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(54) **Title:** CHARGE-TRANSFER SALT COMPRISING AN ORGANIC SEMICONDUCTING MATERIAL

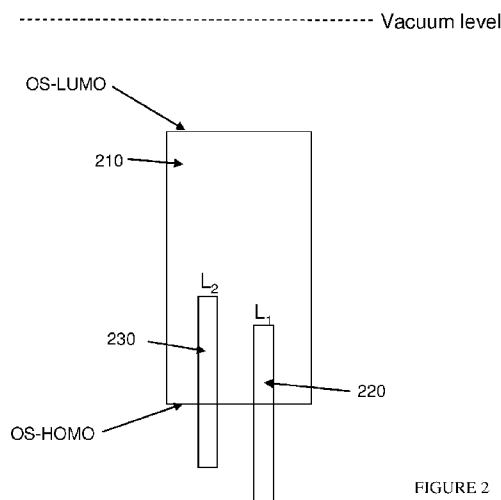


FIGURE 2

(57) **Abstract:** A charge-transfer salt comprising an organic semiconducting material (210) p-doped by a first p-dopant (220) and by a second p-dopant (210) that is different from the first p-dopant. The organic semiconducting material may be a conjugated polymer. The first dopant may have a LUMO level that is at least 0.05 e V further from vacuum than a LUMO level of the second dopant. The charge-transfer salt may be used in organic electronic devices, for example as a hole-injection layer of an organic light-emitting device.

CHARGE-TRANSFER SALT COMPRISING AN ORGANIC SEMICONDUCTING MATERIAL

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) as disclosed in EP 0901176 and EP 0947123, polyacrylic acid or a fluorinated sulfonic acid, for example Nafion ®. PEDT 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.

Hole injection layers formed by p-doping a conjugated material with metal compounds such as FeCl₃ or SbF₅ are disclosed in Chen et al, J. Appl. Phys. 96(1), 454-458, 2004 and in G. Crecelius, M. Stamm, J. Fink and J.J.Ritsko, Phys. Rev. Lett. 50, 1498–1500 (1983).

A hole injection layer formed from a conjugated polymer doped with tetrafluoro-tetracyanoquinodimethane (F4TCNQ) is disclosed in WO 2008/029155.

A hole injection layer formed from a conjugated polymer doped with a partially fluorinated fullerene is disclosed in WO 2012/131314.

Summary of the Invention

In a first aspect the invention provides a charge-transfer salt comprising an organic semiconducting material p-doped by a first p-dopant and by a second p-dopant that is different from the first p-dopant.

In a second aspect the invention provides a formulation comprising a charge-transfer salt according to the first aspect dissolved in a solvent or solvent mixture.

In a third aspect the invention provides an organic electronic device comprising a conductive layer comprising a charge-transfer salt according to any preceding claim.

In a fourth aspect the invention provides a method of forming an organic electronic device according to the third aspect comprising the step of forming the conductive layer by depositing a formulation according to the second aspect and evaporating the solvent or solvent mixture.

For the avoidance of any doubt, the doped organic semiconductor referred to herein has a different conductivity to the organic semiconductor prior to doping, and may be an extrinsic or degenerate organic semiconductor.

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 an embodiment of the invention;

Figure 2 illustrates energy levels of an organic semiconductor, a first dopant and a second dopant used to form a charge-transfer complex of the invention;

Figure 3A is a graph of luminance vs. voltage for a device according to an embodiment of the invention and comparative devices;

Figure 3B is a graph of voltage vs. external quantum efficiency for a device according to an embodiment of the invention and comparative devices;

Figure 3C is a graph of voltage vs. efficiency in lumens per watt for a device according to an embodiment of the invention and comparative devices;

Figure 3D is a graph of luminance vs. time for a device according to an embodiment of the invention and comparative devices;

Figure 3E is a graph of voltage vs. time for a device according to an embodiment of the invention and comparative devices;

Figure 4A is a graph of luminance vs. voltage for a device according to an embodiment of the invention and comparative devices;

Figure 4B is a graph of voltage vs. external quantum efficiency for a device according to an embodiment of the invention and comparative devices; and

Figure 4C is a graph of luminance vs. time for a device according to an embodiment of the invention and comparative devices.

Detailed Description of the Invention

Figure 1 illustrates an OLED 100 according to a first embodiment of the invention comprising an anode 101, a light-emitting layer 105 and a cathode 107 supported on a substrate 109, for example a glass or plastic substrate.

A hole injection layer 103 is provided between the anode and the light-emitting layer. The hole-injection layer is a doped organic semiconductor doped with a first dopant and a second dopant that is different from the first dopant.

With reference to Figure 2, the organic semiconductor 210 has a highest occupied molecular orbital (OS-HOMO) and a lowest unoccupied molecular orbital (OS-LUMO) and is doped with first p-dopant 220 and second p-dopant 230.

The first dopant 220 preferably has a LUMO level L_1 that is deeper (further from vacuum) than LUMO level L_2 of the second dopant 230. It will be appreciated by the skilled person that the first dopant 220 is a stronger dopant than the second dopant 230.

The present inventors have surprisingly found that performance of a device containing an organic semiconductor layer doped by a single dopant can be improved by doping the organic semiconductor layer with dopants of different strengths.

The first dopant may have a LUMO level that is at least 0.05 eV deeper, optionally at least 0.1 eV deeper, than that of the second dopant.

Figure 2 illustrates an organic semiconductor doped with two dopants. In other embodiments, the organic semiconductor may be doped with three or more different dopants wherein at least two of the three or more different dopants may have a difference in LUMO levels as described with reference to the first and second dopants.

One or more further layers may be provided between the anode 101 and cathode 107, for example hole-transporting layers, electron transporting layers, hole blocking layers and electron blocking layers. The device may contain more than one light-emitting layer.

Preferred device structures include:

Anode / Hole-injection layer / Light-emitting layer / Cathode

Anode / Hole-injection layer / Hole-transporting layer / Light-emitting layer / Cathode

Anode / Hole-injection layer / Hole-transporting layer / Light-emitting layer / Electron-transporting layer / Cathode.

Preferably, a semiconducting hole-transporting layer is provided between the hole-injection layer and the light-emitting layer. Preferably, the hole-transporting layer is in contact with the hole-injection layer.

Preferably, at least one of a hole-transporting layer and hole injection layer is present.

Preferably, both a hole injection layer and hole-transporting layer are present.

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

Organic dopants

Exemplary p-dopants include organic and inorganic p-dopants. Organic p-dopants include metallo-organic dopants, for example metal complexes having organic ligands.

Exemplary organic dopants include tetracyano-p-quinodimethane (TCNQ) and fluorinated derivatives thereof, preferably tetrafluorotetracyano-p-quinodimethane (F₄TCNQ); fullerenes, preferably partially fluorinated fullerenes; and hexaazatriphenylene-hexacarbonitrile.

Organic dopants preferably comprise a core structure that may be unsubstituted or substituted with one or more substituents, for example one or more fluorine atoms. The two or more dopants that dope the organic semiconductor may differ in the number and / or position of substituents. Preferably, the first and second dopants have different core structures.

Exemplary dopants include

- fullerenes, which may be unsubstituted or substituted with one or more fluorine atoms, preferably partially fluorinated fullerenes;
- quinones, for example dichloro dicyanoquinine (DDQ); o-chloranil; cyanil; quinonediimine; tetracyano-2,6-naphthoquinodimethane which may be unsubstituted or substituted with one or more fluorine atoms, for example F₆TNAP; and tetracyano-p-quinodimethane (TCNQ) which may be unsubstituted or substituted with one or more fluorine atoms, for example F₂TCNQ, F₃TCNQ or F₄TCNQ;
- Hexaazatriphenylene, which may be unsubstituted or substituted with one or more substituents selected from fluorine and cyano, for example HAT-CN₆
- boranes;
- carbocations;
- bora-tetraazapentalenes;
- onium salts, for example sulfonium, oxonium, selenonium, nitrosonium, arsonium, phosphonium and iodonium salts;

- aminium or ammonium salts;
- silver salts; and
- ammonium salts.

