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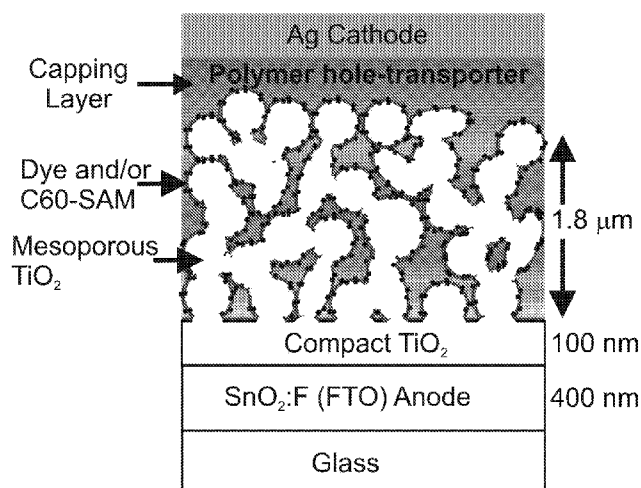


Figure 4. Schematic diagram of a polymer based hybrid solar cell, illustrating either dye-sensitization, surface modification with a C₆₀-SAM, or the combined mixed monolayer.

(57) Abstract: The present invention provides for a solid-state p-n heterojunction comprising an organic polymeric p-type material in contact with a porous layer of n-type material, characterised in that the boundary between the p-type layer and the n-type layer is functionalised with at least a partial monolayer of functionalised electron acceptor moieties and optionally sensitizing agents. The invention also provides devices such as solar cells and photodetectors comprising such heterojunctions and well as methods for making the same.



Optoelectronic Device

The present invention relates to a solid-state p-n heterojunction and to its use in optoelectronic devices, in particular in solid-state solar cells (SSCs), phototransistors and corresponding light sensing devices. Most particularly, the present invention relates to optoelectronic devices having a polymeric hole transporting material and especially polymeric hole transporters which absorb light.

The junction of an n-type semiconductor material (known as an electron transporter) with a p-type semiconductor material (known as a hole-transporter) is perhaps the most fundamental structure in modern electronics. This so-called "p-n heterojunction" forms the basis of most modern diodes, transistors and related devices including opto-electronic devices such as light emitting diodes (LEDs), photovoltaic cells, phototransistors, and electronic photo-sensors.

A realization of the pressing need to secure sustainable future energy supplies has led to a recent explosion of interest in photovoltaics (PV). Conventional semiconductor based solar cells are reasonably efficient at converting solar to electrical energy. However, it is generally accepted that further major cost reductions are necessary to enable widespread uptake of solar electricity generation, especially on a larger scale. Solid-state solar cells such as dye-sensitized solar cells (DSCs) and Polymer Oxide Solar Cells (POSCs) offer a promising solution to the need for low-cost, large-area photovoltaics.

Typically, currently known DSCs are composed of mesoporous TiO_2 (electron transporter) sensitized with a light-absorbing molecular dye, which in turn is contacted by a redox-active hole-transporting medium (electrolyte). Photo-excitation of the sensitizer leads to the transfer (injection) of electrons from the excited dye into the conduction band of the TiO_2 . These photo-generated electrons are subsequently transported to and collected at the anode. The oxidized dye is regenerated via hole-transfer to the redox active medium with the holes being transported through this medium to the cathode.

The most efficient DSCs are composed of TiO_2 in combination with a redox active liquid electrolyte, or a "gel" type semi-solid electrolyte. Those incorporating an

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iodide/triiodide redox couple in a volatile solvent can convert over 12% of the solar energy into electrical energy. However, this efficiency is far from optimum. Even the most effective sensitizer/electrolyte combination which uses a ruthenium complex with an iodide/triiodide redox couple sacrifices approx. 600 mV in order to drive the dye regeneration/iodide oxidation reaction. Furthermore, such systems are optimised to operate with sensitizers which predominantly absorb in the visible region of the spectrum thereby losing out on significant photocurrent and energy conversion. Even in the most efficiently optimised liquid electrolyte-based DSCs, photons which are not absorbed between 600 and 800 nm amount to an equivalent of 7 mA/cm² loss in photocurrent under full sun conditions. Other problems with the use of liquid electrolytes are that these are corrosive and often prone to leakage, factors which become particularly problematical for larger-scale installations or over longer time periods.

More recent work has focused on creating gel or solid-state electrolytes, or entirely replacing the electrolyte with a solid-state molecular hole-transporter, which transports the charge by movement of electrons rather than electrolytes, which rely on movement of ions. Solid phase organic hole-transporters are much more appealing for large scale processing and durability due to their lack of corrosive properties and saving in potential by avoiding the need to drive the redox couple. However, there are a number of obstacles that need to be overcome if organic hole transporting materials can be used efficiently.

Polymeric organic hole transporters offer the potential of high efficiency charge transfer but are considered to be of limited application because it is difficult to cause the polymer to penetrate and fill the porous network of the n-type material (such as mesoporous metal oxide). As a result various workarounds have been proposed, such as the use of monomers that can be polymerised within the device after incorporation and the use of a molecular hole-transporters which dissolve to provide low viscosity solutions and can be incorporated readily into the device.

Since the amount of energy available in a solar cell is fundamentally limited by the amount of solar energy absorbed, it is desirable that the device absorb over a broad range of frequencies. Polymer hole transporters frequently absorb significant amounts of the incident light falling on a solar cell or similar optoelectronic device.

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However there is rarely any measurable current generated by this absorption. The light absorbed by the polymer is therefore, at best, useless and if the absorption of the polymer and the sensitizer overlap then this competition for absorption between the sensitizer and the polymer will reduce efficiency. An efficient polymer-oxide solar cell might utilise the absorption of the polymer itself to perform at least part of the light-harvesting function and ideally would either achieve a broad spectrum of absorption from the polymer or would combine polymer absorption with a sensitizer to maximise light harvesting. However, at present, no known polymer oxide optoelectronic device has achieved any significant photocurrent due to absorption of light by the polymer.

In view of the above, it would be a valuable contribution to the art to provide a means by which the light absorption of the polymer in a polymer/oxide type heterojunction device could be converted into useful current from the device. This would apply both in situations where the polymer was the sole or primary sensitising agent in the device and in devices which additionally incorporated an additional sensitizing agent.

The present inventors have now unexpectedly established that by using certain electron accepting moieties and particularly by functionalising these so that they can be formed into at least a partial monolayer at the interface between the polymer (p-type) material and the n-type material, a significant enhancement of photocurrent can be observed, attributable to photons absorbed by the polymer and transferred to the n-type material by means of the acceptor moieties at the interface.

In a first aspect, the present invention therefore provides a solid-state p-n heterojunction comprising an organic polymeric p-type material in contact with a porous layer of n-type material, characterised in that the boundary between the p-type layer and the n-type layer is functionalised with at least a partial monolayer of functionalised electron acceptor moieties and optionally sensitizing agents. Such a p-n heterojunction will typically be sensitised by at least one sensitizing agent.

Typical electron acceptor moieties as indicated above will comprise at least one 2-dimensional or 3-dimensional network of carbon atoms, optionally including up to 10% of heteroatoms, functionalised by at least one organic group having affinity for

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the n-type material surface. Such moieties will typically have molar masses between 200 and 10000 g/mol. Fullerenes are preferred.

All references to a heterojunction herein may be taken to refer equally to an optoelectronic device, including referring to a solar cell or to a photo-detector where context allows. Similarly, while solid-state polymer-oxide solar cells are frequently used herein as illustration, it will be appreciated that such heterojunctions may equally be applied to other corresponding optoelectronic devices including all those described in all sections herein.

Generally in all heterojunctions and devices as well as all other aspects of the invention indicated herein, the organic p-type material will preferably be an organic polymer, more preferably a conducting polymer or a semi-conducting polymer. The categories of polymer and individual polymers indicated herein are particularly suitable.

A particularly suitable application of the heterojunctions of the present invention (as well as applying to all other aspects of the invention) is in optoelectronic devices. In a further aspect, the present invention therefore provides an optoelectronic device comprising at least one solid state p-n heterojunction as indicated in any embodiment of the present invention and/or formable by any indicated method. Most appropriate optoelectronic devices include all those indicated herein, such as photo-detectors, photo-transistors, solid-state polymer-oxide solar cells, solid state dye sensitised solar cells and/or solid state polymer sensitised solar cells.

In a further embodiment, the present invention additionally provides the use of at least a partial monolayer of functionalised electron acceptor moieties and optionally sensitizing agents to enhance the efficiency of a solid state polymer solar cell, where the electron acceptor is preferably as defined herein. Such a use will generally be to increase the electron transfer from the polymer to the n-type layer, as described above.

A further aspect of the present invention lies in a method for the manufacture of a solid-state p-n heterojunction comprising an organic p-type material in contact with a porous layer of n-type material, said method characterised by;

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- a) coating an anode, preferably a transparent anode (e.g. a Fluorine doped Tin Oxide - FTO anode) with a compact layer of an n-type semiconductor material (such as any of those described herein);
- 5 b) forming a porous (preferably mesoporous) layer of an n-type semiconductor material (such as any of those described herein) on said compact layer,
- c) forming at least a partial monolayer of functionalised electron acceptor moieties (as described herein) and optionally sensitizing agents on the surface of the porous n-type layer;
- 10 d) optionally treating said compact layer and/or said porous layer of n-type material with at least one ionic material such as a lithium salt.
- e) optionally forming a porous barrier layer of an insulating material on said porous layer of n-type material;
- f) contacting said porous layer of n-type material with at least one solution of
- 15 at least one polymeric organic p-type semiconductor material whereby to form a layer of polymeric organic p-type semiconductor interpenetrating the said porous layer of an n-type material;
- f2) optionally treating said layer produced in "f" by coating on top with a solution of ionic material, such as Li-TFSI.
- 20 g) forming a cathode, preferably a metal cathode (e.g. a silver or gold cathode) in contact with said p-type semiconductor material.

Without being bound by theory, it is believed that the use of an ionic material, such as a lithium salt at step d) enhances the generation of an electrically continuous

25 layer of p-type material over the pore-surface within the n-type material. It is therefore preferable that step d) is included. It is more preferable that the ionic material in step d) be a lithium salt and still more preferable that this be Li-TFSI or an analogue or derivative thereof (including any indicated in any section of this application). Devices formed or formable from any of the heterojunctions of the

30 invention or by any of the methods, uses or process of the invention evidently also form additional aspects of the invention in themselves.

In a particularly preferred embodiment optional step d) comprises treating said compact layer and/or said porous layer of n-type material with a mixture of at least

35 two ionic materials. Suitable ionic materials preferably include metal salts

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(especially lithium salts such as lithium bis(trifluoromethylsulfonyl)imide lithium salt) in combination with ionic liquids (such as, 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide).

5 In all aspects and embodiments of the present invention, the term "ionic liquid" is used to indicate an ionic species with a melting point sufficiently low for convenient processing in the formation of the heterojunctions and devices of the invention. Many suitable low melting-point salts are known and in one embodiment, salts having a melting point of 100°C or lower are preferable. Salts having a melting
10 point of below 50°C or even below room temperature may be preferably used. Some suitable ionic liquids, including 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide have a melting point below 0°C. Highly preferable ionic liquids include those selected from 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Butyl-3-methylimidazolium
15 bis(trifluoromethylsulfonyl)imide, 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1,3-Dihydroxy-2-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1,3-Dimethoxy-2-methylimidazolium bis(trifluoromethylsulfonyl)imide and mixtures thereof.

20 The functioning of a polymer oxide solar cell relies initially on the collection of solar light energy in the form of capture of solar photons by the polymer and/or by an additional sensitizer (typically a molecular, metal complex, or polymer dye). The effect of the light absorption is to raise an electron into a higher energy level in the
25 polymer and/or sensitizer. This excited electron will eventually decay back to its ground state, but in a solar cell, the n-type material in close proximity to the excited material provides an alternative (faster) route for the electron to leave its excited state, viz. by "injection" into the n-type semiconductor material. This injection can be direct or via an intermediate material but in all cases results in a charge
30 separation, whereby the n-type semiconductor has gained a net negative charge and the polymer has gained a net positive charge. Where a sensitizer or injecting material is present this may initially take the positive charge but it will rapidly be passed to the polymer charge carrier. This serves to "regenerate" the dye or portion of the polymer close to the heterojunction by passing the positive charge
35 ("hole") on through the p-type semiconductor material of the junction (the "hole

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transporter"). In a solid state polymer oxide device, this hole transporter is in direct contact with the n-type material and/or sensitizer material, while in the more common electrolytic dye sensitised photocells, a redox couple (typically iodide/triiodide) serves to regenerate a dye and transports the "hole species" (triiodide) to the counter electrode. Once the electron is passed into the n-type material, it must then be transported away, with its charge contributing to the current generated by the solar cell.

While the above is a simplified summary of the ideal working of a polymer oxide solar cell, there are certain processes which occur in any practical device in competition with these desired steps and which serve to decrease the conversion of sunlight into useful electrical energy. Decay of the sensitizer back to its ground state was indicated above, but in addition to this, there is the natural tendency of two separated charges of opposite sign to re-combine. This can occur by return of the electron into a lower energy level of the sensitizer, or by recombination of the electron directly from the n-type material to quench the hole in the p-type material. In an electrolytic DSC, there is additionally the opportunity for the separated electron to leave the surface of the n-type material and directly reduce the iodide/iodine redox couple. Evidently, each of these competing pathways results in the loss of potentially useful current and thus a reduction in cell energy-conversion efficiency. It is therefore essential that each of the desired steps occurs at a rate which is considerably faster than the competing undesirable processes to avoid wasting potentially useful energy. It is also important that there is not too much of a disparity in the speeds of the various steps since a fast step followed by a slow step can lead to a build-up of a short-lived intermediate material which may then follow an energy-wasteful path. Thus it is particularly critical that the polymer hole-transporter is capable of effectively carrying charge away from the site of generation.

A schematic diagram indicating a typical structure of the solid-state DSC is given in attached Figure 1a and a diagram indicating some of the key steps in electrical power generation from a polymer oxide solar cell is given in attached Figure 1b .

