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(54) Title: MULTICOMPONENT ORGANIC SOLAR CELLS

(57) Abstract: There is described an organic solar cell (OSC) comprising a multicomponent blend incorporating a semiconducting polymer, an electron acceptor and at least one light harvesting dye such as a porphyrin. There are further disclosed photovoltaic devices and photodetectors comprising the multicomponent blend.



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MULTICOMPONENT ORGANIC SOLAR CELLS**FIELD OF THE INVENTION**

The present invention relates broadly to organic solar cells, and to photodetectors and photovoltaic cells comprising the organic solar cells.

5 **BACKGROUND OF THE INVENTION**

Although the performance of organic solar cells (OSCs) have improved significantly over recent years, the power conversion efficiencies of these devices is only a few percent. These "bulk heterojunction" structures typically consist of a two component blend comprising a semiconducting polymer (electron donor and hole conductor) and a fullerene derivative (electron acceptor and conductor). By carefully controlling phase segregation, two interpenetrating conduction networks are formed resulting in a high density of interfacial dissociation sites for the strongly bound photogenerated excitons. Exciton generation occurs mainly in the polymer and thus the spectral response of these devices is typically limited to wavelengths less than λ_g , the wavelength defined by the polymer band-gap energy. This wavelength is typically around 500nm (green light) and hence most light in the solar spectrum that has a wavelength above λ_g , (eg. red light) cannot be converted into electrical energy.

The current density generated by a photovoltaic device as a function of the incident wavelength $j(\lambda)$, is governed by the incident photon flux $N(\lambda)$, the absorption efficiency $a(\lambda)$, and the internal quantum efficiency $\eta_{int}(\lambda)$, such that:

$$20 \quad j(\lambda) = N(\lambda)\alpha(\lambda)\eta_{int}(\lambda) = N(\lambda)\eta_{ext}(\lambda) \quad (1)$$

where $\eta_{ext}(\lambda)$ is the external quantum efficiency.

The power conversion efficiency of a photovoltaic device η_e is defined in terms of the fill factor FF, the open-circuit voltage V_{oc} , the short-circuit current density J_{sc} , and the incident optical power density L:

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$$\eta_e = \frac{FF V_{oc} J_{sc}}{L} = \left(\frac{FF V_{oc}}{L} \right) \int_{\lambda_1}^{\lambda_2} N(\lambda) \alpha(\lambda) \eta_{int}(\lambda) d\lambda \quad (2)$$

From equation (2) it can be seen that, for a fixed incident photon flux, there are four main routes to improving OSC performance, namely improving the internal quantum efficiency $\eta_{int}(\lambda)$ of converting absorbed photons into current, improving matching of the photon absorption $\alpha(\lambda)$ to the solar spectrum, or by improving the fill factor of FF or the open-circuit voltage V_{oc} .

The recent increases in OSC efficiency can be primarily attributed to improvements in $\eta_{int}(\lambda)$ which itself consists of two factors. Firstly, there is $\eta_{ex}(\lambda)$, the efficiency with which photogenerated excitons reach a dissociation interface prior to recombination. Secondly, there is $\eta_{e-h}(\lambda)$, the efficiency with which the subsequently dissociated charge carriers reach the appropriate electrode without being absorbed by defect or impurity traps in the material, and thus: $\eta_{int} = \eta_{ex} \eta_{e-h}$.

Improvements in η_{ex} have been achieved by optimising the thin film spin coating process to produce a complex phase-separated interpenetrating network thus increasing the density of interfaces in the material to produce a so-called "bulk heterojunction" structure. Most semi-conducting polymers are p-type and hence the electron mobility in these materials is typically low. By making one of the components of the network an efficient electron acceptor, η_{e-h} can be significantly enhanced provided the electron acceptor concentration is high enough to form an efficient electron-transporting percolation network throughout the device. Although these developments led initially to significant increases in OSC power efficiency, only incremental improvements have subsequently been obtained, and bulk heterojunction OSCs (based on blends of polyphenylenevinylene (PPV) and fullerene derivatives) have reported power conversion efficiencies of only up to 3%.

Combining developments in $\eta_{int}(\lambda)$ with improvements in $\alpha(\lambda)$ of organic photodevices has proved to be more problematic. One approach to improving the spectral response of OSCs has been to add a dye, such as porphyrin, with an absorption profile which complements that

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of the semi-conducting polymer. These devices have consisted of a two component system comprising the porphyrin and a semi-conducting polymer.

- Based on the assumption that efficient charge transfer from an excited dye requires intimate molecular contact, previous work on porphyrin based OSCs has focussed upon producing
- 5 complex molecular architectures where the porphyrin is covalently bound to the charge conduction network. Studies of covalently linked two component porphyrin-fullerene systems have demonstrated that electron-transfer can occur rapidly from porphyrin to fullerene moiety and that it is possible to form photoexcited charge separated states that are long-lived.
- 10 Porphyrins have also been studied as sensitising dyes for photoelectrochemical solar cells, as well as for photovoltaic devices based on polymeric and small molecular weight organic materials. However, although the absorption in these two component devices is typically improved, the complex interplay between exciton generation, dissociation and subsequent charge carrier collection, which in turn depends intricately upon the photo-physics, network
- 15 structure and chemistry, means that the development of an efficient broadband organic photovoltaic device has proven elusive.

SUMMARY OF THE INVENTION

- In one aspect of the present invention there is provided an organic solar cell for generating photocurrent from incident light to which it is exposed and comprising a multicomponent
- 20 blend incorporating:
- a semiconducting polymer;
 - an electron acceptor; and
 - at least one light harvesting dye.