Fullerenes may be any carbon allotrope in the form of a hollow sphere or ellipsoid.

The fullerene may consist of carbon atoms arranged in 5, 6 and / or 7 membered rings, preferably 5 and / or 6 membered rings. C₆₀ Buckminster Fullerene is particularly preferred.

The partially fluorinated fullerene may have formula C_aF_b wherein b is in the range of 10 – 60 and a is more than b. a is preferably 60 or 70. Examples include C₆₀F₁₈, C₆₀F₂₀, C₆₀F₃₆, C₆₀F₄₈, C₇₀F₄₄, C₇₀F₄₆, C₇₀F₄₈, and C₇₀F₅₄. Partially fluorinated fullerenes and their synthesis are described in more detail in, for example, Andreas Hirsch and Michael Brettreich, “Fullerenes: Chemistry and Reactions”, 2005 Wiley-VCH Verlag GmbH & Co KGaA, and in “The Chemistry Of Fullerenes”, Roger Taylor (editor) Advanced Series in Fullerenes - Vol. 4 .

The partially fluorinated fullerene may consist of carbon and fluorine only or may include other elements, for example halogens other than fluorine and / or oxygen.

Examples of specific p-dopants are provided in Table 1.

HOMO and LUMO levels as described anywhere herein may be HOMO and LUMO levels as measured by square wave cyclic voltammetry (SQ CV).

Plotting applied potential for forward and backward scans against resulting current gives a typical cyclic voltammogram. The cyclic voltammogram may be used to establish HOMO and/or LUMO levels of a material.

The excitation signal in SQCV consists of a symmetrical square-wave pulse (for example, of amplitude 25mV) superimposed on a staircase waveform of step height (for example, 4mV) where the forward pulse of the square wave coincides with the staircase

step. The resulting current is obtained by taking the difference between the forward and reverse currents. The peak height is directly proportional to the concentration of the electroactive species. An exemplary frequency used for HOMO and LUMO measurements is 15Hz. Oxidation/reduction events (HOMO/LUMO) in Squarewave voltammographs take the shape of peaks with a peak maximum describing occurrence of the event (redox potential).

A solution of the material is spun on a glassy carbon electrode with approximate thickness of 70nm. The electrode is transferred into an electrochemical cell having a reference electrode (commonly Ag/AgCl), and a Pt counter electrode, both immersed in MeCN with 0.1M supporting electrolyte (typically TBAPF6). Measurements of the material spun on the glassy carbon electrode in a negative potential region (vs Ag/AgCl) give rise to reductive currents (LUMO level), and a positive region is resulting from oxidative currents (HOMO level). All measurements are re-referenced vs HOMO level of a standard molecule – Ferrocene equal to -4.8 eV.

Solution CV of a material may be performed in a similar fashion but instead of spun film –dissolved material is used in the electrochemical cell.

Cyclic voltammetry is described in A.J. Bard, L.R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, second ed., Wiley, New York, 2001, *Voltammetric Techniques*, Samuel P. Kounaves, Tufts University, page 720, and *Anal. Chem.*, 1969, 41 (11), pp 1362–1365.

Table 1

p-dopant	LUMO (eV)
Phosphotungstic acid	4.27
Phosphomolybdic acid	4.90
NDP-9, available from Novaled GmbH	4.46

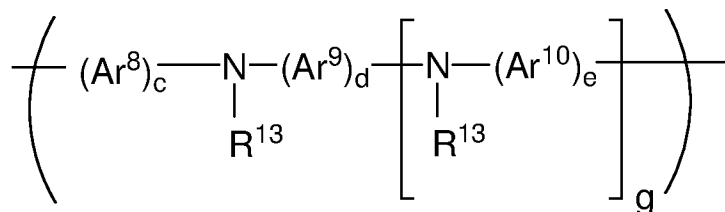
F ₄ TCNQ	4.43
F ₆ TNAP	4.67
HAT-CN ₆	4.32
C ₆₀ F ₁₄	4.17 eV
C ₆₀ F ₃₆	4.53
C ₆₀ F ₄₈	4.98

Organic semiconductor material

The organic semiconductor material may be any form of material, including non-polymeric and polymeric materials, having a HOMO level capable of undergoing p-doping with the dopants. 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 HOMO level of the organic semiconductor material as measured by square wave voltammetry may be any value up to -5.8 eV from vacuum level.

Organic semiconducting polymers include conjugated and non-conjugated polymers. A conjugated polymer may comprise repeat units of formula (I):



(I)

wherein Ar^8 , Ar^9 and Ar^{10} in each occurrence are independently selected from substituted or unsubstituted aryl or heteroaryl, preferably C_{6-20} aryl, g is 0, 1 or 2, preferably 0 or 1, R^{13} independently in each occurrence is H or a substituent, preferably a substituent, and c , d and e are each independently 1, 2 or 3.

R^{13} , which may be the same or different in each occurrence when g is 1 or 2, is preferably selected from the group consisting of alkyl, for example C_{1-20} alkyl, Ar^{11} , a branched or linear chain of Ar^{11} groups, or a crosslinkable unit that is bound directly to the N atom of formula (I) or spaced apart therefrom by a spacer group, wherein Ar^{11} in each occurrence is independently optionally substituted aryl or heteroaryl, preferably C_{6-20} aryl. Exemplary spacer groups are C_{1-20} alkyl, phenyl and phenyl- C_{1-20} alkyl.

Any two aromatic or heteroaromatic groups selected from Ar^8 , Ar^9 , and, if present, Ar^{10} and Ar^{11} directly bound to the same N atom may be linked by a direct bond or a divalent linking atom or group to another of Ar^8 , Ar^9 , Ar^{10} and Ar^{11} . Preferred divalent linking atoms and groups include O, S; substituted N; and substituted C.

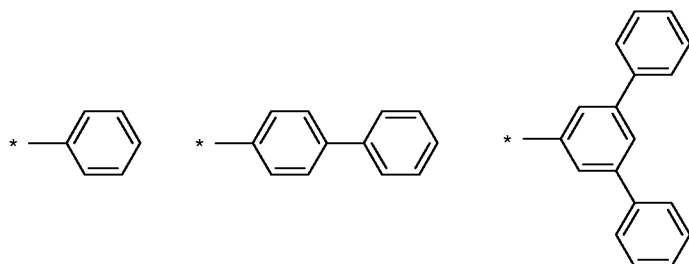
Ar^8 and Ar^{10} are preferably C_{6-20} aryl, more preferably phenyl, that may be unsubstituted or substituted with one or more substituents.

In the case where $g = 0$, Ar^9 is preferably C_{6-20} aryl, more preferably phenyl, that may be unsubstituted or substituted with one or more substituents.

In the case where $g = 1$, Ar^9 is preferably C_{6-20} aryl, more preferably phenyl or a polycyclic aromatic group, for example naphthalene, perylene, anthracene or fluorene, that may be unsubstituted or substituted with one or more substituents.

R^{13} is preferably Ar^{11} or a branched or linear chain of Ar^{11} groups. Ar^{11} in each occurrence is preferably phenyl that may be unsubstituted or substituted with one or more substituents.

Exemplary groups R^{13} include the following, each of which may be unsubstituted or substituted with one or more substituents, and wherein * represents a point of attachment to N:



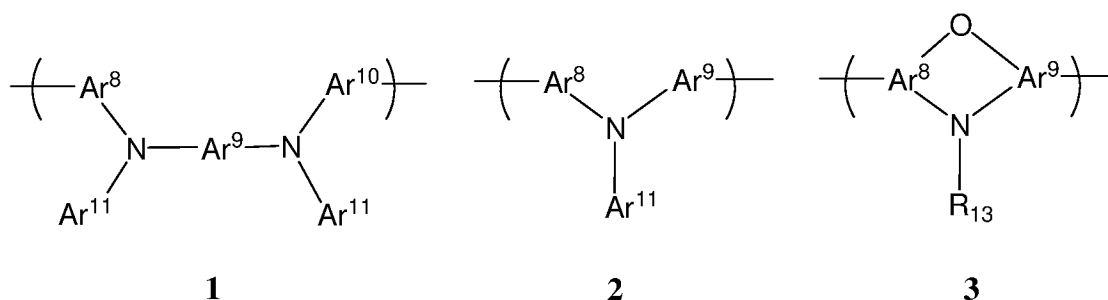
c, d and e are preferably each 1.

