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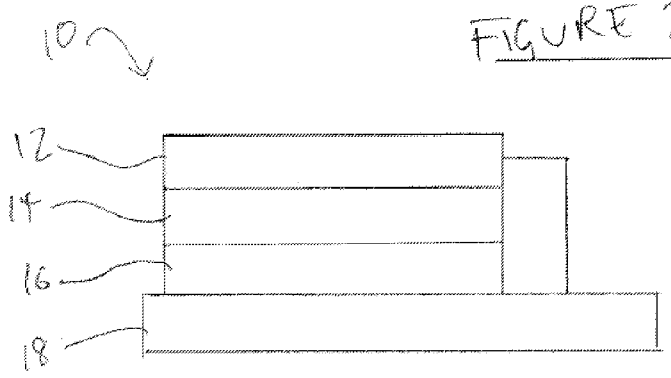
(54) Title: ORGANIC SEMICONDUCTORS

FIGURE 2



(57) Abstract: An optoelectronic device comprising a charge transfer layer including a first semiconductive polymer comprising one or more zwitterions.

Organic Semiconductors

This invention relates to organic semiconductors and, in particular, although not exclusively, to polymeric semiconductors which are usable in optoelectronic, e.g. photo-responsive, devices.

Semiconducting organic materials make remarkably effective substitutes for conventional inorganic semiconductors in a range of optoelectronic devices including light emitting diodes (LEDs), photovoltaic (PV) diodes, field effect transistors (FETs), and lasers. Among the general class of organic semiconductors, conjugated polymers exemplify the considerable material advantages that organic semiconductor may have over inorganic semiconductors including chemically tunable optoelectronic properties and low-temperature, solution-based processing suitable for printed electronics.

Conjugated polyelectrolytes (CPEs), which comprise a semiconductive polymer backbone having charge sites pendant therefrom and counterions associated with those charge sites, have been shown to be in optoelectronic devices, for example as when used as charge transport (*e.g.* electron transport or electron injection) materials. In particular, the electronic properties of the CPEs, in combination with their solubility in polar solvents, makes them attractive candidates for materials in *e.g.* LEDs and PVs.

However, optoelectronic devices including CPEs have slow turn-on times. Without wishing to be bound by any particular theory, it is postulated that this is at least in part owing to the migration of the counter ions, which may also lead to redistribution of the internal field. Moreover, these mobile counter ions also appear to make the device operation mechanism more complicated, as they may alter the work function of the one or both of the electrodes. Furthermore, in OLEDs, for example, the counter ions may impact on the doping characteristics of the light emitting layer.

It is an object of the present invention to provide materials for electronic devices having the advantages of CPEs, while minimising drawbacks such as those described above. It is a further object of the present invention to provide electronic devices including such materials.

In a first aspect, the invention provides an optoelectronic device comprising a charge transfer layer including a first semiconductive polymer comprising one or more zwitterions.

In a second aspect, the invention provides an optoelectronic device comprising a charge transfer layer including a first semiconductive polymer comprising one or more zwitterions covalently attached to the polymer.

In this specification, the term "zwitterion" shall denote a moiety which exists in a stable, charge neutral form having at least one formal positive charge centre and at least one negative charge centre.

In this specification, the term "zwitterionic substituent" refers to a distinct moiety having zwitterionic character attached to a molecule (*e.g.* a polymer).

Preferably, the one or more zwitterions are covalently attached to the semiconductive polymer backbone.

Preferably, the first semiconductive polymer comprises a first repeat unit having at least one zwitterionic substituent.

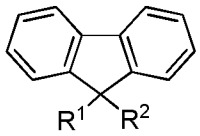
Preferably the zwitterionic substituent comprise at least one quaternary amine group.

Preferably the zwitterionic substituent comprise a sulfonate group.

Preferably, the zwitterionic substituent comprises a cationic centre and an anionic centre separated by at least 1, *e.g.* 2, 3, 4, 5, or more atomic (*e.g.* carbon) centres, for example an integer number between 2 and 20, say 2 and 10.

Preferably, the first repeat unit comprises a fluorene residue.

Preferably, the first repeat unit comprises the structure:



where R^1 comprises the or a zwitterionic substituent.