- The multicomponent blend embodied by the invention can also be utilised as a photovoltaic or
- 25 photodetector for generating photocurrent in response to incident light to which it is exposed.

Hence, in another aspect of the present invention there is provided a photovoltaic device for generating a photocurrent in response to incident light to which it is exposed, the device comprising a multicomponent blend incorporating:

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a semiconducting polymer;
an electron acceptor; and
at least one light harvesting dye.

5 In a yet further aspect of the invention there is provided an organic photodetector for generating a photocurrent in response to incident light to which it is exposed, the organic photodetector comprising a multicomponent blend incorporating:

a semiconducting polymer;
an electron acceptor; and
at least one light harvesting dye.

10 The photodetector may be an organic optoelectronic detector of the type used, for example, in photonic-based industries.

In another aspect of the invention there is provided a method of fabricating a multicomponent blend for generating photocurrent from incident light, the method comprising blending the semiconducting polymer and the electron acceptor with at least one light harvesting dye.

15 Preferably, the method will comprise tailoring the multicomponent blend to generate the photocurrent in response to the incident light. Typically, the tailoring will comprise selecting the semiconducting polymer, the electron acceptor and the at least one light harvesting dye to generate the photocurrent within a predetermined wavelength range when blended together. Alternatively, the tailoring of the multicomponent blend may comprise varying the types of
20 the semiconducting polymer, the electron acceptor and the light harvesting dye used in the fabrication of the multicomponent blend. More preferably, the tailoring will involve varying the ratios of the semiconducting polymer, the electron acceptor and the light harvesting dye in the multicomponent blend. The predetermined wavelength range may comprise a selected bandwidth within the solar spectrum or wavelengths across the solar spectrum.

25 Most preferably, the method of fabricating the multicomponent blend will comprise tailoring the multicomponent blend to generate the photocurrent across substantially the entire solar spectrum.

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The light harvesting dye will normally absorb photon energy in a wavelength range outside of the absorption spectra of the semiconducting polymer and the electron acceptor. Typically, the light harvesting dye will be selected from the group consisting of tetranitrogen containing macrocycles, tetrapyrrolic macrocycles, phthalocyanines, and related macrocycles with large absorbances in the visible and/or near infrared region; the light harvesting dye can also be a chemical that contains multiple chromophores such as porphyrin-appended dendrimers and linked oligoporphyrin systems. Preferably, the tetrapyrrolic macrocycle will be selected from the group consisting of porphyrins and metallated tetracyano porphyrins. Most preferably, the light harvesting dye will be a metallated tetracyanoporphyrin.

- 10 By "organic solar cell" is meant that one or more of the semiconducting polymer, electron acceptor and light harvesting dye(s) of the multicomponent blend is an organic molecule.

In particularly preferred embodiments of the invention, the light harvesting dye is not bonded to the electron acceptor by a covalent or other chemical bond(s).

- 15 Preferably, the multicomponent blend will contain a plurality of different said light harvesting dyes, the light harvesting dyes having a different light absorption spectrum to one another.

Typically, the semiconducting polymer and the electron acceptor will facilitate electron transport and charge transfer in the generation of the photocurrent.

- The inclusion of the light harvesting dye(s) may enhance generation of the photocurrent. Without being limited by theory, the light harvesting dye(s) may act by generating charge and/or excitons in response to absorption of photon energy by the dye(s), and transferring the charge and/or excitons to conducting networks formed by the multicomponent blend.
- 20 However, it will be understood that the invention is not restricted to the mechanism by which the light harvesting dye may contribute to the generation of photocurrent. Indeed, the invention expressly extends to the use of any light harvesting dye that absorbs photon energy
- 25 from incident light and contributes to the generation of photocurrent by the multicomponent blend in response to incident light, irrespective of the mechanism involved.

All publications mentioned in this specification are herein incorporated by reference. Any discussion of documents, acts, materials, devices, articles or the like which has been included

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in the present specification is solely for the purpose of providing a context for the present invention. It is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present invention as it existed anywhere before the priority date of each claim of this application.

- 5 The features and advantages of the present invention will become further apparent from the following details description of preferred embodiments and the accompanying drawings.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1: Graph (a) shows absorption spectra for a PCBM/MEH-PPV/Cu(CN)₄PP film (thinner line) compared to a Cu(CN)₄PP film (thicker line); Graph (b) shows the external quantum efficiency ($\eta_{ext}(\lambda)$) of a MEH-PPV/PCBM/Cu(CN)₄PP OSC (thinner line) (the "porphyrin OSC") compared to that of a conventional MEH-PPV/PCBM OSC (thicker line) (the "conventional OSC"); Graph (c) shows the internal quantum efficiency ($\eta_{int}(\lambda)$) of the porphyrin OSC (thinner line) compared to that of the conventional OSC (thicker line). The labelled vertical lines are provided as guides for comparing the respective maxima in different graphs.

Figure 2: Graph showing current versus voltage curves for the porphyrin OSC (thinner line) and the conventional OSC (thicker line) Fig. 1;

Figure 3: Graph showing shows the spectral response of OSCs embodied by the invention each fabricated with a different porphyrin: methyl-2-cyano-3-(2'-(5', 10', 15', 20'-tetraphenylporphyrinyl)) acrylate (thicker line), methyl-2-cyano-3-(2'-(5', 10', 15', 20'-tetraphenylprphyrinato zinc(II)yl)) acrylate (thinner line), and the diprotonated bistriflate salt of methyl-2-cyano-3-(2'-(5', 10', 15', 20'-tetraphenylporphyrinyl)) acrylate (dashed line). Also shown is the Air Mass 1.5 (AM1.5) standard solar spectrum (left-hand axis) indicating the respective wavelength range of conventional MEH-PPV-based bulk heterojunction OSCs and porphyrin-based bulk heterojunction OSCs embodied by the present invention.