Ar^8 , Ar^9 , and, if present, Ar^{10} and Ar^{11} are each independently unsubstituted or substituted with one or more, optionally 1, 2, 3 or 4, substituents. Exemplary substituents may be selected from:

- substituted or unsubstituted alkyl, optionally C_{1-20} alkyl, wherein one or more non-adjacent C atoms may be replaced with optionally substituted aryl or heteroaryl (preferably phenyl), O, S, C=O or -COO- and one or more H atoms may be replaced with F; and
- a crosslinkable group attached directly to or forming part of Ar^8 , Ar^9 , Ar^{10} or Ar^{11} or spaced apart therefrom by a spacer group, for example a group comprising a double bond such and a vinyl or acrylate group, or a benzocyclobutane group.

Preferred substituents of Ar^8 , Ar^9 , and, if present, Ar^{10} and Ar^{11} are C_{1-40} hydrocarbyl, preferably C_{1-20} alkyl or a hydrocarbyl crosslinking group.

Preferred repeat units of formula (I) include units of formulae 1-3:



Preferably, Ar^8 , Ar^{10} and Ar^{11} of repeat units of formula 1 are phenyl and Ar^9 is phenyl or a polycyclic aromatic group.

Preferably, Ar^8 , Ar^9 and Ar^{11} of repeat units of formulae 2 and 3 are phenyl.

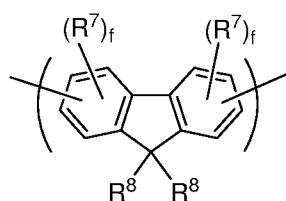
Preferably, Ar^8 and Ar^9 of repeat units of formula 3 are phenyl and R^{11} is phenyl or a branched or linear chain of phenyl groups.

A polymer comprising repeat units of formula (I) may be a homopolymer or a copolymer containing repeat units of formula (I) and one or more co-repeat units.

In the case of a copolymer, repeat units of formula (I) may be provided in a molar amount in the range of about 1-99 mol %, optionally about 1-50 mol %.

Exemplary co-repeat units include arylene repeat units that may be unsubstituted or substituted with one or more substituents, for example one or more C_{1-40} hydrocarbyl groups.

One class of arylene co-repeat unit is optionally substituted fluorene, such as repeat units of formula (II):



(II)

wherein R^7 in each occurrence is the same or different and is a substituent wherein the two groups R^7 may be linked to form a ring; R^8 in each occurrence is the same or different and is a substituent wherein the two groups R^8 may be linked to form a ring; and f is 0, 1, 2 or 3.

Each R^8 may independently be selected from the group consisting of:

- alkyl, optionally C_{1-20} alkyl, wherein one or more non-adjacent C atoms may be replaced with optionally substituted aryl or heteroaryl, O, S, substituted N, $\text{C}=\text{O}$ or $-\text{COO}-$, and one or more H atoms may be replaced with F;

- aryl and heteroaryl groups that may be unsubstituted or substituted with one or more substituents, preferably phenyl substituted with one or more C₁₋₂₀ alkyl groups;
- a linear or branched chain of aryl or heteroaryl groups, each of which groups may independently be substituted, for example a group of formula $-(Ar^7)_r$ wherein each Ar⁷ is independently an aryl or heteroaryl group and r is at least 2, optionally 2 or 3, preferably a branched or linear chain of phenyl groups each of which may be unsubstituted or substituted with one or more C₁₋₂₀ alkyl groups; and
- a crosslinkable-group, for example a group comprising a crosslinkable double bond unit such as a vinyl or acrylate group, or a crosslinkable benzocyclobutane unit.

Preferably, each R⁸ is independently a C₁₋₄₀ hydrocarbyl group.

Substituted N, where present, may be $-NR^6$ - wherein R⁶ is a substituent and is optionally in each occurrence a C₁₋₄₀ hydrocarbyl group, optionally a C₁₋₂₀ alkyl group.

One R⁸ may be C₁₋₂₀ alkyl and the other R⁸ may be unsubstituted or substituted phenyl, for example as described in WO2012/104579, the contents of which are incorporated herein by reference.

The aromatic carbon atoms of the fluorene repeat unit may be unsubstituted, or may be substituted with one or more substituents R⁷.

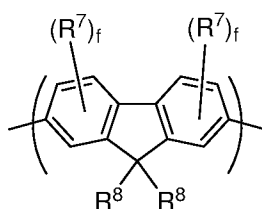
Exemplary substituents R⁷ are alkyl, for example C₁₋₂₀ alkyl, wherein one or more non-adjacent C atoms may be replaced with O, S, C=O and -COO-, optionally substituted aryl, and optionally substituted heteroaryl. Particularly preferred substituents include C₁₋₂₀ alkyl and substituted or unsubstituted aryl, for example phenyl. Optional substituents for the aryl include one or more C₁₋₂₀ alkyl groups.

A crosslinkable group R⁸ may be a crosslinkable unit that is bound directly to the fluorene of formula (II) or that is spaced apart therefrom by a spacer group. Exemplary spacer groups are C₁₋₂₀ alkyl, phenyl and phenyl-C₁₋₂₀ alkyl.

The extent of conjugation of repeat units of formula (II) to aryl or heteroaryl groups of adjacent repeat units in the polymer backbone may be controlled by (a) linking the repeat

unit through the 3- and / or 6- positions to limit the extent of conjugation across the repeat unit, and / or (b) substituting the repeat unit with one or more substituents R^7 in or more positions adjacent to the linking positions in order to create a twist with the adjacent repeat unit or units, for example a 2,7-linked fluorene carrying a C_{1-20} alkyl substituent in one or both of the 3- and 6-positions.

The repeat unit of formula (II) may be a 2,7-linked repeat unit of formula (IIa):

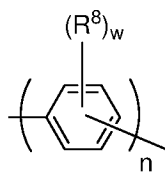


(IIa)

A relatively high degree of conjugation across the repeat unit of formula (IIa) may be provided in the case where each $f = 0$, or where any substituent R^7 is not present at a position adjacent to the linking 2- or 7-positions of formula (IIa).

A relatively low degree of conjugation across the repeat unit of formula (IIa) may be provided in the case where at least one f is at least 1, and where at least one substituent R^7 is present at a position adjacent to the linking 2- or 7- positions of formula (IIa).

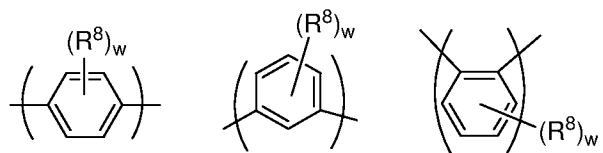
Another class of arylene repeat units is phenylene, such as phenylene repeat units of formula (III):



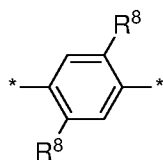
(III)

wherein w in each occurrence is independently 0, 1, 2, 3 or 4, optionally 1 or 2; n is 1, 2 or 3; and R^8 independently in each occurrence is a substituent as described above.