Polymer-oxide solar cells, composed of mesoporous metal oxide electrodes infiltrated with (optionally light absorbing) semiconducting polymers and optionally

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also dye materials, have the potential to deliver high power conversion efficiencies while being compatible with low cost large area chemical processing. However, until recently solar-to-electrical power conversion efficiencies have remained below 1%. For efficient solar cell operation, a suitable fraction of sun light needs to be absorbed in the photoactive layer, excitons formed in the dye and/or polymer need to be ionised at the polymer-oxide heterojunction, and the photo-generated charges need to be separated and carried out of the solar cell to their respective electrodes. The latter requires effective percolation for both charge carriers, electrons and holes, in the oxide and polymer phases respectively. The two main issues thought to be responsible for the relatively poor operation of polymer-oxide solar cells have been an inability to effectively infiltrate semiconducting polymers into random porous networks and ineffective charge transport within the polymer phase due to non-crystalline, un-orientated polymer chains. As noted above, however, there has not previously been any significant contribution to the photocurrent of the device from the light absorbed in the polymer and this has the potential to dramatically improve the efficiency of such a cell.

A measure of the degree to which a p-type material such as a hole-transporting polymer fills the voids within the n-type material is the "pore filling fraction" (PFF). This relates the total volume of the pores to that volume occupied by the p-type material. It is widely believed and reported in the literature that polymeric hole transporters cannot achieve a sufficient filling of the pores of an n-type material. Consequently, various methods have been proposed to overcome this limitation. Methods for overcoming a low PFF with polymeric p-type materials include the use of in-situ polymerisation (e.g. Liu *et al.* Adv. Mater. 22 E1-E6 (2010)) or use of non-polymerised alternatives such as molecular hole transporters (Snaith H. J., Humphry-Baker R., Chen P., Cesar I., Zakeeruddin S. M., Gratzel M., Nanotechnology 2008, 19.). Evidently, polymerisation *in situ* requires additional processing steps at the manufacturing stage and it is yet to be determined whether materials which are activated to polymerise under irradiation can withstand full sun conditions for a potential lifetime of many years. Similarly, although molecular hole transporting material has a great deal of promise, an optimised polymeric p-type material should be capable of faster hole transport with lower resistance. In the present invention, high pore-filling fractions may be used but are not believed essential for the functioning of the invention and thus in one embodiment, PFFS of

50% or less are acceptable. In an alternative embodiment, the PFF will be greater than 50%, e.g 55% to 99%.

In one key embodiment of the present invention the light absorption is provided by the polymeric p-type material and no additional sensitizer is necessary. In such an embodiment, the at least partial monolayer at the interface of the n-type and p-type materials need only comprise functionalised electron absorbing moieties as described herein.

In alternative embodiment, one or more further sensitizers may be used in addition to the absorption of the polymer in the devices of the present invention. These may be used to increase the total absorption (for example in a thin device where the polymer may not absorb completely) or to broaden the spectrum over which light is absorbed. Where a "cascade" of sensitizers of this type is used then it is desirable that there be at least some overlap between the emission spectrum of a first dye and the absorption spectrum of a second so that a "resonance energy transfer" type effect may occur.

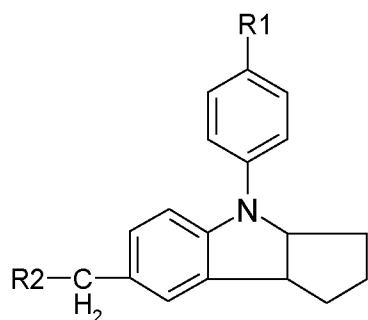
Sensitizers may be chosen, for example, to act as one or more intermediaries serving to aid in transferring the excitation energy from the polymer and complete the charge separation and "injection". However, since in the present invention this function is carried out by the functionalised electron acceptor moieties described herein, it is preferable that any dye or sensitizer present does not serve to aid in transferring the excitation energy from the polymer

The most commonly used light sensitising materials in electrolytic DSCs are organic or metal-complexed dyes. These have been widely reported in the art and the skilled worker will be aware of many existing sensitizers, all of which are suitable in all appropriate aspects of the invention and consequently are reviewed here only briefly.

- 5 A common category of organic dye sensitizers are indolene based dyes, of which D102, D131 and D149 (shown below) are particular examples.

The general structure of indolene dyes is that of Formula SI below:

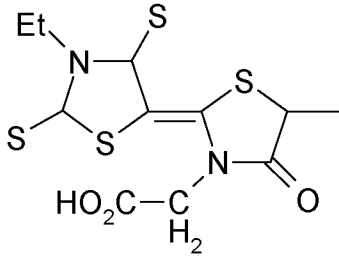
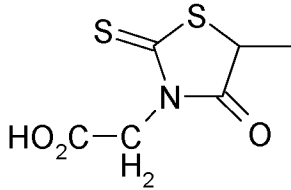
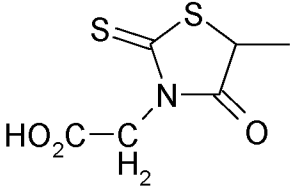
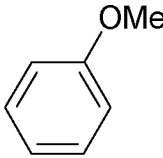
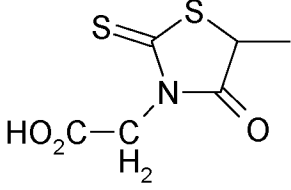
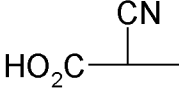
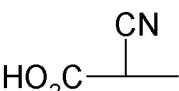
- 10 -



Formula sl

wherein R1 and R2 are independently optionally substituted alkyl, alkenyl, alkoxy,
 5 heterocyclic and/or aromatic groups, preferably with molecular weight less than
 around 360 amu. Most preferably, R1 will comprise aralkyl, alkoxy, alkoxy aryl and/
 or aralkenyl groups (especially groups of formula $C_xH_yO_z$ where x, y and z are each
 0 or a positive integer, $x+z$ is between 1 and 16 and y is between 1 and $2x+1$)
 including any of those indicated below for R1, and R2 will comprise optionally
 10 substituted carbocyclic, heterocyclic (especially S and/or N-containing heterocyclic)
 cycloalkyl, cycloalkenyl and/or aromatic groups, particularly those including a
 carboxylic acid group. All of the groups indicated below for R2 are highly suitable
 examples. One preferred embodiment of R2 adheres to the formula $C_xH_yO_zN_vS_w$
 where x, y, z, v and w are each 0 or a positive integer, $x+z+w+v$ is between 1 and
 15 22 and y is between 1 and $2x+v+1$. Most preferably, $z \geq 2$ and in particular, it is
 preferable that R2 comprises a carboxylic acid group. These R1 and R2 groups
 and especially those indicated below may be used in any combination, but highly
 preferred combinations include those indicated below:

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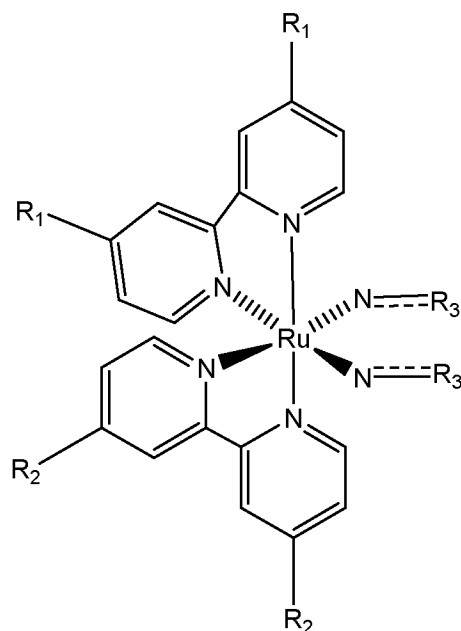
Dye Name	R ₁	R ₂
D ₁₄₉	Ph ₂ C=CH	
D ₁₀₂	Ph ₂ C=CH	
D ₇₇	OMe	
D ₁₀₃		
D ₁₃₁	Ph ₂ C=CH	
D ₁₂₀	OMe	

5

Indolene dyes are discussed, for example, in Horiuchi et al. J Am. Chem. Soc. **126** 12218-12219 (2004), which is hereby incorporated by reference.

10 A further common category of sensitizers are ruthenium metal complexes, particularly those having two bipyridyl coordinating moieties. These are typically of formula sII below

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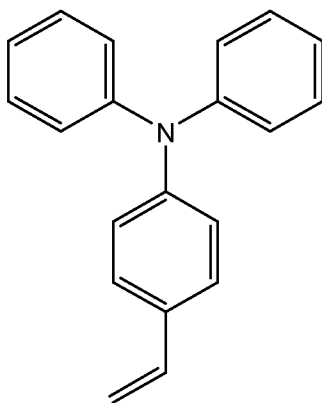


Formula sII

wherein each R1 group is independently a straight or branched chain alkyl or oligo alkoxy chain such as C_nH_{2n+1} where n is 1 to 20, preferably 5 to 15, most preferably 9, 10 or 11, or such as $C(-XC_nH_{2n-})_m-XC_pH_{2p+1}$, where n is 1, 2, 3 or 4, preferably 2, m is 0 to 10, preferably 2, 3 or 4, p is an integer from 1 to 15, preferably 1 to 10, most preferably 1 or 7, and each X is independently O, S or NH, preferably O; and wherein each R2 group is independently a carboxylic acid or alkyl carboxylic acid, or the salt of any such acid (e.g. the sodium, potassium salt etc) such as a $C_nH_{2n}COOY$ group, where n is 0, 1, 2 or 3, preferably 0 and Y is H or a suitable metal such as Na, K, or Li, preferably Na; and wherein each R3 group is single or double bonded to the attached N (preferably double bonded) and is of formula CH_a-Z or $C=Z$, where a is 0, 1 or 2 as appropriate, Z is a hetero atom or group such as S, O, SH or OH, or is an alkyl group (e.g. methylene, ethylene etc) bonded to any such a hetero atom or group as appropriate; R3 is preferably $=C=S$.

A preferred ruthenium sensitizer is of the above formula sII, wherein each R1 is nonyl, each R2 is a carboxylic acid or sodium salt thereof and each R3 is double-bonded to the attached N and of formula $=C=S$. R1 moieties of formula sII may also be of formula sIII below:

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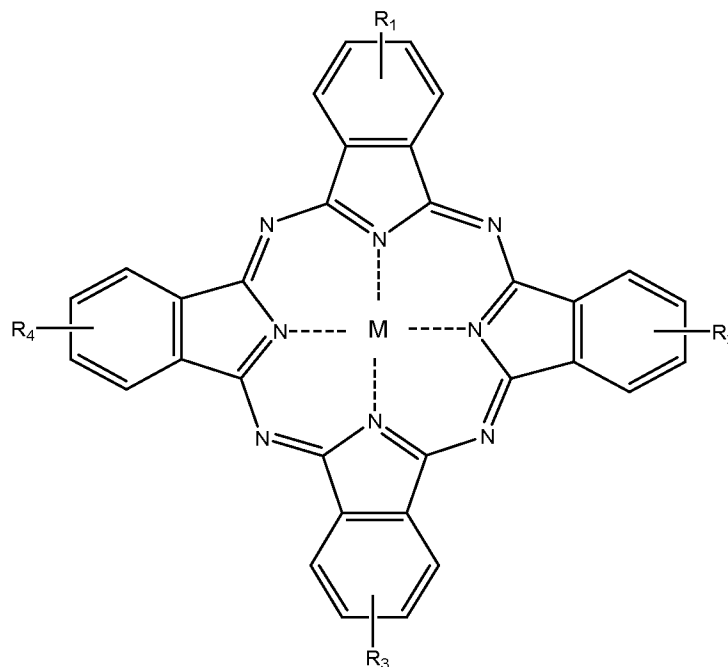
Formula sIII

5 Ruthenium dyes are discussed in many published documents including, for example, Kuang et al. Nano Letters **6** 769-773 (2006), Snaith et al. Angew. Chem. Int. Ed. **44** 6413-6417 (2005), Wang et al. Nature Materials **2**, 402-498 (2003), Kuang et al. Inorganica Chimica Acta **361** 699-706 (2008), and Snaith et al. J Phys, Chem. Lett. **112** 7562-7566 (2008), the disclosures of which are hereby incorporated herein by reference, as are the disclosures of all material cited herein.

10

Other sensitizers which will be known to those of skill in the art include Metal-Phthalocyanine complexes such as zinc phthalocyanine PCH001, the synthesis and structure of which is described by Reddy *et al.* (Angew. Chem. Int. Ed. **46** 373-376 (2007)), the complete disclosure of which (particularly with reference to Scheme 1),
15 is hereby incorporated by reference.

Some typical examples of metal phthalocyanine dyes suitable for use in the present invention include those having a structure as shown in formula sIV below:

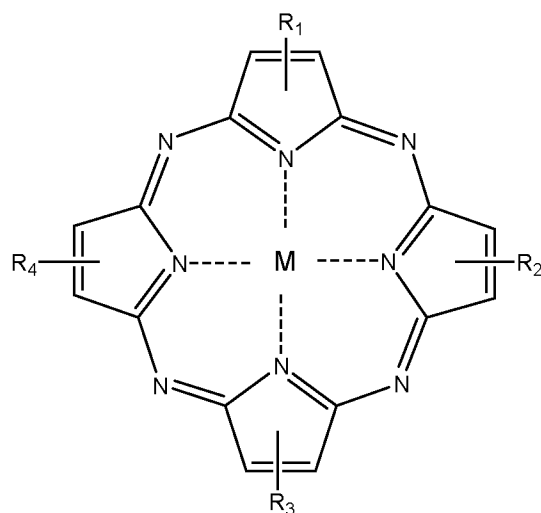


Formula sIV

Wherein M is a metal ion, such as a transition metal ion, and may be an ion of Co, Fe, Ru, Zn or a mixture thereof. Zinc ions are preferred. Each of R1 to R4, which
 5 may be the same or different is preferably straight or branched chain alkyl, alkoxy, carboxylic acid or ester groups such as C_nH_{2n+1} where n is 1 to 15, preferably 2 to 10, most preferably 3, 4 or 5, with butyl, such as tertiary butyl, groups being particularly preferred, or such as OX or CO_2X wherein X is H or a straight or
 10 branched chain alkyl group of those just described. In one preferred option, each of R1 to R3 is an alkyl group as described and R4 is a carboxylic acid CO_2H or ester CO_2X , where X is for example methyl, ethyl, iso- or n-propyl or tert-, iso-, sec- or n-butyl. For example, dye TT1 takes the structure of formula sIV, wherein R1 to R3 are t-butyl and R4 is CO_2H .