Preferably, R^2 comprises the or a zwitterion group (*e.g.* a different zwitterion group), H or a C_1 to C_{10} straight or branched alkyl, alkenyl or alkynyl chain.

More preferably, R^1 and R^2 both comprise zwitterionic substituents, *e.g.* the same zwitterionic substituents.

Preferably, one or more the of the zwitterionic substituents comprises a first cationic charge centre separated from a first anionic charge centre by more than 2 atomic (*e.g.* carbon) centres.

Preferably, the first semiconductive polymer comprises a second repeat unit.

Preferably the second repeat unit comprises a fluorene residue, *e.g.* 9,9-dioctylfluorene.

Preferably the first semiconductive polymer comprises an alternating copolymer of the first repeat unit and the or a second repeat unit.

In some embodiments, the charge transport layer is positioned between a light emissive layer and a cathode, *e.g.* the charge transport layer is positioned directly adjacent the light emissive layer and/or the cathode.

In other embodiments, the charge transport layer is positioned between a photovoltaic layer and a cathode, *e.g.* the charge transport layer is positioned directly adjacent the photovoltaic layer and/or the cathode.

Preferably, the cathode comprises one or more materials selected from aluminium, calcium, indium tin oxide (ITO).

Preferably, the charge transport layer (*e.g.* the electron transport layer) is at least 1nm (*e.g.* at least 2nm, at least 5nm, at least 7nm or at least 9nm) thick.

Preferably, the charge transport layer (*e.g.* the electron transport layer) is between 1nm and 20nm thick. More preferably, the echarge transport layer is between 2nm and 10nm thick.

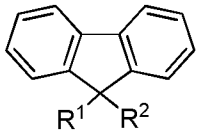
In a further aspect, the invention provides a semiconductive polymer comprising a first repeat unit having at least one zwitterionic substituent, where the zwitterionic substituent comprises a first cationic charge centre separated from a first anionic charge centre by more than 2 atomic (*e.g.* carbon) centres.

Preferably the zwitterionic substituent comprise at least one quaternary amine group.

Preferably the zwitterionic substituent comprise a sulfonate group.

Preferably, the first repeat unit comprises a fluorene residue.

Preferably, the first repeat unit comprises the structure:



where R^1 comprises the or a zwitterionic substituent.

Preferably, R^2 comprises the or a zwitterion group (*e.g.* a different zwitterion group), H or a C_1 to C_{10} straight or branched alkyl, alkenyl or alkynyl chain.

More preferably, R^1 and R^2 both comprise zwitterionic substituents, *e.g.* the same zwitterionic substituents.

Preferably, the semiconductive polymer comprises a second repeat unit.

Preferably the second repeat unit comprises a fluorene residue, *e.g.* 9,9-dioctylfluorene.

Preferably the semiconductive polymer comprises an alternating copolymer of the first repeat unit and the or a second repeat unit.

In a further aspect, the invention provides an electron injection material comprising a semiconductive polymer as described above.

In a further aspect, the invention provides an electron transport material comprising a polymer as described above.

In a further aspect, the invention comprises a method of manufacturing an electrically semiconductive zwitterionic polymer comprising: polymerising at least a first conjugated monomer to form a conductive polymer and reacting the polymer with at least one zwitterion forming reactant to form the conductive zwitterionic polymer.

Preferably, the first conjugated monomer comprises at least one tertiary amine substitution, *e.g.* such that the semiconductive polymer formed therefrom comprises a tertiary amine substituted polymer.

Preferably, the first zwitterion forming reactant comprises a negative charge carrying species or precursor thereof, for example for reacting with the or a tertiary amine group.

Preferably the negative charge carrying species or precursor thereof comprises a sulfone.

Preferably the method comprises copolymerising the first monomer with at least one further monomer, *e.g.* an amine free monomer.

Preferably the polymerisation comprises a Suzuki polymerisation.

In some embodiments, the polymerisation comprises a Yamamoto or Stille polymerisation.

