cu, Mg, Ba, ZnO, and Ca.

11. Photovoltaic device according to any of claims

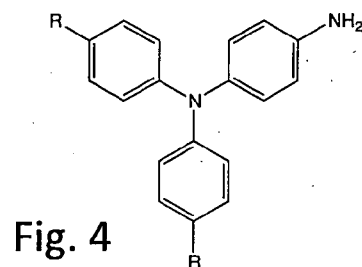
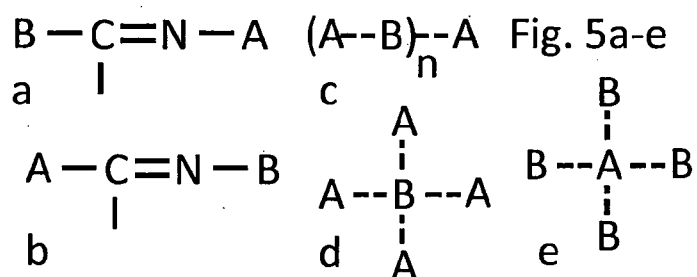
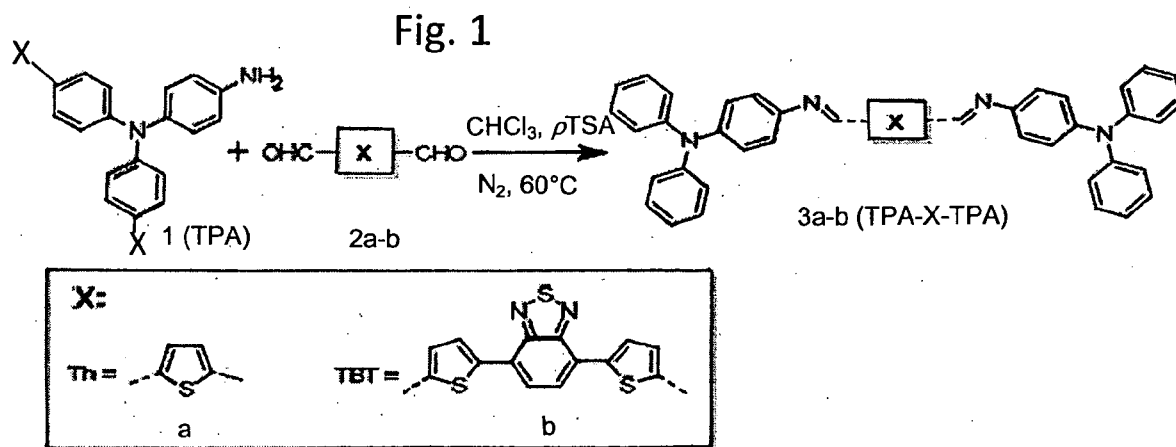
8-10, further comprising a hole transport layer, wherein the hole transport layer is preferably selected from PEDOT-PSS, MoO<sub>x</sub>, NiO, V<sub>2</sub>O<sub>5</sub>, and combinations thereof, an electron transport layer.

- 5           12. Photovoltaic device according to any of claims 8-11, having a sequence of layers comprising one or more of  
a 20-200 nm anode layer,  
a 3-100 nm hole transport layer,  
a 20-200 nm photovoltaic layer, comprising an azome-  
10 thine as disclosed in any of claims 1-6 and [70]PCBM,  
an 0.5-50 nm electron transport layer, and  
a 20-200 nm cathode layer.

- 15           13. Solar cell comprising a photovoltaic molecule as disclosed in any of claims 1-6 and/or a photovoltaic device according to any of claims 8-12.

14. Film comprising a photovoltaic molecule as disclosed in any of claims 1-6.

- 20           15. Sensor for detecting an intensity and/or frequency of light, comprising a film according to claim 14, or a photovoltaic molecule as disclosed in any of claims 1-6.