If n is 1 then exemplary repeat units of formula (III) include the following:



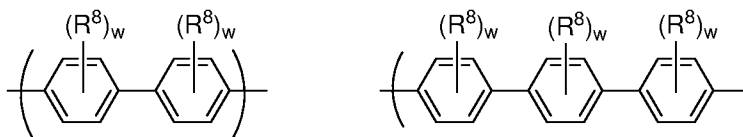
A particularly preferred repeat unit of formula (III) has formula (IIIa):



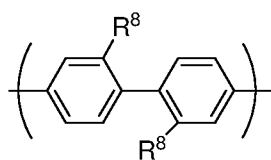
(IIIa)

Substituents R^8 of formula (IIIa) are adjacent to linking positions of the repeat unit, which may cause steric hindrance between the repeat unit of formula (IIIa) and adjacent repeat units, resulting in the repeat unit of formula (IIIa) twisting out of plane relative to one or both adjacent repeat units.

Exemplary repeat units where n is 2 or 3 include the following:



A preferred repeat unit has formula (IIIb):



(IIIb)

The two R^8 groups of formula (IIIb) may cause steric hindrance between the phenyl rings they are bound to, resulting in twisting of the two phenyl rings relative to one another.

Solution processing

The organic semiconductor material, the first dopant and the second dopant are preferably soluble. Preferably, solvents for forming solutions of the organic semiconductor material, the first dopant and the second dopant are miscible. A charge-transfer salt may be formed by mixing separate solutions of the organic semiconductor material, the first dopant and the second dopant, or mixing a solution of the organic semiconductor material with a solution of the first and second dopants. The solvent or solvent mixture may be selected so as to dissolve not only the starting materials but also the charge-transfer salt formed upon doping of the organic semiconductor.

Solutions of the first dopant, the second dopant and / or the organic semiconductor material may be filtered before being combined.

The concentrations of the first dopant and second 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.

The doping concentration may be selected so as to control resistivity of a film formed from the doped organic semiconductor. The resistivity of a film formed from the organic semiconductor may be greater than about 5×10^5 Ohm cm.

The total doping concentration (first dopant + second dopant concentration) may be in the range of 0.1 mol % to 10 mol %

Organic semiconductor polymers comprising arylene repeat units, in particular alkyl-substituted arylene repeat units as described above, are soluble in mono- or poly-alkylated benzenes such as toluene, ortho-, meta- and para-xylene, mesitylene, tetraline, ethylbenzene and cyclohexylbenzene.

Suitable solvents for organic dopants include chlorinated solvents such as chlorinated benzenes, for example dichlorobenzene and mono- or poly-alkylated benzenes as described above.

The number, size and / or position of substituents on an arylene solvent may be selected to control solubility of the organic semiconductor, dopants and / or charge transfer salt, and / or to control the boiling point, viscosity and / or contact angle of the solvent according to the deposition technique to be used in forming a film of the doped organic semiconductor.

A film comprising the charge-transfer salt may be formed by depositing a formulation comprising the charge-transfer salt and one or more solvents, and evaporating the one or more solvents. Preferably, the formulation is a solution.

Deposition methods include coating techniques, such as spin-coating, dip-coating and blade coating and printing techniques such as inkjet printing, flexographic printing, screen printing and roll printing.

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 one colour (in the case of a monochrome device) or multiple colours (in the case of a multicolour, in particular full colour device). The patterned layer is typically a layer of photoresist that is patterned to define wells as described in, for example, EP 0880303.

As an alternative to wells, the ink 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.

Further layers of a device containing a layer of the charge-transfer salt may be formed by a deposition method described herein. The light-emitting layer of an OLED and, if present, any charge-transporting layer of an OLED, may be formed by a method described herein.

If a layer, for example a hole-transporting layer or light-emitting layer, is formed on the layer of the charge-transfer salt by a solution deposition method such as a printing or coating method described herein then the charge-transfer salt layer may be crosslinked

before the overlying layer is formed. The organic semiconductor of the charge-transfer salt may carry crosslinking groups, for example as described above, that are reacted to crosslink the layer comprising the charge-transfer salt. Preferably, crosslinking groups are reacted by thermal treatment, for example by heating to a temperature in the range of about 100°C-250°C.

Applications

The charge-transfer salt formed upon doping of the organic semiconductor may be used as a conducting layer of an organic electronic device.

Exemplary applications include use as a hole-injection layer of an OLED, as described with reference to Figure 1; use as an anode of an OLED, an organic photovoltaic device or an organic photosensor; and use as an electrode of an organic thin-film transistor.

A layer of a device comprising the charge-transfer salt may consist essentially of the charge-transfer salt or may contain one or more further materials.

Preferably, the charge-transfer salt is used to form a hole-injection layer of an OLED.

Anodes

Suitable materials for forming the anode of an OLED 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.

Hole transporting layer

An OLED may comprise a hole transporting layer between a doped hole injection layer formed from a charge transfer salt as described herein and the light-emitting layer.

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

The material used to form the hole transporting layer may be selected from any hole transporting material. 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 the first and / or second 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 -5.8 eV or shallower as measured by square wave voltammetry.

The hole transporting material may be provided with crosslinkable groups, for example crosslinkable groups as described above.

Light emitting layer

Suitable light-emitting materials for use in the light-emitting layer include non-polymeric materials, polymeric materials, and compositions thereof. Suitable light-emitting polymers include conjugated polymers, for example optionally substituted poly(arylene

vinylenes) such as poly(p-phenylene vinylenes) and optionally substituted 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 optionally substituted amine repeat units of formula (I) and / or optionally substituted arylene or heteroarylene repeat units as described above, in particular fluorene repeat units of formula (II) 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.

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, such as 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.

Two or more light-emitting layers may be present. For example, emission from two or more layers may combine to produce white light.

Light produced by the OLED may be fluorescent light, phosphorescent light or a combination of fluorescent and phosphorescent light.

A 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 is at least the same as or 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. In the case of a phosphorescent light-emitting dopant the triplet excited state energy level (T_1) of the host material is at least the same as or higher than that of the phosphorescent light-emitting dopant in order that triplet excitons may be transferred from the host material to the phosphorescent light-emitting dopant. The host and dopant materials may be separate materials that are mixed together in the light-emitting layer, or the host and dopant materials may be covalently bound. If the host is a polymer then the dopant may be provided in a side-group of the polymer, as a repeat unit in the polymer main chain, or as an end-group of the polymer.

Exemplary phosphorescent light-emitting dopants include metal complexes, for example complexes of ruthenium, rhodium, palladium, rhenium, osmium, iridium, platinum and gold. Iridium complexes are particularly preferred.

The light-emitting layer may be patterned or unpatterned. A device comprising an unpatterned layer may be used as 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.

Cathode

The cathode 107 is selected from materials that have a workfunction allowing injection of electrons into the light-emitting layer or layers of the OLED. Other factors influence the selection of the cathode such as the possibility of adverse interactions between the cathode and the light-emitting material. The cathode may consist of a single material such as a layer of aluminium. Alternatively, it may comprise a plurality of conductive materials such as metals, for example a bilayer of a low workfunction material and a high workfunction material such as calcium and aluminium, for example as disclosed in WO 98/10621. The cathode may comprise elemental barium, for example as disclosed in WO 98/57381, Appl. Phys. Lett. 2002, 81(4), 634 and WO 02/84759. The cathode may comprise a thin (e.g. 0.5-5 nm) layer of metal compound, in particular an oxide or fluoride of an alkali or alkali earth metal, between the organic layers of the device and one or more conductive cathode layers to assist electron injection, for example lithium fluoride as disclosed in WO 00/48258; barium fluoride as disclosed 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 comprises 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.

Encapsulation

Organic electronic devices 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 US 6268695 which discloses a substrate of alternating plastic and barrier layers or a laminate of thin glass and plastic as disclosed in 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.

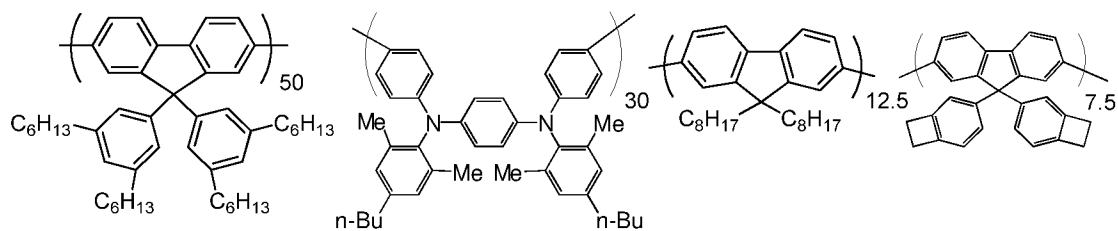
Examples

Material properties

Semiconductor Polymer 1, illustrated below, was doped with first and second dopants.

