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1110565.7 22 June 2011 (22.06.2011) GB(71) Applicants (for all designated States except US): **CAMBRIDGE DISPLAY TECHNOLOGY LIMITED** [GB/GB]; Building 2020 Cambourne Business Park, Cambridgeshire CB23 6DW (GB). **SUMITOMO CHEMICAL COMPANY LIMITED** [JP/JP]; Floor 18, Sumitomo Twin Buildings, 27-1 Shinkawa 2-chome, Chuo-Ku, Tokyo 104-8260 (JP).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **ZUBERI, Tania** [GB/GB]; Cambridge Display Technology Ltd, Building 2020, Cambourne Business Park, Cambridgeshire CB23 6DW (GB). **DOUST, Alexander** [GB/GB]; Cambridge

Display Technology Ltd, Building 2020, Cambourne Business Park, Cambridgeshire CB23 6DW (GB).

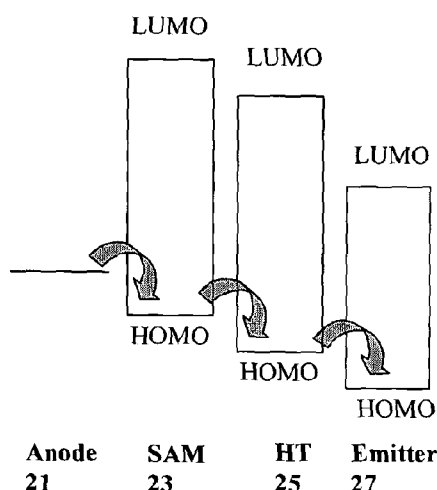
(74) Agent: **SHARP, Alan**; IP Department, Cambridge Display Technology Ltd, Building 2020, Cambourne Business Park, Cambridgeshire CB23 6DW (GB).

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(54) Title: ORGANIC OPTOELECTRONIC MATERIAL, DEVICE AND METHOD

FIGURE 5

(57) Abstract: A method of forming an organic electronic device comprises: providing an anode having a surface; modifying the surface by forming a self-assembled monolayer on the surface; forming a layer of hole transporting material over the self-assembled monolayer; forming a layer of an organic semiconductor material over the charge transporting layer; and forming a second electrode over the organic semiconducting layer, wherein the modified first electrode surface has a work function that is closer to the HOMO level of the charge-transporting layer than the work function of the first electrode surface prior to modification, and wherein the self-assembled monolayer is formed by depositing a self-assembling material comprising a binding group for binding to the first electrode surface and a hole-transporting group having a HOMO energy level.



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ORGANIC OPTOELECTRONIC MATERIAL, DEVICE AND METHOD

Summary of the Invention

This invention relates to organic optoelectronic devices, materials and methods of making the same.

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.

With reference to Figure 1, an organic optoelectronic device may comprise a substrate 1 carrying an anode 2, a cathode 4 and an organic semiconducting layer 3 between the anode and cathode comprising a light-emitting material.

The active organic layer 3 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 2 (for example indium tin oxide, or ITO) and electrons are injected through the cathode 4 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 3 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, such as a hole-transporting layer between the anode and the light-emitting layer and / or an electron-transporting layer between the cathode and the light-emitting layer.

One known class of hole transporting materials is electron-rich triphenylamines. WO 01/66618 discloses an organic light-emitting device in which triphenylamine repeat units of a hole transporting polymer are substituted with electron-withdrawing trifluoromethyl groups to adjust the HOMO level of those repeat units.

Additionally, or alternatively, a hole-injection layer may be provided between the anode and the light-emitting layer. Known hole injection layers include conductive organic materials such as poly(ethylene dioxythiophene) (PEDT), in particular PEDT doped with a charge-balancing polyacid such as polystyrene sulfonate (PSS) as disclosed in EP 0901176, and conductive inorganic materials such as VOx, MoOx and RuOx as disclosed in *Journal of Physics D: Applied Physics* (1996), 29(11), 2750-2753.

Self-assembling monolayers that modify the workfunction of an anode are disclosed in E. L. Hanson, J. Guo, N. Koch, J. Schwartz, S. L. Bernasek, *J. Am. Chem. Soc.* 2005, 127, 10058; J. Morgado, A. Charas, N. Barbagallo, L. Alcacer, M. Matos, F. Cacialli, *Macromol. Symp.* 2004, 212, 381; C. Ganzorig, K. J. Kwak, K. Yagi, M. Fujihira, *Appl. Phys. Lett.* 2001, 79, 272; H. Ishii, K. Sugiyama, E. Ito, K. Seki, *Adv. Mater.* 1999, 11, 605; F. Nuesch, E. W. Forsythe, Q. T. Le, Y. Gao, L. J. Rothberg, *J. Appl. Phys.* 2000, 87, 7973; Jones et al *Adv. Funct. Mat.* 2004, 14, 1205; and Marder et al *App. Phys. Lett.* 2008, 93, 163308

Hole-transporting materials comprising organosiloxanes as ITO modification/adhesion layers are disclosed in *J. Am. Chem. Soc.* 2005 (127) 3172, 10227; *J. Am. Chem. Soc.* 2005 (127) 10227; and *J. Am. Chem. Soc.* 2003 (125) 3172, p14704.

Gratzel et al Eur Phys J B 1, 1999 505 discloses self-assembled monolayers (SAMs) comprising carbazole functionalized with various carboxylic acid alkyl-spacer groups.

Bardecker et al, Adv. Funct. Mater. 2008, 1, 3964-3971 discloses an OLED having a SAM on the surface of an ITO anode and a hole-transporting layer over the SAM comprising crosslinked 4,4',4''-tris(N-carbazolyl)triphenylamine bis(vinylbenzyl-ether), or "BVB-TCTA". Devices were formed using SAMs having phosphonic acid groups to bind to ITO. The modified ITO surface is has a shallower work function than untreated ITO (Figure 8).

Polymers comprising pendant hole-transporting groups are disclosed in J. Mater. Chem., 2001, 11, 3023-3030 which discloses polyphenylenevinylene derivatives with carbazole pendant groups are described. Single layer devices are described.

Adv. Mater. 2009, 21, 1972-1975 discloses polystyrene with pendant hole transporting groups cross linked on top of an anode / hole injection bilayer of ITO / PEDT:PSS.

Photo-cross linkable hole transporting polymers are discussed in Macromolecules 2005, 38, 1640-1647. Macromolecules 2009, 42, 4053-4062 discloses polyfluorene with pendant charge transporting groups.

Adv. Mater. 2009, 21, 4496-4501 discloses modification of the surface properties of indium tin oxide with benzylphosphonic acids.

J. Appl. Phys. 105, 084507, 2009 discloses electrophosphorescent OLEDs in which the surface of ITO electrodes has been modified using phosphonic acids.

J. Appl. Phys. 105, 074511, 2009 discloses modification of ITO electrodes using phosphonic acids in organic single-layer diodes.