Figure 4: Graph showing spectral response of further OSCs embodied by the invention.

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DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The light harvesting dye may be any suitable dye which absorbs photon energy for charge transfer to conduction networks formed by the multicomponent blend. Free-based porphyrins and metallated porphyrins may be utilised. The metallated porphyrins which may be utilised

5 incorporate any heteroatom that binds in the inner periphery or at the outer periphery of the porphyrin. Typically the heteroatom bound to the porphyrin will be a metal ion, most typically Zn(II) Cu(II) or Mg(II). Examples of light harvesting dyes which may be used include methyl-2-cyano-3-(2'-(5', 10', 15', 20'-tetraphenylporphyrinyl)) acrylate, the diprotonated bistriflate salt of methyl-2-cyano-3-(2'-(5', 10', 15', 20'-tetraphenylporphyrinyl)

10 acrylate, methyl-2-cyano-3-(2'(5', 10', 15', 20'-tetraphenylporphyrinato zinc(II)yl)) acrylate, (2, 3, 12, 13-tetracyano-5', 10', 15', 20'-tetrakis(3, 5-di-tert-butylphenyl) porphyrinato copper (II)) (Cu(CN)₄PP), (2,3,12,13-tetracyano-5, 10, 15, 20-tetrakis(3,5-di-tert-butylphenyl)porphyrinato)copper(II) (Cu(CN)₄PP) and its free base and zinc(II) and Mg(II) analogues and other (2,3,12,13-tetracyano-5,10,15,20-tetra-arylporphyrinato)copper(II)

15 compounds and their free-base and zinc(II) and Mg(II) analogues. Typically, the porphyrin-containing component will be soluble in the same solvents as the semiconducting polymer and electron acceptor for the purpose of fabrication of the device.

The electron acceptor may for instance be selected from the group consisting of fullerenes, fullerene derivatives, pyrenes, pyrene derivatives, naphthimides, naphthimide derivatives,

20 viologen, viologen derivatives, nicotinamide, nicotinamide derivatives, 7,7',8,8'-tetracyanoquinodimethanes, 7,7',8,8'-tetracyanoquinodimethane derivatives, perylenes, and perylene derivatives and titanium dioxide. Examples of electron acceptors that may be used include buckminsterfullerene, methano-fullerene derivatives, ((6,6)-phenyl-C₆₁-butyric acid methyl ester (PCBM), pyrene, 1-pyreneacetic acid, *N*-(1-pyrenyl)maleimide, 1-

25 hydroxypyrene, 1,8-naphthalimide, 1,4,5,8-naphthalendiimide, *N,N'*-dicyclohexylnaphthalene-1,4,5,8-tetracarboxylic acid diimide, methyl viologen dichloride (paraquat), methyl viologen bis(hexafluorophosphate), ethyl viologen dichloride, 1,1'-Dimethyl-2,2'-dipyridylium dichloride, 1-methylpyridinium chloride, 1-ethylpyridinium chloride, 1-methyl-2-picolinium chloride, 1-methyl isonicotinic acid chloride, beta-nicotinamide adenine dinucleotide sodium

30 salt (NAD⁺), beta-nicotinamide adenine dinucleotide phosphate hydrate (NADP⁺),

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tetracyano-*p*-quinodimethane (TCNQ), 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyano-*p*-quinodimethane, perylene, 3,4,9,10-perylenecarboxylic diimide, anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone, and 5,6,12,13-tetrakis[4-(1,1-dimethylethyl)phenoxy]- (9CI). Preferably, the electron acceptor will be a methano-fullerene derivative and most preferably, PCBM.

The semiconducting polymer may be selected from polymeric materials containing extended pi-systems for charge conduction. Examples of such semiconducting polymers include (poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene]) (MEH-PPV).. MEH-PPV will preferably be used in the multicomponent blend.

Typically, the multicomponent blend will contain the electron acceptor in a weight ratio of greater than 2 relative to the semiconducting polymer and the light harvesting dye. The electron acceptor will generally be present in a weight ratio of the semiconducting polymer, electron acceptor and light harvesting dye of from between about 1:1:1 to about 1:10:1 and preferably, from about 1:2:1 to about 1:10:1. More preferably, the weight ratio will be in a range of from about 1:4:1 to about 1:10:1 and most preferably, the weight ratio will be essentially 1:8:1.

It will also be understood that the multicomponent blend of an OSC of the invention may comprise more than one electron acceptor and/or semiconducting polymer in combination with the selected light harvesting dye(s). The amounts of each of these components may be varied to modify the light wavelength absorbtion profile of the blend and the bandwidth within which photocurrent is generated. By tailoring the chemistry of the multicomponent blend in this way, broadband generation of photocurrent may be obtained. Alternatively, photocurrent generation may be limited to within a predetermined wavelength range.