In order that the invention is better understood, it will now be described by way of example only, with reference to the following drawings, in which:

Figure 1 shows a synthetic pathway for a conductive polymer according to the invention;

Figure 2 shows a schematic diagram of an optoelectronic device according to the present invention;

Figure 3 shows a plot of luminance against voltage for devices according to the invention and the prior art;

Figure 4 shows a plot of efficiency against voltage for devices according to the invention and the prior art;

Figure 5 shows a plot of absorption intensity against wavelength for materials according to the present invention and the prior art;

Figure 6 shows a plot of photoluminescent intensity against wavelength for materials according to the present invention and the prior art;

Figure 7 shows plots of luminescence and current density against time for devices according to the present invention;

Figure 8 shows plots of capacitive charge and charge density versus voltage for devices according to the present invention and the prior art.

A charge-neutral conjugated polyelectrolyte was synthesised according to the following method.

Neutral tertiary amine polymers were synthesised by Pd-mediated Suzuki condensation polymerisation of 2,7-bis(1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (1) with 2,7-dibromo-9,9-bis((N,N-dimethylamino)ethanyl) fluorene (2), under conditions as are well known in the art. The neutral tertiary amine polymer (3) so-formed is soluble in organic solvents such as chloroform, THF and toluene, but insoluble in methanol, DMSO and water.

The polymer was then quaternised by refluxing for 3 days at 70°C in toluene/methanol with 1,4-butane sultone. The resulting zwitterionic conjugated polyelectrolyte (4) was soluble in methanol and DMSO. Elemental analysis of the polyelectrolyte showed a near 100% conversion of the tertiary amines of the first polymer into the sulfobetaine zwitterionic groups.

A synthetic pathway for the above described series of reactions is shown in Figure 1.

Figure 2 shows a simple optoelectronic device 10 according to the invention. The device 10 comprises in series an aluminium cathode layer 12, a 2nm thick electron transfer layer 14 comprising the zwitterionic polyelectrolyte, a 100nm thick light emissive layer 16 comprising poly(9,9-dioctylfluorene)-co-benothiadazole (F8BT) and an ITO/PEDOT:PSS anode 18.

The device 10 was manufactured by successively spin coating the anode 18, light emissive layer 18 and electron transfer layer 14 onto a glass substrate,

followed by depositing the aluminium cathode 12 onto the electron transfer layer 14.

Example 1

The device 10 as described above was tested for luminance against voltage. The results of the test are plotted in Figure 3. The turn-on voltage (defined as the voltage at which the luminance reached 1cd/m^2) was 2.3V and the brightness increased to 1900cd/m^2 at 3V and a maximum of 80000cd/m^2 at 5.8V.

Example 2

The same device 10 was tested for current efficiency against voltage. The results of the test are plotted in Figure 4. The efficiency at 5.8V was found to be 8.8 cd/A (the corresponding current density being 910.5 cd/m^2), the maximum efficiency being 10.4 cd/A (at a brightness of 26000 cd/m^2). It is notable that the device efficiency is stable at operating voltages, with no significant decrease observed up to 5.8V.

Comparative Examples

A first comparative device was prepared to comprise, in series, an aluminium/calcium cathode, an F8BT emissive layer and a PEDOT:PSS anode.

A second comparative device was prepared to comprise, in series, an aluminium cathode, an F8BT emissive layer and a PEDOT:PSS anode.

Comparative Example 1

The first comparative device was tested for luminance against voltage and efficiency against voltage. The results are plotted in Figures 3 and 4 respectively.

As expected, the first comparative device performed very poorly in both tests, owing to poor electron injection. In particular, it is noted that the

turn-on voltage was around 7.5V, far higher than the 2.3V observed for Example 1.

Comparative Example 2

The second comparative device was also tested for luminance against voltage and efficiency against voltage. The results are plotted in Figures 3 and 4 respectively.

The turn-on voltage of the second comparative device was found to be substantially the same as that of Example 1, which can be explained by the small difference between the LUMO of F8BT (2.94eV) and the work function of Ca (2.87eV). However, the maximum brightness of the second comparative device was found to be only 30,000cd/m^2, less than half of that of the device of Example 1. Moreover, the energy conversion efficiency of the second comparative device was found to be approximately half that observed in Example 2.

Example 3

A film of the zwitterionic polyelectrolyte was tested for its absorption (Example 3a) and photoluminescent (Example 3b) properties. The results are plotted in Figures 5 and 6 respectively.

