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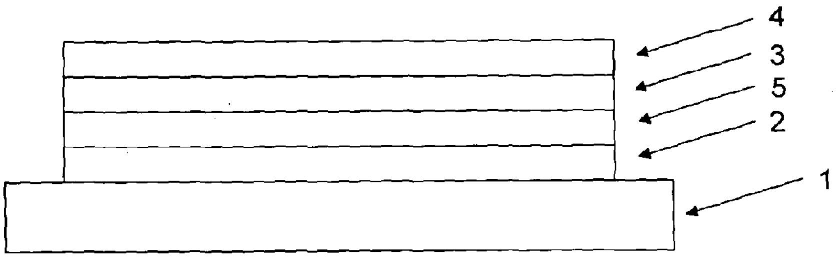
(54) Title: ORGANIC SEMICONDUCTOR SOLUTION

Figure 1



(57) Abstract: A solution comprises an organic semiconducting polymer doped with a transition metal compound comprising a transition metal having an oxidation state of at least five dissolved in at least one solvent. The dopant is preferably present in the range of 0.1-10 wt % relative to the organic semiconducting polymer, and the at least one solvent is a substituted or unsubstituted cyclic ether. The transition metal compound is preferably a heteropoly acid selected from the group consisting of phosphomolybdic acid, phosphotungstic acid and tungstosilicic acid.

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ORGANIC SEMICONDUCTOR SOLUTION

Field of the Invention

This invention relates to a solution comprising a doped organic semiconductor, and its use in making organic electronic devices.

Background of the Invention

Electronic devices comprising active organic materials are attracting increasing attention for use in devices such as organic light emitting diodes, organic photoresponsive devices (in particular organic photovoltaic devices and organic photosensors), organic transistors and memory array devices. Devices comprising organic materials offer benefits such as low weight, low power consumption and flexibility. Moreover, use of soluble organic materials allows use of solution processing in device manufacture, for example inkjet printing or spin-coating.

An organic optoelectronic device may comprise a substrate carrying an anode, a cathode and an organic semiconducting layer between the anode and cathode.

The organic semiconducting layer is an organic light-emitting layer in the case where the device is an organic light-emitting device (OLED). Holes are injected into the device through the anode (for example indium tin oxide, or ITO) and electrons are injected through the cathode during operation of the device. Holes in the highest occupied molecular orbital (HOMO) and electrons in the lowest unoccupied molecular orbital (LUMO) of the light combine to form an exciton that releases its energy as light. Suitable light-emitting materials include small molecule, polymeric and dendrimeric materials. Suitable light-emitting polymers for use in layer include poly(arylene vinylenes) such as poly(p-phenylene vinylenes) and polyarylenes such as polyfluorenes. Alternatively or additionally, the light-emitting layer may comprise a host material and a light-emitting dopant, for example a fluorescent or phosphorescent dopant.

The operation of an organic photovoltaic device or photosensor entails the reverse of the above-described process in that photons incident on the organic semiconducting layer generate excitons that are separated into holes and electrons.

In order to facilitate the transfer of holes and electrons into the light-emitting layer of an OLED (or transfer of separated charges towards the electrodes in the case of a photovoltaic or photosensor device) additional layers may be provided between the anode and the cathode.

A doped hole injection layer, which may be formed from a conductive organic or inorganic material, may be provided between the anode and the semiconducting layer or layers.

An example of a doped organic hole injection material is doped poly(ethylene dioxythiophene) (PEDT), in particular PEDT doped with a charge-balancing polyacid such as polystyrene sulfonate (PSS), polyacrylic acid or a fluorinated sulfonic acid, for example Nafion ® as disclosed in "Built-in field electroabsorption spectroscopy of polymer light-emitting diodes incorporating a doped poly(3,4-ethylene dioxythiophene) hole injection layer", T. M. Brown, J. S. Kim, R. H. Friend, F. Cacialli, R. Daik, and W. J. Feast, Appl. Phys. Lett. 75, 1679 (1999), EP 0901176 and EP 0947123PEDT is deposited from an aqueous formulation.

Examples of conductive inorganic materials used as hole injection layers include transition metal oxides such as VOx MoOx and RuOx as disclosed in Journal of Physics D: Applied Physics (1996), 29(11), 2750-2753 and "Electronic structure of anode interface with molybdenum oxide buffer layer", Kaname Kanai, Kenji Koizumi, Satoru Ouchi, Yoshiaki Tsukamoto, Kei Sakanoue, Yukio Ouchi, Kazuhiko Seki, Organic Electronics 11, 188-194 (2010).

N. Ballav and M. Biswas, Materials Letters, 60, 514-517 (2006) discloses conductive composites of polyaniline and polypyrrole with MoO_3

A hole injection layer formed by doping a conjugated polymer with tetrafluoro-tetracyanoquinodimethane (F4TCNQ) is disclosed in WO2008/029155.

US 2011/0108825 discloses an anode formed from a doped polymer compound.

Chen et al, J. Appl. Phys. 96(1), 454-458, 2004 discloses the use of poly(3-hexylthiophene) p-doped with $FeCl_3$ in a polymer-based thin-film transistor.

G. Crecelius, M. Stamm, J. Fink and J.J.Ritsko, Phys. Rev. Lett. 50, 1498–1500 (1983) discloses doping of polyparaphenylene with AsF_5.

US 2009/0299031 discloses formation of a polythiophene film by deposition of a solution comprising bithiophene or terthiophene monomers and phosphomolybdic acid, followed by oxidative polymerisation.

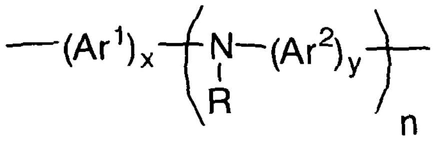
Summary of the Invention

In a first aspect the invention provides a solution comprising at least one solvent and an organic semiconducting polymer doped with a transition metal compound comprising a transition metal having an oxidation state of at least five dissolved in the at least one solvent.

Preferably, the organic semiconducting polymer is present in a concentration of at least 0.1 weight percent, optionally 0.4 weight percent, relative to the at least one solvent.

Optionally, the dopant is present in the range of about 0.1-20 wt %, optionally 0.1-5 wt % relative to the organic semiconducting polymer.

Optionally, the organic semiconducting polymer comprises repeat units of formula (I):



$$-(\mathrm{Ar}^1)_x-\left(\underset{\substack{|\\ \mathrm{R}}}{\mathrm{N}}-(\mathrm{Ar}^2)_y\right)_n-$$

(I)

wherein Ar^1 and Ar^2 in each occurrence are independently selected from substituted or unsubstituted aryl or heteroaryl groups; n is greater than or equal to 1, preferably 1 or 2; R is H or a substituent; any of Ar^1, Ar^2 and R may be linked by a direct bond or linking group; and x and y are each independently 1, 2 or 3.

Optionally, H is a substituent.

Optionally,the organic semiconducting polymer is a copolymer comprising less than 50 mol% of repeat units of formula (I).

Optionally,the organic semiconducting polymer comprises an substituted or unsubstituted arylene repeat unit.

Optionally,the substituted or unsubstituted arylene repeat unit is an substituted or unsubstituted fluorene repeat unit or an substituted or unsubstituted phenylene repeat unit.

Optionally,at least one repeat unit of the organic semiconducting polymer is substituted with one or more alkyl groups, optionally one or more C_{1-20} alkyl groups.

Optionally, the polymer is crosslinkable.

Optionally, the at least one solvent is an substituted or unsubstituted cyclic ether, optionally tetrahydrofuran.

Optionally, the transition metal compound is a heteropoly acid.

Optionally, the heteropoly acid is selected from the group consisting of phosphomolybdic acid, phosphotungstic acid and tungstosilicic acid.

Optionally, the oxidation state of the transition metal is 5, 6 or 7.

Optionally, the oxidation state of the transition metal is 6.

In a second aspect the invention provides a method of forming an organic electronic device comprising the step of forming an active layer of the device by depositing a solution according to the first aspect and evaporating the at least one solvent.

Optionally according to the second aspect, the organic electronic device is an organic light-emitting device.

According to the second aspect, the active layer is preferably a hole injection layer formed on an anode layer of the organic light-emitting device, the device further comprising a light-emitting layer between the hole injection layer and a cathode of the organic light-emitting device.

Optionally according to the second aspect, the anode is selected from the group consisting of indium tin oxide, indium zinc oxide, fluorine-doped tin oxide, tungsten trioxide, titanium dioxide, molybdenum trioxide, aluminium zinc oxide, gallium indium zinc oxide, aluminium, silver, palladium, copper, gold, platinum, and alloys thereof, for example silver-palladium-copper and molybdenum-chrome.

Optionally according to the second aspect, the method comprises the step of crosslinking the active layer.

Optionally according to the second aspect, the method comprises the step of forming a hole-transporting layer between the hole injection layer and the light-emitting layer by deposition of a substantially undoped hole transporting material.

Optionally according to the second aspect, the hole injection layer, the light-emitting layer and, if present, the hole-transporting layer are formed by inkjet printing.

Optionally according to the second aspect, the hole injection layer, the light-emitting layer and, if present, the hole-transporting layer are deposited into a well formed from a single bank material.