When light harvesting dyes comprising porphyrins are used, porphyrin mixtures with different Q-band absorption peaks may significantly extend the spectral range of photocurrent generation in OSCs embodied by the present invention. By tailoring porphyrin mixtures in the multicomponent blend, OSCs may be fabricated whose spectral response has been matched to the solar spectrum, with a concomitant increase in power efficiency. Similarly, by using porphyrins whose absorption is tailored to particular bands, OSC devices may be

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provided that are ideally suited for use as low-cost photodetectors whose response is limited to particular wavelength range(s). Tailoring the chemical structure of the porphyrin either by functionalisation or metallation alters the size and position of its characteristic absorption peaks, see for instance Fukuzumi, S.; The Porphyrin Handbook, Kadish, K. Metal (Eds),
5 Academic Press: San Diego, CA, 8,115,(2000)), the contents of which is incorporated herein in its entirety.

In a preferred embodiment, an OSC embodied by the invention or device incorporating an OSC embodied by the invention may generate photocurrent across substantially the entire solar spectrum. By "solar spectrum" is meant incident light with wavelengths in a range of
10 from 200nm to 3000nm and so expressly includes visible light with wavelengths in a range of from 400nm to 700nm and for instance, infra-red light. The wavelength of infra-red light is generally accepted to range from about 700nm to about 3000nm.

An OSC embodied by the invention can be fabricated using any suitable conventionally known method including, but not limited to, spin coating, drop casting, screen printing,
15 chemical vapour deposition, sputter coating and vacuum deposition.

A photovoltaic device will typically incorporate a plurality of OSCs embodied by the invention arranged in an array in a conventionally known manner for generation of photocurrent in response to incident light. A photodetector device can also comprise an array of OSCs embodied by the invention for detecting incident light. The photodetector device
20 may be provided for detecting incident light of any wavelength within the solar spectrum including infra-red light or within a narrow predetermined bandwidth, and can be connected to switching or control circuitry in use for activation of same by the photocurrent generated in response to the light to obtain a desired outcome. As with a photodetector device, an OSC or photodetector embodied by the invention may likewise be provided that is responsive to a
25 predetermined narrow bandwidth of visible light, infra-red light, or light within another predetermined wavelength range.

In a particularly preferred embodiment, the multicomponent blend will comprise the semiconducting polymer MEH-PPV, PCBM (a soluble fullerene derivative), and the porphyrin $\text{Cu}(\text{CN})_4\text{PP}$.

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An organic solar cell embodied by the invention may be provided in the form of a plastic sheet for generating electricity when exposed to incident light. The sheet can, for instance, be in the form of a laminate bonded to a suitable substrate. The substrate may be any substrate suitable for the intended use and can be selected from metals, oxides, polymers, fabrics, textiles, building (eg. roofs or windows), vehicles (eg. bodywork or windows), or electronic devices such as laptop computers and spacecraft or other extra-terrestrial structures.

The present invention will now be further described by way of non-limiting examples.

EXAMPLE 1: Fabrication of organic solar cells**1.1 Materials**

MEH-PPV was supplied by American Dye Source (Baue d'Urfé, Quebec, Canada) and was purified before use. PCBM was supplied by the Hummelen Group at the University of Groningen, The Netherlands. The porphyrin $\text{Cu}(\text{CN})_4\text{PP}$ was supplied by Prof. Maxwell Crossley of the School of Chemistry, The University of Sydney, New South Wales, Australia. Other porphyrins were provided by Prof. David Officer of Nanomaterials Research Centre and MacDiarmid Institute for Advanced Materials and Nanotechnology, Massey University, Palmerston North, New Zealand.

1.2 Preparation of OSC devices

Films of PEDOT:PSS (Baytron P available from Bayer AG, Germany) were deposited onto pre-cleaned patterned indium tin oxide (ITO) substrates by spin coating from an aqueous solution to give a thickness of 80 nm. Blended films of MEH-PPV and PCBM were spin-coated from a chlorobenzene solution with a weight ratio of 1:4 (MEH-PPV:PCBM) yielding films of approximately 110 nm thick. Blended films of PCBM, MEH-PPV and the porphyrin $\text{Cu}(\text{CN})_4\text{PP}$ were similarly spin coated from a chlorobenzene solution containing all three materials with a weight ratio of 1:8:1 (polymer:fullerene:porphyrin) to give a film thickness of approximately 120 nm. Finally, the top metal electrode of total thickness approximately 150 nm was deposited by thermal evaporation of approximately 50 nm of calcium followed by approximately 100 nm of silver. Due to the patterned ITO substrate, six individually

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addressable devices were fabricated from each prepared film, with the active area of each device (determined by the overlap between the ITO and the metal) approximately 4 mm.

1.3 PV measurements

For PV-measurements, a Solux quartz halogen lamp (4700 Kelvin, 10° beam spread) was used, which, when placed at 300 mm from the solar cell, delivered a power density of approximately 100 mW/cm². The intensity of the light incident upon the photocells was measured using a calibrated silicon (Newport 818 – SL head & 840 meter). IV curves were collected using a Keithley 2400 source measure unit.

1.4 Spectral response measurements

Photocurrent action spectra were collected using a lock-in amplifier (Ithaco Dynatrac, Narrowband Voltmeter Model 395, Ithaca, new York, United States) to measure the short circuit-current signal from the devices when illuminated by chopped light from a tungsten halogen lamp passed through a monochromator (Oriel Cornerstone 130, Cornerstone 130, Newport Corporation, Oriel Instruments, Stratford, Connecticut, United States). A pre-amplifier was employed prior to the lock-in that served to hold the devices at virtual short-circuit and convert the current signal to a voltage.

1.5 UV/Vis measurements

UV/Vis measurements were carried out using a Cary spectrometer (Model 1E, Varian Inc., Palo Alto, California, United States). The measurements were performed on films which had a thickness of approximately 100 nm.