Summary of the Invention

In a first aspect the invention provides a method of forming an organic electronic device as specified in claim 1. The method comprises the steps of:

providing a first electrode having a surface;

modifying the surface of the first electrode by forming a self-assembled monolayer on the first electrode surface;

forming a charge-transporting layer comprising a charge transporting material over the self-assembled monolayer, the charge-transporting layer having an energy level;

forming an organic semiconductor layer comprising an organic semiconductor material over the charge transporting layer, the organic semiconductor layer having an energy level; and

forming a second electrode over the organic semiconducting layer,

wherein the modified first electrode surface has a work function that is closer to the energy level of the charge-transporting layer than that of the first electrode surface prior to modification, and wherein the self-assembled monolayer is formed by depositing a self-assembling material comprising a binding group for binding to the first electrode surface and a charge-transporting group.

Optionally, the energy level of the charge transporting group of the self-assembling material falls between the work function of the modified first electrode surface and the energy level of the charge-transporting layer.

Optionally, the self-assembling layer comprises at least two different charge transporting groups providing at least two different energy levels.

Optionally, the energy level of the charge transporting layer falls between the energy level of the charge transporting group of the self-assembling material and the organic semiconductor layer energy level.

Optionally, the self-assembled material is formed from a compound of formula (I):



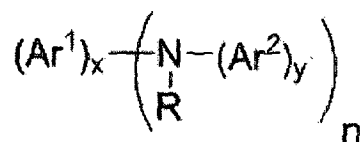
(I)

wherein Bind represents a binding group; Sp^1 in each occurrence independently represents a spacer group; CT in each occurrence independently represents a charge-transporting group; EWG is an electron-withdrawing group; m in each occurrence is independently 0 or 1; p is 0 or 1; and q is 0 or an integer.

Optionally, Bind comprises a phosphonic acid group.

Optionally, Sp^1 is an optionally substituted alkyl group.

Optionally, CT comprises a group of formula (V):



(V)

wherein Ar^1 and Ar^2 in each occurrence are independently selected from optionally substituted aryl or heteroaryl groups; R in each occurrence is independently H, a substituent or $-(Sp)_m$ -Bind, preferably a substituent or $-(Sp)_m$ -Bind; n is greater than or equal to 1, preferably 1 or 2; x and y are each independently 1, 2 or 3; and wherein any of the aryl or heteroaryl groups of the group of formula (V) may be linked by a direct bond or a divalent linking group.

Optionally, CT comprises an optionally substituted carbazole or an optionally substituted phenoxazine.

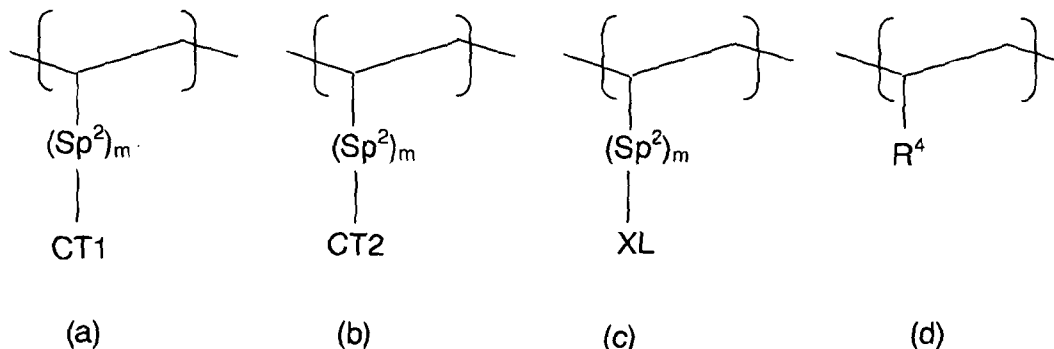
Optionally, CT comprises an optionally substituted fused thiophene, preferably optionally substituted thieno[3,2-b]thiophene or thienobenzothiophene.

Optionally, the charge transporting material is a polymer.

Optionally, the polymer comprises a polymer backbone with charge transporting groups pendant from the backbone.

Optionally, the polymer comprises at least two different charge transporting groups pendant from the backbone.

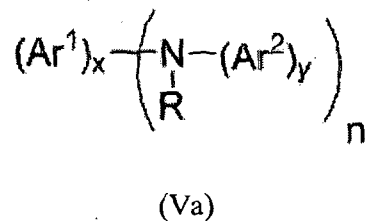
Optionally, a backbone of the polymer comprises repeat units of formula a and optionally comprises repeat units of formulae b, c and / or d:



wherein CT1 is a first charge transporting group; CT2 is a second charge transporting group; XL is a crosslinkable group; each Sp^2 is independently a spacer group; R^4 in each occurrence is independently H or a substituent; and each m is independently 0 or 1.

Optionally, Sp^2 in each occurrence is selected from the group consisting of optionally substituted alkyl, optionally substituted arylalkyl and optionally substituted heteroarylalkyl.

Optionally, CT1 and / or, where present, CT2 comprises a group of formula (Va)



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

Optionally, CT1 and / or, where present, CT2 comprises an optionally substituted fused thiophene, preferably optionally substituted thieno[3,2-b]thiophene or thienobenzothiophene.

Optionally, XL comprises a polymerisable double bond.

Optionally, the device is an organic light-emitting device; the organic semiconductor is a light-emitting material; and the organic semiconductor energy level is a HOMO level or a LUMO level.

Optionally, the organic semiconductor energy level is a HOMO level that is separated from the workfunction of the anode by at least 0.2 eV, optionally at least 0.35 eV, optionally at least 0.5 eV.

Optionally, the first electrode is an anode, preferably indium tin oxide, the second electrode is a cathode; the charge-transporting material is a hole transporting material; the organic semiconductor energy level is a HOMO level; the energy level of the charge transporting layer is a HOMO level; the charge transporting group of the self-assembling monolayer is a hole-transporting group; the energy level of the charge transporting group of the self-assembling monolayer is a HOMO level; and the charge-transporting layer is a hole transporting layer.

In a second aspect the invention provides a method of forming an organic electronic device comprising the steps of:

forming a self-assembled monolayer on a first electrode by bringing at least one self-assembling material into contact with the first electrode;

forming a charge-transporting layer by depositing at least one charge transporting polymer onto the self-assembled monolayer

forming an organic semiconductor layer comprising an organic semiconductor over the self-assembled monolayer; and

forming a cathode over the organic semiconductor layer, wherein:

the first electrode has a work function value;

the organic semiconductor has an organic semiconductor energy level;

the charge-transporting polymer provides the charge transporting layer with at least one energy level falling between the work function value of the first electrode and the organic semiconductor energy level; and

the at least one self-assembling material provides the self-assembled monolayer with at least one energy level falling between the work function value of the first electrode and the organic semiconductor energy level.

Optionally according to the second aspect, the charge-transporting polymer is deposited onto the self-assembled monolayer from a solution in a solvent.

Optionally according to the second aspect, the charge-transporting polymer comprises a crosslinkable group and wherein the crosslinkable group is crosslinked following deposition of the charge transporting polymer.

Optionally according to the second aspect, the organic semiconductor layer is formed by depositing a formulation comprising a solvent and the organic semiconductor and evaporating the solvent.

In a third aspect the invention provides an organic light-emitting device comprising an anode; a self-assembled monolayer on the anode; a hole-transporting layer on the self-assembled monolayer; an organic light-emitting layer over the hole-transporting layer; and a cathode over the organic light-emitting layer; wherein the organic light-emitting layer comprises a material having a photoluminescent CIE(y) value of no greater than 0.1.

Optionally according to the third aspect, the material of the organic light-emitting layer emits light when the device is in operation.