Description of the Figures

The invention will now be described in more detail with reference to the drawings, in which:

Figure 1 illustrates an OLED according to a first embodiment of the invention;

Figure 2 illustrates an OLED according to a second embodiment of the invention;

Figure 3 illustrates an inkjet printed pixel of an OLED according to an embodiment of the invention;

Figure 4A illustrates the UV-visible spectrum of an undoped organic semiconductor;

Figure 4B illustrates the UV-visible spectra of solutions of doped organic semiconductors of varying dopant concentrations according to an embodiment of the invention formed by doping of the organic semiconductor of Figure 4A;

Figure 5A illustrates the UV-visible spectrum of an undoped organic semiconductor;

Figure 5B illustrates the UV-visible spectra of solutions of doped organic semiconductors of varying dopant concentrations according to an embodiment of the invention formed by doping of the organic semiconductor of Figure 5A;

Figure 5C illustrates a magnification of the UV-visible spectrum of Figure 5B; and

Figure 6 illustrates the UV-visible spectra of films of doped organic semiconductors according to an embodiment of the invention.

Detailed Description of the Invention

Figure 1 illustrates an OLED according to a first embodiment of the invention comprising a substrate 1, an anode 2, a light-emitting layer 3 and a cathode 4.

A hole injection layer 5 comprising an organic semiconductor doped with a transition metal compound dopant, as described in more detail below, is provided between anode 2 and light-emitting layer 3.

Figure 2 illustrates an OLED according to a second embodiment of the invention comprising the elements of Figure 1 and a hole-transporting layer 6 between the hole injection layer 5 and the light-emitting layer 3.

Additional layers may be provided between the anode 2 and cathode 4 of Figures 1 and 2, for example one or more of electron transporting layers, hole transporting layers (which would be further hole transporting layers in the case of Figure 2), electron blocking layers and / or hole blocking layers.

The hole injection layer may have a thickness in the range of 1-200 nm, optionally 1-100 nm, optionally 20-50 nm, optionally 35-45 nm.

In another embodiment (not illustrated) the doped organic semiconductor may be used as an anode.

In other embodiments, the doped organic semiconductor may form an active layer of another organic electronic device, for example a photoresponsive device or an organic thin film transistor.

Dopant

The high oxidation state of the transition metal compound dopant, which may for example be 5+, 6+ or 7+, is such that the transition metal compound is a highly electron deficient, making the compounds particularly strong p-dopants.

Exemplary transition metal compounds are acidic compounds comprising acidic hydrogen atoms, for example heteropoly acids.

Exemplary heteropoly acid formulae include $H_nXM_{12}O_{40}$ (Keggin structure) and $H_nX_2M_{18}O_{62}$ (Dawson structure) wherein X is a p-block element, for example Si, Ge, P or As, M is a transition metal and n is an integer having a value to satisfy the valency of X.

Specific preferred examples of heteropoly acids are phosphomolybdic acid, phosphotungstic acid and tungstosilicic acid.

Specific structures include the following:

- $H_4X^{n+}M_{12}O_{40}$, wherein X is Si or Ge and M is Mo, W
- $H_3X^{n+}M_{12}O_{40}$, wherein X is P or As and M is Mo or W
- $H_6X_2M_{18}O_{62}$, wherein X is P or As and M is Mo or W

Heteropoly acids may exist in the form of a hydrate, for example:

- Phosphomolybdic acid hydrate: $12MoO_3 \bullet H_3PO_4 \bullet xH_2O$
- Phosphotungstic acid hydrate: $12WO_3 \bullet H_3PO_4 \bullet xH_2O$
- Tungstosilicic acid hydrate: $H_4[Si(W_3O_{10})_4] \bullet xH_2O$

Exemplary transition metal compounds having a 5+ oxidation state include vanadium and niobium compounds such as Vanadium(V) oxytripropoxide, Vanadium(V) oxytriisopropoxide, and Vanadium(V) oxytriethoxide.

Exemplary transition metal compounds having a 7+ oxidation state include manganese, technetium, and rhenium compounds, for example trioxo(triphenylsilyloxy)rhenium (VII) and rhenium oxide (Re_2O_7).

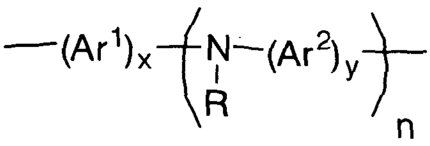
Organic semiconducting polymer

The organic semiconducting polymer may be any polymer having a HOMO level capable of undergoing p-doping with the transition metal compound dopant. Doping of an organic semiconductor is apparent from doping-induced features in the UV-visible absorption spectrum of a solution of the organic semiconductor and dopant.

The organic semiconducting polymer may have a weight average molecular weight of at least 5000. The polymer may have a polydispersity greater than 1.

The organic semiconductor is preferably a hole-transporting material. The ionisation potential of the organic semiconductor material as measured by photoelectron spectroscopy is preferably be any value up to about – 6 eV from vacuum level, optionally up to about -5.5 eV from vacuum level (for the avoidance of any doubt, "up to" as used herein means the gap from vacuum level; for example, "up to -6 eV" includes -5.9 eV but exclude -6.1 eV).

The organic semiconducting polymer may comprise amine-containing repeat units, for example amine repeat units of formula (I):



$$-(Ar^1)_x\left(\underset{R}{\overset{}{N}}-(Ar^2)_y\right)_n-$$

(I)

wherein Ar^1 and Ar^2 in each occurrence are independently selected from substituted or unsubstituted aryl or heteroaryl groups, n is greater than or equal to 1, preferably 1 or 2, R is H or a substituent, preferably a substituent, and x and y are each independently 1, 2 or 3.

R is preferably alkyl, for example C_{1-20} alkyl, Ar^3, or a branched or linear chain of Ar^3 groups, for example $-(Ar^3)_r$, wherein Ar^3 in each occurrence is independently selected from aryl or heteroaryl and r is at least 1, optionally 1, 2 or 3.

Any of Ar^1, Ar^2 and Ar^3 may independently be substituted with one or more substituents. Preferred substituents are selected from the group R^3 consisting of:

alkyl, for example C_{1-20} alkyl, wherein one or more non-adjacent C atoms may be replaced with O, S, substituted N, C=O and -COO- and one or more H atoms of the alkyl group may be replaced with F or aryl or heteroaryl optionally substituted with one or more groups R^4,

aryl or heteroaryl optionally substituted with one or more groups R^4,

NR^5_2, OR^5, SR^5,

fluorine, nitro and cyano, and

crosslinkable groups;

wherein each R^4 is independently alkyl, for example C_{1-20} alkyl, in which one or more non-adjacent C atoms may be replaced with O, S, substituted N, C=O and -COO- and one or more H atoms of the alkyl group may be replaced with F, and each R^5 is independently selected from the group consisting of alkyl and aryl or heteroaryl optionally substituted with one or more alkyl groups.

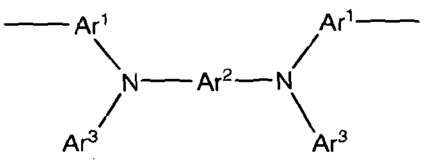
R may comprise a crosslinkable-group, for example a group comprising a polymerisable double bond such and a vinyl or acrylate group, or a benzocyclobutane group.

Any of the aryl or heteroaryl groups in the repeat unit of Formula (I) may be linked by a direct bond or a divalent linking atom or group. Preferred divalent linking atoms and groups include O, S; substituted N; and substituted C.

Where present, substituted N or substituted C of R^3, R^4 or of the divalent linking group may independently in each occurrence be NR^6 or CR^6_2 respectively wherein R^6 is alkyl, e.g. C_{1-20} alkyl, or substituted or unsubstituted aryl or heteroaryl, e.g. phenyl substituted with one or more C_{1-20} alkyl groups. Optional substituents for aryl or heteroaryl groups R^6 may be selected from R^4 or R^5.

In one preferred arrangement, R is Ar^3 and each of Ar^1, Ar^2 and Ar^3 are independently and optionally substituted with one or more C_{1-20} alkyl groups.

Particularly preferred units satisfying Formula 1 include units of Formulae 1-3:



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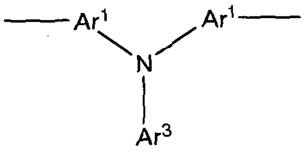

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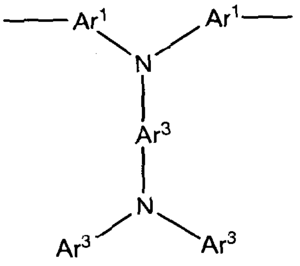


3

wherein Ar^1 and Ar^2 are as defined above; and Ar^3 is substituted or unsubstituted aryl or heteroaryl. Where present, preferred substituents for Ar^3 include substituents as described forAr^1 and Ar^2, in particular alkyl and alkoxy groups.

Ar^1, Ar^2 and Ar^3 are preferably phenyl, each of which may independently be substituted with one or more substituents as described above.

In another preferred arrangement, aryl or heteroaryl groups of formula (I) are phenyl, each phenyl group being optionally substituted with one or more alkyl groups.

In another preferred arrangement, Ar^1, Ar^2 and Ar^3 are phenyl, each of which may be substituted with one or more C_{1-20} alkyl groups, and $r = 1$.

In another preferred arrangement, Ar^1 and Ar^2 are phenyl, each of which may be substituted with one or more C_{1-20} alkyl groups, and R is 3,5-diphenylbenzene wherein each phenyl may be substituted with one or more alkyl groups.

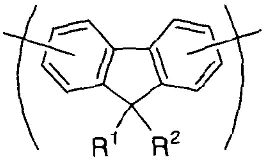
The hole-transporting polymer may be a homopolymer comprising repeat units of formula (I). Alternatively, the hole transporting polymer may be a copolymer, for example a random, alternating or block copolymer comprising one or more repeat units of formula (I) and further repeat units.