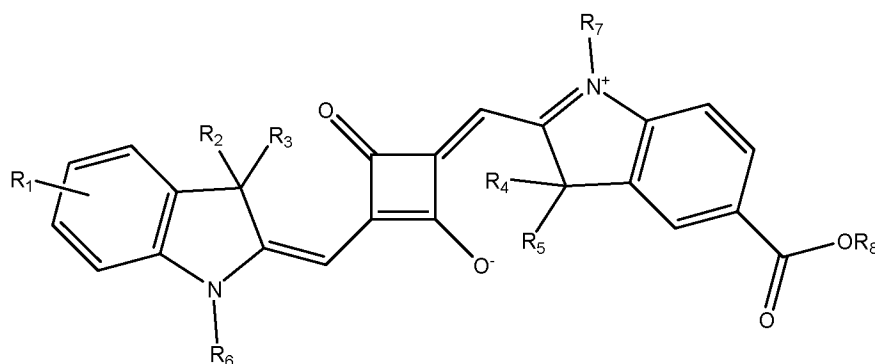
15 Further examples of suitable categories of dyes include Metal-Porphyrin complexes, Squaraine dyes, Thiophene based dyes, fluorine based dyes, molecular dyes and polymer dyes. Examples of Squaraine dyes may be found, for example in Burke et al., *Chem. Commun.* **2007**, 234, and examples of polyfluorene and polythiophene polymers in McNeill et al., *Appl. Phys. Lett.* **2007**, 90, both of which
 20 are incorporated herein by reference. Metal porphyrin complexes include, for example, those of formula sV and related structures, where each of M and R1 to R4 can be any appropriate group, such as those specified above for the related phthalocyanine dyes:

- 15 -



Formula sV

- 5 Squaraine dyes form a preferred category of dye for use in the present invention. The above Burke citation provides information on Squaraine dyes, but briefly, these may be, for example, of the following formula sVI



Formula sVI

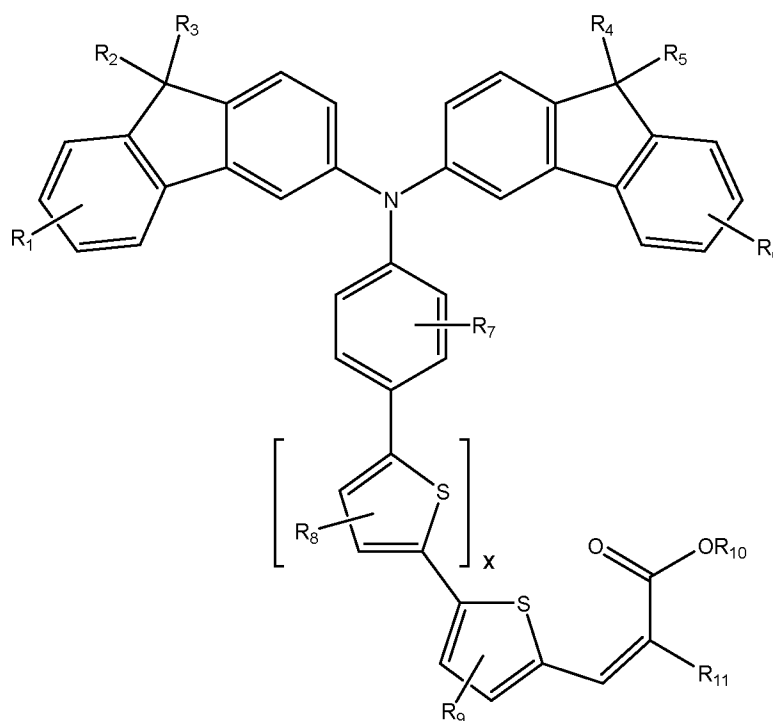
10

- Wherein any of R1 to R8 may independently be a straight or branched chain alkyl group or any of R1 to R5 may independently be a straight or branched chain alkyloxy group such as C_nH_{2n+1} or $C_nH_{2n+1}O$ respectively where n is 1 to 20, preferably 1 to 12, more preferably 1 to 9. Preferably each R1 to R5 will be H, C_nH_{2n+1} or $C_nH_{2n+1}O$ wherein n is 1 to 8 preferably 1 to 3 more preferably 1 or two. Most preferably R1 is H and each R5 is methyl. Preferably each R6 to R8 group is H or C_nH_{2n+1} wherein n is 1 to 20, such as 1 to 12. For R6, n with preferably be 1 to 5 more preferably 1 to 3 and most preferably ethyl. For R7 n will preferably be 4 to 12, more preferably 6 to 10, most preferably 8, and for R8, preferred groups are H, methyl or ethyl. preferably H. One preferred squaraine dye referred to herein is
- 15
- 20

- 16 -

SQ02, which is of formula sVI wherein R1 and R8 are H, each of R2 to R5 is methyl, R6 is ethyl, and R7 is octyl (e.g. n-octyl).

5 A further example category of valuable sensitizers are polythiophene (e.g. dithiophene)-based dyes, which may take the structure indicated below as formula sVII



Formula sVII

10 Wherein x is an integer between 0 and 10, preferably 1, 2, 3, 4 or 5, more preferably 1, and wherein any of R1 to R10 may independently be hydrogen, a straight or branched chain alkyl group or any of R1 to R9 may independently be a straight or branched chain alkyloxy group such as C_nH_{2n+1} or $C_nH_{2n+1}O$ respectively where n is 1 to 20, preferably 1 to 12, more preferably 1 to 5. It is preferred that
 15 each if R1 to R10 will independently be a hydrogen or C_nH_{2n+1} group where n is 1 to 5, preferably methyl, ethyl, n- or iso-propyl or n-, iso-, sec- or t-butyl. Most preferably, each of R2 to R4 will be methyl or ethyl and each of R1 and R6 to R10 will be hydrogen. The group R11 may be any small organic group (e.g. molecular weight less than 100) but will preferably be unsaturated and may be conjugated to
 20 the extended pi-system of the dithiophene groups. Preferred R11 groups include alkenyl or alkynyl groups (such as C_nH_{2n-1} and C_nH_{2n-3} groups respectively, e.g. where n is 2 to 10, preferably 2 to 7), cyclic, including aromatic groups, such as substituted

or unsubstituted phenyl, piridyl, pyrimidyly, pyrrolyl or imidazyl groups, and unsaturated hetero-groups such as oxo, nitrile and cyano groups. A most preferred R11 group is cyano. One preferred dithiophene based dye is 2-cyanoacrylic acid-4-(bis-dimethylfluorene aniline)dithiophene, known as JK2.

5

No dye sensitizer is necessary for the functioning of the present invention since light may be absorbed either by the polymeric p-type material and/or by sensitizers of other types, such as inorganic films or nanoparticles. Where present, in one embodiment, only a single dye sensitizer will be employed in the p-n

10 heterojunctions herein described (and thus all compatible aspects of the invention), and this may serve to absorb over a broad range of wavelengths and/or may act to increase absorption in regions of the spectrum where the absorption of the polymer material is relatively low. In an alternative embodiment, two or more dye sensitizers may nevertheless be used. For example, all aspects of the present invention are

15 suitable for use with co-sensitisation using a plurality of (e.g. at least 2, such as 2, 3, 4 or 5) different sensitizing agents, including dye sensitizing agents. If two or more dye sensitizers are used, these may be chosen such that their respective emission and absorption spectra overlap. In this case, resonance energy transfer (RET) results in a cascade of transfers by which an electron excitation steps down

20 from one dye to another of lower energy, from which it is then injected into the n-type material. Alternatively, it may be preferred that the emission and absorption spectra of the individual dyes do not overlap to any significant extent. This ensures that all dye sensitizers are effective in the injection of electrons into the n-type material. Where two or more dye sensitizers are used, these will preferably have

25 complimentary absorption characteristics. Some complimentary parings include, for example, the near-infra red absorbing zinc phthalocyanine dyes referred to above in combination with indoline or ruthenuim-based sensitizers to absorb the bulk of the visible radiation. As an alternative, a polymeric or molecular visible light absorbing material may be used in conjunction with a near IR absorbing dye, such as a visible

30 light absorbing polyfluorene polymer with a near IR absorbing zinc phlaocianine or squaraine dye.

Other types of sensitizers may also be used in the various aspects of the present invention and in each case may form all or the bulk of the light-absorbing material

35 or may be used in conjunction with absorption from the polymeric p-type material and/or in combination with other sensitizers of the same or different types.

Preferred sensitizing agents include at least one inorganic light absorbing thin film or semiconductor nanoparticle layer, where the film or layer is formed from materials selected from, for example, PbS, PbSe, SnS, SnSe SbS, SbSe, CdSe, Ge, Si.

5 Although many of the dyes indicated above show broad spectrum absorption in the visible region, plasmonic nanoparticles allow injection of electrons which result from excitation of surface plasmon modes by lower energy solar photons including those of near infra-red frequencies. These are therefore advantageously combined with suitable dye sensitizers.

10

A highly preferred sensitizer for use in the present invention is the widely known indoline based organic dye D131.

15

As referred to in the context of this patent, a p-type polymer is a material which exhibits good hole-transport characteristics and functions as a hole-transporter in the operating heterojunction (especially solar cell). Its function is to 1. Transfer an electron from the highest occupied molecular orbital (HOMO) level of the p-type polymer to the HOMO level of the photo-oxidized dye or other sensitizer (where present - also known as dye regeneration). 2. Transfer an electron from photoexcitations directly on the p-type polymer to the n-type oxide resulting in generated charge. 3. Transport the holes remaining on the polymer to the cathode and into the external circuit.

20

In all aspects of the present invention, a polymerised material is used as the p-type material of the heterojunction or device. There are a number of polymeric p-type materials which have been used previously in reported polymer oxide solar cells and any of these may be used. Preferably, the polymeric p-type material is an organic polymer selected from poly fluorenes, poly carbazolenes, poly thiophenes, poly selophenes, polythiadiazoles, poly thienopyrazines, poly p-phenylene vinylenes, poly thienylene vinylenes, poly(thienylenevinylenes) and mixtures, copolymers and derivatives thereof. Highly suitable polymers include those disclosed in Kroon Et Al. (Polymer Reviews **48**, 531-582 (2008), which is hereby incorporated by reference. In particular, the polymers set out in Table 1 and compounds 1 to 10 (thiophene and thioselenophene polymers), Table 2 (donor-acceptor polymers), Table 3 and Figs 12 to 14 (Poly thenylene vinylene polymers),

Table 4 (Thienylene vinylene copolymers), Table 5 and Fig 15 (fluorene polymers) and in Table 6 and Figs 16-18 (carbazolene polymers) are highly suitable.

A particularly effective example of conducting polymers include poly(3-hexylthiophene) (P3HT) poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene) (MDMO-PPV), poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene), poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-5,5-(40,70-di-2-thienyl-20,10,30-benzothiadiazole)] (APFO-3)

Low band gap polymers are particularly preferred in the present invention.****

Examples of low band gap polymers include poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b0] dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT), APFO-Green5.

The alternating co-polymers described and disclosed in Zhang et al. (Advanced Materials **18**, 2169-2173 (2006)) are highly appropriate and are hereby incorporated by reference. In particular, the structure of APFO-Green5 is given in Figure 1 and its synthesis in the experimental section thereof.

Further information on PCPDTBT may be found from Lee et al. J. AM. CHEM. SOC. 2008, **130**, 3619-3623, Chen et al., Macromolecules, Vol. **43**, No. 2, 2010 -D and Muhlbacher et al. Adv. Mater. 2006, **18**, 2884. These are again incorporated herein by reference.

By "band-gap" as used herein in the context of organic semiconductors is intended the energy of the transition from the lowest energy singlet ground state (S_0) to first excited state (S_1). "low band gap" in this context thus refers to having a low energy for this transition and "high band gap" refers to a high energy transition. Typical transition energies for "low band gap" organic semiconductors may be, for example, less than 2.0 eV (e.g. 1.0 eV to 2.0 eV), preferably less than 1.9 eV, more preferably 1.8 eV or lower. 1.7 eV or lower is highly preferred (e.g. less than 1.6 eV or less than 1.5 eV).

The said functionalised electron acceptor moieties for a key aspect of the present invention and are believed to allow the transfer of energy absorbed by the p-type polymer into useful electrical energy by promoting charge transfer to the n-type

material. Such functionalised electron acceptor moieties typically comprise at least one 2-dimensional or 3-dimensional network of carbon atoms, optionally including up to 10% of heteroatoms, functionalised by at least one organic group having affinity for the n-type material surface.

Fullerenes are particularly suitable as the 2-dimensional or 3-dimensional network of carbon atoms referred to herein and may comprise heteroatoms as indicated herein. Fullerenes as indicated herein may be in the form of a hollow sphere, ellipsoid, or tube. Spherical fullerenes are also known as buckyballs, cylindrical ones are called carbon nanotubes or buckytubes. All such fullerenes are suitable in the present invention. Fullerenes are similar in structure to graphite, which is composed of stacked graphene sheets of linked hexagonal rings; but they may also contain pentagonal (or sometimes heptagonal) rings. Single graphene sheets and small numbers of stacked graphene sheets (e.g. 2-5) are also suitable in the present invention. Molar masses of 200 to 10000 g/mol would be typical for the electron absorbing moieties, preferably 300 to 3000 and more preferably 500 to 1200. Any of the well known fullerenes are suitable with C60 and C70 fullerenes (and their equivalents with one or more carbon substituted with heteroatom(s)) being highly appropriate.

The electron absorbing moieties of the present invention are "functionalised" in that they are covalently bound to at least one organic group that is not part of the fullerene-type 2-dimensional or 3-dimensional atom network. Such functional groups will preferably serve to provide an affinity for the n-type material and thus may vary depending upon the n-type material used. Typical groups include polar groups such as carboxylic acids, phosphonic acids, cyano acrylic acids, thioacids, esters, amides, hydroxyl, hydroxamate, thiol and amine groups.

In all aspects, the n-type semiconductor material for use in the solid state heterojunctions (e.g. DSCs) relating to the present invention may be any of those which are well known in the art. Oxides of Ti, Al, Sn, Mg and mixtures thereof are among those suitable. TiO₂ and Al₂O₃ are common examples, as are MgO and SnO₂. The n-type material is used in the form of a layer and will typically be mesoporous providing a relatively thick layer of around 0.05 - 100 μm over which the second sensitizing agent may be absorbed at the surface.