Semiconductor Polymer 1 has a HOMO level of 5.1 eV as measured by square wave voltammetry.

Semiconductor Polymer 1 was formed by Suzuki polymerisation as described in WO 00/53656 of monomers for forming the illustrated repeat units.



Semiconducting Polymer 1

Semiconducting Polymer 1 was doped with either the combination of dopants of Table 2 or the combination of dopants of Table 3. NDP-9 was obtained from Novaled GmbH. Dopant LUMO levels were measured by square wave voltammetry.

Table 2

Material	LUMO (eV)
F ₄ TCNQ First dopant A	4.43
HAT-CN6 Second dopant A	4.32

Table 3

Material	LUMO (eV)
C ₆₀ F ₃₆ First dopant B	4.53
NDP-9 Second dopant B	4.46

Formulation Examples

Semiconducting Polymer 1, illustrated below, was dissolved in o-xylene.

First and second dopants of Table 2 and Table 3 were individually dissolved in o-xylene.

The polymer solution and dopant solutions were separately filtered through syringe filter discs having a pore size of 0.45 microns.

Formulation A containing 0.6 wt % of the doped polymer was formed by mixing the solution of Semiconducting Polymer 1 with solutions of first dopant A and second dopant A (Semiconducting Polymer 1 : first dopant A : second dopant A = 95.9 : 1.7 : 2.4 wt %).

Formulation B of the doped polymer was formed by mixing the solution of Semiconducting Polymer 1 with solutions of first dopant B and second dopant B.

Device Examples - General Device Process

A substrate carrying an 45 nm thick ITO anode layer was cleaned using UV / Ozone. A 35 nm thick crosslinked and doped hole-injection layer was formed by spin-coating Formulation A or Formulation B, evaporating the solvent and thermally crosslinking the polymer. A 22 nm thick hole-transporting layer, was formed by spin-coating undoped Semiconducting Polymer 1 from an o-xylene solution followed by thermal crosslinking. A light-emitting layer of a blend of a fluorescent blue light-emitting polymer and an additive polymer (90 : 10 wt %) was formed by spin-coating from o-xylene solution. A cathode was formed by evaporation of a first layer of sodium fluoride to a thickness of about 2 nm, a second layer of aluminium to a thickness of about 100 nm and a third layer of silver to a thickness of about 100 nm.

The fluorescent blue light-emitting polymer was formed by Suzuki polymerisation as described in WO 00/53656 of fluorene monomers of formula (II), a diamine monomer of formula (I-1) and an amine monomer of formula (I-3).

Device Example A

A device was prepared according to the General Device Process wherein the hole injection layer is formed by spin-coating Formulation A.

Comparative Devices 1 and 2

For the purpose of comparison, devices in which the hole-injection layer is doped with only one of first dopant A and second dopant A were prepared, as summarized in Table 4.

Table 4

Device	First dopant A	Second dopant A
Device Example A	1.7 wt % 3.5 mol %	2.4 wt % 3.5 mol %
Comparative Device 1	1.7 wt % 3.5 mol %	-
Comparative Device 2	3.5 wt % 7.0 mol %	-

Device Example A - Results

In the graphs of Figures 3A-3E, traces for Device Example A are shown as dotted lines; traces for Comparative Device 1 are shown as dashed lines; and traces for Comparative Device 2 are shown as solid lines.

With reference to Figure 3A, Device Example A has higher luminance at any given measured voltage Comparative Device 1 or Comparative Device 2. Voltage at 1,000 cd/m^2 is about 4.5 V for Device Example A compared to about 5.1 V for Comparative Device 1, and about 4.9 V for Comparative Device 2.

With reference to Figure 3B, the maximum external quantum efficiency for Device Example A is about 5.6 eV compared to about 4.3 eV for Comparative Device 1, and about 4.7 eV for Comparative Device 2.

With reference to Figure 3C, efficiency measured in Lm / W is higher for Device Example A than for Comparative Device 1 or Comparative Device 2. Efficiency at $1,000 \text{ cd/m}^2$ is about $4.4 \text{ Lm} / \text{W}$ for Device Example A compared to about $2.9 \text{ Lm} / \text{W}$ for Comparative Device 1, and about $3.3 \text{ Lm} / \text{W}$ for Comparative Device 2.

Surprisingly, the effect on efficiency of doubling the concentration of first dopant A in going from Comparative Device 1 to Comparative Device 2 is relatively small compared to the effect of using second dopant A in combination with first dopant A, even though second dopant A is a weaker dopant having a shallower LUMO than first dopant A.

With reference to Figure 3D, the time taken for luminance of Device Example A to decay to 50 % of a starting luminance at constant current is surprisingly much longer than the corresponding time for Comparative Device 1 or Comparative Device 2.

With reference to Figure 3E, surprisingly the increase in drive voltage over time at a constant current is significantly slower for Device Example A than for Comparative Device 1 or Comparative Device 2.

Device Example B

A device was prepared according to the General Device Process wherein the hole injection layer is formed by spin-coating Formulation B.

Comparative Devices 3 and 4

For the purpose of comparison, devices were prepared according to the General Device Process in which the hole-injection layer is doped with only one of first dopant B and second dopant B, as summarized in Table 5.

Table 5

Device	First dopant B	Second dopant B

Device Example B	15.45 wt %	3 wt %
Comparative Device 3	15.45 wt %	-
Comparative Device 4	-	3 wt %

Device Example B - Results

In the graphs of Figures 4A-4C, traces for Device Example B are shown as dotted lines; traces for Comparative Device 3 are shown as dashed lines; and traces for Comparative Device 4 are shown as solid lines.

With reference to Figure 4A, luminance at a given voltage is slightly higher Device Example B compared to either Comparative Device 4, but slightly lower compared to Comparative Device 3.

With reference to Figure 4B, external quantum efficiency of Device Example B is higher than that of Comparative Device 4 but lower than that of Comparative Device 3.

With reference to Figure 4C, the time taken for luminance of Comparative Device 3 to decay to 50 % of a starting luminance at constant current is relatively short compared to that of Comparative Device 4. Surprisingly, adding second dopant B to Comparative Device 3 to give Device Example B results in a lifetime that is very similar to that of Comparative Device 4.

Accordingly, using the combination of first dopant B and second dopant B achieves the long lifetime of Comparative Device 4 as compared to Comparative Device 3 whilst increasing the efficiency of Comparative Device 4 as compared to Comparative Device 3.

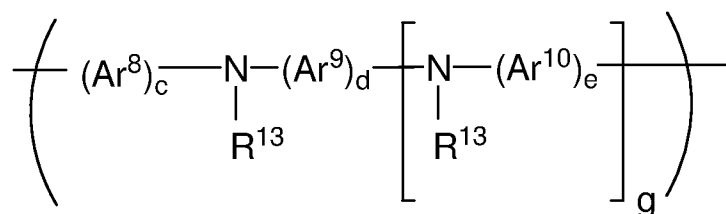
Although the present invention has been described in terms of specific exemplary embodiments, it will be appreciated that various modifications, alterations and/or

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 charge-transfer salt comprising an organic semiconducting material p-doped by a first p-dopant and by a second p-dopant that is different from the first p-dopant.
2. A charge-transfer salt according to claim 1 wherein the first dopant has a LUMO level that is at least 0.05 eV further from vacuum than a LUMO level of the second dopant.
3. A charge-transfer salt according to claim 2 wherein the first dopant LUMO level is at least 0.1 eV further from vacuum than the LUMO level of the second dopant.
4. A charge-transfer salt according to any preceding claim wherein the first dopant is a neutral compound.
5. A charge-transfer salt according to any preceding claim wherein the second dopant is a neutral compound.
6. A charge-transfer salt according to any preceding claim wherein the first dopant is a fluorinated tetracyano-p-quinodimethane.
7. A charge-transfer salt according to any preceding claim wherein the first dopant is tetrafluorotetracyano-p-quinodimethane.
8. A charge-transfer salt according to claim 6 or 7 wherein the second dopant is dipyrzino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile.
9. A charge-transfer salt according to any of claims 1-5 wherein the first dopant is a partially fluorinated Buckminster fullerene.
10. A charge-transfer salt according to claim 9 wherein the first dopant is a partially fluorinated C₆₀ Buckminster fullerene.
11. A charge-transfer salt according to any preceding claim wherein the organic semiconducting material is a polymer.