Further repeat units may be selected from:

- one or more further repeat units of formula (I) that are different to the first repeat unit; and
- one or more substituted or unsubstituted (hetero)arylene repeat units, for example substituted or unsubstituted fluorene, phenylene and / or indenofluorene repeat units.

Repeat units of formula (I) may make up 50 mol %, more than 50 mol % or less than 50 mol% of the repeat units of a copolymer.

Exemplary fluorene repeat units include repeat units of formula (II):



(II)

wherein R^1 and R^2 are independently H or a substituent and wherein R^1 and R^2 may be linked to form a ring.

R^1 and R^2 are optionally selected from the group consisting of hydrogen; substituted or unsubstituted Ar^3 or a linear or branched chain of Ar^3 groups, wherein Ar^3 is as described above; and substituted or unsubstituted alkyl, for example C_{1-20} alkyl, wherein one or more non-adjacent C atoms of the alkyl group may be replaced with O, S, substituted N, C=O and -COO-.

In the case where R^1 or R^2 comprises alkyl, optional substituents of the alkyl group include F, CN, nitro, and aryl or heteroaryl optionally substituted with one or more groups R^4 wherein R^4 is as described above.

In the case where R^1 or R^2 comprises aryl or heteroaryl, each aryl or heteroaryl group may independently be substituted. Preferred optional substituents for the aryl or heteroaryl groups include one or more substituents R^3.

Optional substituents for the fluorene unit, other than substituents R^1 and R^2, are preferably selected from the group consisting of alkyl, e.g. C_{1-20} alkyl, wherein one or more non-adjacent C atoms may be replaced with O, S, substituted N, C=O and -COO-, substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, fluorine, cyano and nitro.

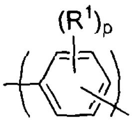
Where present, substituted N in repeat units of formula (II) may independently in each occurrence be NR^5 or NR^6.

In one preferred arrangement, at least one of R^1 and R^2 comprises an optionally substituted C_1-C_{20} alkyl or an optionally substituted aryl group, in particular phenyl substituted with one or more C_{1-20} alkyl groups.

R^1 and / or R^2 may be crosslinkable. For example, R^1 and / or R^2 may comprise a polymerisable double bond such and a vinyl or acrylate group, or a benzocyclobutane group.

The repeat units of formula (II) may be 2,7-linked.

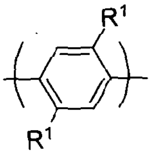
Exemplary phenylene repeat units include repeat units of formula (III):



(III)

wherein R^1 is as described above with reference to formula (II) and p is 1, 2, 3 or 4, optionally 1 or 2. In one arrangement, the repeat unit is a 1,4-phenylene repeat unit. In another arrangement, the repeat unit is a 1,3-phenylene repeat unit.

The repeat unit of formula (III) may have formula (IIIa), wherein R^1 in each occurrence may be the same or different:



(IIIa)

Substituents that enhance solubility of the polymer in organic solvents may include, without limitation, alkyl substituents as described above, for example C_{1-20} alkyl groups, bonded directly or indirectly to an arylene unit in the backbone of a polymer.

Doped organic semiconductor

The transition metal compound dopant is optionally provided in an amount of greater than or equal to 0.05 weight %, optionally greater than or equal to 0.2 weight % or 0.5

weight % up to 10 weight %, optionally up to 5 weight %, optionally in the range of 1-2 weight %.

The doping concentration may be selected so as to control resistivity of a film formed from the doped organic semiconductor.

Resistivity of the doped film may be in the range of 100000 – 10 Ohm-cm, preferably 100000 – 100 Ohm-cm, most preferably 100000 – 1000 Ohm-cm.

It will be appreciated that the doped organic semiconductor will have a different conductivity to the organic semiconductor prior to doping, and may be an extrinsic or degenerate organic semiconductor.

The present inventors have surprisingly found that the products resulting from charge-transfer doping may be soluble in organic solvents, allowing a film of the doped organic semiconductor to be formed by solution processing methods, including printing and coating methods as described in more detail below.

Exemplary solvents include ethers, including:

- Substituted or unsubstituted cyclic ethers including, without limitation, tetrahydrofuran, 1,3-dioxolane or 1,4-dioxolane. The cyclic ether solvents may be substituted with one or more substituents, for example one or more C_{1-10} alkyl or C_{1-5} alkyl groups. Exemplary substituted cyclic ethers include methyl-substituted tetrahydrofurans.
- Asymmetric ethers, such as:
    (i) Cycloalkyl alkyl ethers. Exemplary cycloalkyl groups include cyclopentyl and cyclohexyl. Exemplary solvents include cyclopentyl methyl ether and cyclohexyl methyl ether.

    (ii) Asymmetric ethers comprising a tertiary alkyl group, such as t-butyl. Examples include t-butyl methyl ether.

    (iii) Alkyl tetrahydrofurfuryl ethers, for example tetrahydrofurfuryl ethyl ethers.

Accordingly, a solution of the doped composition may be formed by adding the dopant, in solid form or in solution, to a solution of the organic semiconductor.

Both the dopant and the organic semiconductor, including but not limited to polymers comprising arylene repeat units, in particular alkyl-substituted arylene repeat units as described above, may be soluble in organic solvents, for example substituted or unsubstituted cyclic ethers as described above.

A solvent or solvent system may be selected based not only on its ability to dissolve the doped organic semiconductor but also based on the boiling point, viscosity and / or contact angle of the solvent. The choice of solvent or solvent system may be selected according to the deposition technique to be used in forming a film of the doped organic semiconductor. Exemplary solution deposition methods are described below.

Charge-transfer occurs following mixing of the organic semiconductor and the transition metal compound dopant, and the solvent or solvent mixture used may be selected so as to dissolve not only the starting materials but also the products resulting from charge-transfer occurring following combination of the solutions. Alternatively or additionally, the concentration of dopant may be selected to give a concentration of the charge transfer salt that is below the solubility limit for the charge transfer salt in the selected solvent or solvent mixture.

Hole transporting layer

A hole transporting layer may be provided between the doped hole injection layer and the light-emitting layer.

The hole transporting layer may have a thickness in the range of 10-200 nm, optionally in the range of 10-100 nm.

The material used to form the hole transporting layer may be selected from any hole transporting material capable of providing little or no barrier to hole transport from the hole-injection layer to the light-emitting layer. Exemplary hole-transporting materials may be selected from any of the organic semiconductor materials described above, for example a polymer (homopolymer or copolymer) comprising a repeat unit of formula (I).

This layer may be formed from the same organic semiconductor used to form the doped hole injection layer in order to provide little or no barrier to charge transport from the hole injection layer to the light-emitting layer.

The organic semiconductor used to form the hole transporting layer is substantially undoped. Following deposition of the substantially undoped organic semiconductor onto the hole injection layer, there may be some diffusion of the transition metal compound dopant from the hole injection layer resulting in some doping of the previously undoped organic semiconductor and a dopant gradient in an interface region between the hole injection layer and the hole transporting layer. This diffusion may occur in particular if the hole-transporting layer is heated following deposition, for example to crosslink or otherwise anneal the hole transporting layer. The material used to form the hole transporting layer may have a HOMO level of -6.0 eV or shallower, optionally no deeper than -5.8 eV or -5.5 eV as measured by photoelectron spectroscopy.

The hole transporting material may be provided with crosslinkable groups, for example crosslinkable groups as described above. The crosslinkable groups may be crosslinked following deposition of the hole transporting material, for example by UV light or thermal treatment, to render the hole-transporting layer substantially insoluble in solvents used to form the layer deposited onto the hole transporting layer. If the layer deposited onto the hole transporting layer is deposited from a solvent or solvent system in which the hole transporting layer is substantially insoluble, or if this layer is deposited by a non-solution processing method, then crosslinking may not take place.

Light emitting layer

Suitable light-emitting materials for use in the light-emitting layer include small molecule, polymeric and dendrimeric materials, and compositions thereof. Suitable light-emitting polymers include conjugated polymers, for example substituted or unsubstituted poly(arylene vinylenes) such as poly(p-phenylene vinylenes) and substituted or unsubstituted polyarylenes such as: polyfluorenes, particularly 2,7-linked 9,9 dialkyl polyfluorenes or 2,7-linked 9,9 diaryl polyfluorenes; polyspirofluorenes, particularly 2,7-linked poly-9,9-spirofluorene; polyindenofluorenes, particularly 2,7-linked polyindenofluorenes; polyphenylenes, particularly alkyl or alkoxy substituted poly-1,4-phenylene. Such polymers as disclosed in, for example, Adv. Mater. 2000 12(23) 1737-1750 and references therein.

Polymers for use as light-emitting materials in devices according to the present invention may comprise a repeat unit selected from substituted or unsubstituted amine repeat units of formula (I) and / or substituted or unsubstituted arylene or heteroarylene repeat units as described above, in particular fluorene repeat units of formula (II) and / or phenylene repeat units of formula (III) described above.

The light-emitting layer may consist of a light-emitting material alone, or may comprise this material in combination with one or more further materials. In particular, the light-emitting material may be blended with hole and / or electron transporting materials or alternatively may be covalently bound to hole and / or electron transporting materials as disclosed in for example, WO 99/48160.

Light-emitting copolymers may comprise a light-emitting region and at least one of a hole transporting region and an electron transporting region as disclosed in, for example, WO 00/55927 and US 6353083. If only one of a hole transporting region and electron transporting region is provided then the electroluminescent region may also provide the other of hole transport and electron transport functionality – for example, an amine unit of formula (I) as described above may provide both hole transport and light-emission functionality. A light-emitting copolymer comprising light-emitting repeat units and one or both of a hole transporting repeat units and electron transporting repeat units may provide said units in a polymer main-chain, as per US 6353083, or in polymer side-groups pendant from the polymer backbone.