Comparative Example 3

A film of the neutral tertiary amine polymer (3) was tested for its absorption (Comparative Example 3a) and photoluminescent (Comparative Example 3b) properties. The results are plotted in Figures 5 and 6 respectively.

Example 4

A solution of the zwitterionic polyelectrolyte in methanol was tested for its solution absorption (Example 4a) and solution photoluminescent properties (Example 4b). The results are plotted in Figures 5 and 6 respectively.

Comparative Example 4

A solution of the neutral tertiary amine polymer (3) in chloroform was tested for its solution absorption (Comparative Example 4a) and solution photoluminescent properties (Comparative Example 4b). The results are plotted in Figures 5 and 6 respectively.

As can be seen from Figures 5 and 6, the film absorption and photoluminescent spectra for the zwitterionic polyelectrolyte and the neutral polymer F8BT are very similar, suggesting that the electronic properties of the zwitterionic polyelectrolyte are not affected by the strong dipole of the zwitterionic side chains.

The HOMO of the zwitterionic polyelectrolyte and F8BT were found, by cyclic voltammetry, each to be 5.6eV . The corresponding LUMOs were found through the absorption onset to be 2.67eV and 2.64eV respectively. These figures might suggest to the skilled person that including an additional zwitterionic polyelectrolyte layer between an aluminium electrode (work function 4.28eV) and an F8BT emissive layer would in fact increase the electron injection barrier. The opposite has been surprisingly shown to be so.

Example 5

An device similar to that tested in Example 1, but having a 7nm thick electron transfer layer comprising the zwitterionic polyelectrolyte, was tested to measure its luminescence (Example 5a) and current density dynamics (Example 5b) during rectangular 1Hz voltage pulses of 4.9V. The results are plotted in Figure 7.

It was observed that the response time at 4.9V was around 10μs, which is in agreement with the use of metal electrodes. The response time is understood to be faster than response times for other devices utilising conjugated polyelectrolytes as electron injection layers.

Examples 6 and 7

The time-dependence of the current measured in Example 5 (and as shown in Figure 7), and equivalent data for a similar device having an electron transfer layer comprising the zwitterionic polymer 10nm thick (Examples 6 and 7 respectively) are integrated to show charge accumulated in the device. The capacitive charge accumulation and charge density are shown in a plot against voltage in Figure 8.

Comparative Example 5

Similar current time-dependence data for a standard comparative device was integrated to show charge accumulated in the device. The capacitive charge accumulation and charge density are shown in a plot against voltage in Figure 8.

These data show that in addition to the capacitive charging of the standard device that rises linearly with voltage, the zwitterion-containing devices shows an extra charging above a threshold near 3 V. Without wishing to be bound by any particular theory, it is postulated that this extra charging arises from reorientation of the zwitterion during the timescale 0 – 10 μs.

The zwitterionic polyelectrolyte of the invention therefore offers excellent performance as a charge transport material, while maintaining fast switching times and high efficiency, and without compromising emission frequency.

It will be readily appreciated by the skilled person, that alternative or additional ionic species may be incorporated into the polymeric structure. It will be further appreciated that other zwitterionic CPEs and molecular semiconductors (e.g. fullerenes) may be used in the invention outlined herein.

Claims

1. An optoelectronic device comprising a charge transfer layer including a first semiconductive polymer comprising one or more zwitterions.

2. An optoelectronic device according to Claim 1, wherein the first semiconductive polymer comprises a first repeat unit having at least one zwitterionic substituent.

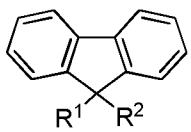
3. An optoelectronic device according to Claim 2, wherein the zwitterionic substituent comprises at least one quaternary amine group.

4. An optoelectronic device according to Claim 2 or Claim 3, wherein the zwitterionic substituent comprise a sulfonate group.

5. An optoelectronic device according to any of Claims 2 to 4, wherein the zwitterionic substituent comprises a cationic centre and an anionic centre separated by at least 1, *e.g.* 2, 3, 4, 5, or more atomic (*e.g.* carbon) centres.

6. An optoelectronic device according to any of Claims 2 to 5, wherein the first repeat unit comprises a fluorene residue.

7. An optoelectronic device according to any of Claims 2 to 6, wherein the first repeat unit comprises the structure:



where R^1 comprises the or a zwitterionic substituent.