In one optional but preferred embodiment, a thin surface coating of a high band-gap / high band gap edge (insulating) material, may be deposited on the surface of a lower band gap n-type semiconductor such as SnO_2 . This can greatly reduce the fast recombination from the n-type electrode, which is a much more severe issue in solid state DSCs than in the more widely investigated electrolyte utilising cells. Such a surface coating may be applied before the oxide particles (e.g. SnO_2) are sintered into a film or after sintering.

The n-type material of the solid state heterojunctions relating to all aspects of the present invention is generally a metal compound such as a metal oxide, compound metal oxide, doped metal oxide, selenide, teluride, and/or multicomponent semiconductor, any of which may be coated as described above. Suitable materials include single metal oxides such as Al_2O_3 , ZrO , ZnO , TiO_2 , SnO_2 , Ta_2O_5 , Nb_2O_5 , WO_3 , W_2O_5 , In_2O_3 , Ga_2O_3 , Nd_2O_3 , Sm_2O_3 , La_2O_3 , Sc_2O_3 , Y_2O_3 , NiO , MoO_3 , PbO , CdO and/or MnO ; compound metal oxides such as $\text{Zn}_x\text{Ti}_y\text{O}_z$, ZrTiO_4 , ZrW_2O_8 , $\text{SiAlO}_{3.5}$, $\text{Si}_2\text{AlO}_{5.5}$, SiTiO_4 and/or AlTiO_5 ; doped metal oxides such as any of the single or compound metal oxides indicated above doped with at least one of Al, F, Ge, S, N, In, Mg, Si, C, Pb and/or Sb; carbides such as Cs_2C_5 ; sulphides such as PbS , CdS , CuS ; selenides such as PbSe , CdSe ; telurides such as CdTe ; nitrides such as TiN ; and/or multicomponent semiconductors such as ClGaS_2 .

It is common practice in the art to generate p-n heterojunctions, especially for optical applications, from a mesoporous layer of the n-type material so that light can interact with the junction at a greater surface than could be provided by a flat junction. In the present case, this mesoporous layer may be conveniently generated by sintering of appropriate semiconductor particles using methods well known in the art and described, for example in Green et al. (J. Phys. Chem. B **109** 12525-12533 (2005)) and Kay et al. (Chem. Mater. **17** 2930-2835 (2002)), which are both hereby incorporated by reference. With respect to the surface coatings, where present, these may be applied before the particles are sintered into a film, after sintering, or two or more layers may be applied at different stages.

Typical particle diameters for the semiconductors will be dependent upon the application of the device, but might typically be in the range of 5 to 1000nm, preferably 10 to 100 nm, more preferably still 10 to 30 nm, such as around 20 nm. Surface areas of $1\text{-}1000\text{ m}^2\text{g}^{-1}$ are preferable in the finished film, more preferably

30-200 m²g⁻¹, such as 40 - 100 m²g⁻¹. The film will preferably be electrically continuous (or at least substantially so) in order to allow the injected charge to be conducted out of the device. The thickness of the film will be dependent upon factors such as the photon-capture efficiency of the photo-sensitizer, but may be in the range 0.05 - 100 µm, preferably 0.5 to 20 µm, more preferably 0.5 -10 µm, e.g. 1 to 5 µm. Typical thicknesses include 0.05 to 30 µm, preferably 1 to 5 µm, more preferably 2 to 3 µm. In one alternative embodiment, the film is planar or substantially planar rather than highly porous, and for example has a surface area of 1 to 20 m²g⁻¹ preferably 1 to 10 m²g⁻¹. Such a substantially planar film may also or alternatively have a thickness of 0.005 to 5 µm, preferably 0.025 to 0.2 µm, and more preferably 0.05 to 0.1 µm.

Where the n-type material is surface coated, materials which are suitable as the coating material (the "surface coating material") may have a conduction band edge closer to or further from the vacuum level (vacuum energy) than that of the principal n-type semiconductor material, depending upon how the property of the material is to be tuned. They may have a conduction band edge relative to vacuum level of at around -4.8 eV, or higher (less negative) for example -4.8 or -4.7 to -1 eV, such as -4.7 to -2.5 eV, or -4.5 to -3 eV

Suitable coating materials, where present, include single metal oxides such as MgO, Al₂O₃, ZrO, ZnO, HfO₂, TiO₂, Ta₂O₅, Nb₂O₅, WO₃, W₂O₅, In₂O₃, Ga₂O₃, Nd₂O₃, Sm₂O₃, La₂O₃, Sc₂O₃, Y₂O₃, NiO, MoO₃, PbO, CdO and/or MnO; compound metal oxides such as Zn_xTi_yO_z, ZrTiO₄, ZrW₂O₈, SiAlO_{3.5}, Si₂AlO_{5.5}, SiTiO₄ and/or AlTiO₅; doped metal oxides such as any of the single or compound metal oxides indicated above doped with at least one of Al, F, Ge, S, N, In, Mg, Si, C, Pb and/or Sb; carbonates such as Cs₂C₅; sulphides such as PbS, CdS, CuS; selenides such as PbSe, CdSe; telurides such as CdTe; nitrides such as TiN; and/or multicomponent semiconductors such as ClGaS₂. Some suitable materials are discussed in Grätzel (Nature **414** 338-344 (2001)). The most preferred surface coating material is MgO.

Where present, the coating on the n-type material will typically be formed by the deposition of a thin coating of material on the surface of the n-type semiconductor film or the particles which are to generate such a film. In most cases, however, the material will be fired or sintered prior to use, and this may result in the complete or partial integration of the surface coating material into the bulk semiconductor. Thus

although the surface coating may be a fully discrete layer at the surface of the semiconductor film, the coating may equally be a surface region in which the semiconductor is merged, integrated, or co-dispersed with the coating material.

- 5 Since any coating on the n-type material may not be a fully discrete layer of material, it is difficult to indicate the exact thickness of an appropriate layer. The appropriate thickness will in any case be evident to the skilled worker from routine testing, since a sufficiently thick layer will retard electron-hole recombination without undue loss of charge injection into the n-type material. Coatings from a monolayer
10 to a few nm in thickness are appropriate in most cases (e.g. 0.1 to 100 nm, preferably 1 to 5 nm).

- The bulk or "core" of the n-type material in all embodiments of the present invention may be essentially pure semiconductor material, e.g. having only unavoidable
15 impurities, or may alternatively be doped in order to optimise the function of the p-n-heterojunction device, for example by increasing or reducing the conductivity of the n-type semiconductor material or by matching the conduction band in the n-type semiconductor material to the excited state of the chosen sensitizer.

- Thus the n-type semiconductor and oxides such as TiO_2 , ZnO , SnO_2 and WO_3 referred to herein (where context allows) may be essentially pure semiconductor (e.g. having only unavoidable impurities). Alternatively they may be doped throughout with at least one dopant material of greater valency than the bulk (to provide n-type doping) and/or may be doped with at least one dopant material of lower valency than the bulk (to give p-type doping). n-type doping will tend to increase the n-type character of the semiconductor material while p-type doping will tend to reduce the degree of the natural n-type state (e.g. due to defects).

- 20 Such doping may be made with any suitable element including F, Sb, N, Ge, Si, C, In, InO and/or Al. Suitable dopants and doping levels will be evident to those of skill in the art. Doping levels may range from 0.01 to 49% such as 0.5 to 20%, preferably in the range of 5 to 15%. All percentages indicated herein are by weight
25 where context allows, unless indicated otherwise.

In addition to the n-type, p-type and optional sensitizer components, an optional by preferable ionic material such as a lithium salt may also be included in all aspects of

the present invention. In one embodiment therefore, this ionic additive will be present. In a more preferable embodiment, this ionic additive will be present and will comprise a lithium salt or compound. Particularly preferable ionic additives are lithium salts such as lithium perchlorate or ionic liquids, such as 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1,3-Dihydroxy-2-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1,3-Dimethoxy-2-methylimidazolium bis(trifluoromethylsulfonyl)imide. Mixtures of such materials are also highly suitable.

The invention is illustrated further in the following non-limiting examples and in the attached Figures, in which:

- 5 Figure 1a - is a schematic diagram of an organic solid state dye sensitized solar cell formed with a mesoporous TiO_2 n-type semiconductor material;
- Figure 1b - shows a schematic representation of charge transfers taking place in DSC operation. $h\nu$ indicates light absorption, e^- inj = electron injection, rec = recombination between electrons in the n-type and holes in the p-type material, h^+ inj = hole-transfer (dye regeneration), and CB = conduction band;
- 10 Figure 2 - shows the absorption spectra of a TiO_2 /PCPDTBT spin coated from a 30 mg/mL solution in CB (lower line) and TiO_2 /D131/PCPDTBT (upper line);
- Figure 3 - shows the absorption spectra of a C_{60} -SAM on the TiO_2 surface;
- 15 Figure 4 - is a schematic diagram of a polymer based hybrid solar cell, illustrating either dye-sensitization, surface modification with a C_{60} -SAM, or the combined mixed monolayer;

- Figure 5a - shows the external quantum efficiency spectra of a TiO_2 /PCPDTBT (triangles); TiO_2 /D131/P3HT (squares); TiO_2 /D131/PCPDTBT (circles) based dye-sensitized solar cell;
- 5 Figure 5b - Shows the Solar cell performance parameters extracted from current-voltage curves of a TiO_2 /PCPDTBT based solar cells, a TiO_2 /D131/PCPDTBT based dye-sensitized solar cell and also of TiO_2 /D131/P3HT based dye-sensitized solar cell measured under AM1.5 simulated sun light of 100mWcm^{-2} .
- 10
- Figure 6 - Top: Pump-probe spectrum of TiO_2 /PCPDTBT collected at different pump-probe delay, from 200fs to 100ps, as indicated in the legend. Down: Normalized $\Delta T/T$ dynamics at 570nm and at 960nm as a
- 15 function of pump-probe delay.
- Figure 7 - shows the pump-probe spectrum of a) TiO_2 /C₆₀-SAM/PCPDTBT and c) TiO_2 /D131/C₆₀-SAM/PCPDTBT collected at different pump-probe delay, from 200fs to 100ps, as indicated in the legend. b) and d)
- 20 show respective $\Delta T/T$ dynamics as 960nm probe wavelength and 780nm pump wavelength. Pump 780nm;
- Figure 8 - shows normalized $\Delta T/T$ dynamics at 960nm probe wavelength of TiO_2 /PCPDTBT (circles), TiO_2 /C₆₀-SAM/PCPDTBT (squares) and TiO_2 /D131/C₆₀-SAM/PCPDTBT (triangles) on long (a) and short time
- 25 scale (b). The table in (c) table indicates the fit parameters. 780nm pump;
- Figure 9 - shows (a) J_{sc} and V_{oc} dependence on Li salts concentration on PCPDTBT/C₆₀-SAM/ TiO_2 devices; (b) device parameters; and (c)
- 30 external quantum efficiency spectra for corresponding devices presented in Figure 9a and 9b;

Figure 10 - shows (a) external quantum efficiency spectra and (b) device performances for a series of PCPDTBT based DSSC with and without C₆₀-SAM and D131 co-sensitization.

5 Example 1 - Solar cell fabrication

1.1 Materials

10 A low band gap polymer poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b0] dithiophene)-alt-4,7-(2,1,3-benzothiadiazole), (PCPDTBT), was used as the hole transporter in solid-state hybrid solar cells. This material has been the first candidate of a new class of copolymers for organic photovoltaics utilizing a cyclopentadithiophene unit as the donor block in the polymer chain. It shows improved charge-transport properties, mobility values as high as $2 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and good processability (see D. Mühlbacher *Adv. Mater.* **18**: 2884-2889, 2006 and J. Peet *Nat Mater* **6**: 498-500, 2007). The ideal energy gap of PCPDTBT of $E_g = 1.46 \text{ eV}$ and the improved light harvesting in the near-infrared region make it a good candidate for solar photovoltaic applications. The combination of these properties allowed efficiencies up to 5.5% when blended with PC₇₁BM in standard bulk
15
20 heterojunction solar cells, with short-circuit current values up to 16 mAcm^{-2} and a high EQE approaching 50% over the spectral range from 400 to 800 nm (D. Mühlbacher and J. Peet *supra*).

25 The absorption spectrum of the PCPDTBT is shown by the lower line in Figure 2, it peaks around 700nm, with a minor peak around 400nm. Its molecular structure is presented in the inset. We infiltrate the PCPDTBT into the mesoporous TiO₂ layer, sensitized with high molar extinction coefficient metal free indoline-based dyes (D131) (see the chemical structure in Figure 2). The upper line in Figure 2 represents the absorption spectrum of the dye-sensitized TiO₂ peaked around
30 400nm and 700nm, corresponding to D131 and PCPDTBT absorption, respectively. Combining the D131 with the PCPDTBT a panchromatic light absorption in the whole visible-near IR spectral region (from 400 to 900nm) is achieved.

35 The chemical structure of the C60-based self-assembled monolayer (SAM) we used to modify the TiO₂ surface is functionalized as shown in Figure 3 and the

synthesis procedure reported elsewhere (see S. K. Hau *et al.* Interfacial modification J. Mater Chem. 18: 5113-5119, 2008 and S. K. Hau Applied Materials and Interfaces 27: 1892-1902, 2010). The C60 SAM exhibits a very weak absorption in the visible spectral region, with an onset at around 320nm, as shown in Figure 3.

1.2 Methods: ultrafast pump-probe set-up

In order to elucidate the energy transfer and charge generation mechanism in the complete photovoltaic composites, and measure the time scale in which this process occurs we performed transient absorption measurements with sub ps time resolution. In a typical pump-probe experiment, the system under study is photoexcited by a short pump pulse and its subsequent dynamical evolution is detected by measuring the transmission changes ΔT of a delayed probe pulse as a function of pump-probe delay τ and probe wavelength λ . The signal is given by the differential transmission $\Delta T/T [(T_{\text{pump on}} - T_{\text{pump off}})/T_{\text{pump off}}]$. The pump probe set-up is driven by 1 kHz repetition rate pulse train at $\lambda = 780$ nm centre wavelength with 150 fs duration coming from a regeneratively amplified modelocked Ti: sapphire laser (Clark-MXR Model CPA-1) (Cerullo, G *et al.*, *Photochem. Photobiol. Sci.* 6: 135, 2007; G. Cerullo *et al.*, *Phys. Rev. B* 57, 12: 806, 1998). A fraction of this beam is used as the excitation pulse at 390 nm wavelength, generated via second harmonic process in a non-linear crystal. Another small fraction of the Ti: sapphire amplified output is independently focused into a 2-mm-thick sapphire plate to generate a stable single-filament white-light supercontinuum which serves as a probe pulse, in the visible and near-infrared region spanning from 400nm to 1000nm. The pump and probe beams are spatially overlapped on the sample and the time delay is controlled by motorized slit. The experimental pump-probe system has a 150fs temporal resolution. Details of the system used can be found elsewhere (see Cerullo G. *et al.*, *supra*). The pump beam density energy used in the experiment is kept deliberately low (10-50 nJ energy, 50 μ m beam size). All the measurements were taken with the samples in a vacuum chamber, to prevent any influence from oxygen or sample degradation.