12. A charge-transfer salt according to claim 11 wherein the polymer comprises repeat units of formula (I):



(I)

- wherein Ar^8 , Ar^9 and Ar^{10} in each occurrence are independently selected from substituted or unsubstituted aryl or heteroaryl; g is 0, 1 or 2; R^{13} independently in each occurrence is H or a substituent; c , d and e are each independently 1, 2 or 3; and any of Ar^8 , Ar^9 , Ar^{10} and R^{11} linked directly to the same N atom may be linked by a direct bond or a divalent linking group.
13. A charge-transfer salt according to any preceding claim wherein the dopants are present in the range of about 0.1 mol % to 10 mol %
14. A charge-transfer salt according to any preceding claim wherein the organic semiconducting material comprises crosslinkable groups.
15. A formulation comprising a charge-transfer salt according to any of claims 1-14 dissolved in a solvent or solvent mixture.
16. An organic electronic device comprising a conductive layer comprising a charge-transfer salt according to any preceding claim.
17. An organic electronic device according to claim 16 wherein the device is an organic light-emitting device comprising an anode; a hole injection layer in contact with the anode; a light-emitting layer over the hole injection layer; and a cathode over the light-emitting layer, wherein the hole injection layer comprises a charge-transfer salt according to any of claims 1-14.

18. An organic electronic device according to claim 17 wherein the organic light-emitting device comprises a hole-transporting layer between the hole-injection layer and the light-emitting layer.
19. A method of forming an organic electronic device according to any of claims 16-18 comprising the step of forming the conductive layer by depositing a formulation according to claim 15 and evaporating the solvent or solvent mixture.
20. A method according to any of claims 17-19 wherein the charge-transfer salt is crosslinked prior to formation of the light-emitting layer.