8. An optoelectronic device according to Claim 7, wherein R^2 comprises the or a different group, H or a C_1 to C_{10} straight or branched alkyl, alkenyl or alkynyl chain.

9. An optoelectronic device according to Claim 7, wherein R^1 and R^2 comprise the same zwitterionic substituents.

10. An optoelectronic device according to any of Claims 2 to 9, wherein, the first semiconductive polymer comprises a second repeat unit.

11. An optoelectronic device according to Claim 10, wherein the second repeat unit comprises a fluorene residue, *e.g.* 9,9-dioctylfluorene.

12. An optoelectronic device according to Claim 10 or Claim 11, wherein the first semiconductive polymer comprises an alternating copolymer of the first repeat unit and the second repeat unit.

13. An optoelectronic device according to any preceding Claim, wherein the charge transport layer is positioned between a light emissive layer and a cathode, *e.g.* the charge transport layer is positioned directly adjacent the light emissive layer and/or the cathode.

14. An optoelectronic device according to any of Claims 1 to 12, wherein the charge transport layer is positioned between a photovoltaic layer and a cathode, *e.g.* the charge transport layer is positioned directly adjacent the photovoltaic layer and/or the cathode.

15. An optoelectronic device according to Claims 13 or 14, wherein the cathode comprises one or more materials selected from aluminium, calcium, indium tin oxide (ITO), gold, silver.

16. An optoelectronic device according to any preceding Claim, wherein the charge (*e.g.* electron) transport layer is at least 1nm thick.

17. An optoelectronic device according to Claim 16, wherein the charge transfer layer is from 1nm to 20nm thick.

18. A semiconductive polymer comprising a first repeat unit having at least one zwitterionic substituent, where the zwitterionic substituent comprises a first cationic charge centre separated from a first anionic charge centre by more than 2 atomic (*e.g.* carbon) centres.

19. A semiconductive polymer according to Claim 18, wherein the zwitterionic substituent comprises at least one quaternary amine group.

20. A semiconductive polymer according to Claim 18 or 19, wherein the zwitterionic substituent comprises a sulfonate group.

21. A semiconductive polymer according to any of Claims 18 to 20, wherein the first repeat unit comprises a fluorene residue.

22. A semiconductive polymer according to any of Claims 18 to 21, wherein the first repeat unit comprises the structure:

where R^1 comprises the or a zwitterionic substituent.

23. A semiconductive polymer according to Claim 22, wherein R^2 comprises a second different zwitterion group, H or a C_1 to C_{10} straight or branched alkyl, alkenyl or alkynyl chain.

24. A semiconductive polymer according to Claim 22, wherein R^1 and R^2 comprise the same zwitterionic substituents.

25. A semiconductive polymer according to any of Claims 18 to 24, wherein comprises a second repeat unit.

26. A semiconductive polymer according to Claim 25, wherein the second repeat unit comprises a fluorene residue, *e.g.* 9,9-dioctylfluorene.

27. A semiconductive polymer according to Claim 25 or 26, comprising an alternating copolymer of the first repeat unit and the or a second repeat unit.

28. An electron injection material comprising a semiconductive polymer according to any of Claims 18 to 27.

29. An electron transport material comprising a semiconductive polymer according to any of Claims 18 to 28.

30. A method of manufacturing an electrically semiconductive zwitterionic polymer comprising:

- polymerising at least a first conjugated monomer to form a conductive polymer; and,
- reacting the polymer with at least one zwitterion forming reactant to form a conductive zwitterionic polymer.

31. A method according to Claim 30, wherein the first conjugated monomer comprises at least one tertiary amine substitution, *e.g.* such that the conductive polymer formed therefrom comprises a tertiary amine substituted polymer.