The pump-probe measurements were taken on PCPDTBT film spin cast on the TiO₂ substrates, fabricated following DSSC procedure, sensitized with/without C60 SAM and D131. In order to separate the contribution of the single interface and understand the photophysical process occurring in the system, also TiO₂/C60-SAM and TiO₂/PCPDTBT films were fabricated, serving as reference samples. We tuned the pump beam from 390nm to 780nm in order to mainly excite the C60 SAM, and the PCPDTBT component, respectively.

1.3 Device Fabrication

The devices are composed of mesoporous TiO₂ (or other metal oxides) with film thicknesses ranging from 100 nm to 2 μ m. The mesoporous film is optionally sensitized with a dye layer or other surface treatments, specifically here with a C₆₀-SAM, and infiltrated with a polymeric hole-transporter via spin-coating. The devices are then capped with a silver metallic cathode. In Figure 4 we show a schematic representation of these devices. For the most basic two component systems, light is absorbed in the hole-transporter and an exciton is formed. The exciton then diffuses within the film and hopefully reaches the heterojunction between the metal oxide and the hole-transporter, where the energy levels are suitably set to facilitate electron transfer into the metal oxide. Once charge has been generated the respective charge percolates through the hole-transporting and electron transporting phases to be collected at the electrodes (H. Snaith, book chapter Wiley, Yanagida *et al.*, Adv. Funct. Mater. 19, 2481–2485, 2009, B. Wenger *et al.*, J. Am. Chem. Soc. 127: 12150, 2005, and T. Forster, *Annalen Der Physik* 2: 55, 1948).

The detailed fabrication procedure is explained in the following. Fluorine doped tin oxide (FTO) coated glass sheets (15 $\Omega/\square$ Pilkington) were etched with zinc powder and HCl (2 Molar) to obtain the required electrode pattern. The sheets were then washed with soap (Hellmanex at 2% in water), de-ionized water, acetone, methanol and finally treated under an oxygen plasma for 10 minutes to remove the last traces of organic residues. The FTO sheets were subsequently coated with a compact layer of TiO₂ (100 nm) by aerosol spray pyrolysis deposition at 450°C, using air as the carrier gas.

The standard Dyesol TiO₂ paste was previously diluted down 1:3.5 in anhydrous ethanol and stirred and ultrasonicated until completely mixed. The paste was then doctor-bladed by hand using scotch tape and a pipette on the TiO₂ compact layer coated FTO sheets to get a TiO₂ average thickness of 1 μm. The sheets were then slowly heated to 550°C (ramped over 1½ hours) and baked at this temperature for 30 minutes in air. After cooling, slides were cut down to size and soaked in a 15 mM of TiCl₄ in water bath and oven-baked for 1 hour at 70°C. After rinsing in water, ethanol and drying in air, they were subsequently baked once more at 550°C for 45 minutes in air, then cooled down to 70°C and finally introduced in a dye solution for 1 hour.

The indolene dye used was D131 in a 1:1 volume ratio of tert-butanol and acetonitrile at 0.3 mM concentration. The dyed films were briefly rinsed in acetonitrile and dried in air for 1 minute.

The synthesis of C₆₀-substituted carboxylic acid is reported elsewhere (see S. K. Hau et al. *supra*). Functionalized C₆₀-SAMs with carboxylic acid end-group can be formed onto the surface of dye-sensitized TiO₂ by a solution immersion technique. First, a 1mM solution containing the C₆₀-SAM molecules in a 1:1 (v:v) cosolvent in tetrahydrofuran:chlorobenzene (THF:CB) is prepared. The solutions are filtered through a 0.2 μm PTFE filter prior to immersion of the samples into the solution. The TiO₂ substrates, optionally dye sensitized, were immersed into a 5 mL solution of the C₆₀-SAMs and left in solution for a set period of time (from 1 min up to 240 min). The samples were then removed from the solution and thoroughly rinsed with THF:CB to remove any excess unbound molecules and dried under a nitrogen stream. Samples were annealed at 140°C for 5 minutes to promote the improve the uniformity of the chemical bonding of the SAM to the TiO₂ surface.

PCPDTBT was dissolved in chlorobenzene at 30mg/mL concentration, heated at 70°C for 1 hour and stirred overnight. A solution of lithium bis(trifluoromethylsulfonyl)imide salt (Li-TFSI) at 0.01 to 0.12 M concentration in acetonitrile was prepared to treat the dye and C₆₀-SAM sensitized TiO₂ surface prior to PCPDTBT spin-coating. A small quantity of Li-TFSI solution (25 μl) was dispensed onto each substrate and left to wet the films for 20 secs before spin-

coating at 1000 rpm for 60 secs in air. Then the PCPDTBT solution was spin coated on the substrate at 1000rpm for 45 seconds in air.

5 The films were then placed in a thermal evaporator where 150 nm thick silver electrodes were deposited through a shadow mask under high vacuum (10^{-6} mbar), to give rectangular cells with an active area of $\sim 0.12\text{cm}^2$. During testing under simulated sun light, the active areas of the devices were defined by single aperture metal optical masks with a round aperture of 2.5 mm giving an area of 0.0491cm^2 . All light was excluded from entering the sides of the devices by having them in a
10 "light-tight" sample holder, and the only light entering the solar cell substrate was through the single mask aperture.

Example 2 - Solar cell testing

15 2.1 Polymer based dye-sensitized solar cells

The solar cell characteristics of dye-sensitized TiO_2 polymer solar cells are shown in Figure 5, evaluated at AM 1.5G solar conditions. Here we compare the low band gap polymer PCPDTBT with the previously used P3HT. In Figure 5a we show the
20 external quantum efficiency EQE versus wavelength of fully processed devices (FTO conductive glass/compact TiO_2 /mesoporous TiO_2 /hole transporter/Ag electrode, as schematically illustrated in Figure 4). The EQE of the PCPDTBT based DSSC is shown and compared to the standard P3HT based DSSC and the TiO_2 /PCPDTBT device. In P3HT based DSSC the conversion efficiency from light
25 absorbed in the dye is significantly greater than light absorbed in the P3HT, as founded in established literature (K.-J. Jiang *et al.* *Adv. Func. Matter.* 19: 1, 2009). In this case the dye molecules absorb the incident light and contribute to the charge generation, and P3HT acts as the hole transporter, to regenerate the oxidized dye molecules (referred to as dye regenerative mechanism - see Rui Zhu *et al.* *Adv.*
30 *Mater.* 21: 994–1000, 2009). The EQE shows that the photoaction originates from light absorption in the dye indicating that charge generation from light absorbed in the P3HT is still relatively low. The EQE measurement on the PCPDTBT based DSSC reveals a predominant contribution from the dye at shorter wavelengths (note the lack of this band for the pristine PCPDTBT, used as a reference),
35 however, there is a significant photoresponse from light harvested by the polymer in

the near IR region (~5%), indicating that the PCPDTBT could be excited by the incident light and acts as the electron donor to donate electrons to the TiO₂. The dye molecules at the TiO₂/PCPDTBT interface act as an energy tunnel or an electronic mediator to improve the electron injection efficiency (referred to as "electron-mediating" mechanism - see Rui Zhu *et al. supra*).

We demonstrated a power-conversion efficiency of 3.3% under simulated AM1.5 sun light (100mWcm⁻²) and remarkably high Voc (~0.8V), indicating that this is a promising material to optimize in this class of solar cells.

2.2. Enhancing photoinduced electron transfer from the polymer to the mesoporous TiO₂

It is clear that PCPDTBT acts as a very good hole-transporter in solid-state dye-sensitized solar cells. However, the photo response is predominantly from the light absorbed in the dye, indicating that excitons formed on the polymer are not effectively at the TiO₂ polymer heterojunction. In order to assess if this is correct we performed pump-probe spectroscopy on mesoporous TiO₂ films infiltrated with PCPDTBT.

Figure 6 shows the pump probe spectrum of TiO₂/PCPDTBT after excitation at 780 nm, corresponding to the absorption peak of the PCPDTBT. The primary photoexcitation dynamics of TiO₂/PCPDTBT resemble the ones in a pure PCPDTBT film (In-Wook Hwang *et al.*, Adv. Mater. 19: 2307–2312, 2007). The positive band from 650nm to near IR is attributed to photobleaching (PB) and stimulated emission (SE), while the negative band at shorter wavelength is due to photo induced absorption (PA) of the singlet exciton, decaying within a hundred ps. After a few tens of ps a negative band appears around 570 and 950 nm. This signal is attributed to a small population of charges created after exciton separation at the TiO₂ interface. These charges (as shown from the $\Delta T/T$ dynamics) are long-lived and contribute to the small current measured in TiO₂/PCPDTBT device, showing very low photovoltaics performance.

As a means to improve electron transfer into the TiO₂, we functionalised the surface of the metal oxide with a C₆₀-SAM. In order to investigate if this aids charge

generation, we once again performed pump-probe spectroscopy which is presented in Figure 7a. It is apparent that with the presence of the C₆₀-SAM, the spectra is completely different to that with the unmodified PCPDTBT-TiO₂ interface. Firstly the signal is negative from the earliest time, indicating a strong photoinduced absorption which we assign to an ultrafast photoinduced generation of charges. There is a rapid decay of this signal, but a residual longer lived species which could result in efficient photocurrent generation in the complete solar cells.

Since the polymer absorbs strongly in the infra red and relatively weakly in the visible region of the spectrum it would be advantageous to "co-functionalize" the surface of the mesoporous oxide with both an electron acceptor and a dye-sensitizer. To determine if this co-functionalisation is possible and still delivers the signature of the enhanced charge generation, we fabricated films with mixed monolayers of an organic indolene dye, termed D131, and the C₆₀-SAM. As presented in Figure 7c, the signature of charge generation still occurs in the co-functionalised sample, with similar features, though even stronger signal strength. For means of comparison, the normalised dynamics, probed at 960 nm (the hole on the polymer) are shown in Figure 8 for the three different samples. The sample without the presence of the C₆₀-SAM is upside down, with respect to the other two traces. It is clear that ultrafast charge generation is only present when the C₆₀-SAM is employed.

2.3 Enhanced photovoltaic performance with C₆₀-SAM surface modification and co-functionalized dye -electron acceptor heterojunction

In order to verify if the enhanced signature of charge generation observed spectroscopically really translates into enhanced photovoltaic performance, we first fabricated hybrid solar cells with C₆₀-SAM modified TiO₂ with PCPDTBT (with no dye). In comparison to the unmodified mesoporous TiO₂, the photocurrent for the solar cells measured under simulated AM1.5 solar illumination increases by about one order of magnitude from 0.23 to 2 mAcm⁻² with an open-circuit voltage of 0.64V, and efficiency of 0.8%. For a hybrid solar cell, this is already one of the best efficiencies reported to date. However, the external quantum efficiency maximum is only around 5% and this polymer has the potential to generate over 25 mAcm⁻² if the external quantum efficiency can be increased to 90%. One possible reason for

the relatively low photocurrent could be that the lowest unoccupied molecular orbital (LUMO) of the C₆₀-SAM is deeper than the conduction band edge of the TiO₂. In order to assess this, and to create a positive shift in the TiO₂ conduction band level, we coated the functionalised TiO₂ surface with Li-TFSI prior to coating with
5 PCPDTBT.

The evolution of the short-circuit current, open-circuit voltage and other solar cell performance parameters are shown in Figures 9a and 9b. As expected the open-circuit voltage drops monotonically with increasing Li-TFSI concentration. Quite
10 remarkably, the short-circuit photocurrent increases by a further factor of 3, up to 5.5 mAcm⁻² over the range studied and the efficiency is over 1%. This is the first time that mesoporous metal oxide hybrid solar cells, employing the polymer as the sole absorber, have delivered over 1% power conversion efficiency. In Figure 9c, we show the external quantum efficiency spectra for the same devices which were
15 tested under the simulated sun light. We note that the EQE increases up to 30% at 700nm.

As last step to maximise the photocurrent generation in these polymer based hybrid solar cells, we optimized the co-functionalisation of the TiO₂ surface with a mixed
20 layer of D131 and C₆₀-SAM layer on the top. The co-sensitisation is performed by immersing the TiO₂ substrate first for 30 minutes in the D131 and second for 1 hour in the C₆₀-SAM solution. Figure 10 shows the obtained EQE results and device performances, respectively. From the EQE measurements the presence of the D131 dye appears to even enhance the photoaction from the polymer, and
25 simultaneously delivers good photovoltaic response from the dye. The highest photocurrent for the co-functionalized device is over 8 mAcm⁻² and the corresponding power conversion efficiency is 1.4%. This demonstrates a novel concept for photovoltaic response from polymer based hybrid solar cells.

30 2.4 Conclusions

We have demonstrated that charge generation between the low bandgap polymer PCPDTBT and mesoporous TiO₂ is very inefficient, even though PCPDTBT acts as a very good hole-transporter in dye-sensitized solar cells. We have subsequently
35 modified the TiO₂ surface with a carboxylic acid functionalised C₆₀ molecule which

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enhances the photoinduced electron transfer into the TiO_2 and the subsequent photocurrent generation in the solar cells by an order of magnitude. By tuning the surface potential of the metal oxide with the addition of Li-TFSI, the photocurrent is increased further, to deliver hybrid solar cells with over 30% EQE from light
5 absorbed in the polymer. To create a panchromatic photoresponse, we have introduced a new concept of co-functionalising the surface with both dye-sensitizer and electron accepting components, which creates a further increase in photocurrent.