Optionally according to the third aspect, the material of the organic light-emitting layer is a host material for a light-emitting dopant that emits light when the device is in operation.

Optionally according to the third aspect, the anode carrying the self-assembled monolayer has a workfunction that is further from vacuum level than the anode without the self-assembled monolayer.

Optionally according to the third aspect, the SAM is formed from a self-assembly material comprising a phosphonic acid and wherein the anode is indium-tin oxide.

Optionally according to the third aspect, the SAM has at least one HOMO level; the charge transporting layer has at least one HOMO level; said HOMO levels both falling

between a workfunction of the anode and a HOMO level of the material of the light-emitting layer.

In a fourth aspect the invention provides an organic electronic device comprising a first electrode; a second electrode; an organic semiconducting layer comprising an organic semiconductor between the first and second electrodes; a self-assembled monolayer on the first electrode; and a charge-transporting layer between the self-assembled monolayer and the organic semiconducting layer, wherein:

the first electrode has a work function value;

the organic semiconductor has an organic semiconductor energy level;

the charge-transporting layer comprises at least one charge-transporting material providing the charge transporting layer with at least one energy level falling between the work function value of the first electrode and the organic semiconductor energy level;

the self-assembled monolayer comprises at least one self-assembled material providing the self-assembled monolayer with at least one energy level falling between the work function value of the first electrode and the organic semiconductor energy level; and

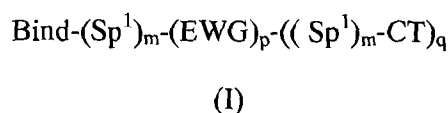
wherein at least one of the at least one charge-transporting material and the at least one self-assembled material provide their respective layers with at least two energy levels falling between the work function value of the first electrode and the organic semiconductor energy level.

In a fifth aspect the invention provides a self-assembling material comprising a binding group, a first charge-transporting group having a first energy level and at least one further charge transporting group having at least one further energy level wherein the first and at least one further energy levels are different.

Optionally according to the fifth aspect the first charge-transporting group and the at least one further charge-transporting group are spaced apart by a spacer group that breaks any conjugation path between the first charge-transporting group and the at least one further charge-transporting group

Optionally according to the fifth aspect the first and at least one further energy levels are HOMO levels.

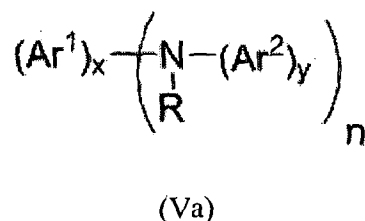
Optionally according to the fifth aspect the self-assembling material has optionally substituted formula (I):



wherein Bind represents a binding group; Sp^1 in each occurrence independently represents the spacer group; CT in a first occurrence represents the first charge-transporting group; CT in each further occurrence represents the at least one further charge transporting group; EWG is an electron-withdrawing group; m in each occurrence is independently 0 or 1; p is 0 or 1; and q is at least 2, optionally 2 or 3.

Bind, Sp^1 and EWG of the fifth aspect may be as described with reference to the first aspect of the invention.

Optionally according to the fifth aspect one or more of the first charge transporting group and the at least one further charge-transporting group comprises a group of formula (Va)



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

Optionally according to the fifth aspect one or more of the first charge transporting group and the at least one further charge-transporting group is selected from optionally substituted carbazole and optionally substituted phenoxazine.

Optionally according to the fifth aspect one or more of the first charge transporting group and the at least one further charge-transporting group is an optionally substituted fused

thiophene, preferably optionally substituted thieno[3,2-b]thiophene or thienobenzothiophene.

Optionally according to the fifth aspect the binding group comprises a phosphonic acid group.

Optionally according to the fifth aspect the spacer group is an optionally substituted alkyl group.

In a sixth aspect the invention provides an organic electronic device comprising an electrode layer carrying a self-assembled monolayer comprising the self assembling material according to the fifth aspect, the self-assembling material being bound to the electrode layer through the binding group

Optionally according to the sixth aspect the device is an organic light-emitting device and the electrode is an anode, the device further comprising a cathode and a light-emitting layer between the self-assembled monolayer and the cathode.

Optionally according to the sixth aspect a hole-transporting layer is provided between the self-assembled monolayer and the light-emitting layer.

The hole transporting layer of the sixth aspect may be a polymer as described in the first aspect of the invention. The hole-transporting layer may be formed as described with reference to the second aspect of the invention.

Optionally according to the sixth aspect the anode layer comprises indium-tin oxide.

In a seventh aspect the invention provides a method of forming an organic electronic device according to the sixth aspect, the method comprising the steps of:

forming the self-assembled monolayer on the anode layer by bringing the self-assembling material into contact with the anode layer;

forming the organic light-emitting layer by depositing an organic light-emitting material over the self-assembled monolayer; and

forming a cathode over the organic light-emitting layer.

Optionally, the seventh aspect comprises the further step of forming a hole-transporting layer between the self-assembled monolayer and the light-emitting layer by depositing a hole-transporting material over the self-assembled monolayer.

Any of the optional features described with reference to any one of the aforementioned aspects may be applied to any one of the other aforementioned aspects.

Description of the Figures

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

Figure 1 is a schematic illustration of a prior art organic light-emitting device;

Figure 2 is a schematic illustration of an organic light-emitting device according to an example of the invention;

Figure 3 is an energy diagram illustrating the effect of SAM formation on anode workfunction;

Figure 4 is an energy diagram of a first exemplary organic light-emitting device;

Figure 5 is an energy diagram of a second exemplary organic light-emitting device;

Figure 6 is an energy diagram of a third exemplary organic light-emitting device;

Figure 7 is an energy diagram of a fourth exemplary organic light-emitting device;

Figure 8 is an energy diagram of a fifth exemplary organic light-emitting device;

Figure 9 is a graph of hole current density of an exemplary organic light-emitting device and a comparative device;

Figure 10a is a graph of current density vs voltage for an exemplary organic light-emitting device; and

Figure 10b is a graph of the electroluminescence spectrum of an exemplary organic light-emitting device.

Detailed Description of the Invention

With reference to Figure 2, an exemplary OLED comprises an anode 21 supported on a substrate, a self-assembled monolayer 23, a hole-transporting layer 25, an organic light-emitting layer 27 and a cathode 29.

Binding of a self-assembling material to the anode to form SAM 23 may have the effect of modifying the anode workfunction, and accordingly the modified workfunction of an electrode as referred to herein means the workfunction at the surface of the electrode following formation of the SAM. For example, self-assembling materials comprising phosphonic acid binding groups may deepen the workfunction of ITO, which is beneficial if the light-emitting layer comprises an emitter or host material with a deep HOMO level because the gap between the anode workfunction and the HOMO level is narrowed by the anode modification treatment.

In the embodiment of Figure 3, application of a suitable SAM to an anode material (such as a suitable phosphonic acid to ITO) causes the workfunction of the anode to move further from vacuum level. With reference to Figure 4, this anode may be used for enhanced hole injection into a hole transporting layer HT (for the avoidance of any doubt, energy levels illustrated herein are not drawn to any scale).