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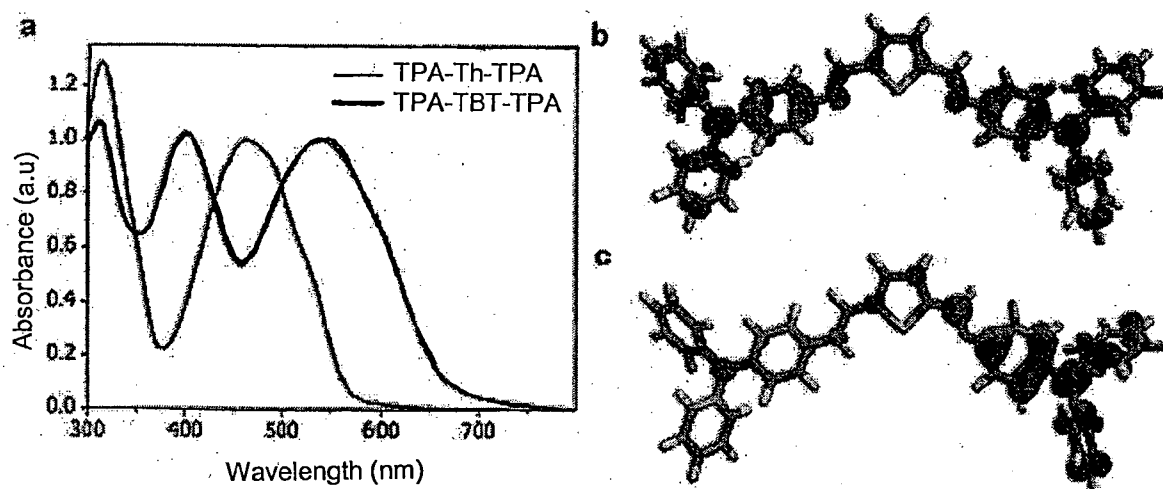


Fig. 2

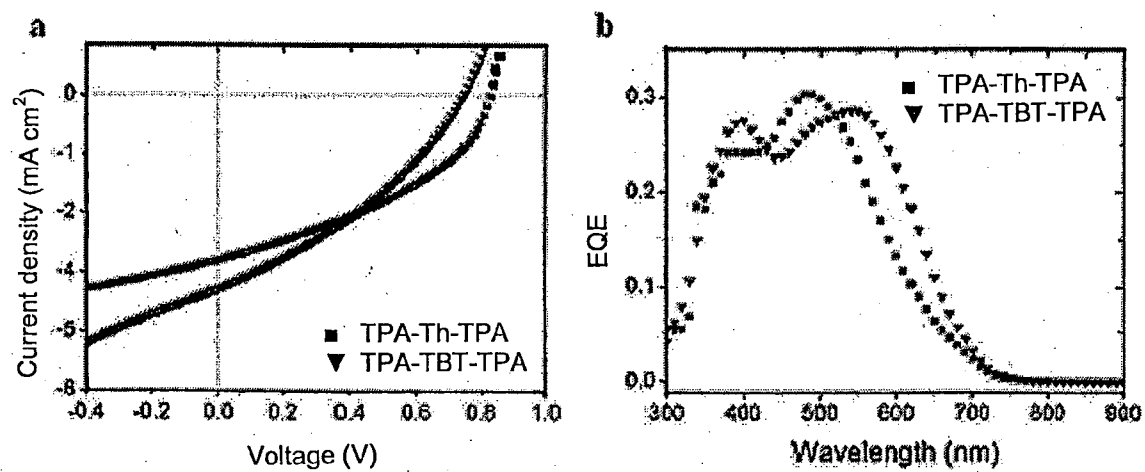


Fig. 3

# INTERNATIONAL SEARCH REPORT

International application No

PCT/NL2015/050172

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C07D333/22 C07D417/14 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)

C07D

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

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

EPO-Internal, CHEM ABS Data, WPI Data, BEILSTEIN Data

## C. 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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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

6 May 2015

Date of mailing of the international search report

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| X         | <p>DATABASE CA [Online]<br/>CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US;<br/>2009,<br/>IWAN, AGNIESZKA ET AL: "Mesomorphic behavior of symmetrical and unsymmetrical azomethines with two imine groups", XP002732317, retrieved from STN<br/>Database accession no. 2009:892480 the abstract; and the compounds with the Registry Numbers: [1270950-24-7] en [1270950-25-8]<br/>&amp; IWAN, AGNIESZKA ET AL: "Mesomorphic behavior of symmetrical and unsymmetrical azomethines with two imine groups", MATERIALS , 2(1), 38-61 CODEN: MATEG9; ISSN: 1996-1944 URL: <a href="http://www.mdpi.com/1996-1944/2/1/38/PDF">HTTP://WWW.MDPI.COM/1996-1944/2/1/38/PDF</a>, 2009, DOI: 10.3390/MA2010038 10.3390/MA2010038</p> <p>-----</p> <p style="text-align: center;">-/--</p> | 6,7                   |

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