Claims:

- 1) A solid-state p-n heterojunction comprising an organic polymeric p-type material in contact with a porous layer of n-type material, characterised in that the boundary between the p-type layer and the n-type layer is functionalised with at least a partial monolayer of functionalised electron acceptor moieties and optionally sensitizing agents.
- 2) A solid-state p-n heterojunction as claimed in the preceding claim wherein said heterojunction is sensitised by at least one sensitizing agent.
- 3) A solid-state p-n heterojunction as claimed in any preceding claim wherein said functionalised electron acceptor moieties comprise at least one 2-dimensional or 3-dimensional network of carbon atoms, optionally including up to 10% of heteroatoms, functionalised by at least one organic group having affinity for the n-type material surface.
- 4) A solid-state p-n heterojunction as claimed in claim 3 wherein said 2-dimensional or 3-dimensional networks of carbon atoms are selected from single-layer graphene, graphene having two, three, four or five layers, carbon nanotubes, and fullerenes, all optionally doped with up to 10% of at least one heteroatom selected from oxygen, boron, sulphur and nitrogen, preferably C60 or C70 fullerenes.
- 5) A solid-state p-n heterojunction as claimed in claim 3 or claim 4 wherein said organic group having affinity for the n-type material surface is at least one group selected from an organic acid and an organic thio-acid.
- 6) A solid-state p-n heterojunction as claimed in any preceding claim wherein the surface of the n-type layer is functionalised with at least a partial mixed monolayer of at least one functionalised electron acceptor and at least one sensitising agent.

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- 7) A solid-state p-n heterojunction as claimed in any preceding claim wherein the pore-filling-fraction of the porous layer of n-type material by the organic p-type material is no more than 50%.
- 5 8) A solid state p-n heterojunction as claimed in any preceding claim wherein said sensitizing agent comprises at least one dye selected from a ruthenium complex dye, a metal-phalocianine complex dye, a metal-porphyrin complex dye, a squaraine dye, a thiophene based dye, a fluorine based dye, a polymer dye, and mixtures thereof.
- 10 9) A solid state p-n heterojunction as claimed in any preceding claim wherein said sensitizing agent comprises at least one inorganic light absorbing thin film or semiconductor nanoparticle layer formed from a material selected from PbS, PbSe, SnS, SnSe SbS, SbSe, CdSe, Ge, Si.
- 15 10) A solid-state p-n heterojunction as claimed in preceding claim wherein said heterojunction comprises at least one ionic additive.
- 20 11) A solid-state p-n heterojunction as claimed in claim 7 wherein said ionic additive is a lithium salt such as lithium bis(trifluoromethylsulphonyl)imide salt (Li-TFSI) or Li perchlorate.
- 25 12) A solid-state p-n heterojunction as claimed in claim 7 or claim 8 wherein said ionic additive is a mixture of a metal salt and an ionic liquid.
- 30 13) A solid-state p-n heterojunction as claimed in any of claims 7 to 9 wherein said ionic additive comprises or consists of an ionic liquid, selected from 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1,3-Dihydroxy-2-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1,3-Dimethoxy-2-methylimidazolium bis(trifluoromethylsulfonyl)imide and mixtures thereof.

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- 14) A solid-state p-n heterojunction as claimed in preceding claim wherein said p-type material is an organic polymer selected from – poly thiophenes, poly p-phenylene vinylenes, mixtures, derivatives and copolymers thereof, most preferably PCPDTBT. ****
- 5
- 15) A solid-state p-n heterojunction as claimed in preceding claim wherein said p-type material is an organic polymer having a molecular weight M_n of greater than 15,000.
- 10
- 16) A solid-state p-n heterojunction as claimed in preceding claim wherein said p-type material is substantially electrically continuous throughout the mesoporous film.
- 15
- 17) A solid-state p-n heterojunction as claimed in preceding claim wherein said n-type semiconductor material comprises at least one single metal oxide, compound metal oxide, doped metal oxide, carbonate, sulphide, selenide, teluride, nitrides and/or multicomponent semiconductor, most preferably TiO_2 , SnO_2 or ZnO .
- 20
- 18) A solid state p-n heterojunction as claimed in preceding claim wherein said n-type material has a surface area of $1-1000\text{ m}^2\text{g}^{-1}$ and preferably in the form of an electrically continuous layer.
- 25
- 19) A solid state p-n heterojunction as claimed in preceding claim wherein said n-type material has a thickness of 0.05 to 30 μm , preferably 1 to 5 μm , more preferably 2 to 3 μm .
- 30
- 20) A solid-state p-n heterojunction as claimed in preceding claim wherein said n-type material is selected from oxides of Ti, Zn, Sn, W and mixtures thereof, and wherein said n-type material is optionally surface coated.
- 21) An optoelectronic device comprising at least one solid state p-n heterojunction as claimed in preceding claim.

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- 22) An optoelectronic device as claimed in claim 21 wherein said device is a solar cell, phototransistor or photo-detector, preferably a solid state dye sensitised solar cell and/or solid state polymer sensitised solar cell.
- 5 23) An optoelectronic device as claimed in any of claims 21 to 22 wherein said device is encapsulated so as to be substantially isolated from atmospheric oxygen.
- 24) Use of at least a partial monolayer of functionalised electron acceptor moieties and optionally sensitizing agents to enhance the efficiency of a solid state
10 polymer solar cell, where the electron acceptor is preferably as defined in claims 3 to 5.
- 25) Use as claimed in claim 24 to increase the photo induced electron transfer from the polymer to the n-type layer.
15
- 26) A method for the manufacture of a solid-state p-n heterojunction comprising an organic p-type material in contact with a porous layer of n-type material, said method characterised by;
- 20 a) coating an anode, preferably a transparent anode (e.g. a Fluorine doped Tin Oxide - FTO anode) with a compact layer of an n-type semiconductor material (such as any of those described herein);
- b) forming a porous (preferably mesoporous) layer of an n-type semiconductor material (such as any of those described herein) on said compact layer,
- 25 c) forming at least a partial monolayer of functionalised electron acceptor moieties (as described herein) and optionally sensitizing agents on the surface of the porous n-type layer;
- d) optionally treating said compact layer and/or said porous layer of n-type material with at least one ionic material such as a lithium salt.
- 30 e) optionally forming a porous barrier layer of an insulating material on said porous layer of n-type material;
- f) contacting said porous layer of n-type material with at least one solution of at least one polymeric organic p-type semiconductor material whereby to form a layer of polymeric organic p-type semiconductor interpenetrating the said porous
35 layer of an n-type material;

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f2) optionally treating said layer produced in "f" by coating on top with a solution of ionic material, such as Li-TFSI.

g) forming a cathode, preferably a metal cathode (e.g. a silver or gold cathode) in contact with said p-type semiconductor material.

5

27) A method as claimed in claim 26 wherein optional step d) is included and comprises treating said compact layer and/or said porous layer of n-type material with a mixture of at least two ionic materials.

10

28) A method as claimed in claim 27 wherein said ionic materials comprise at least one metal salt, preferably at least one lithium salt, and at least one ionic liquid, preferably 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

15

29) A method as claimed in any of claims 26 to 28 wherein step d) takes place and comprises contacting the porous layer of n-type material with a solution of Li-TFSI.

20

30) An optoelectronic device such as a photovoltaic cell, phototransistor or light sensing device comprising at least one solid-state p-n heterojunction formed or formable by the method of and of claims 26 to 29.

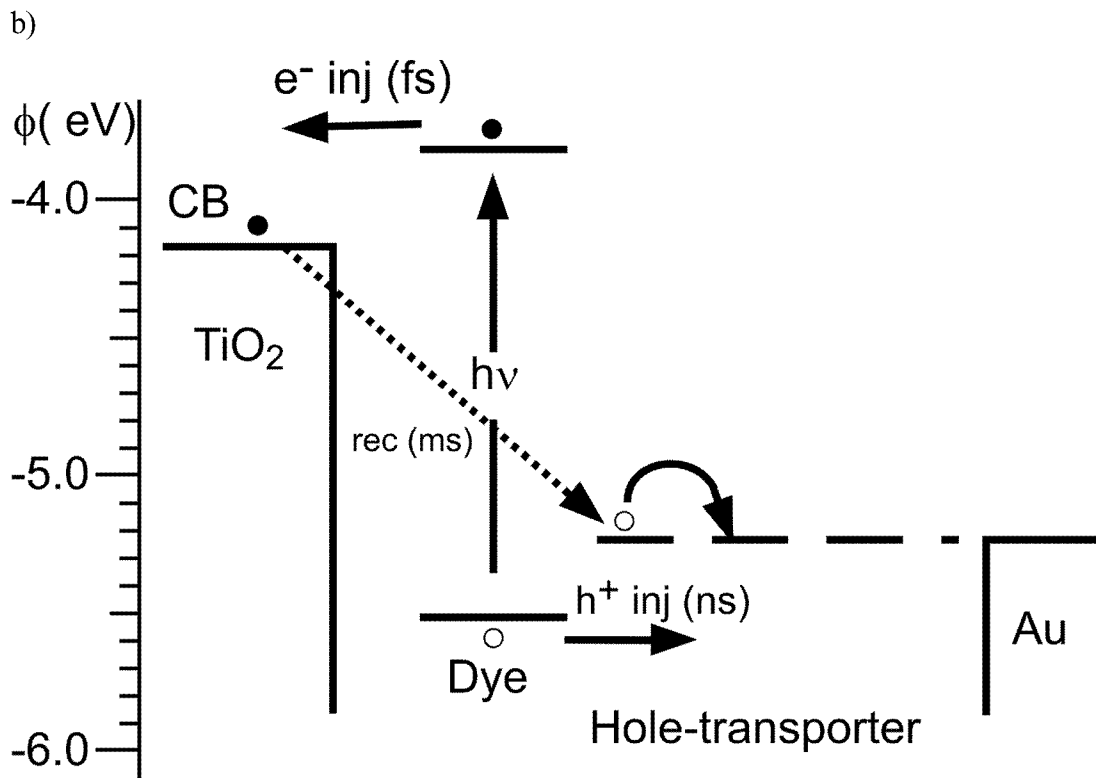
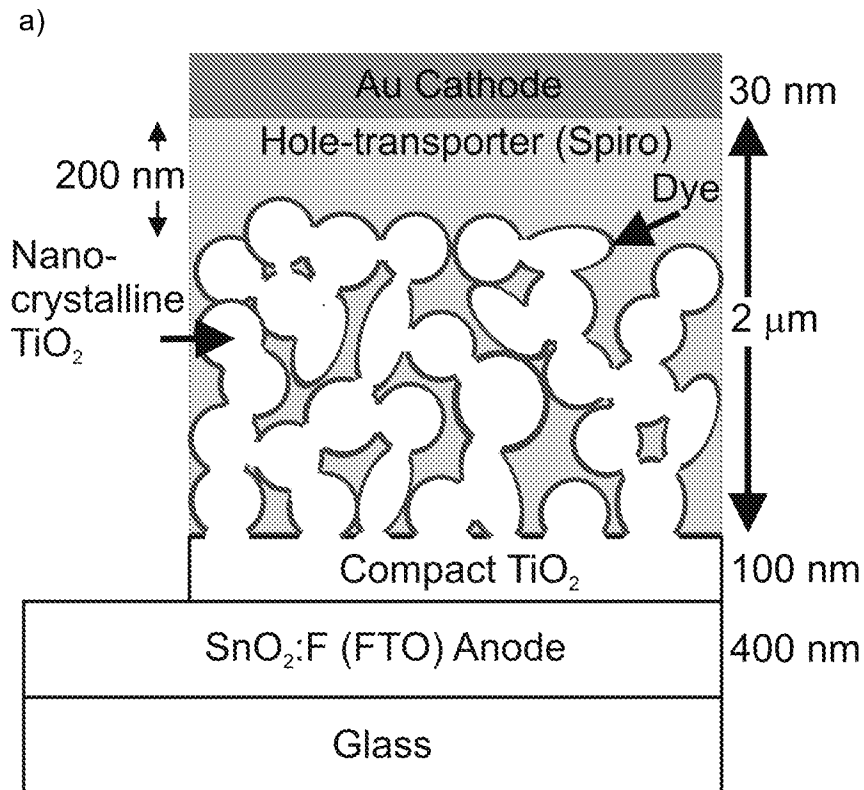


Figure 1. a) A schematic illustration of a cross section of a solid-state dye-sensitized solar cell using SnO_2 as the n-type metal oxide. b) An illustrative energy level diagram for a conventional solid-state dye sensitized solar cell.

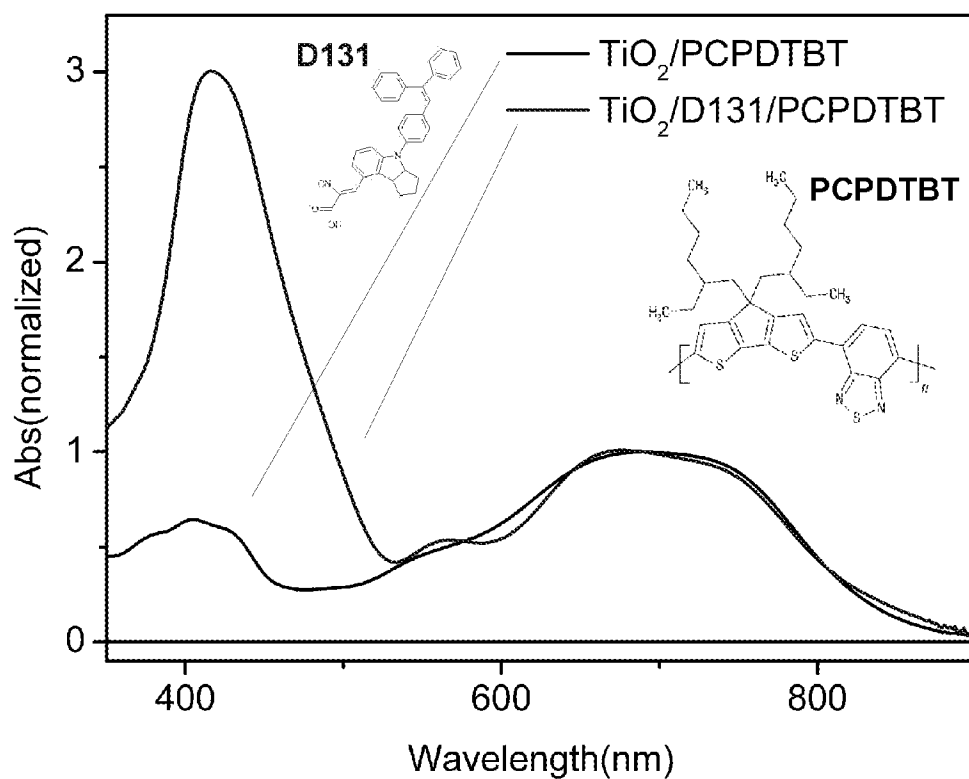


Figure 2. The absorption spectra of a $\text{TiO}_2/\text{PCPDTBT}$ spin coated from a 30 mg/mL solution in CB (lower line) and $\text{TiO}_2/\text{D131}/\text{PCPDTBT}$ (upper line). The insets show the D131 and PCPDTBT molecular structures.