In other arrangements, illustrated in Figures 5-8, the SAM 23 is formed from a material or materials that contain one or more charge transporting groups, thus providing the SAM with one or more HOMO levels. In the embodiments of Figures 5-8, the anode may or may not have a deepened workfunction following SAM treatment, although the workfunction preferably is deepened by the SAM treatment, or at least not moved closer to the vacuum level.

With reference to Figure 5, in one arrangement the SAM is formed from a self-assembling material comprising a hole-transporting group having a HOMO level falling between that of the anode and that of the hole transporting layer HT, and hole transporting layer HT comprises a material providing a HOMO level between the HOMO level of SAM and the HOMO level of the light-emitting material. In operation, stepped hole injection from the anode to the emitter is provided.

With reference to Figure 6, in another arrangement the self-assembled monolayer 23 comprises self-assembled monolayer SAM1 which comprises a hole-transporting material having a HOMO level falling between that of the anode and those of the hole transporting layer 25, and hole transporting layer 25 comprises a material or materials providing two HOMO levels HT1 and HT2 between the HOMO level of SAM1 and the light-emitting material.

With reference to Figure 7, in another arrangement self-assembled monolayer 23 is formed from two different self-assembling materials, SAM1 and SAM2, with charge-transporting groups having different HOMO levels which, in combination with the HOMO level HT1 of the hole transporting layer 25 provides stepped hole injection from the anode to the emitter. Alternatively, a single self-assembling material comprising two different charge transporting groups may be used.

With reference to Figure 8, the self-assembled monolayer 23 has two different HOMO levels SAM1 and SAM2, and the hole transporting layer 25 provides two HOMO levels HT1 and HT2.

In the examples of Figures 6-8, the self-assembled monolayer 23 and / or the hole transporting layer 25 provide two HOMO levels to provide stepped hole transport. However, it will be appreciated that either or both of these layer may provide more than two HOMO levels to provide further incremental steps in stepped hole transport.

Self-assembled monolayer

The self-assembled monolayer may be formed from any material capable of binding to the anode.

The binding group and / or substituents of the self-assembling material may be selected so as to deepen the work function of the anode surface. For example, the binding group may be substituted with one or more electron-withdrawing groups, and the electron withdrawing properties of those substituents may be selected so as to control the effect on workfunction of the anode surface.

Self-assembling materials that can deepen the workfunction of an anode include optionally fluorinated phenyl phosphonic acids, for example 3,4,5-

trifluorophenylphosphonic acid, 2,3,4,5,6-pentaphenylphosphonic acid and phenylphosphonic acid substituted with one or more trifluoromethyl groups. Other materials that may be used to deepen the workfunction of ITO include phosphonic acids with cyano-, nitro- or chloro- substituents in the para-position to the phosphonic acid group. Materials comprising an optionally substituted benzoyl chloride binding group may also be used to deepen the ITO workfunction, for example 4-chlorobenzoyl chloride.

The SAM may provide at least one HOMO level lying between the work function of the anode and a HOMO level of the hole transporting layer. In this case, formation of a SAM may not only deepen the workfunction at the surface of the modified anode, thereby moving it closer to the HOMO level of the hole transporting layer, but also provide an intermediate step between the modified anode and the hole transporting layer.

The self-assembling material may be an optionally substituted compound of formula (I):



(I)

wherein Bind represents a binding group; Sp^1 in each occurrence independently represents a spacer group; CT in each occurrence independently represents a charge-transporting group; EWG is an electron-withdrawing group; m in each occurrence is independently 0 or 1; p is 0 or 1; and q is 0 or an integer.

Suitable EWG groups include, for example, phenyl substituted with electron-withdrawing groups such as one or more fluorine or trifluoromethyl groups.

In one case, $q = 0$ and $m = 0$ or 1. In this case, the SAM formed from the self-assembling material does not comprise a CT group providing a HOMO level lying between the work function of the anode and a HOMO level of the hole transporting layer.

In another arrangement, $p = 0$, q is at least 1 and m in each occurrence is 0 or 1. In this case, at least one CT group providing at least one HOMO level lying between the work function of the anode and a HOMO level of the hole transporting layer is provided by the SAM formed from the self-assembling material.

In one case, p is 0 and the compound of formula (I) has formula $\text{Bind}-(\text{Sp}^1)_m-\text{CT}$, i.e. it contains only one charge transporting group. However, in the case where p is an integer

the compound contains at least two charge transporting groups. These CT groups may be the same or different, however in one arrangement they are different and moreover these different CT groups may be arranged to provide two or more steps between the workfunction of the modified anode and the HOMO of the charge transporting layer. In particular, the CT groups may be arranged such that the CT group closest to Bind is the CT group having a HOMO level that is closest to the workfunction of the modified anode, and the CT group furthest from Bind is the CT group with a HOMO level that is furthest from the workfunction of the modified anode (and optionally closest to the HOMO level of the charge transporting layer). Any further CT groups between these two CT groups may likewise be arranged to provide a "ladder" of HOMO levels. In yet another case, p is 1, q is at least 1 and m in each occurrence is 0 or 1.

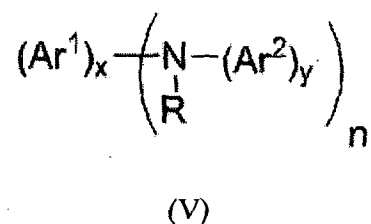
In this way, the self-assembling material may be designed so as to (a) control the effect that SAM formation has on workfunction at the anode surface by choice of EWG (or, indeed, exclusion of EWG altogether) and / or (b) provide at least one HOMO level lying between the work function of the anode and a HOMO level of the hole transporting layer.

Bind may be any group that binds to the material that the anode is formed from. For example, if the anode is ITO then Bind may comprise a phosphonic acid that binds to ITO as described in, for example, Bardecker et al, Adv. Funct. Mater. 2008, 1, 3964-3971. Siloxanes, benzoic acids, benzoyl chlorides and sulfonyl chlorides are also suitable for use as binding groups, in particular in combination with ITO.

The spacer group may be any group spacing the CT and Bind groups or, where present, two CT groups. The optional spacer group Sp may provide flexibility to the self-assembling material, in particular between Bind and the first CT group, and may be an alkyl chain, for example a C₁₋₂₀ alkyl chain which may optionally be substituted; a cycloalkyl group or an alkoxy group. Optionally, the spacer group Sp comprises at least 3 carbon atoms. In the case where p is an integer, spacer groups may be any group providing a break in conjugation between two CT groups.

CT may comprise any charge transporting group providing a HOMO level between the workfunction of the anode and a HOMO level of the hole transporting layer. Exemplary

charge transporting groups comprise (hetero)arylamine groups, for example groups of formula (V):



wherein Ar^1 and Ar^2 in each occurrence are independently selected from optionally substituted aryl or heteroaryl groups, n is greater than or equal to 1, preferably 1 or 2, R in each occurrence is independently H, a substituent or $-(\text{Sp})_m\text{-Bind}$, preferably a substituent or $-(\text{Sp})_m\text{-Bind}$, and x and y are each independently 1, 2 or 3.

Any of the aryl or heteroaryl groups in the repeat unit of Formula (V) 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.

Substituents R are preferably selected from alkyl, Ar^3 , or a branched or linear chain of Ar^3 groups, for example $-(\text{Ar}^3)_r$, 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 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;

wherein each R^4 is independently 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.

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 or optionally substituted aryl or heteroaryl. 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.