Suitable light-emitting materials may emit in the UV, visible and / or infra-red region of the electromagnetic spectrum. The OLED may contain one or more of red, green and blue light-emitting materials.

A blue light-emitting material may have photoluminescent spectrum with a peak wavelength in the range of less than or equal to 480 nm, e.g. in the range of 400-480 nm

A green light-emitting material may have photoluminescent spectrum with a peak wavelength in the range of above 480 nm – 560 nm.

A red light-emitting material may have photoluminescent spectrum with a peak wavelength in the range of above 560 nm – 630 nm.

More than one light-emitting material may be used. For example, red, green and blue light-emitting dopants may be used to obtain white light emission.

The light emitting layer may comprise a host material and at least one light-emitting dopant. The host material may be a material as described above that would, in the absence of a dopant, emit light itself. When a host material and dopant are used in a device, the dopant alone may emit light. Alternatively, the host material and one or more dopants may emit light. White light may be generated by emission from multiple light sources, such as emission from both the host and one or more dopants or emission from multiple dopants.

In the case of a fluorescent light-emitting dopant the singlet excited state energy level (S_1) of the host material should be higher than that of the fluorescent light-emitting dopant in order that singlet excitons may be transferred from the host material to the fluorescent light-emitting dopant. Likewise, in the case of a phosphorescent light-emitting dopant the triplet excited state energy level (T_1) of the host material should be higher than that of the phosphorescent light-emitting dopant in order that triplet excitons may be transferred from the host material to the fluorescent light-emitting dopant.

Exemplary phosphorescent light-emitting dopants include metal complexes comprising substituted or unsubstituted complexes of formula (IV):

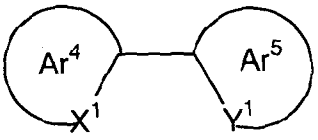
$$ML^1_qL^2_rL^3_s$$

(IV)

wherein M is a metal; each of L^1, L^2 and L^3 is a coordinating group; q is an integer; r and s are each independently 0 or an integer; and the sum of (a. q) + (b. r) + (c.s) is equal to the number of coordination sites available on M, wherein a is the number of coordination sites on L^1, b is the number of coordination sites on L^2 and c is the number of coordination sites on L^3.

Heavy elements M induce strong spin-orbit coupling to allow rapid intersystem crossing and emission from triplet or higher states (phosphorescence). Suitable heavy metals M include d-block metals, in particular those in rows 2 and 3 i.e. elements 39 to 48 and 72 to 80, in particular ruthenium, rhodium, palladium, rhenium, osmium, iridium, platinum and gold. Iridium are particularly preferred.

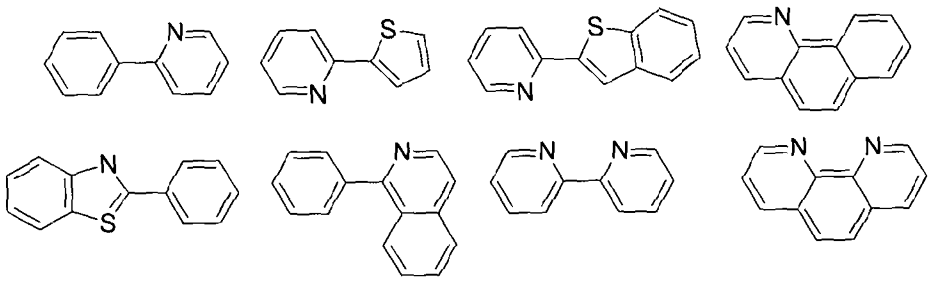
Exemplary ligands L^1, L^2 and L^3 include carbon or nitrogen donors such as porphyrin or bidentate ligands of formula (V):



(V)

wherein Ar^4 and Ar^5 may be the same or different and are independently selected from substituted or unsubstituted aryl or heteroaryl; X^1 and Y^1 may be the same or different and are independently selected from carbon or nitrogen; and Ar^4 and Ar^5 may be fused together. Ligands wherein X^1 is carbon and Y^1 is nitrogen are particularly preferred.

Examples of bidentate ligands are illustrated below:



Each of Ar^4 and Ar^5 may carry one or more substituents. Two or more of these substituents may be linked to form a ring, for example an aromatic ring.

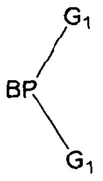
Other ligands suitable for use with d-block elements include diketonates, in particular acetylacetonate (acac); triarylphosphines and pyridine, each of which may be substituted.

Exemplary substituents include groups R^3 groups R^3 as described above with reference to Formula (I). Particularly preferred substituents include fluorine or trifluoromethyl which may be used to blue-shift the emission of the complex, for example as disclosed in WO 02/45466, WO 02/44189, US 2002-117662 and US 2002-182441; alkyl or alkoxy groups, for example C_{1-20} alkyl or alkoxy, which may be as disclosed in JP 2002-324679;

carbazole which may be used to assist hole transport to the complex when used as an emissive material, for example as disclosed in WO 02/81448; bromine, chlorine or iodine which can serve to functionalise the ligand for attachment of further groups, for example as disclosed in WO 02/68435 and EP 1245659; and dendrons which may be used to obtain or enhance solution processability of the metal complex, for example as disclosed in WO 02/66552.

A light-emitting dendrimer typically comprises a light-emitting core bound to one or more dendrons, wherein each dendron comprises a branching point and two or more dendritic branches. Preferably, the dendron is at least partially conjugated, and at least one of the branching points and dendritic branches comprises an aryl or heteroaryl group, for example a phenyl group. In one arrangement, the branching point group and the branching groups are all phenyl, and each phenyl may independently be substituted with one or more substituents, for example alkyl or alkoxy.

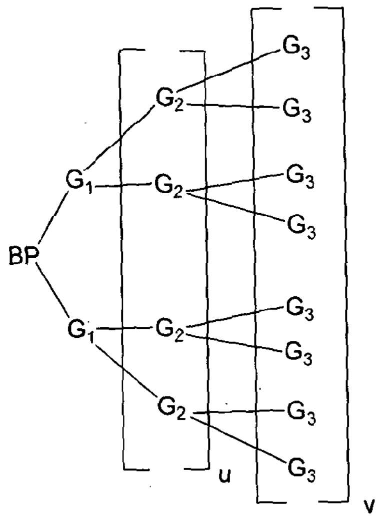
A dendron may have optionally substituted formula (VI)



(VI)

wherein BP represents a branching point for attachment to a core and G_1 represents first generation branching groups.

The dendron may be a first, second, third or higher generation dendron. G_1 may be substituted with two or more second generation branching groups G_2, and so on, as in optionally substituted formula (VIa):



(VIa)

wherein u is 0 or 1; v is 0 if u is 0 or may be 0 or 1 if u is 1; BP represents a branching point for attachment to a core and G_1, G_2 and G_3 represent first, second and third generation dendron branching groups.

BP and / or any group G may be substituted with one or more substituents, for example one or more C_{1-20} alkyl or alkoxy groups.

Where used, a light-emitting dopant may be present in an amount of about 0.05 mol % up to about 20 mol %, optionally about 0.1-10 mol % relative to their host material.

The light-emitting dopant may be physically mixed with the host material or it may be chemically bound to the host material in the same manner described above with respect to binding of the light-emitting dopant to the charge transporting material.

More than one light-emitting layer may be present. Multiple light-emitting layers may together produce white light.

The light-emitting layer may be patterned or unpatterned. A device comprising an unpatterned layer may be used an illumination source, for example. A white light emitting device is particularly suitable for this purpose. A device comprising a patterned layer may be, for example, an active matrix display or a passive matrix display. In the case of an active matrix display, a patterned electroluminescent layer is typically used in combination with a patterned anode layer and an unpatterned cathode. In the case of a passive matrix display, the anode layer is formed of parallel stripes of anode material, and parallel stripes of electroluminescent material and cathode material arranged perpendicular to the anode material wherein the stripes of electroluminescent material and cathode material are typically separated by stripes of insulating material ("cathode separators") formed by photolithography.

Anodes

Suitable materials for forming the anode include metals, metal alloys, conductive metal oxides and mixtures thereof. The anode may be formed by a non-solution deposition process, for example evaporation or sputtering, and may be patternable by photolithography.

Exemplary metals include aluminium, silver, palladium, copper, gold, platinum, and alloys thereof, for example silver-palladium-copper and molybdenum-chrome.

Exemplary conductive metal oxides include indium tin oxide, indium zinc oxide, fluorine-doped tin oxide, tungsten trioxide, titanium dioxide, molybdenum trioxide, aluminium zinc oxide and gallium indium zinc oxide. Indium tin oxide is particularly preferred.

The anode may have only one layer, or may have two or more layers. For example, the anode of a transparent cathode may be formed from a layer of indium tin oxide onto which the hole injection layer is formed, and an underlying layer of reflective metal such as aluminium in order that light emitted towards the anode may be reflected through the anode.