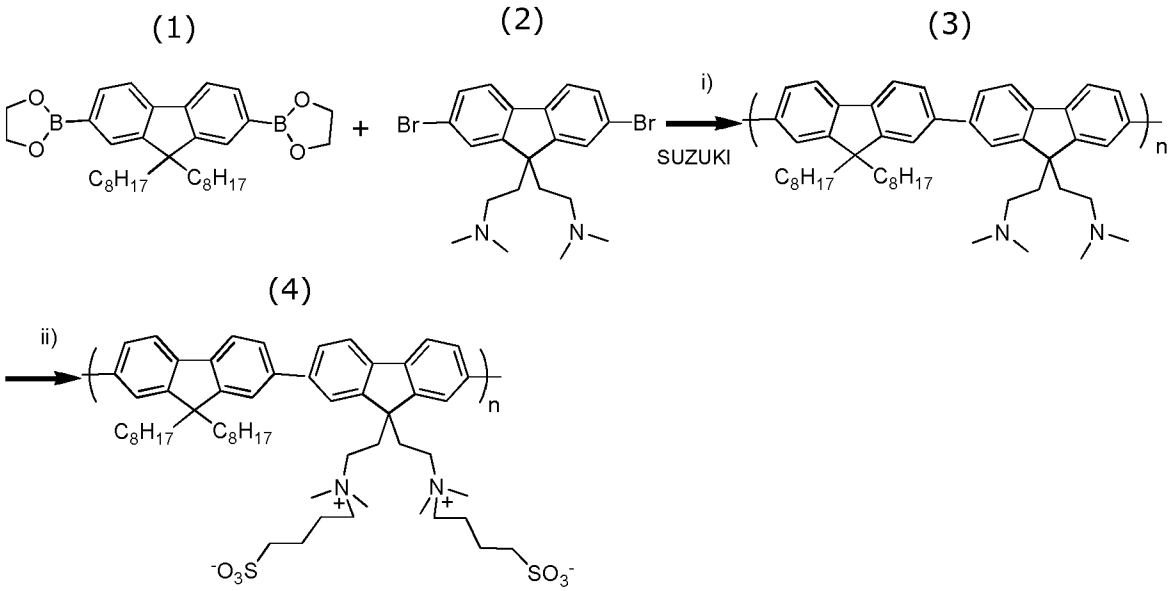
32. A method according to Claim 30 or 31, wherein the first zwitterion forming reactant comprises a negative charge carrying species or precursor thereof, for example for reacting with the or a tertiary amine group.

33. A method according to Claim 32, wherein the negative charge carrying species or precursor thereof comprises a sulfone.

34. A method according to any of Claims 30 to 333, where the first monomer is copolymerised with at least one further monomer, *e.g.* an amine free monomer.

35. A method according to any of Claims 30 to 34, wherein the polymerisation comprises a Suzuki polymerisation.

36. A method according to any of Claims 30 to 34, wherein the polymerisation comprises a Yamamoto or Stille polymerisation.



Conditions: i) $Pd(PPh_3)_4$, 2M K_2CO_3, toluene, reflux, 3 days;
ii) THF/Methanol, 1,4-butane sultone, 70°C, 3 days