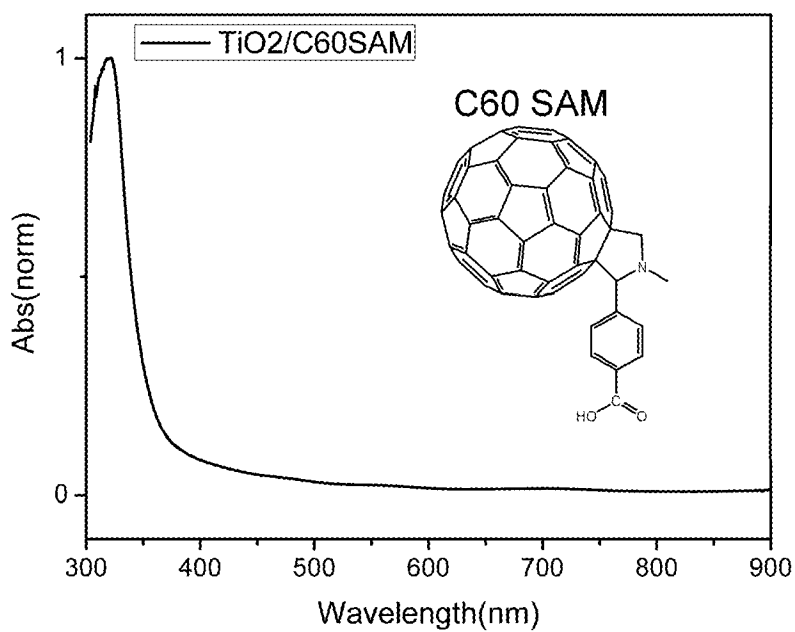


Figure 3. The absorption spectra of a C_{60} -SAM on the TiO_2 surface. Its molecular structure is shown in the inset.

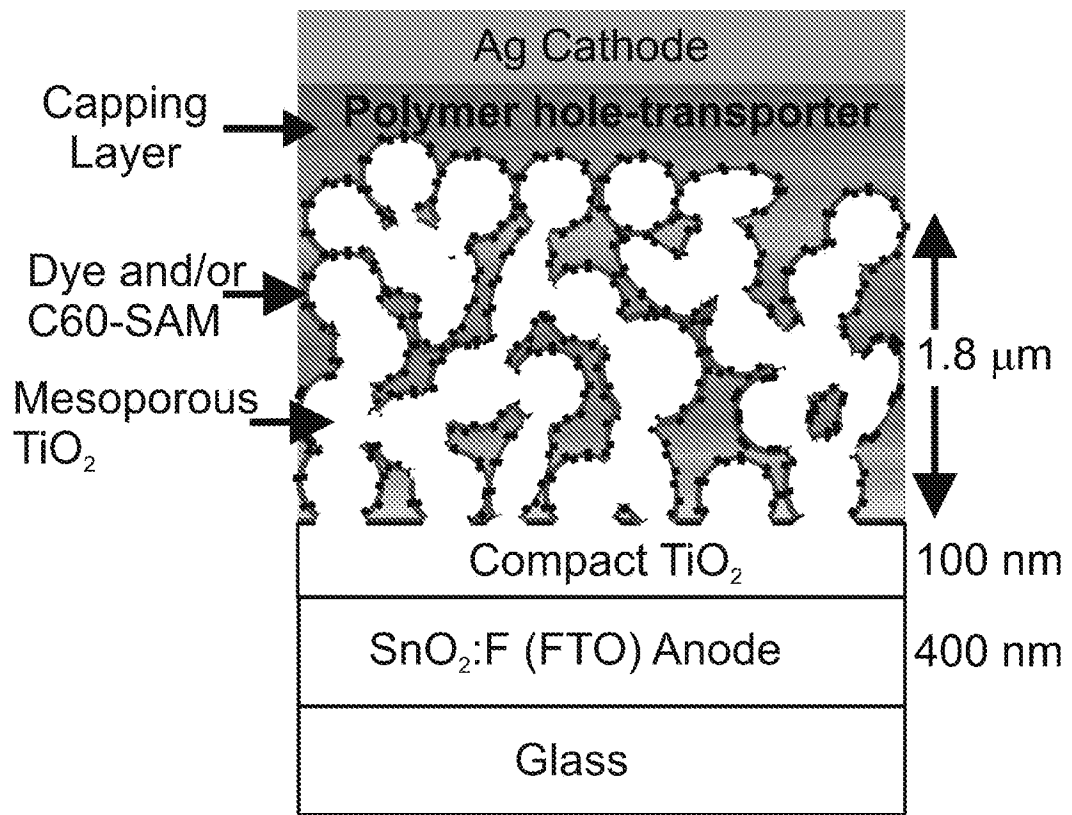


Figure 4. Schematic diagram of a polymer based hybrid solar cell, illustrating either dye-sensitization, surface modification with a C₆₀-SAM, or the combined mixed monolayer.

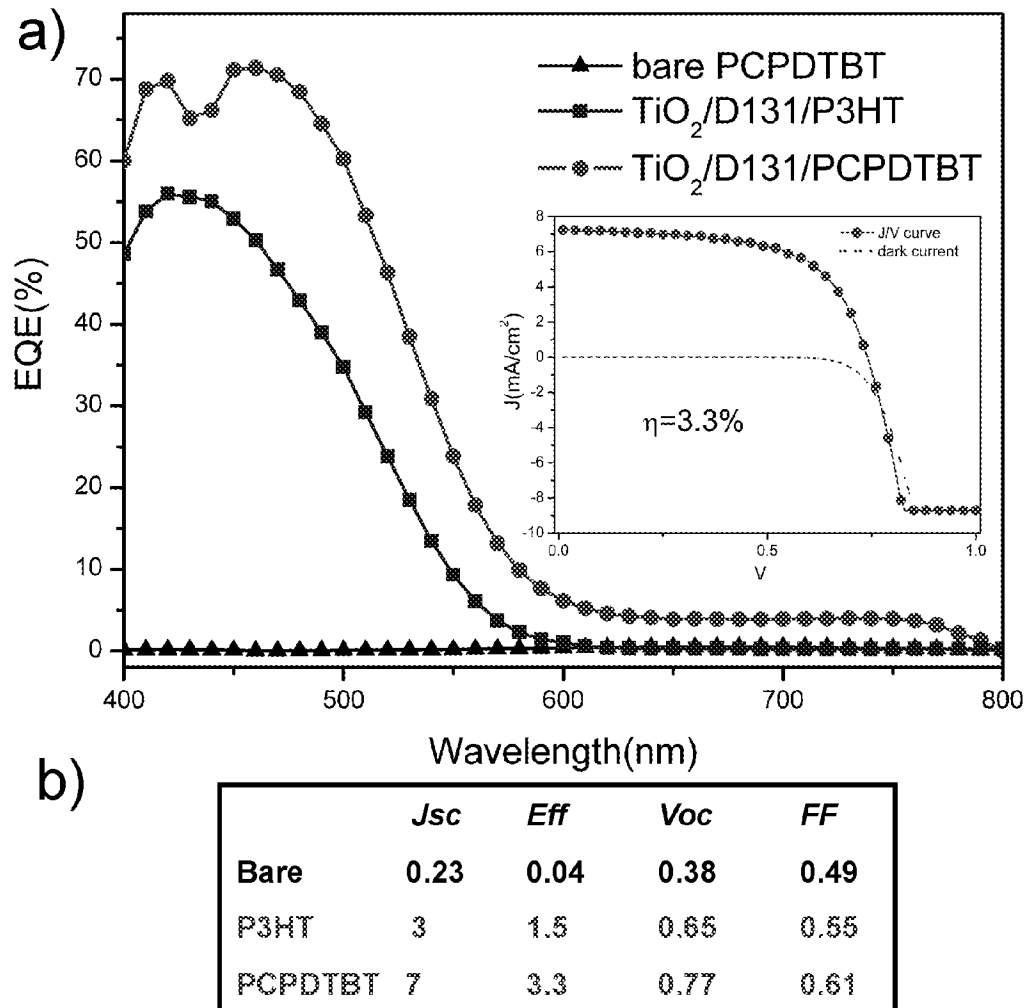


Figure 5 (a) External quantum efficiency spectra of a $\text{TiO}_2/\text{PCPDTBT}$ (triangles); $\text{TiO}_2/\text{D131}/\text{P3HT}$ (squares); $\text{TiO}_2/\text{D131}/\text{PCPDTBT}$ (circles) based dye-sensitized solar cell. (b) Solar cell performance parameters extracted from current-voltage curves of a $\text{TiO}_2/\text{PCPDTBT}$ based solar cells, a $\text{TiO}_2/\text{D131}/\text{PCPDTBT}$ based dye-sensitized solar cell and also of $\text{TiO}_2/\text{D131}/\text{P3HT}$ based dye-sensitized solar cell measured under AM1.5 simulated sun light of 100mWcm^{-2} .

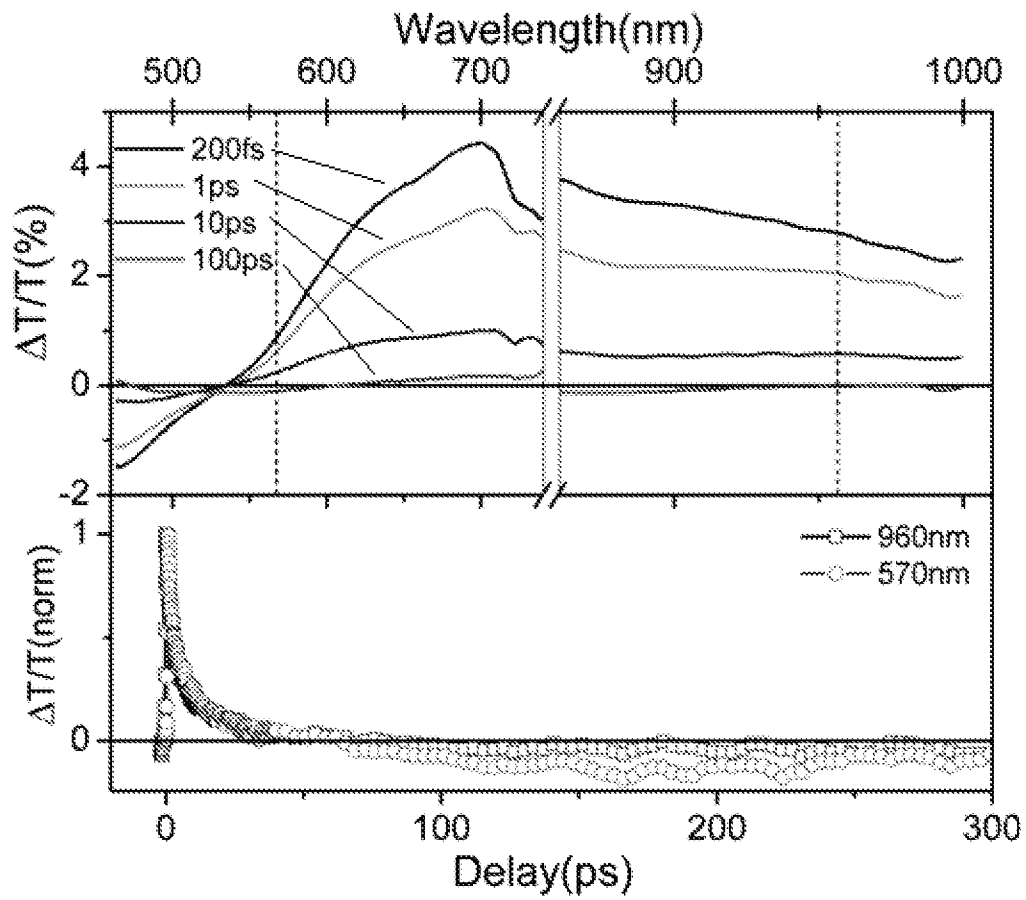


Figure 6 Top: Pump-probe spectrum of $\text{TiO}_2/\text{PCPDTBT}$ collected at different pump-probe delay, from 200fs to 100ps, as indicated in the legend. Down: Normalized $\Delta T/T$ dynamics at 570nm and at 960nm as a function of pump-probe delay.