1.6 Results

Figure 1 shows graphs illustrating the photocurrent spectrum measuring the short-circuit current generated by (i) the conventional MEH-PPV/PCBM bulk-heterojunction OSC (thicker line) and (ii) the porphyrin based MEH-PPV/PCBM/Cu(CN)₄PP OSC (thinner line) as a function of incident wavelength.

A comparison of the absorption spectra for the MEH-PPV/PCBM/Cu(CN)₄PP blend with Cu(CN)₄PP alone (see Fig. 1a) shows that, although slightly shifted to the right, there is a

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strong absorption peak in the blended material at approximately 460 nm associated with the large Soret band absorption of the porphyrin (labelled "Soret") and further smaller peaks at 600, 640 and 740 nm associated with the much weaker Q-band absorption of the porphyrin (labelled "Q₁", "Q₂", "Q₃").

- 5 Figure 1b shows the external quantum efficiency ($\eta_{\text{ext}}(\lambda)$) of the MEH-PPV/PCBM / Cu(CN)₄PP OSC (the "porphyrin OSC") compared with that of the conventional MEH-PPV/PCBM OSC (the "conventional OSC"). The MEH-PPV/PCBM OSC has a band gap of 2.1 eV and hence the majority of the short-circuit current is produced for incident wavelengths below $\lambda_g = 590$ nm. Indeed, below λ_g the responses of the two devices are comparable, with a
- 10 high external quantum efficiency of approximately 30 %. However, above λ_g the two responses diverge, with the MEH-PPV/PCBM / Cu(CN)₄PP device exhibiting a strong photocurrent response at 650 nm, together with smaller responses at 640 nm and 740 nm, associated with the Q-band absorption of the porphyrin.

- As shown in Fig 1c, the difference between the *internal* quantum efficiency ($\eta_{\text{int}}(\lambda)$) of the
- 15 two devices is even more marked. Despite the fact that the addition of porphyrin necessarily reduces the relative polymer content of the film, the porphyrin OSC exhibits an increased response across the entire spectral range compared to the conventional OSC. In addition to the spectral features associated with the conventional OSC there are now clear peaks in the response that can be attributed to the Soret and Q-band features in the porphyrin UV-Vis
- 20 spectrum.

- The photocurrent associated with the Q-band absorption for the MEH-PPV/PCBM/Cu(CN)₄PP OSC device is generated from photons with energy less than the band gap energy of the semi-conducting polymer and as such must originate from charge transfer from the porphyrin. Light absorbed by the Q-bands of the porphyrin creates excitons,
- 25 ie excited molecular states, that must transfer their charge to the conducting networks in order to contribute to the photocurrent. What makes the spectral response of the porphyrin based device so broad is the surprisingly high level of photocurrent generated by the Q-bands. The internal quantum efficiency of the Q₂-peak, for example, is over 60% of that due to the MEH-PPV at its peak value. The origin of this enhanced photocurrent in the Q-band region of the

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porphyrin absorption spectrum lies in the efficient charge transfer from the (absorbing) porphyrin molecule to the charge conducting networks. For photogenerated electrons, this conduction network is formed by the PCBM percolation network whereas the photogenerated holes (+ve charge) are transferred to the MEH-PPV semiconducting polymer network.

- 5 For the three component blend of PCBM/MEH-PPV/Cu(CN)₄PP, it appears that the polymer-porphyrin-methanofullerene conduction networks are sufficiently intimately mixed to allow for efficient electron transfer from porphyrin to methanofullerene and for efficient hole (+ve charge) transfer from porphyrin to the semiconducting polymer. Cyclic voltammetry measurements of the PCBM and Cu(CN)₄PP materials, both separately and as a mixture,
- 10 showed that the position of the first reduction peaks of the two materials were equivalent to within 0.1 eV. These measurements indicate that there is essentially no energetic barrier to charge transfer from the Cu(CN)₄PP to the PCBM moiety.

- Fig 2 shows current versus voltage (IV) curves for the MEH-PPV/PCBM/Cu(CN)₄PP OSC (thinner line) and the conventional MEH-PPV/PCBM OSC (thicker line). The current-
- 15 voltage (IV) curves for these devices demonstrates that, despite reducing the relative polymer content of the films, the short-circuit current produced by the porphyrin-based OSC is comparable to, or slightly higher than, that of the conventional OSC. The overall efficiency of these heterostructured devices is governed by the competing effects of $\alpha(\lambda)$ and $\eta_{int}(\lambda)$.
- While increasing $\alpha(\lambda)$, the addition of porphyrin to the blend necessarily displaces both
- 20 semiconducting polymer and fullerene, potentially limiting the effectiveness of the hole and electron conduction networks respectively, as well as possibly reducing exciton generation from the semiconducting polymer below λ_g . Nevertheless, significant increases in OSC performance may be obtained with optimisation of the blend composition and active layer thickness.

25 **EXAMPLE 2: Organic solar cells containing multiple porphyrins**

As shown in Fig. 3, enhanced Q-band photocurrent generation was observed for a variety of porphyrin molecules in the three component blended OSC structure embodied by the present invention. This demonstrates that charge transfer from porphyrin to the conduction networks is a generic feature of many porphyrins. The different porphyrins exhibit complementary

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$\eta_{int}(\lambda)$ spectra, which effectively span the wavelength range that is not covered by the conventional MEH-PPV based conventional OSC device and much better match the solar spectrum (hatched area).

Fig. 4 shows the photocurrent action spectra for three OSC devices wherein the porphyrin component is: (A) Cu CN COO Me, (B) Cu(CN)₄PP or (C) a 50:50 ratio of A and B. The results again demonstrate that OSC's containing blends of more than one porphyrin generate photocurrent across regions of the solar spectrum more effectively.