In another preferred arrangement, aryl or heteroaryl groups of formula (V) 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, x and y are each 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.

In yet 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, $r = 1$ and Ar^1 and Ar^2 are linked by an O or S atom, for example phenoxazine substituted by one or more alkyl groups.

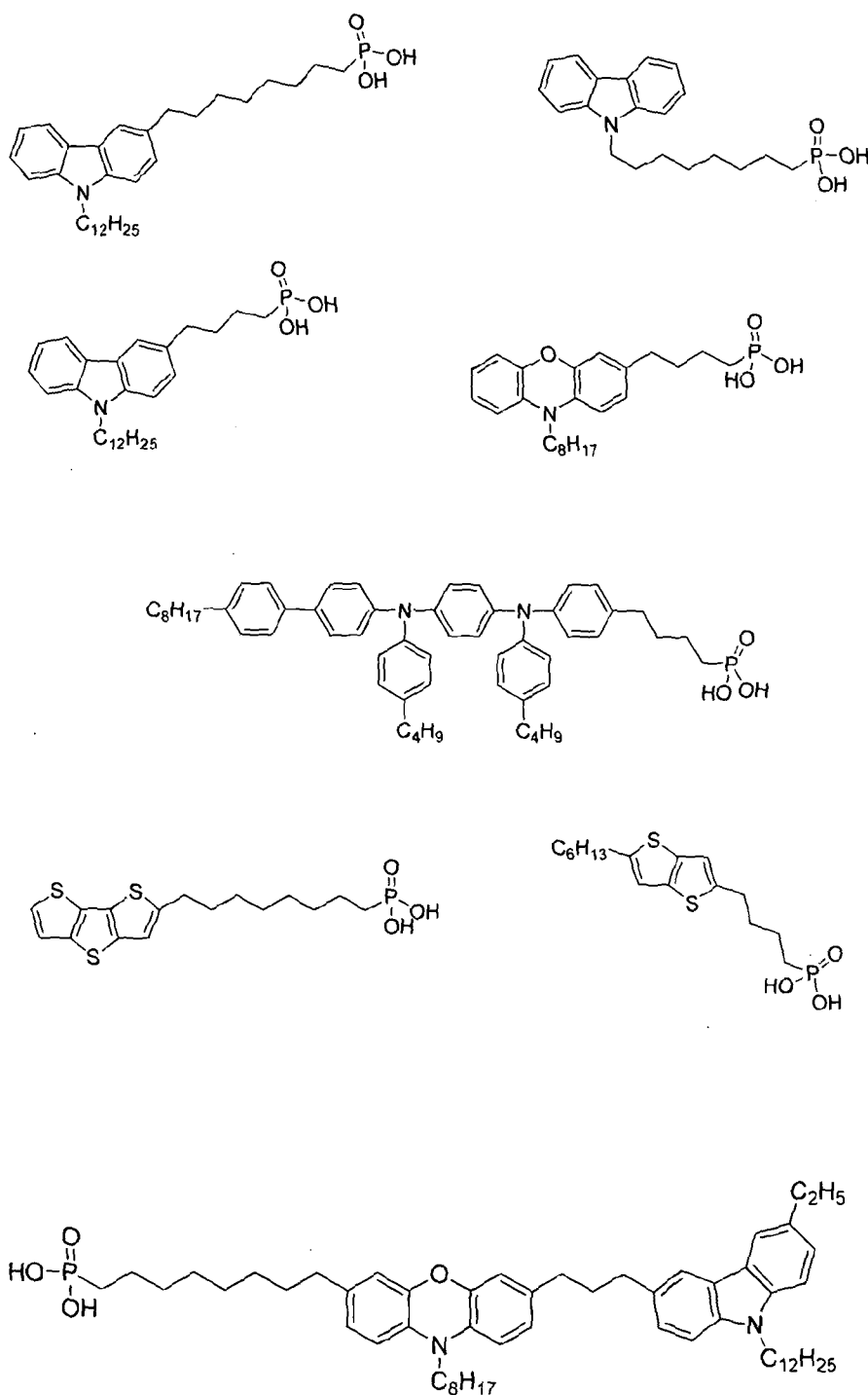
In yet another preferred arrangement, Ar^1 and Ar^2 are phenyl, each of which may be substituted with one or more C_{1-20} alkyl groups, R is C_{1-20} alkyl or phenyl substituted by one or more C_{1-20} alkyl groups; n, r, x and y are each 1, and Ar^1 and Ar^2 are linked by a direct bond, for example carbazole substituted by one or more alkyl groups.

Optionally, the CT group has low basicity in order to avoid formation of zwitterions with acidic binding groups.

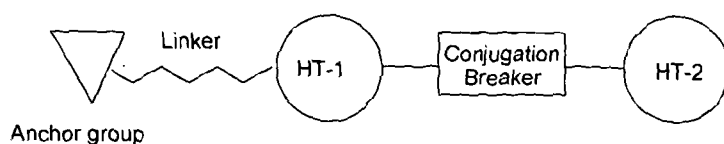
Other charge transporting groups include fused thiophenes, for example, thieno[2,3-b]thiophene and thienobenzothiophene, each of which may optionally be substituted with one or more substituents, for example alkyl.

Sp may be bound to any atom of the CT group, for example a N atom of the group of formula (V) or an aromatic C atom of the group of formula (V).

Exemplary self-assembling materials include the following:



In the last example illustrated above, p of formula (I) is 1. The HOMO level of the phenoxazine unit is shallower (i.e. closer to vacuum level) than that of the carbazole unit. The alkyl spacer unit breaks conjugation between the phenoxazine and carbazole units to give separate and definite HOMO domains. Other non-conjugating spacer groups include alkyl, for example. Binding the phosphonic acid of such a compound to an ITO anode provides a “ladder” of deepening HOMO levels in moving from the anode towards the hole transporting layer. Compounds comprising two hole-transporting groups may be illustrated generally as follows:



in which the Anchor group may be selected from any of the groups Bind described with respect to Formula (I); the Linker and Conjugation Breaker may each independently be selected from groups Sp1 of Formula (I); and HT-1 and HT-2 are selected from hole transporting groups CT of Formula (I).

Use of multiple CT groups in a single self-assembling material is described above. Additionally or alternatively, two or more self-assembly materials with different CT groups may be provided to provide a SAM with different HOMO levels.

Hole transporting material

The hole transporting material(s) of hole transporting layer 25 may be any material that provides a HOMO level between a HOMO level of the SAM and a HOMO level of the light-emitting layer.

The hole transporting material may be a polymer with hole-transporting groups pendant from the polymer backbone, in particular a polymer with a non-conjugated backbone such as a polyethene, polystyrene, polyacrylate or copolymer thereof.

The polymer may be formed by polymerization or copolymerization of monomers comprising polymerisable double bond groups substituted with charge transporting groups. The non-conjugated backbone of such a polymer allows the polymer to be used with wide bandgap light-emitting materials, for example deep blue fluorescent light

emitting materials. These materials typically have a deep HOMO level and accordingly stepped hole transport as described herein can provide for efficient hole injection and transport without use of narrow bandgap charge transporting materials, such as charge-transporting polymers with extensive conjugation in the polymer backbone, that may quench the luminescence of a wider bandgap material. The wide bandgap of such a polymer may also function as an exciton blocking layer (that is, the bandgap of the polymer is larger than the bandgap of the light-emitting material). Moreover, this wide bandgap may also provide electron blocking functionality if the LUMO level of the polymer is shallower (closer to vacuum) than that of the light-emitting material. This is illustrated in Figures 4-8, wherein the charge-transporting material or materials of the hole-transporting layer 25 have a wider HOMO-LUMO bandgap and a shallower LUMO level than the light-emitting material of light-emitting layer 27.