Cathode

The cathode is selected from materials that have a workfunction allowing injection of electrons into the light-emitting layer. Other factors influence the selection of the cathode such as the possibility of adverse interactions between the cathode and the materials of the light-emitting layer. The cathode may consist of a single material such as a layer of aluminium. Alternatively, it may comprise a plurality of metals, for example a bilayer of a low workfunction material and a high workfunction material such as calcium and aluminium as disclosed in, for example, WO 98/10621; elemental barium as disclosed in, for example, WO 98/57381, Appl. Phys. Lett. 2002, 81(4), 634 and WO 02/84759; or a thin layer of metal compound, in particular an oxide or fluoride of an alkali or alkali earth metal, to assist electron injection, for example lithium fluoride as disclosed in, for example, WO 00/48258; barium fluoride as disclosed, for example, in Appl. Phys. Lett. 2001, 79(5), 2001; and barium oxide. In order to provide efficient injection of electrons into the device, the cathode preferably has a workfunction of less than 3.5 eV, more preferably less than 3.2 eV, most preferably less than 3 eV. Work functions of metals can be found in, for example, Michaelson, J. Appl. Phys. 48(11), 4729, 1977.

The cathode may be opaque or transparent. Transparent cathodes are particularly advantageous for active matrix devices because emission through a transparent anode in such devices is at least partially blocked by drive circuitry located underneath the emissive pixels. A transparent cathode will comprise a layer of an electron injecting material that is sufficiently thin to be transparent. Typically, the lateral conductivity of this layer will be low as a result of its thinness. In this case, the layer of electron injecting material is used in combination with a thicker layer of transparent conducting material such as indium tin oxide.

It will be appreciated that a transparent cathode device need not have a transparent anode (unless, of course, a fully transparent device is desired), and so the transparent anode used for bottom-emitting devices may be replaced or supplemented with a layer of reflective material such as a layer of aluminium. Examples of transparent cathode devices are disclosed in, for example, GB 2348316.

In one arrangement, the surface of the cathode contacts a surface of the light-emitting layer. In another arrangement, one or more layers may be provided between the cathode and the light-emitting layer. For example, an organic electron-transporting layer may be provided between the light-emitting layer and the cathode.

Encapsulation

OLEDs tend to be sensitive to moisture and oxygen. Accordingly, the substrate preferably has good barrier properties for prevention of ingress of moisture and oxygen into the device. The substrate is commonly glass, however alternative substrates may be used, in particular where flexibility of the device is desirable. For example, the substrate may comprise a plastic as in, for example, US 6268695 which discloses a substrate of alternating plastic and barrier layers or a laminate of thin glass and plastic as disclosed in, for example, EP 0949850. The substrate may be opaque in the case of an OLED with a transparent cathode.

The device is preferably encapsulated with an encapsulant (not shown) to prevent ingress of moisture and oxygen. Suitable encapsulants include a sheet of glass, films having suitable barrier properties such as silicon dioxide, silicon monoxide, silicon nitride or alternating stacks of polymer and dielectric as disclosed in, for example, WO 01/81649 or an airtight container as disclosed in, for example, WO 01/19142. In the case of a transparent cathode device, a transparent encapsulating layer such as silicon monoxide or silicon dioxide may be deposited to micron levels of thickness, although in one preferred embodiment the thickness of such a layer is in the range of 20-300 nm. A getter material for absorption of any atmospheric moisture and / or oxygen that may permeate through the substrate or encapsulant may be disposed between the substrate and the encapsulant.

Solution processing

A film of the doped organic semiconductor may be formed by deposition of a solution of the doped organic semiconductor from a solution in at least one solvent followed by evaporation of the at least one solvent.

The organic semiconductor may be provided in the solution at a concentration of at least 0.1 weight %, optionally 0.4 weight %. The solution may be stable in the sense that the organic semiconducting polymer does not precipitate out of the solution over time.

Solution deposition methods include coating techniques, such as spin-coating, dip-coating and blade coating and printing techniques such as inkjet printing, screen printing and roll to roll printing such as gravure or flexographic printing.

Spin-coating is particularly suitable for devices wherein patterning of the electroluminescent material is unnecessary – for example for lighting applications or simple monochrome segmented displays.

Inkjet printing is particularly suitable for high information content displays, in particular full colour displays. A device may be inkjet printed by providing a patterned layer over the first electrode and defining wells for printing of the doped organic semiconductor to form a hole injection layer followed by printing of one colour (in the case of a monochrome device) or multiple colours (in the case of a multicolour, in particular full colour device) to form a light-emitting layer.

The patterned layer is typically a layer of photoresist that is patterned to define wells as described in, for example, EP 0880303. One or more further organic layers may be printed into each well, including charge transporting or charge blocking layers, for example a hole-transporting layer between the hole-injection layer and the light-emitting layer.

As an alternative to wells, the doped organic semiconductor and the light-emitting material may be printed into channels defined within a patterned layer. In particular, the photoresist may be patterned to form channels which, unlike wells, extend over a plurality of pixels and which may be closed or open at the channel ends.

Figure 3 illustrates a doped hole injection layer 305 on anode surface 302 and a light-emitting layer 303 formed in an inkjet well by inkjet printing. The well perimeter is defined by a bank material 310, which may be a photoresist that has been patterned to define a well. A hole-transporting layer (not shown) may likewise by printed into the well.

The doped organic semiconductor used to form the hole injection layer may be soluble in organic solvents such as cyclic ethers, as described above. Hole transport layers and light-emitting layers are typically formed by printing relevant materials in an organic solvent. In contrast, hole injection materials such as PEDOT:PSS are deposited from an aqueous formulation.

Printing of a hole injection material deposited from an aqueous formulation may involve use of a bank structure to form the wells wherein a first layer of the bank structure is formed from a material optimised for printing of an aqueous formulation and a second layer is formed from a material optimised for printing of an organic formulation. Printing of only organic formulations may allow this structure to be dispensed with.

It will be appreciated that organic layers of an OLED other than the hole injection layer, for example the light-emitting layer(s) and, if present, charge-transporting or charge-blocking layers, may be deposited by methods other than solution deposition, for example by evaporation.

If multiple layers of an OLED are formed by solution processing, for example as illustrated in Figure 4 then techniques to prevent intermixing of adjacent layers include crosslinking of one layer before deposition of a subsequent layer and / or selection of materials for adjacent layers such that the material from which the first of these layers is formed is not soluble in the solvent used to deposit the second layer. Crosslinking may be thermal or photo-crosslinking.

The organic semiconductor used to form a doped hole injection layer or an undoped hole transporting layer may be substituted with a crosslinkable group, for example as described above with reference to substituents R, R^1 and R^2 of repeat units of formulae (I), (II) and (III). In the case of a hole-transporting polymer, a crosslinkable group may be provided as a substituent of one or more polymeric repeat units. Suitable crosslinkable groups include groups comprising a reactive carbon-carbon double bond such as vinyl and acrylate groups, in particular double bond groups including a CH_2 group, and groups comprising an substituted or unsubstituted benzocyclobutane. Following deposition of the organic semiconductor, the crosslinkable groups may be crosslinked by any suitable method, for example heating or exposure to UV light.

If the layer deposited onto the hole injection layer is deposited from a solvent or solvent system in which the doped hole injection layer is substantially insoluble, or if that layer is deposited by a non-solution deposition method, then crosslinking of the hole injection layer may not take place.

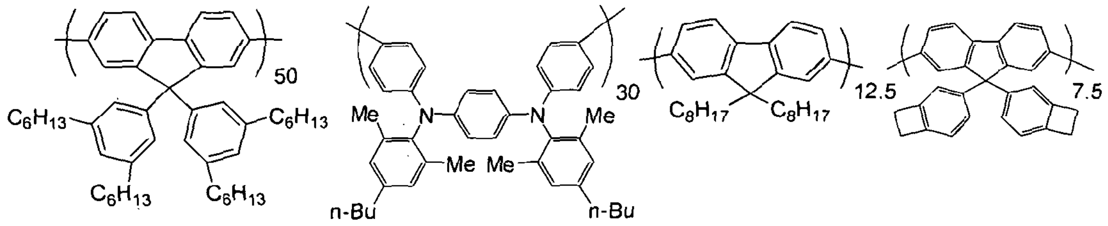
A film of the doped organic semiconductor formed by solution deposition, for example a hole injection layer of an OLED, optionally has a thickness of up to about 200 nm, optionally a thickness in the range of about 10-100 nm. The film may consist essentially of the doped organic semiconductor or it may comprise one or more further materials.

Examples

Formulation Example 1

Organic Semiconductor 1, illustrated below, was prepared by Suzuki polymerisation of fluorene and amine monomers as described in WO 00/53656. Organic Semiconductor 1 has an ionisation potential of about -5.2 eV as measured by photoelectron spectroscopy, described below.

A solution of 47.5 mg of Organic Semiconductor 1 in 4.75 ml of tetrahydrofuran (1 wt % solution) was mixed with 0.25mL of a 1 wt % solution of phosphomolybdic acid in tetrahydrofuran to give a solution of doped Organic Semiconductor 1 with a doping level of 5 wt %.



Organic Semiconductor 1

The solution of Organic Semiconductor 1 is intensely yellow. The solution of phosphomolybdic acid is bright yellow. The solution formed by mixing of these two solutions is dark green, and remains so following filtration through 0.45 micron syringe filter discs.

Figure 4A illustrates the UV-visible absorption spectrum for the undoped solution of Organic Semiconductor 1, and the spectrum for a film formed from this solution.

Figure 4B illustrates spectra of solutions of doped Organic Semiconductor 1, illustrating doping-induced features at around 500 nm and above 800 nm. The spectra are of increasingly dilute solutions, and the direction of the arrow illustrates the increasing dilution.

Formulation Example 2

47.5mg of polyvinylcarbazole (PVK) in 4.75mL of tetrahydrofuran (1 wt % solution) was mixed with 0.25mL of solution comprising phosphomolybdic acid in tetrahydrofuran (1 wt % solution) to give a solution of polyvinycarbazole having a doping level of 5 wt %.