Now that preferred embodiments of the invention has been described in some detail, it will be apparent to those skilled in the art that at least the described embodiments of the organic solar cell and photodetector have the following advantages:

1. The multicomponent blend may allow for broadband solar collection in an organic solar cell;
2. The chemistry of the multicomponent blend may be tailored so that it is responsive to light of a specific wavelength;
3. The multicomponent blend can be utilised in a photodetector whose light response is tailored to a specific wavelength;
4. The organic solar cells are relatively cheap, flexible and can provide of a large surface area for generating electricity.

It will also be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive. For example, the multicomponent blend is not limited to those compounds described and extends to other semiconducting polymers, electron acceptors and light-harvesting dyes. Moreover, the organic solar cells and photodetectors embodied by the invention may be utilised in applications other than those specifically described.

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CLAIMS:

1. An organic solar cell for generating photocurrent from incident light to which it is exposed and comprising a multicomponent blend incorporating:
a semiconducting polymer;
5 an electron acceptor; and
at least one light harvesting dye.
2. An organic solar cell according to claim 1 wherein the light harvesting dye is not bonded to the electron acceptor by a chemical bond.
3. An organic solar cell according to claim 1 or 2 wherein the multicomponent blend is
10 adapted to generate photocurrent in response to incident light across essentially the entire solar spectrum.
4. An organic solar cell according to any one of claims 1 to 3 wherein the multicomponent blend generates a photocurrent in response to incident light within a predetermined wavelength range.
- 15 5. An organic solar cell according to any one of claims 1 to 4 wherein the multicomponent blend contains the electron acceptor in a weight ratio of greater than 2 relative to the semiconducting polymer and the light harvesting dye.
6. An organic solar cell according to claim 5 wherein the multicomponent blend contains the semiconductor polymer, the electron acceptor and the at least one light harvesting
20 dye in a weight ratio of substantially 1:8:1, respectively.
7. An organic solar cell according to any one of claims 1 to 6 wherein the light harvesting dye is selected from the group consisting of tetranitrogen macrocycles, tetrapyrrolic macrocycles, phthalocyanines, porphyrins and metallated tetracyanoporphyrins.
- 25 8. An organic solar cell according to claim 7 wherein the light harvesting dye comprises a porphyrin.

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9. An organic solar cell according to any one of claims 1 to 6 wherein the multicomponent blend contains a plurality of different said light harvesting dyes, the light harvesting dyes having a different light absorption spectrum to one another.
10. An organic solar cell according to claim 9 wherein the light harvesting dyes are porphyrins with different Q-band absorption spectrums to one another.
11. An organic solar cell according to any one of claims 5 to 8 wherein the, or each, light harvesting dye is selected from the group consisting of methyl-2-cyano-3-(2'-(5',10',15',20'-tetraphenylporphyrinyl)) acrylate, methyl-2-cyano-3-(2'-(5',10',15',20'-tetraphenylporphyrinato zinc(II)yl)) acrylate, and a diprotonated bistriflate salt of methyl-2-cyano-3-(2'-(5',10',15',20'-tetraphenylporphyrinyl)) acrylate.
12. An organic solar cell according to any one of claims 1 to 11 wherein the electron acceptor is selected from the group consisting of fullerenes, fullerene derivatives, pyrenes, pyrene derivatives, naphthimides, naphthimide derivatives, viologen, viologen derivatives, nicotinamide, nicotinamide derivatives, 7,7',8,8'-tetracyanoquinodimethanes, 7,7',8,8'-tetracyanoquinodimethane derivatives, perylenes, and perylene derivatives and titanium dioxide.
13. An organic solar cell according to claim 12 wherein the electron acceptor comprises (6,6)-phenyl-C₆₁-butyric acid methyl ester.
14. An organic solar cell according to any one of claims 1 to 13 wherein the semiconducting polymer may be selected from polymeric materials containing extended pi-systems for charge conduction.
15. An organic solar cell according to claim 14 wherein the semiconducting polymer comprises poly[2-methoxy-5-(2'-ethyl-hexyloxy-1,4-phenylene vinylene)].
16. A photovoltaic device for generating photocurrent from incident light to which it is exposed and comprising a multicomponent blend incorporating:
a semiconducting polymer;

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an electron acceptor; and
at least one light harvesting dye.

17. A photovoltaic device according to claim 16 wherein the light harvesting dye is not bonded to the electron acceptor by a chemical bond.
- 5 18. A photovoltaic device according to claim 16 or 17 wherein the multicomponent blend is adapted to generate the photocurrent across essentially the entire solar spectrum.
19. A photovoltaic device according to any one of claims 16 or 17 wherein the multicomponent blend generates a photocurrent in response to incident light within a predetermined wavelength range.
- 10 20. A photovoltaic device according to any one of claims 16 to 19 wherein the multicomponent blend contains the electron acceptor in a weight ratio of greater than 2 relative to the electron acceptor and the light harvesting dye.
- 15 21. A photovoltaic device according to claim 20 wherein the multicomponent blend contains the semiconducting polymer, the electron acceptor, and the at least one light harvesting dye in a weight ratio of substantially 1:8:1, respectively.
22. A photovoltaic device according to any one of claims 16 to 21 wherein the light harvesting dye is selected from the group consisting of tetranitrogen macrocycles, tetrapyrrolic macrocycles, phthalocyanines, porphyrins and metallated tetracyanoporphyrins.
- 20 23. A photovoltaic device according to claim 22 wherein the light harvesting dye comprises a porphyrin.
24. A photovoltaic device according to any one of claims 16 to 21 wherein the multicomponent blend contains a plurality of different said light harvesting dyes, the light harvesting dyes having a different light absorption spectrum to one another.
- 25 25. A photovoltaic device according to claim 24 wherein the light harvesting dyes comprise porphyrins with different Q-band absorption spectrums to one another.