The hole-transporting layer may also function as an electron blocking layer and / or an exciton blocking layer. Alternatively, these further functionalities may be provided by separate blocking layers.

High hole mobility of these polymers may allow formation of thick hole transporting layers (e.g. up to 100 nm or up to 80 nm) with little or no increase in drive voltage.

The substituent charge transporting groups may be linked to the polymer backbone by a spacer group, such as an alkyl group or a (hetero)arylalkyl group such as a phenylalkyl group.

The charge-transporting group or groups of the polymer may be selected from any of the groups described above with respect to the self-assembling material. In the case of charge transporting groups of formula (V), R in one arrangement may be H or a substituent and the charge transporting group may be bound to the polymer through an atom of Ar¹, Ar² or R. In another arrangement, the polymer may be linked to a N atom of the group of formula (V), in which case the R group of that N atom represents the polymer, wherein the polymer backbone may be linked directly to the N atom or linked through a spacer group.

The polymer may be a homopolymer comprising a repeat unit carrying a hole-transporting group CT1 or it may be a copolymer comprising a repeat unit carrying a hole-transporting group CT1 and one or more co-repeat units such as:

- co-repeat units comprising at least one hole transporting group (CT2, CT3, CT4 ...) in order to provide the hole transporting layer with more than one HOMO level;
- co-repeat units substituted with a crosslinking group, including but not limited to a polymerisable double bond group, a benzocyclobutane group, or an oxetane group, each of which may optionally be substituted. If the light-emitting layer is formed by deposition of a formulation comprising the light-emitting material and a solvent then the hole-transporting material may be crosslinked in order to avoid dissolution of the hole transporting layer by the solvent(s) used to deposit the light-emitting layer; and
- spacing co-repeat units, such as styrene or acrylate repeat units.

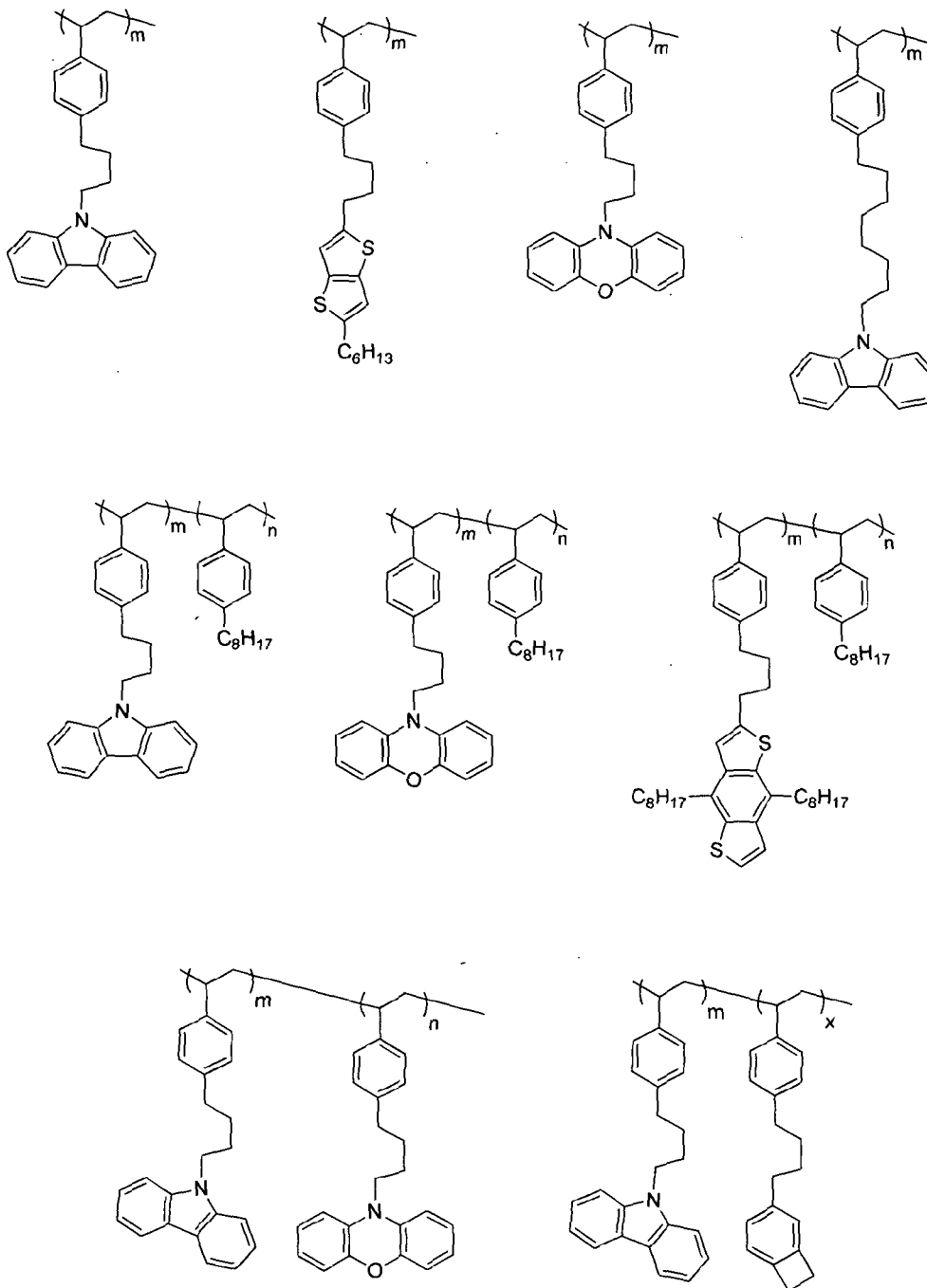
Copolymers may be random, regular or block copolymers, and may be formed by an addition polymerisation reaction of the relevant monomers using methods known to the skilled person. The nature and quantity of monomers may be selected so as to tune the properties of the resultant polymer, for example the charge transporting or crosslinking properties.

The polymers are preferably soluble in order to allow their deposition from a solution in a solvent. The polymers are preferably soluble in common organic solvents such as alkylated benzenes (such as xylene and toluene) and chlorinated solvents such as chloroform.

Following deposition from solution, the sidechains of the polymer may undergo pi-pi stacking, which may serve to increase the hole mobility of the hole transporting layer.

As an alternative to providing a crosslinking repeat unit, the hole transporting material may be deposited with a crosslinking additive for crosslinking following deposition.

Exemplary polymers include the following:



wherein m , n and x represent a molar percentage of a repeat unit in the polymer. In the case of a homopolymer, $m = 100$. In the case of a copolymer, $m + n$ or $m + x$ may equal 100. If further repeat units are present then $m + n$ or $m + x$ may be less than 100.