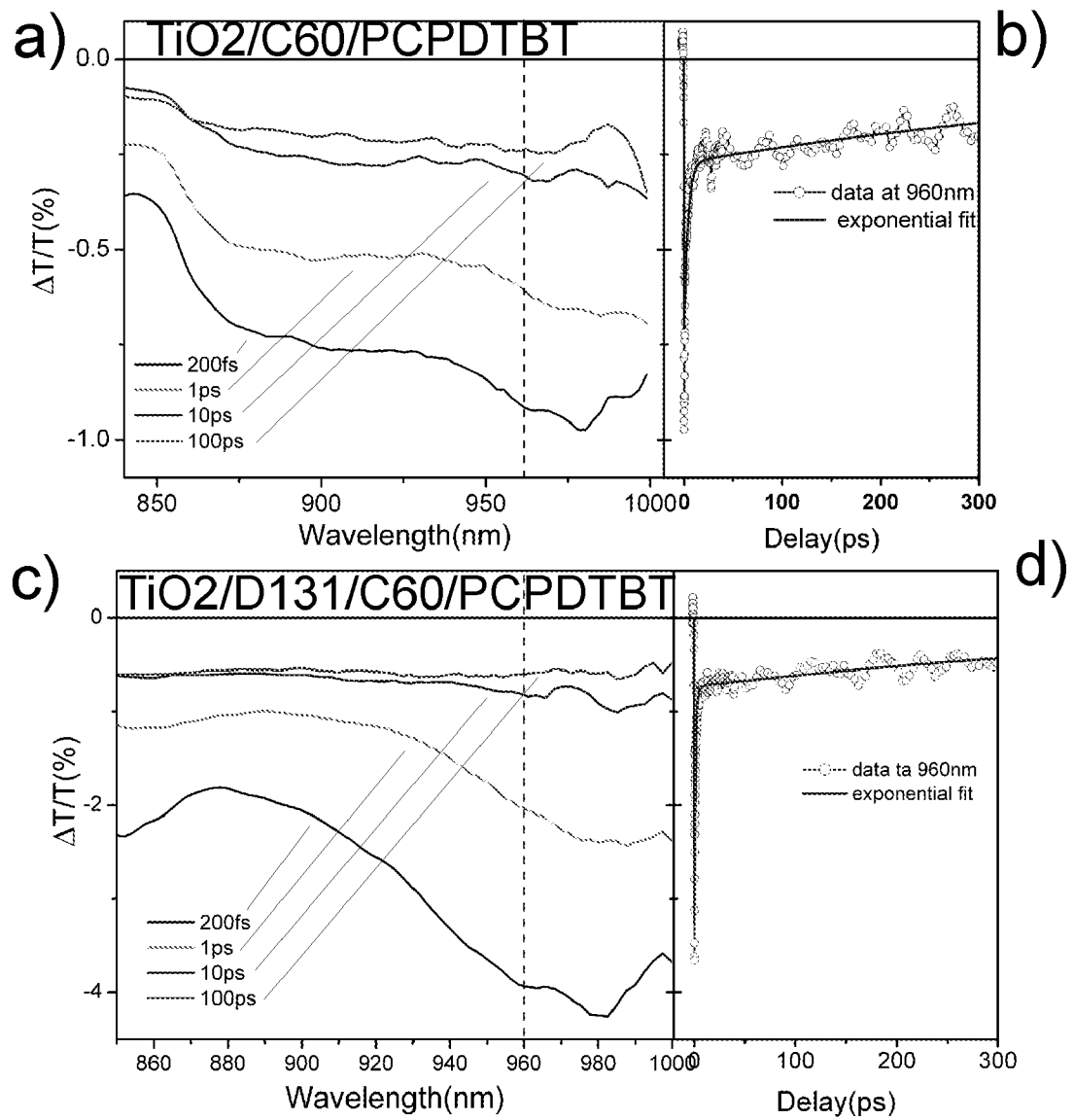


Figure 7. Pump-probe spectrum of a) $\text{TiO}_2/\text{C}_{60}\text{-SAM/PCPDTBT}$ and c) $\text{TiO}_2/\text{D131}/\text{C}_{60}\text{-SAM/PCPDTBT}$ collected at different pump-probe delay, from 200fs to 100ps, as indicated in the legend. b) and d) respective $\Delta T/T$ dynamics as 960nm probe wavelength and 780nm pump wavelength. Pump 780nm.

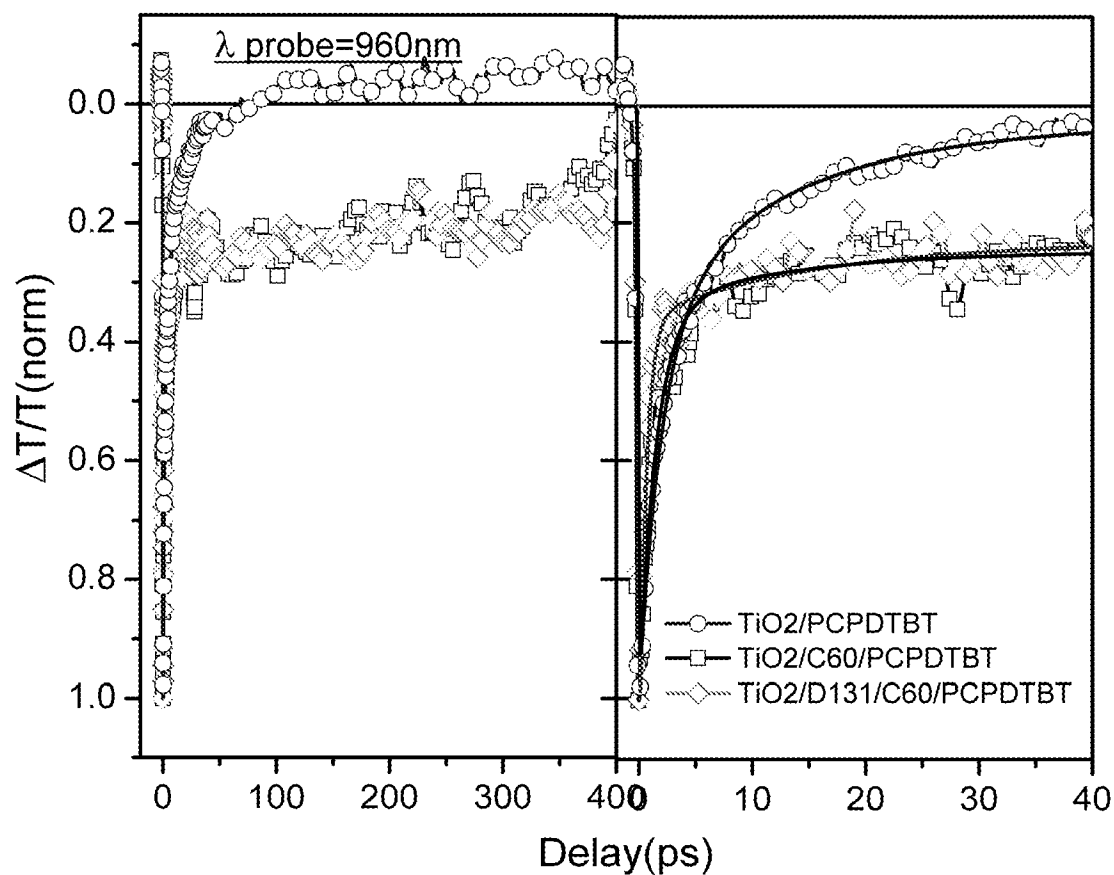


Figure 8. Normalized $\Delta T/T$ dynamics as 960nm probe wavelength of TiO₂/PCPDTBT (circles), TiO₂/C₆₀-SAM/PCPDTBT (squares) and TiO₂/D131/C₆₀-SAM/PCPDTBT (triangles) on long (a) and short time scale (b). In (c) table indicating the fit parameters. 780nm pump.

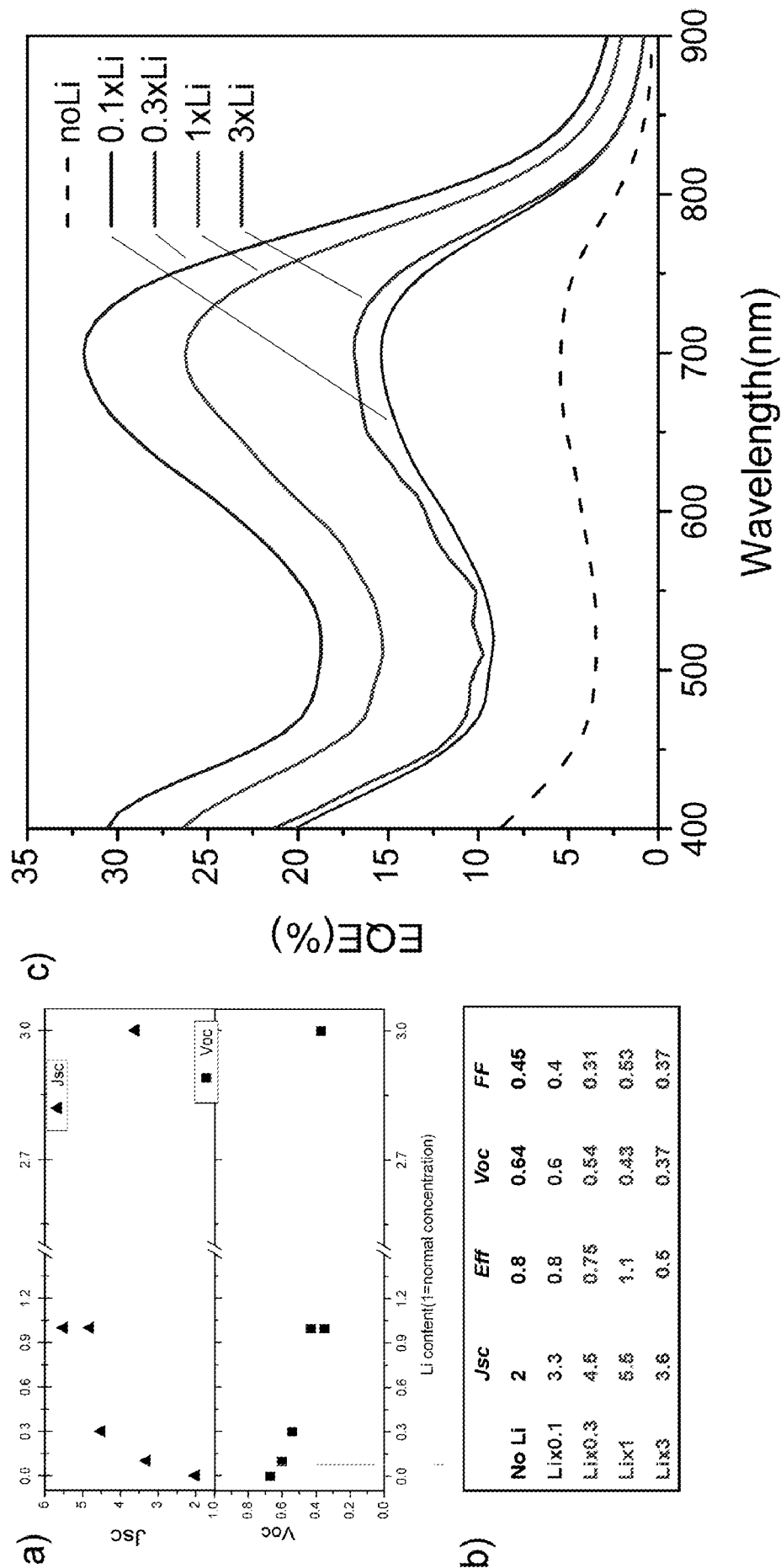
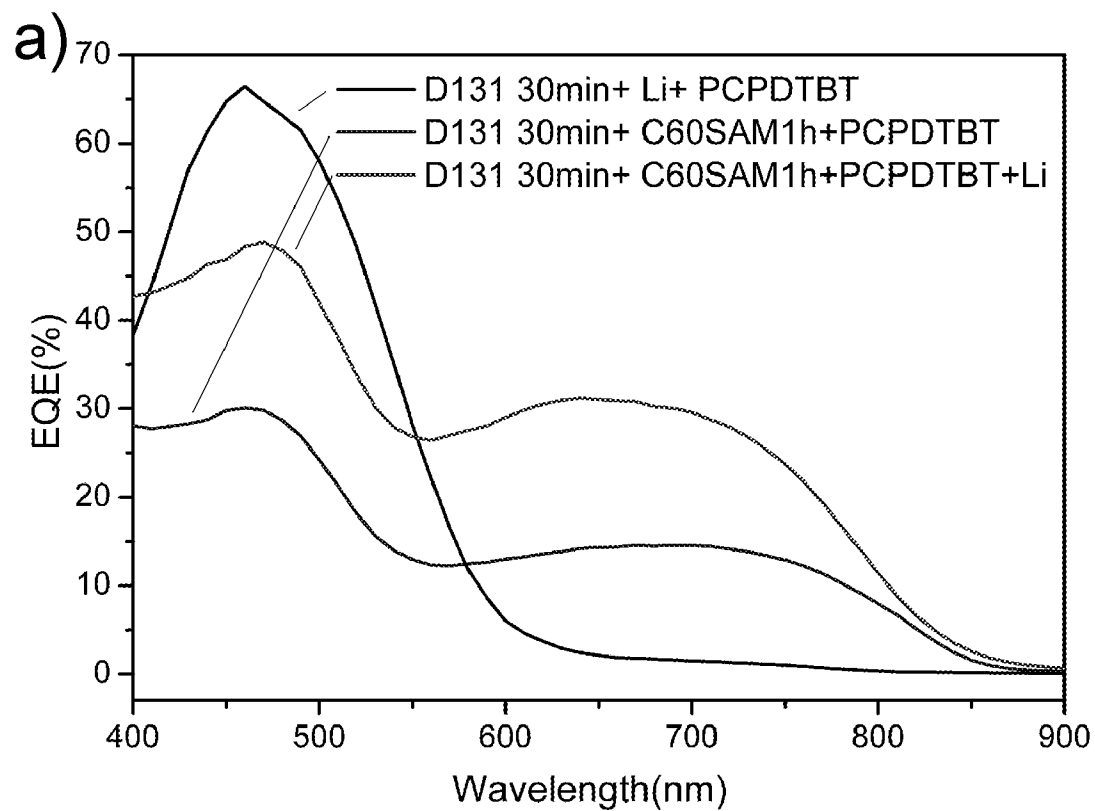


Figure 9 (a) Jsc and Voc dependence on Li salts concentration on PCPDTBT/C₆₀-SAM/TiO₂ devices. (b) Device parameters and (c) External quantum efficiency spectra for corresponding devices presented in Figure 9a and 9b.



b)

	Jsc	Eff	Voc	FF
TiO ₂ /D131/Li/PCPDTBT	5	1.25	0.4	0.57
TiO ₂ /D131/ <u>C60SAM</u> /PCPDTBT	4.3	1.2	0.55	0.5
TiO ₂ /D131/ <u>C60SAM</u> / <u>Li</u> /PCPDTBT	8	1.44	0.4	0.5

Figure 10 (a) External quantum efficiency spectra and (b) device performances for a series of PCPDTBT based DSSC with and without C₆₀-SAM and D131 co-sensitization. Note that all the samples belong to the same device batch, where the controller without C₆₀-SAM shows relatively low performances compared to the best devices obtained.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2012/051080

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01L51/42 H01L51/44 H01G9/20 H01L51/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01L H01G

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, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RUI ZHU ET AL: "Highly Efficient Nanoporous TiO₂-Polythiophene Hybrid Solar Cells Based on Interfacial Modification Using a Metal-Free Organic Dye", ADVANCED MATERIALS, vol. 21, no. 9, 6 March 2009 (2009-03-06), pages 994-1000, XP55034084, ISSN: 0935-9648, DOI: 10.1002/adma.200802388 cited in the application page 994, column 2, line 19 - line 26; figure 1 page 996, column 2, line 33 - line 37 page 997, column 2, line 15 - line 21; figure 4(B) page 998, column 2, line 33 - page 999, column 1, line 13 ----- -/--	1,2,5, 10-14, 16,17, 19-22, 24-30



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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INTERNATIONAL SEARCH REPORT

International application No
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