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26. A photovoltaic device according to any one of claims 16 to 25 incorporating a plurality of organic solar cells arranged in an array, each of the organic solar cells comprising the multicomponent blend of the semiconducting polymer, the electron acceptor and the at least one light harvesting dye, respectively.
- 5 27. An organic photodetector for generating a photocurrent in response to incident light to which it is exposed, the organic photodetector comprising a multicomponent blend incorporating:
- 10 a semiconducting polymer;
an electron acceptor; and
at least one light harvesting dye.
28. A photodetector according to claim 27 wherein the light harvesting dye is not bonded to the electron acceptor by a chemical bond.
29. A photodetector according to claim 27 or 28 wherein the multicomponent blend is adapted to generate photocurrent in response to incident light within a predetermined wavelength range.
- 15 30. A photodetector according to any one of claims 27 to 29 wherein the multicomponent blend contains the electron acceptor in a weight ratio of greater than 2 relative to the semiconducting polymer and the light harvesting dye.
31. A photodetector according to claim 30 wherein the multicomponent blend contains the semiconducting polymer, the electron acceptor, and the at least one light harvesting dye in a weight ratio of substantially 1:8:1, respectively.
- 20 32. A photodetector according to any one of claims 27 to 31 wherein the light harvesting dye is selected from the group consisting of tetranitrogen macrocycles, tetrapyrrolic macrocycles, phthalocyanines, porphyrins, metallated tetracyanoporphyrins, ...
- 25 33. A photodetector according to claim 32 wherein the light harvesting dye comprises a porphyrin.

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34. A photodetector according to any one of claims 27 to 31 wherein the multicomponent blend contains a plurality of different said light harvesting dyes, the light harvesting dyes having a different light absorption spectrum to one another.
35. A photodetector according to claim 34 wherein the light harvesting dyes comprise porphyrins with different Q-band absorption spectrums to one another.
36. A photodetector according to any one of claims 27 to 35 incorporating a plurality of organic solar cells arranged in an array, each of the organic solar cells comprising the multicomponent blend of the semiconducting polymer, the electron acceptor and the at least one light harvesting dye, respectively.
37. A method of fabricating a multicomponent blend for generating photocurrent from incident light, the method comprising blending a semiconducting polymer and an electron acceptor with at least one light harvesting dye.
38. A method according to claim 37 wherein the light harvesting dye is not bonded to the electron acceptor in the multicomponent blend by a chemical bond.
39. A method according to claim 37 or 38 further comprising tailoring the multicomponent blend to generate photocurrent in response to incident light in a predetermined wavelength range.
40. A method according to claim 39 wherein the tailoring comprises selecting the semiconducting polymer, the electron acceptor and the at least one light harvesting dye to generate the photocurrent in the predetermined wavelength range when blended together.
41. A method according to claim 39 or 40 wherein the multicomponent blend is tailored to generate the photocurrent across substantially the entire said predetermined wavelength range.
42. A method according to any one of claims 37 to 41 wherein the electron acceptor is blended in the multicomponent blend in a weight ratio of greater than 2 relative to the semiconducting polymer and the light harvesting dye.

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43. A method according to claim 42 wherein the semiconducting polymer, the electron acceptor and the light harvesting dye are blended together in a weight ratio of substantially 1:8:1, respectively.
- 5 44. A method according to any one of claims 37 to 43 wherein the light harvesting dye is selected from the group consisting of tetranitrogen macrocycles, tetrapyrrolic macrocycles, phthalocyanines, porphyrins and metallated tetracyanoporphyrins.
45. A method according to claim 45 wherein the light harvesting dye comprises a porphyrin.
- 10 46. A method according to any one of claims 37 to 44 wherein more than one said light harvesting dye is blended with the semiconducting polymer and the electron acceptor, the light harvesting dyes having a different light absorption spectrum to one another.
47. A method according to claim 46 wherein the light harvesting dyes are porphyrins with different Q-band absorption spectrums to one another.

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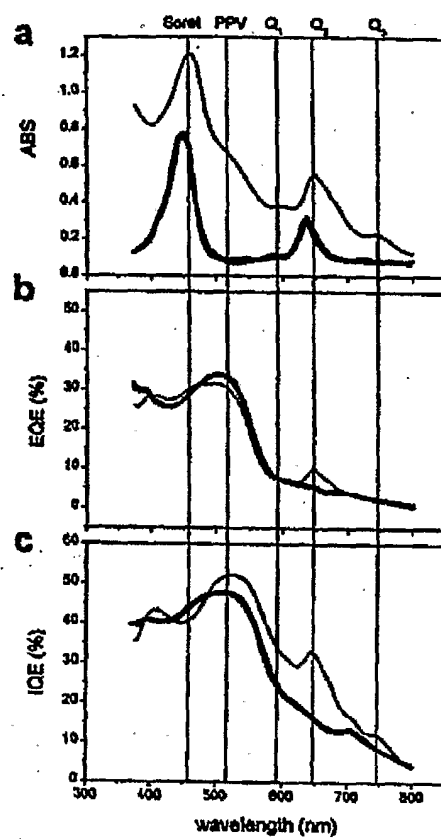