PVK has an ionisation potential of about -5.8 eV as measured by photoelectron spectroscopy, described below.

The non-doped PVK solution is colourless. The solution of phosphomolybdic acid in THF is bright yellow, as is the doped polymer solution.

Figure 5A illustrates the UV-visible absorption spectrum for the undoped solution of PVK, and the spectrum for a film formed from this solution.

Figure 5B illustrates spectra of solutions of doped PVK, showing doping-induced features at around 500 nm and above 800 nm. The spectra are of increasingly dilute solutions, and the direction of the arrow illustrates the increasing dilution.

Figure 5C illustrates a 20x magnification of the spectra of Figure 5B, illustrating doping features of a shoulder above 380 nm and 980 nm. Although doping for PVK, which has a particularly deep ionisation potential, is not as pronounced for Organic Semiconductor 1, Figure still illustrates that the highly electron deficient transition metal compound dopants of the invention are capable of doping materials with a deep ionisation potential.

Figure 6 illustrates the UV-Visible absorption spectra for films formed by spin-coating Organic Semiconductor 1 and phosphomolybdic acid at increasing dopant concentration levels. The intensity of doping-induced features at around 480 nm and above 700 nm increase with increasing dopant concentrations.

Ionisation Potential Measurement

Energy level values of organic semiconductors were measured by photoelectron spectroscopy, using the AC-2 photoelectron spectrometer available from RK Instruments Inc.

Measurements are performed in air, and result in plots of photoelectron yield vs. photon energy

The measurements are performed by probing a sample that is typically several square millimetres in area, and includes the following steps:

- UV photons emitted from a deuterium lamp are monochromatized through a grating monochromator.
- The monocromatized UV photons are focused on a sample surface in the air.
- The energy of UV photon is increased in increments from -3.4eV to -6.2eV.
- When the energy of the UV photon is higher than the threshold energy of photoemission of the sample material (i.e. the Ionisation Potential), the photoelectrons are emitted from the sample surface.
- Photoelectrons emitted from the sample are detected and counted in the air by the open counter.
- Photoemission threshold (Ionisation Potential) is determined from the energy of an intersecting point between a background line and the extended line of the square root of the photoelectric quantum yield.

Device Examples

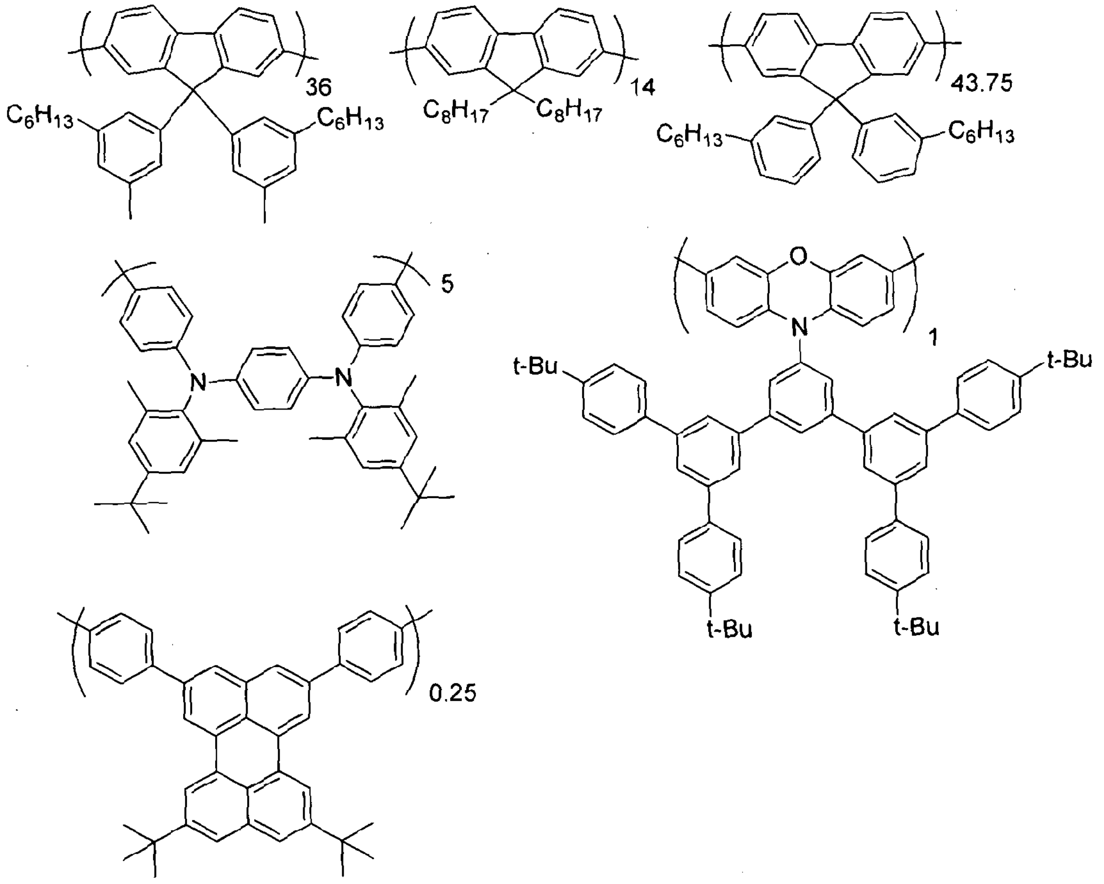
A substrate carrying ITO was cleaned using UV / Ozone.

53.46mg of Organic Semiconductor 1 was dissolved in 8.9mL of THF, and blended with 0.09mL of a 0.6% solution of phosphomolybdic acid in THF. After Vortex mixing, the resulting combined solution was spin-coated in a glove box in a nitrogen atmosphere onto the ITO to form a 35 nm hole injection layer. The crosslinkable groups of Organic Semiconductor 1 were crosslinked by thermal cross-linking on a hot plate in a glove box in a nitrogen atmosphere at 200°C for 30 – 60 minutes.

A 22 nm thick hole transporting layer was formed on the hole injection layer by spin-coating undoped Organic Semiconductor 1 onto the crosslinked hole injection layer. The crosslinkable groups of Organic Semiconductor 1 were crosslinked by thermal cross-linking on a hot plate in a glove box in a nitrogen atmosphere at 200°C for 30 – 60 minutes

A solution of Light-Emitting Polymer 1, illustrated below, in ortho-xylene (0.8 wt %) was deposited onto the hole transporting layer by spin-coating to form a 70 nm thick light-emitting layer. The resulting layer was dried by heating at 100°C for 10 minutes.

A cathode was formed by evaporation of a first layer of a metal fluoride to a thickness of about 2 nm, a second layer of aluminium to a thickness of about 200 nm and a third layer of silver.



Light Emitting Polymer 1

Devices with dopant concentrations in the hole injection layer of 0.1 wt %, 1 wt % and 5 wt %. were prepared as described above. The external quantum efficiency was about 3 % at a doping level of 0.1 wt %; about 3.5 % at a doping level of 1 wt %; and about 2.5 % at a doping level of 5 wt %.

The invention has been described herein with reference to organic light-emitting diodes, however it will be appreciated that a doped organic semiconductor layer as described herein may be provided as a layer of other organic electronic devices, including without limitation organic photoresponsive devices, including photosensors and photovoltaic devices such as solar cells, and organic thin film transistors.

Although the present invention has been described in terms of specific exemplary embodiments, it will be appreciated that various modifications, alterations and/or combinations of features disclosed herein will be apparent to those skilled in the art without departing from the scope of the invention as set forth in the following claims.

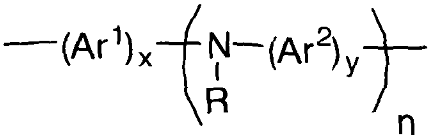
CLAIMS

1. A solution comprising at least one solvent and an organic semiconducting polymer doped with a transition metal compound comprising a transition metal having an oxidation state of at least five dissolved in the at least one solvent.

2. A solution according to claim 1 wherein the organic semiconducting polymer is present in a concentration of greater than or equal to 0.1 % weight percent relative to the at least one solvent.

3. A solution according to any preceding claim wherein the dopant is present in the range of 0.1-10 wt % relative to the organic semiconducting polymer.

4. A solution according to claim 3 wherein the organic semiconducting polymer comprises repeat units of formula (I):



$$-(Ar^1)_x-\left(\underset{R}{\underset{|}{N}}-(Ar^2)_y\right)_n-$$

(I)

wherein Ar^1 and Ar^2 in each occurrence are independently selected from substituted or unsubstituted aryl or heteroaryl groups; n is an integer greater than or equal to 1, preferably 1 or 2; R is H or a substituent; any of Ar^1, Ar^2 and R may be linked by a direct bond or linking group; and x and y are each independently 1, 2 or 3.

5. A solution according to claim 4 wherein H is a substituent.

6. A solution according to claim 4 or 5 wherein the organic semiconducting polymer is a copolymer comprising less than 50 mol% of repeat units of formula (I).

7. A solution according to any preceding claim wherein the organic semiconducting polymer comprises a substituted or unsubstituted arylene repeat unit.

8. A solution according to claim 7 wherein the substituted or unsubstituted arylene repeat unit is a substituted or unsubstituted fluorene repeat unit or an substituted or unsubstituted phenylene repeat unit.

9. A solution according to any preceding claim wherein at least one repeat unit of the organic semiconducting polymer is substituted with one or more alkyl groups, optionally one or more C_{1-20} alkyl groups.