These polymers include examples of polymers comprising one charge transporting group and a spacing co-repeat unit, and polymers comprising two different charge transporting groups (e.g. carbazole and phenoxazine), and polymer comprising a charge-transporting group and a crosslinkable group.

Anode

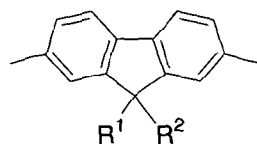
The anode may comprise any material with a workfunction suitable for injection of holes into the OLED. Exemplary materials for use as a transparent anode in the case where light is emitted through the anode include indium tin oxide (ITO) and indium zinc oxide (IZO). In the case where light is not emitted through the anode, for example if the cathode is transparent, then opaque conducting materials such as opaque metals may be used as the anode material, and the binding group of the SAM may be selected accordingly.

Light emitting material

Suitable light-emitting materials for use in layer 3 include small molecule, polymeric and dendrimeric materials, and compositions thereof. Suitable light-emitting polymers for use in layer 3 include poly(arylene vinylenes) such as poly(p-phenylene vinylenes) and polyarylenes such as: polyfluorenes; polyindenofluorenes, particularly 2,7-linked polyindenofluorenes; and polyphenylenes, poly-1,4-phenylene.

The repeat units of each of these polymers are optionally substituted. Examples of substituents include solubilising groups such as C₁₋₂₀ alkyl or alkoxy; electron withdrawing groups such as fluorine, nitro or cyano; and substituents for increasing the glass transition temperature (T_g) of the polymer.

Examples of such polymers as disclosed in, for example, Adv. Mater. 2000 12(23) 1737-1750 and references therein. Particularly preferred polyfluorenes comprise repeat units of formula (V):



(IV)

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; optionally substituted $-(Ar^3)_r$, wherein Ar^3 and r are as described above; and optionally substituted 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 wherein one or more non-adjacent C atoms may be replaced with O, S, substituted N, C=O and -COO-, optionally substituted aryl, optionally substituted heteroaryl, fluorine, cyano and nitro.

Where present, substituted N in repeat units of formula (IV) 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 optionally substituted with one or more C_{1-20} alkyl groups.

The light-emitting layer may comprise a host / dopant arrangement in which a host material (such as one of the light-emitting materials described above) is used in combination with a light-emitting dopant. Suitable light-emitting dopants include fluorescent and / or phosphorescent (such as heavy metal complex, e.g. iridium complex) light-emitting dopants.

Light-emitting layer 3 may comprise one or more light-emitting materials that emit light of any wavelength. The combination of a SAM and wide-bandgap charge transporting layer providing stepped hole transport may be used for materials having a relatively deep

HOMO level (that is, relatively far from vacuum level), in particular blue light emitting materials having aCIE (y) value of no more than 0.1 on the CIE 1931 chromaticity diagram..

Materials having a aCIE (y) value of no more than 0.1 may also be used as host materials for luminescent dopants, for example fluorescent dopants with a singlet excited state (S_1) level lower than that of the host material, or phosphorescent dopants with a triplet excited state (T_1) level lower than that of the host material.

Cathode

Cathode 29 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 light-emitting material. 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 WO 98/10621; elemental barium as disclosed in 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 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 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, and the choice of binding group for the SAM may be selected according to the anode material. Examples of transparent cathode devices are disclosed in, for example, GB 2348316.

Further layers

Further layers may be provided between the anode and the cathode. For example, an electron transporting and / or hole blocking layer may be provided between the light-emitting layer 27 and the cathode 29.

An electron transporting layer may be provided to assist transport of electrons into the LUMO of the light emitting layer by providing a material having a LUMO level falling between that of the light emitting layer and the workfunction of the cathode 29.

Similarly, a hole blocking layer may comprise a material having a HOMO level that serves to block transport of holes from the light-emitting layer to the cathode.

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 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.

Energy level measurement

HOMO, LUMO and electrode workfunction values may be calculated by any method known to the skilled person in order to determine the energy levels required to provide stepped charge transport from the relevant electrode to the light-emitting material. A suitable measurement method is photoelectron spectroscopy using AC-2 apparatus available from RK Instruments Inc, as described in more detail below.

Measurements may alternatively be made using ultraviolet photoelectron spectroscopy measurements performed in a vacuum system, by irradiating the sample surface with ultraviolet light of a fixed wavelength. This measurement results in plots of the Photoelectron Intensity as a function of Kinetic Energy, which are 1:1-projections of the Density-Of-State in the sample substrate.

Examples

Example 1 – effect of SAM on anode workfunction

A substrates was washed successively in Acetone, THF, water and dried using N₂ air supply. A 2 minute UV/Ozone treatment was followed by substrate sonication in Ethanol for 15 minutes. The ITO surface was cleaned and activated in a 1:1:2 ratio of H₂O₂ (30%):NH₄OH(30%):H₂O for 1 hour and then washed with H₂O and THF and dried using N₂ air supply. The substrates were then placed into a phosphonic acid SAM solution (5mmol in Chloroform:Methanol 70:30 ratio) for 2 hours and baked at 140°C in the glove box for 1 hour. Following this step, the substrates were washed with H₂O, ortho-xylene and THF and dried using N₂ air supply. Prior to depositing the hole

transport material, the substrates were given an addition bake at 140°C in a glovebox for 10 minutes.

The workfunctions of ITO before and after SAM modifications were measured by photoelectron spectroscopy using the AC-2 photoelectron spectrometer available from RK Instruments Inc.

Measurements were performed in air, to produce plots of photoelectron yield vs. photon energy. The measurements were performed by probing a sample that is typically several square millimetres in area, and included the following steps:

- UV photons emitted from a deuterium lamp are monochromatized through the grating monochromator
- The monochromatized UV photons are focused on a sample surface in the air
- The energy of UV photon is increased from 3.4eV to 6.2eV, step by step
- 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.

The workfunction of ITO without any SAM was determined to be in the range of 4.85-5 eV.

The workfunction of modified ITO comprising a SAM formed from 3,4,5-trifluorophenylphosphonic acid was 5.33 eV, and 5.07 for a SAM formed from 2,3,4,5,6-pentaphenylphosphonic acid. The deepening of the workfunction (i.e. move further from vacuum level) is beneficial in improving injection of holes into the device.

Figure 9 is a comparison of hole current densities for a device comprising ITO and a SAM formed from 2,3,4,5,6-pentaphenylphosphonic acid and a device comprising ITO

and PEDT / PSS, with the same hole transporting layer (interlayer) coated on top. The current densities are comparable, illustrating that the effect on current density of providing this SAM is comparable to that of providing a hole injection layer of PEDT:PSS.

Example 2

An example of a device fabricated with a materials stack comprised of ITO:dipole SAM:Interlayer:Blue Emitter is shown below. Here we have ITO treated with pentafluorophenylphosphonic acid, followed by the spin coating of a cross-linkable interlayer, followed by the light emitting polymer and cathode. Figure 10a shows the current density and Figure 10b shows the emission characteristics of this bipolar devices:

Example 3

A hole-transporting polymer comprising a repeat unit carrying a pendant phenoxazine charge transporting group and a repeat unit carrying a pendant crosslinkable benzocyclobutane group was prepared according to the following method:

Intermediate (I)

To a solution of bromostyrene (5g, 0.03mol) in THF (100ml) at -78°C under nitrogen, was added n-butyllithium (11ml, 1.0eq, 2.5M in hexanes) dropwise. After stirring at this temperature for 1hr, 1-4,dibromobutane (58g, 0.3mol) was added rapidly and the reaction mixture allowed to warm to ambient temperature overnight. Water (100ml) was then added and the solvent removed under reduced pressure. The organic phase was extracted with DCM (3x50ml), washed with water, dried (MgSO₄) and concentrated in vaco. The resulting yellow oil was treated with 3,5-di-t-butyl-catechol (1%) and excess dibromobutane removed via distillation (99°C, ~10mbar pressure). The orange residue was filtered through a silica plug, (100% hexane to 3%EtOAc) and the filtrate evaporated to give the 4-(4-bromo-butyl)-styrene as a clear oil (3.6g, 65%).