FIGURE 1

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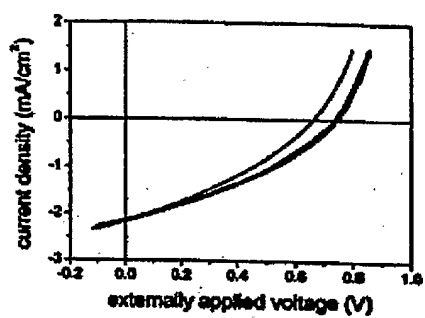


FIGURE 2

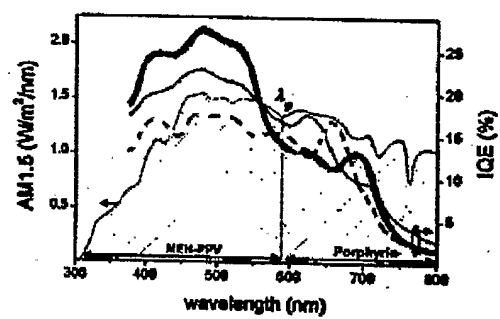


FIGURE 3

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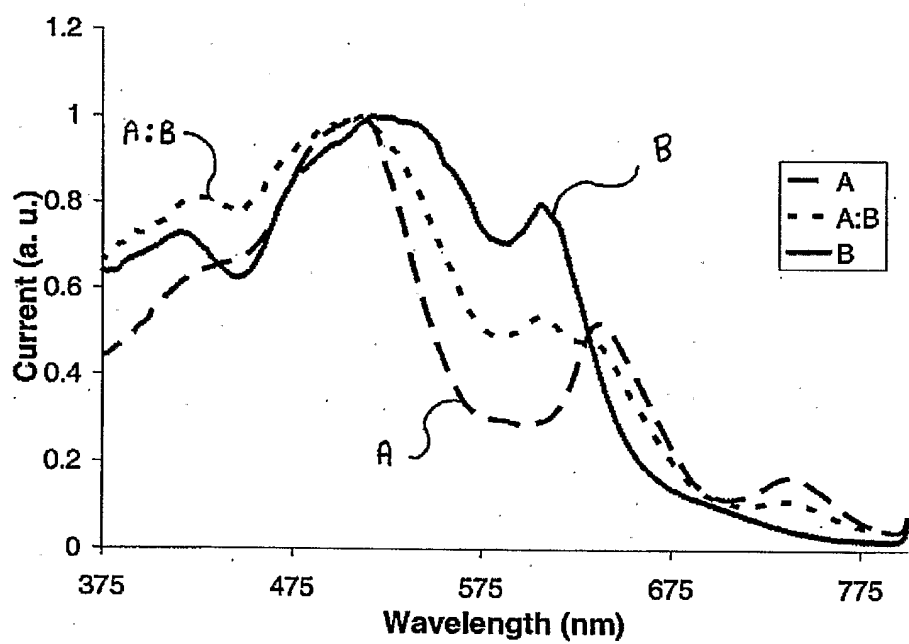


FIGURE 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2005/000637

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl. ⁷ : H01L 31/0256, 31/042 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) 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) DWPI, JAPIO, IEEE: solar cell, photovoltaic, dye, pigment, fullerene, electron acceptor, semiconductive polymer, meh-ppv and similar terms					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.			
E, X	WO 2005/050757 A2 (RENSSELAER POLYTECHNIC INSTITUTE) 2 June 2005 Whole document, paragraphs 15, 50-52 in particular	1-47			
A	US 2003/0013843 A1 (PEI) 16 January 2003 Paragraphs 148-153				
A	DE 19927981 A1 (FRAUNHOFER-GESELLSCHAFT ZUR FORDERUNG DER ANGEWANDTEN FORSCHUNG E.V. et al) 4 January 2001 Abstract				
A	Derwent Abstract Accession No. 2002-246669/30, Classes A85, E19, L03, A89, JP 2001-257012 A (FUJI PHOTO FILM CO LTD) 21 September 2001 Abstract				
<div style="display: flex; justify-content: space-between;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex </div>					
<table style="width: 100%; border: none;"> <tr> <td style="width: 33%; vertical-align: top;"> * Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 33%; vertical-align: top;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family </td> <td style="width: 33%;"></td> </tr> </table>			* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
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Date of the actual completion of the international search 7 July 2005		Date of mailing of the international search report 12 JUL 2005			
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929		Authorized officer GREG POWELL Telephone No : (02) 6283 2308			

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2005/000637

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Bailey S.G. et al, "Thin-Film Organic-Based Solar Cells for Space Power", IEEE Electron Devices Society, 37 th Intersociety Energy Conversion Engineering Conference, August 2002, retrieved from the Internet <URL: http://gltrs.grc.nasa.gov/reports/2002/TM-2002-211833.pdf > See Section entitled "Fullerene-containing Polymeric Devices", page 4	
P, A	US 2004/0084080 A1 (SAGER et al) 6 May 2004 Paragraphs 73-78	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2005/000637

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Member				
WO	2005050757	NONE					
US	2003013843	EP	1401916	US	6723828	US	6800722
		US	2002193551	US	2005033015	WO	02094910
DE	19927981	NONE					
JP	2001257012	NONE					
US	2004084080	AU	2003253672	AU	2003291756	AU	2003301934
		US	6852920	US	2004237101	US	2004250848
		US	2005098204	US	2005098205	US	2005121068
		WO	2004001926	WO	2004042432	WO	2004044948
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.							
END OF ANNEX							