10. A solution according to any preceding claim wherein the polymer is crosslinkable.

11. A solution according to any preceding claim wherein the at least one solvent is a substituted or unsubstituted cyclic ether.

12. A solution according to any preceding claim wherein the transition metal compound is a heteropoly acid.

13. A solution according to claim 12 wherein the heteropoly acid is selected from the group consisting of phosphomolybdic acid, phosphotungstic acid and tungstosilicic acid.

14. A solution according to any preceding claim wherein the oxidation state of the transition metal is 5, 6 or 7.

15. A solution according to any preceding claim wherein the oxidation state of the transition metal is 6.

16. A method of forming an organic electronic device comprising the step of forming an active layer of the device by depositing a solution according to any preceding claim and evaporating the at least one solvent.

17. A method according to claim 16 wherein the organic electronic device is an organic light-emitting device.

18. A method according to claim 17 wherein the active layer is a hole injection layer formed on an anode layer of the organic light-emitting device, the device further comprising a light-emitting layer between the hole injection layer and a cathode of the organic light-emitting device.

19. A method according to claim 18 wherein the anode is selected from the group consisting of indium tin oxide, indium zinc oxide, fluorine-doped tin oxide, tungsten trioxide, titanium dioxide, molybdenum trioxide, aluminium zinc oxide, gallium indium zinc oxide, aluminium, silver, palladium, copper, gold, platinum, and alloys thereof, for example silver-palladium-copper and molybdenum-chrome.

20. A method according to any of claims 16-19 comprising the step of crosslinking the active layer.

21. A method according to any of claims 18-20 comprising the step of forming a hole-transporting layer between the hole injection layer and the light-emitting layer by deposition of a substantially undoped hole transporting material.

22. A method according to any of claims 18-21 wherein the hole injection layer, the light-emitting layer and, if present, the hole-transporting layer are formed by inkjet printing.

23. A method according to claim 22 wherein the hole injection layer, the light-emitting layer and, if present, the hole-transporting layer are deposited into a well formed from a single bank material.

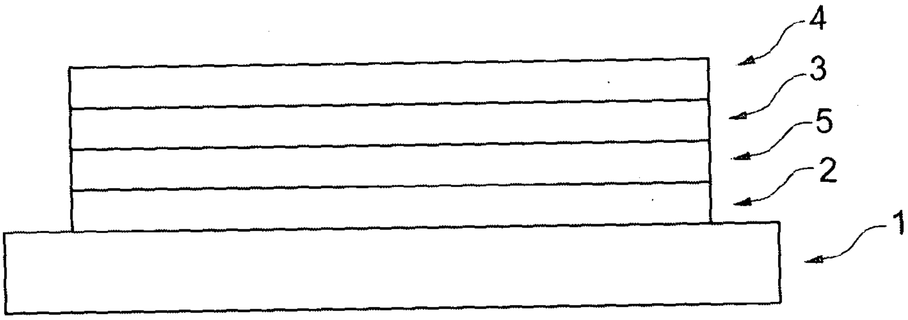


Fig. 1

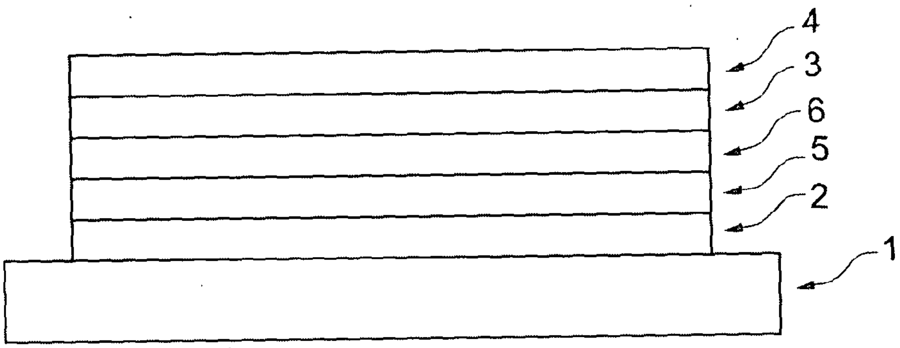


Fig. 2

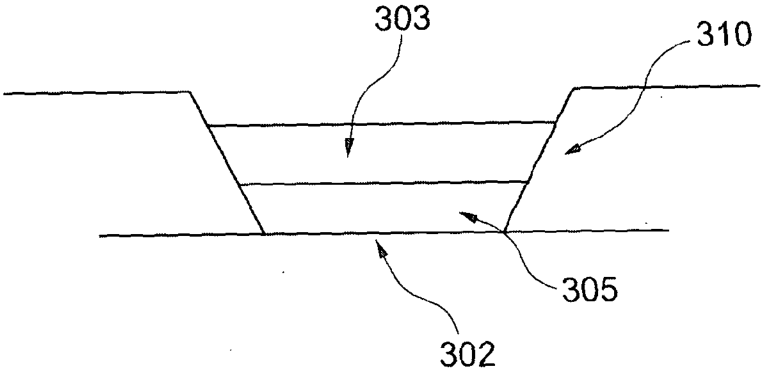


Fig. 3

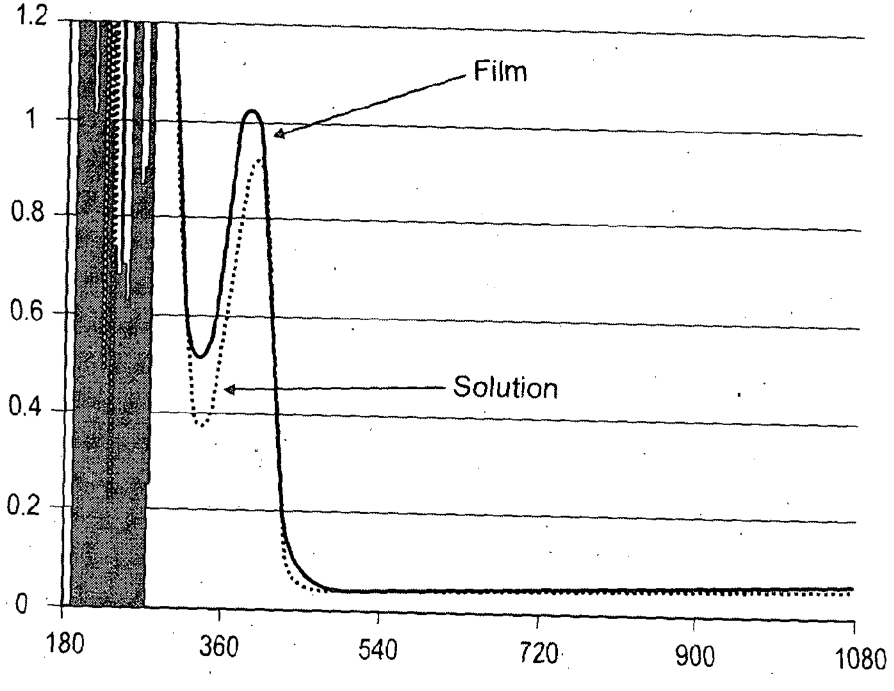

1.2
1
0.8
0.6
0.4
0.2
0
180
360
540
720
900
1080
Film
Solution

Fig. 4A

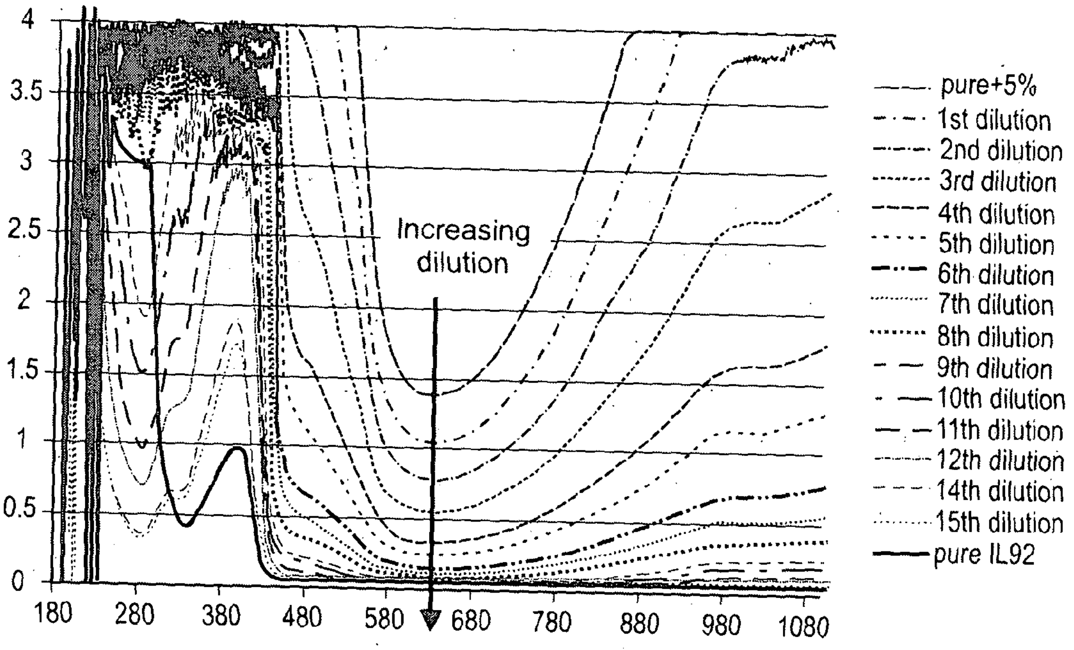

4
3.5
3
2.5
2
1.5
1
0.5
0
180
280
380
480
580
680
780
880
980
1080
Increasing dilution
pure+5%
1st dilution
2nd dilution
3rd dilution
4th dilution
5th dilution
6th dilution
7th dilution
8th dilution
9th dilution
10th dilution
11th dilution
12th dilution
14th dilution
15th dilution
pure IL92