FIGURE 1

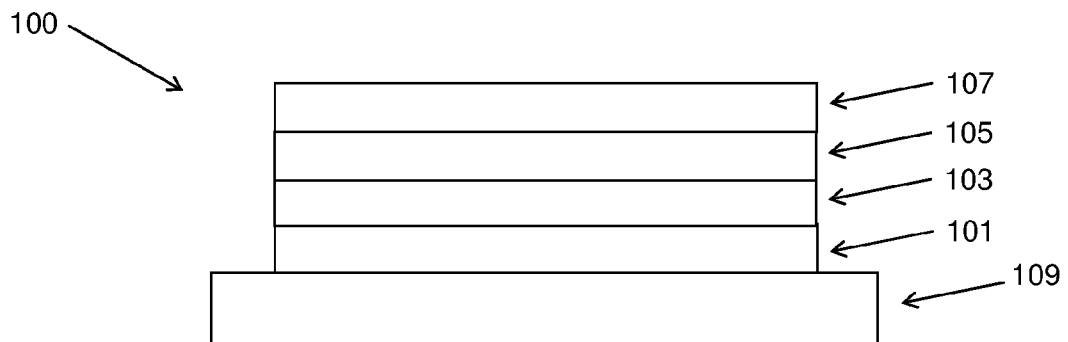


FIGURE 2

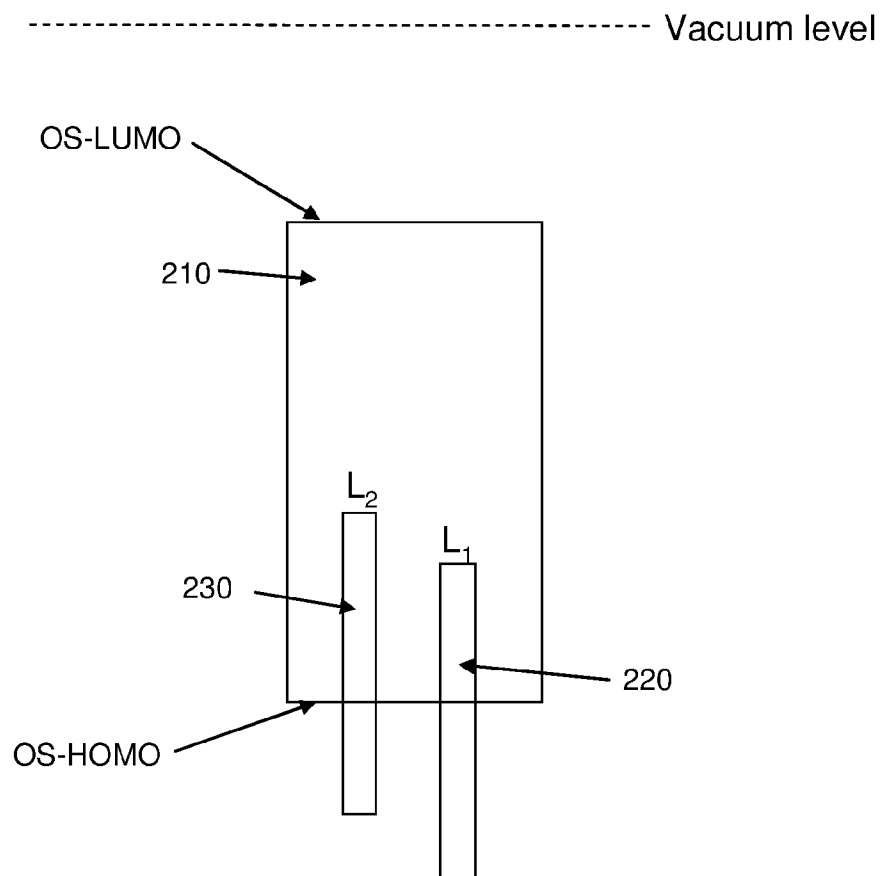


FIGURE 3A

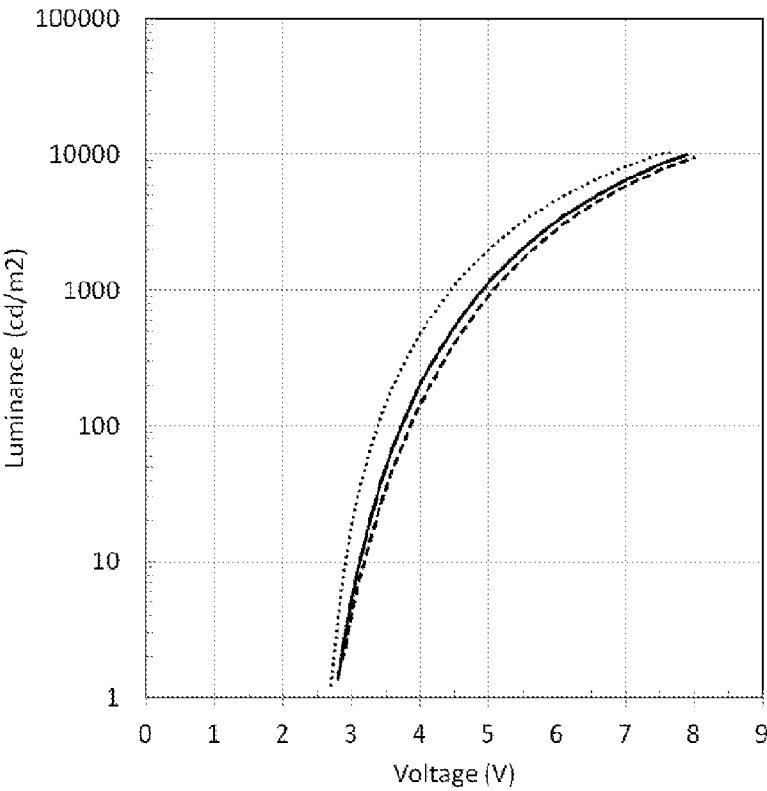


FIGURE 3B

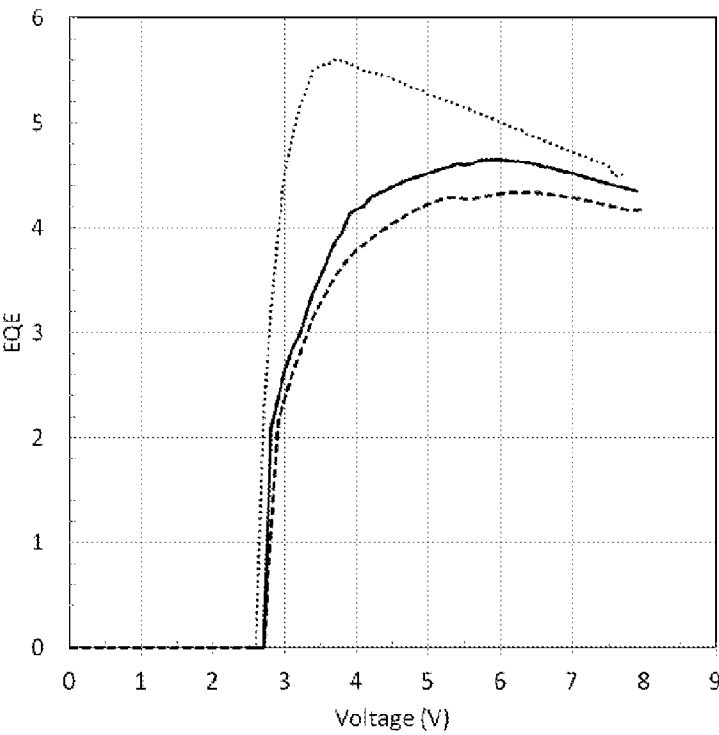


FIGURE 3C

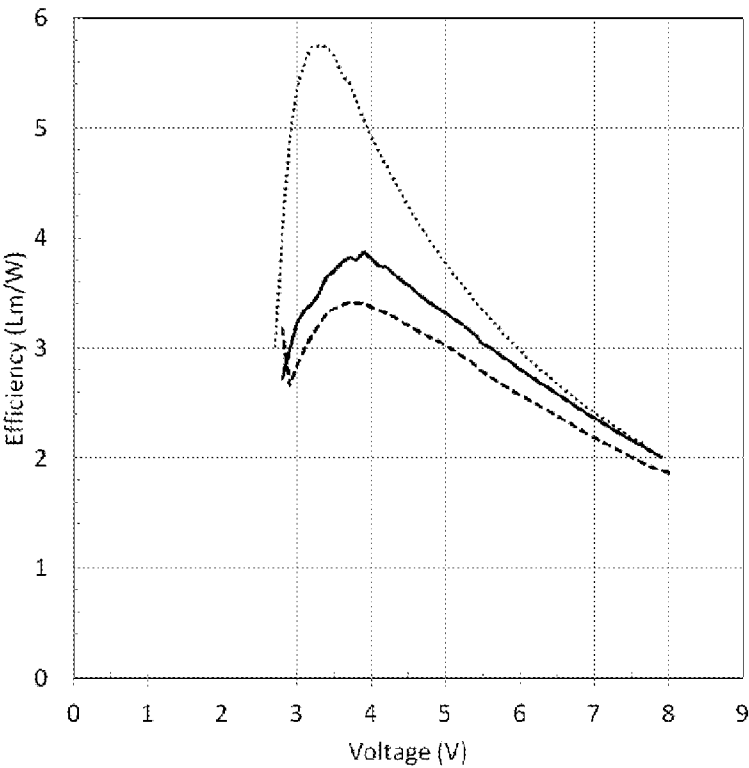


FIGURE 3D

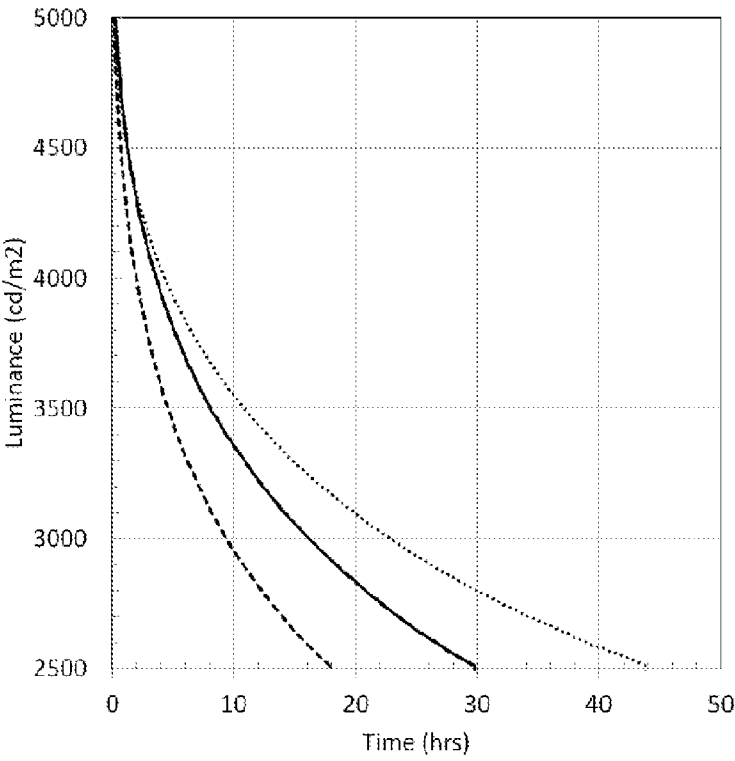


FIGURE 3E

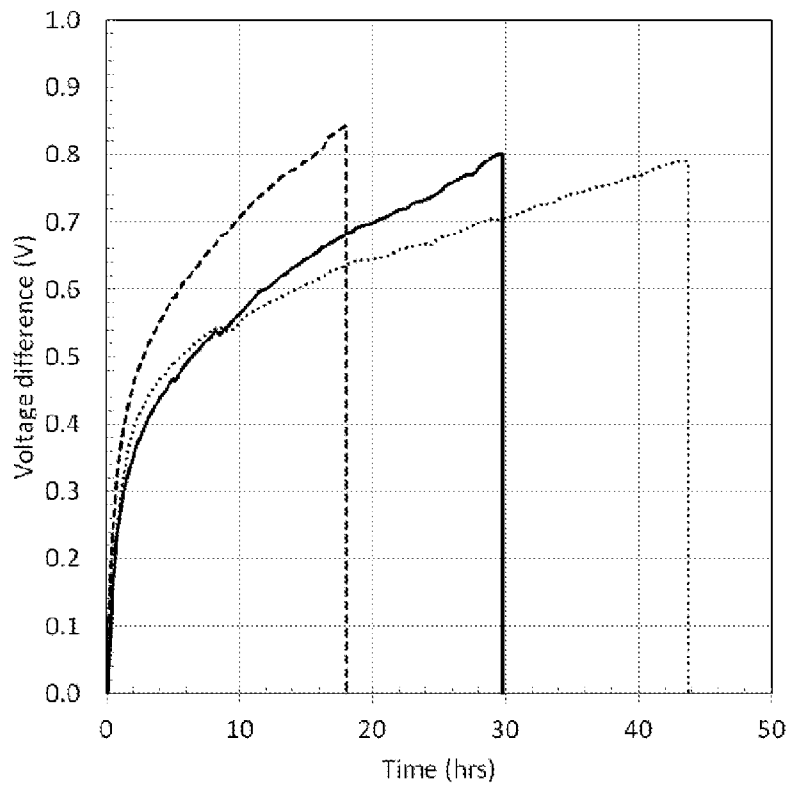


FIGURE 4A

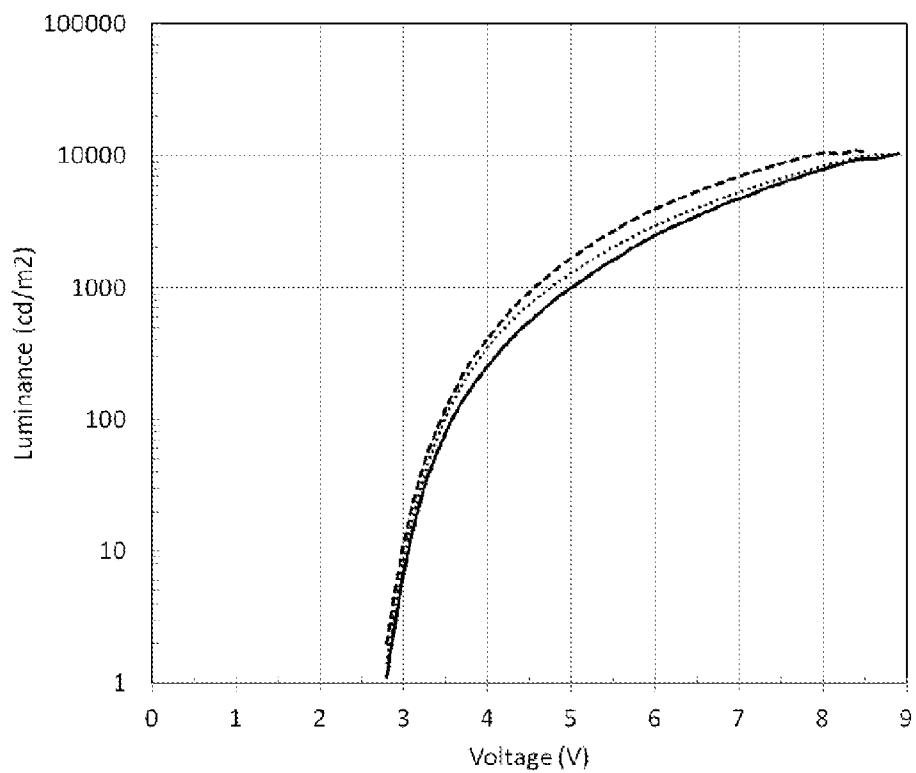


FIGURE 4B

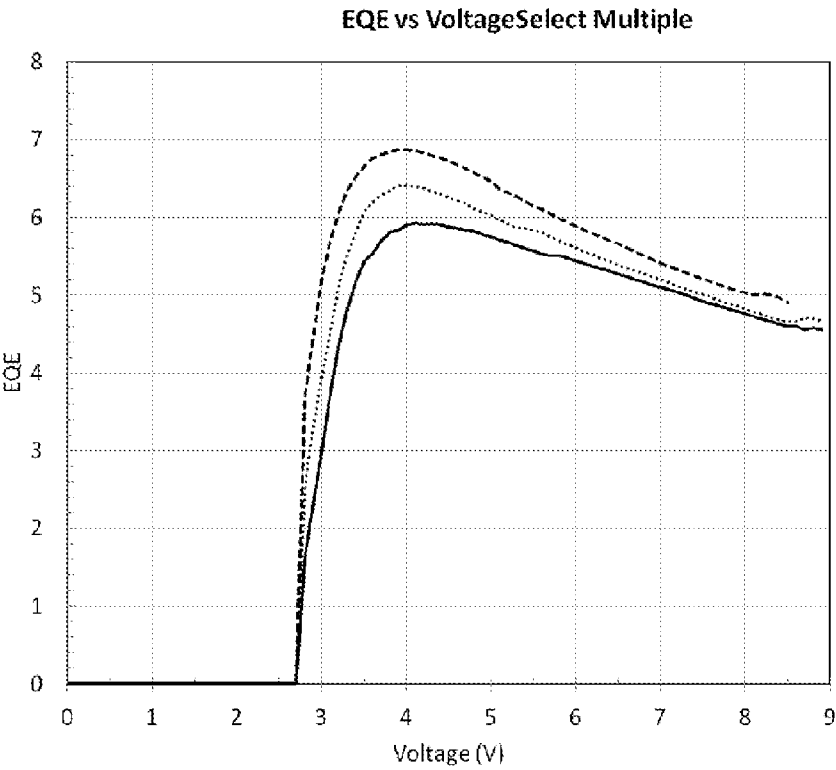
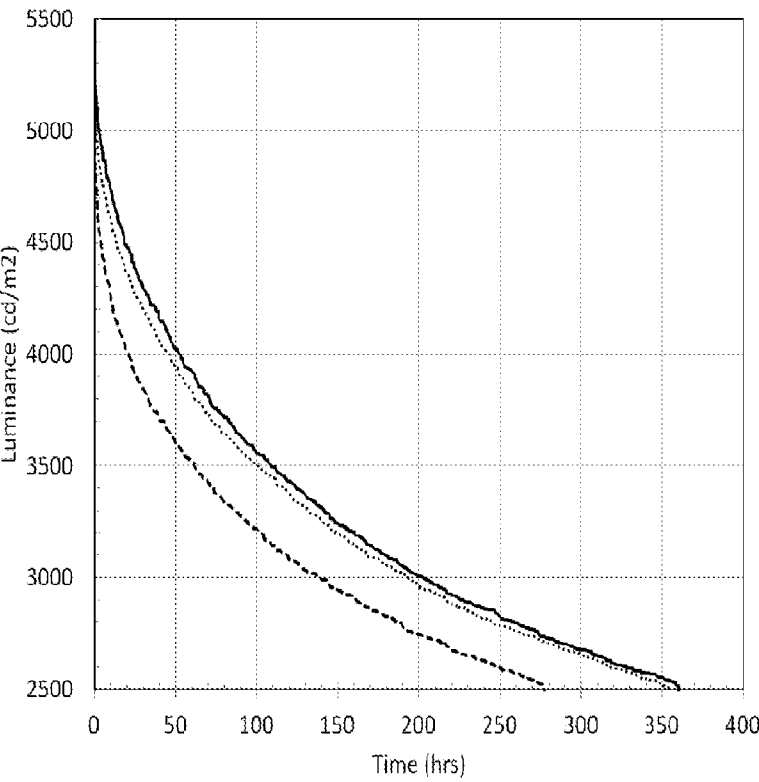


FIGURE 4C



INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2015/051879

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01L51/56 H01L51/50
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)

EP0-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	WO 2013/098648 A1 (IMP INNOVATIONS LTD [GB]) 4 July 2013 (2013-07-04) page 8 - page 13 -----	1-20
X	WO 2012/131314 A1 (CAMBRIDGE DISPLAY TECH [GB]; SUMITOMO CHEMICAL CO [JP]; KUGLER THOMAS) 4 October 2012 (2012-10-04) cited in the application the whole document -----	1-20
X	US 2011/156019 A1 (TESSLER NIR [IL] ET AL) 30 June 2011 (2011-06-30) the whole document -----	1-20
X	DE 10 2011 084304 A1 (ARDENNE ANLAGENTECH GMBH [DE]) 11 April 2013 (2013-04-11) paragraphs [0006], [0012] - [0013]; figure 2 -----	1

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

☒ See patent family annex.

* Special categories of cited documents :

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

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"&" document member of the same patent family

Date of the actual completion of the international search

20 August 2015

Date of mailing of the international search report

26/08/2015

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Authorized officer

Wolfbauer, Georg

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2015/051879

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013098648 A1	04-07-2013	TW 201348241 A WO 2013098648 A1	01-12-2013 04-07-2013
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