Figure 1

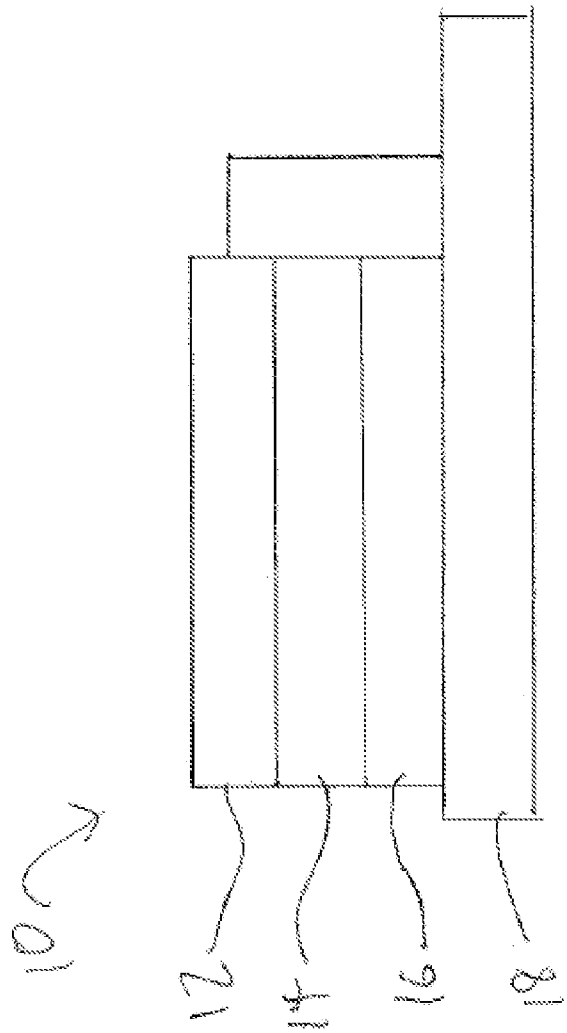


FIGURE 2

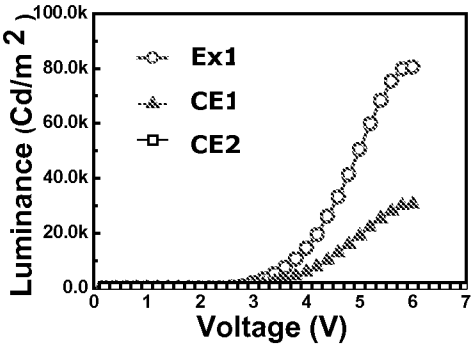


Figure 3

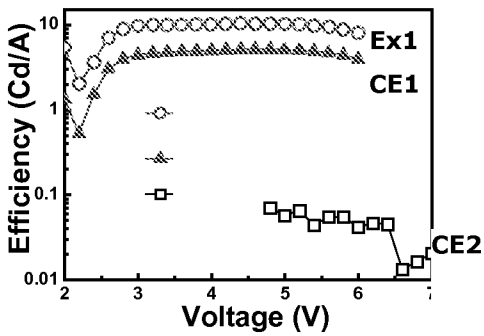


Figure 4

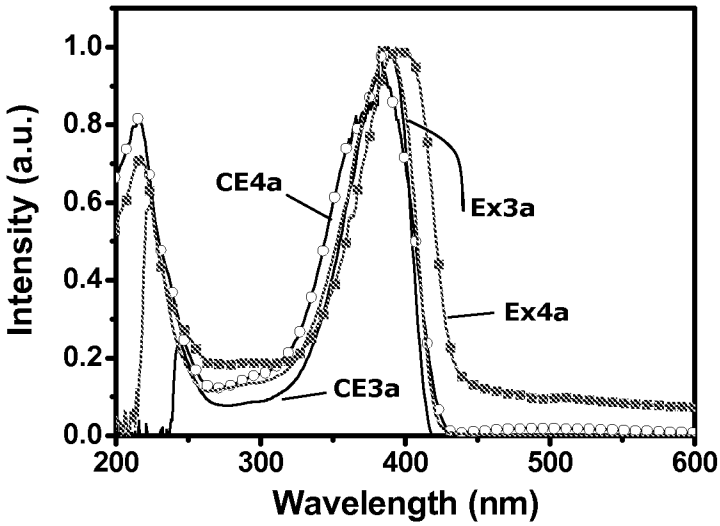


Figure 5

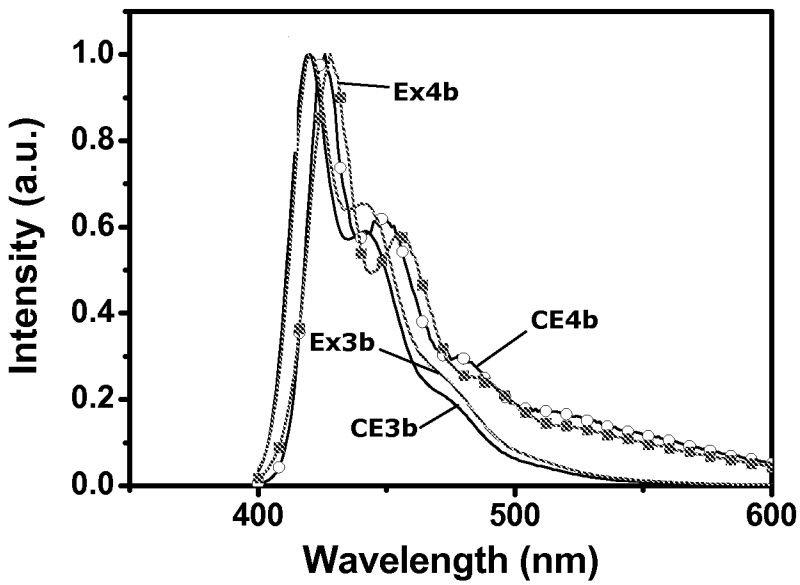


Figure 6

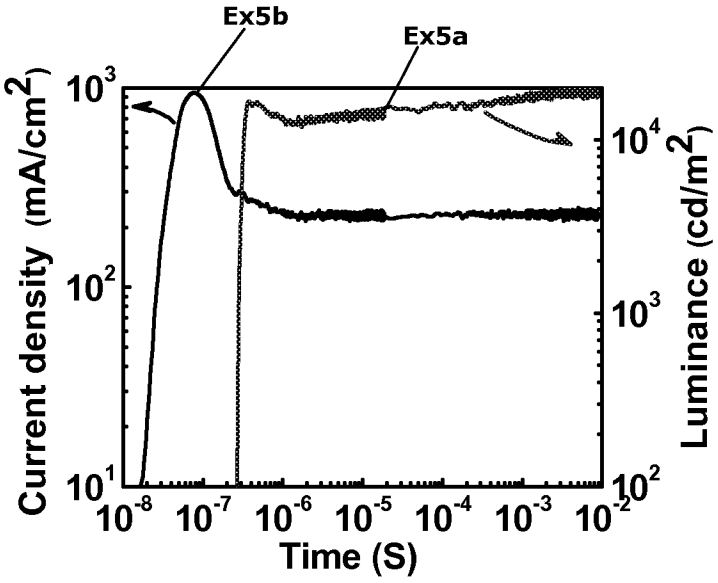


Figure 7

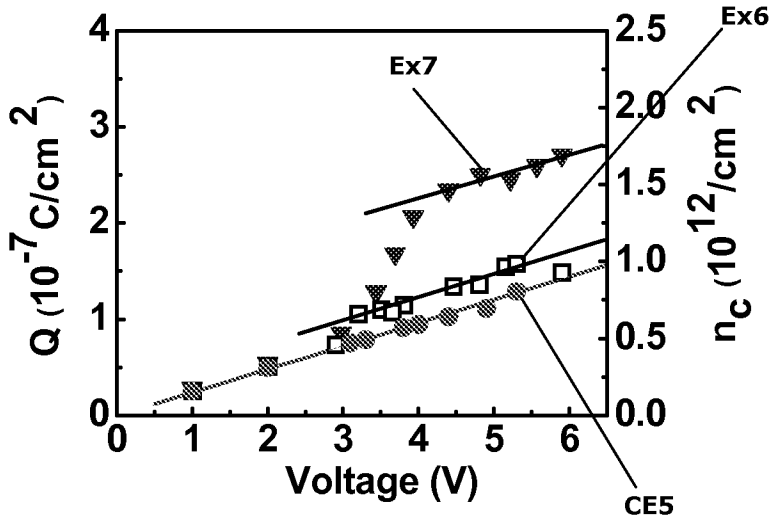


Figure 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2011/052503

A. CLASSIFICATION OF SUBJECT MATTER
INV. 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)
H01G H01L

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	F. C. KREBS AND M. BIANCARDO: "Dye sensitized photovoltaic cells: Attaching conjugated polymers to zwitterionic ruthenium dyes.", SOLAR ENERGY MATERIALS AND SOLAR CELLS, vol. 90, 18 April 2005 (2005-04-18), pages 142-165, XP002670047,	1-3,5, 13-19, 28-31, 35,36
Y	ITO/PEDOT:PSS/16/Al; page 158; figure 2; table 1; compound 16 page 149, paragraph 2.12; compound 16	4,6-12, 21-24,26
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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24 February 2012	06/03/2012

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2011/052503

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	page 451, column 2; figure Chart 3; compound polymer 19	4

Y	WO 2010/125403 A1 (CAMBRIDGE ENTPR LTD [GB]; FRIEND RICHARD [GB]; HODGKISS JUSTIN [NZ]; H) 4 November 2010 (2010-11-04) claim 1; figure 6; compounds FN-BF4	6-12, 21-24,26

A	EP 1 734 595 A2 (SEIKO EPSON CORP [JP]) 20 December 2006 (2006-12-20) the whole document	1-36

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2011/052503

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