Fig. 4B

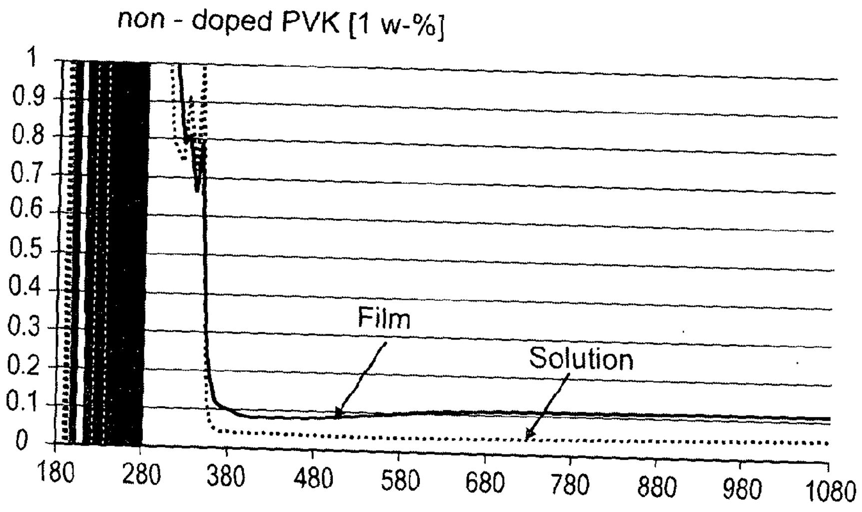

non - doped PVK [1 w-%]
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
180
280
380
480
580
680
780
880
980
1080
Film
Solution

Fig. 5A

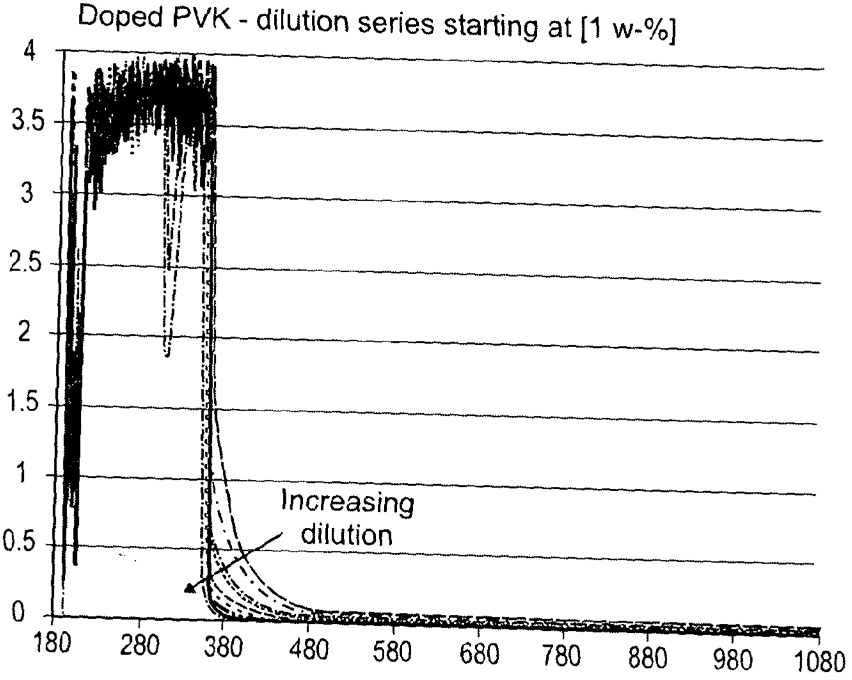

Doped PVK - dilution series starting at [1 w-%]
4
3.5
3
2.5
2
1.5
1
0.5
0
180
280
380
480
580
680
780
880
980
1080
Increasing dilution

Fig. 5B

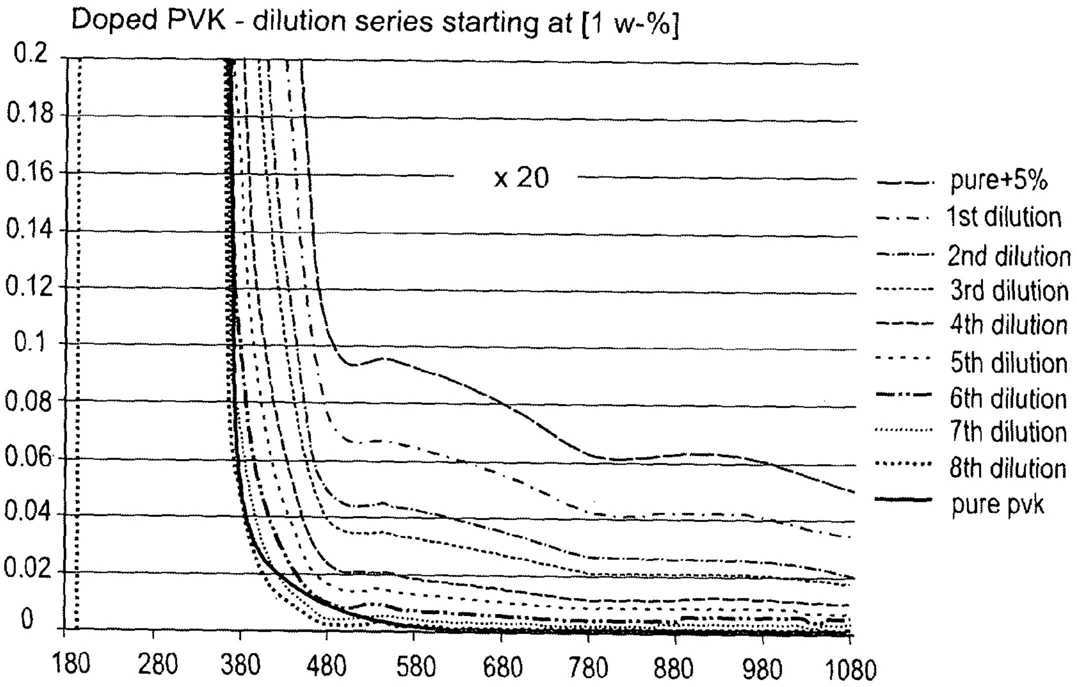

Doped PVK - dilution series starting at [1 w-%]
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
180
280
380
480
580
680
780
880
980
1080
x 20
pure+5%
1st dilution
2nd dilution
3rd dilution
4th dilution
5th dilution
6th dilution
7th dilution
8th dilution
pure pvk

Fig. 5C

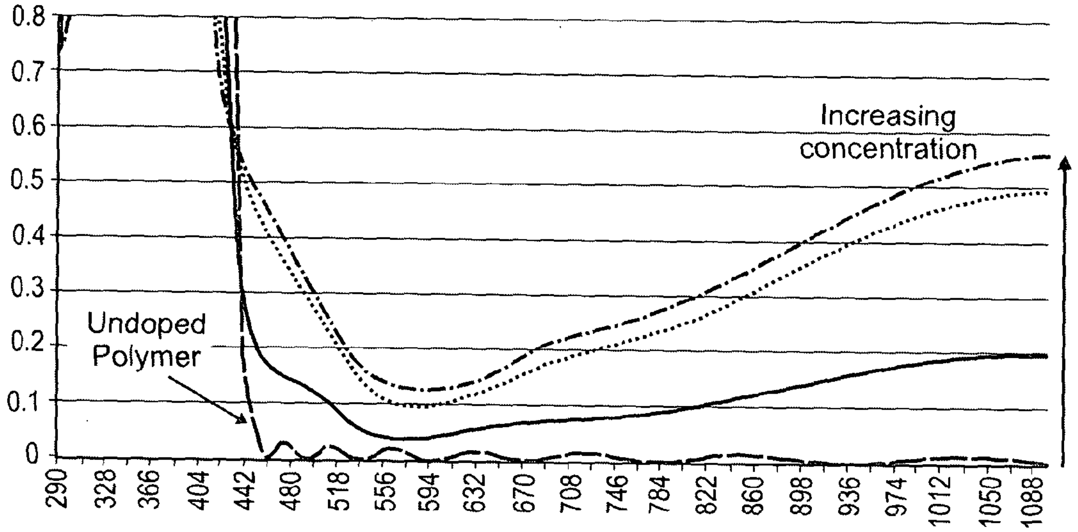

0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
290
328
366
404
442
480
518
556
594
632
670
708
746
784
822
860
898
936
974
1012
1050
1088
Increasing concentration
Undoped Polymer

Fig. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2012/000558

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L51/54
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L

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

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

EPO-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	DE 10 2009 022117 A1 (SIEMENS AG [DE]) 25 November 2010 (2010-11-25)	1,3-5, 7-9,11, 14, 16-19,22
Y	paragraph [0042] - paragraph [0043] paragraph [0057] - paragraph [0061] paragraph [0031] paragraph [0019] paragraph [0049] - paragraph [0050] -----	6,10,20, 21,23
X	EP 0 323 351 A1 (COMMISSARIAT ENERGIE ATOMIQUE [FR]) 5 July 1989 (1989-07-05) column 6, lines 19-34 column 2, lines 26-32 ----- -/--	1,2, 12-15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

5 October 2012

Date of mailing of the international search report

26/10/2012

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Beierlein, Udo

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2012/000558

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