¹H-NMR (400MHz, CDCl₃) δ in ppm: 7.34 (2H, d, ArH), 7.14 (2H, d, ArH), 6.38 (1H, dd, =CH₂), 5.71 (1H, d, CH=), 5.20 (1H, d), 3.42 (2H, t, ArCH₂), 2.64 (2H, t, Br-CH₂), 1.89 (2H, m, CH₂CH₂), 1.78 (2H, m, CH₂CH₂); MS: M⁺238 (100%).

Intermediate (II)

To a suspension of NaH (8.4g, 21mmol, 60% in mineral oil) in DMF (250ml) at 0°C under nitrogen, was added a solution of phenoxazine (35g, 19mmol) in DMF (50ml) dropwise so as to maintain an internal temperature of <5°C. After stirring for 1hr, a solution of the (I) (45.7ml, 19mmol) in DMF (50ml) was added dropwise and the reaction mixture allowed to warm to ambient temperature overnight. Water (100ml) was added to the reaction mixture and the organic phase extracted with toluene (3x50ml), washed with water, dried (MgSO₄) and concentrated under reduced pressure. The resulting crude material was dissolved in toluene, filtered (florisil/silica plug), concentrated and the resulting oil recrystallized (IPA/toluene) to give the product as a white solid (53g, 81%) MS: M⁺341 (100%).

Intermediate (III)

To a suspension of magnesium turnings (1.32g, 55mmol) and an iodine crystal, in THF (26ml) under nitrogen, was added dropwise the first part of a solution of styrene (I) (9.8g, 41mmol) in THF (15ml). The mixture was heated to initiate the reaction and the addition of (I) continued dropwise so as to maintain gentle reflux. After the addition was complete, the reaction mixture was heated to 60°C for 1hr 30mins cooled to room temperature and added dropwise to a solution of benzocyclobutyl bromide (BCBBBr) (5g, 27mmol), PdCl₂(dppf) (1.11g, 0.05eq) and dppf (1.51g, 0.1eq) in THF (50ml) and the resulting mixture heated at 70°C overnight. The mixture was then cooled to room temperature quenched with water (500ml), extracted with toluene (3x50ml) and the organic phase washed with water, dried (MgSO₄) and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO₂, hexane) to give the product as a clear oil (1.3g, 18%).

MS: M⁺ 262 (100%)

Polymer Example 1

A suspension of (II) (7.37g, 21mmol) and (III) (0.63g, 2.4mmol) in heptanone 20ml (degassed with nitrogen for 30mins before use) was heated to 40°C. Azobisisobutyronitrile (AIBN) (9.6mg, 1mol%) was added and the reaction mixture

heated at 60°C for 24hrs. The reaction mixture was diluted with toluene (30ml) and added dropwise to diethyl ether (500ml) to precipitate the polymer. The resulting polymer was redissolved in toluene (20ml) and reprecipitated into diethyl ether (400ml) to give the product.

Mw 95,000, Mp 85,000, PD 2.01.

Thus in one embodiment the method of forming an organic electronic device comprises: providing an anode having a surface; modifying the surface by forming a self-assembled monolayer (SAM) on the surface; forming a layer of hole transporting material over the self-assembled monolayer; forming a layer of an organic light-emissive semiconductor material over the charge transporting layer; and forming a second electrode over the organic light-emissive semiconducting layer, wherein the modified first electrode surface has a work function that is closer to the HOMO level of the hole-transporting layer than the work function of the first electrode surface prior to modification, and wherein the self-assembled monolayer is formed by depositing a self-assembling material comprising a binding group for binding to the first electrode surface and a hole-transporting group having a HOMO energy level. Preferably the HOMO level of the hole transporting group of the SAM and the HOMO level of the hole-transporting layer both fall between the work function of the anode and a HOMO level of the material of the light-emitting layer.

The HOMO levels and work functions should be measured in the same way under the same experimental conditions (such as temperature, etc.) for all the materials. They are preferably measured by photoelectron spectroscopy in air using a AC-2 photoelectron spectrometer.

The present invention has been illustrated with reference to injection of charge into organic light-emitting devices for recombination in an organic light-emitting layer, however the skilled person will understand that the teaching of the present invention may equally be applied to separation of charges in a photoresponsive device.

Although the invention is described herein with respect to injection of holes from an anode into the HOMO levels of a SAM and a hole transporting layer, it will be appreciated that the teachings herein may analogously be applied to injection of electrons

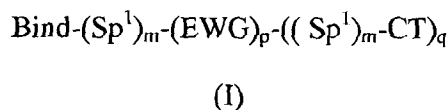
into the LUMO levels of a SAM and an electron-transporting layer in order to provide stepped electron transport into the LUMO of a light-emitting layer. For example, an OLED may be constructed in the reverse order to that described above wherein a cathode is provided on a substrate, an electron-transporting SAM is formed on the cathode, an electron transporting layer is formed on the SAM and light-emitting and anode layers are formed over the electron transporting layer.

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

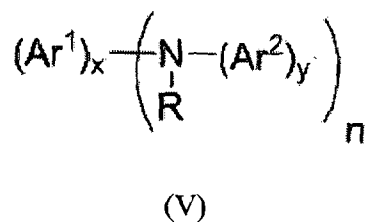
- 1) A method of forming an organic electronic device comprising:
providing a first electrode having a surface;
modifying the surface of the first electrode by forming a self-assembled monolayer on the first electrode surface;
forming a charge-transporting layer comprising a charge transporting material over the self-assembled monolayer, the charge-transporting layer having an energy level;
forming an organic semiconductor layer comprising an organic semiconductor material over the charge transporting layer, the organic semiconductor layer having an energy level; and
forming a second electrode over the organic semiconducting layer,
wherein the modified first electrode surface has a work function that is closer to the energy level of the charge-transporting layer than that of the first electrode surface prior to modification, and wherein the self-assembled monolayer is formed by depositing a self-assembling material comprising a binding group for binding to the first electrode surface and a charge-transporting group having an energy level.
- 2) A method according to claim 1 wherein the energy level of the charge transporting group of the self-assembling material falls between the work function of the modified first electrode surface and the energy level of the charge-transporting layer.
- 3) A method according to claim 1 or 2 wherein the self-assembling layer comprises at least two different charge transporting groups providing at least two different energy levels.

- 4) A method according to any preceding claim wherein the energy level of the charge transporting layer falls between the energy level of the charge transporting group of the self-assembling material and the organic semiconductor layer energy level.
- 5) A method according to any preceding claim wherein the self-assembled material is formed from a compound of formula (I):



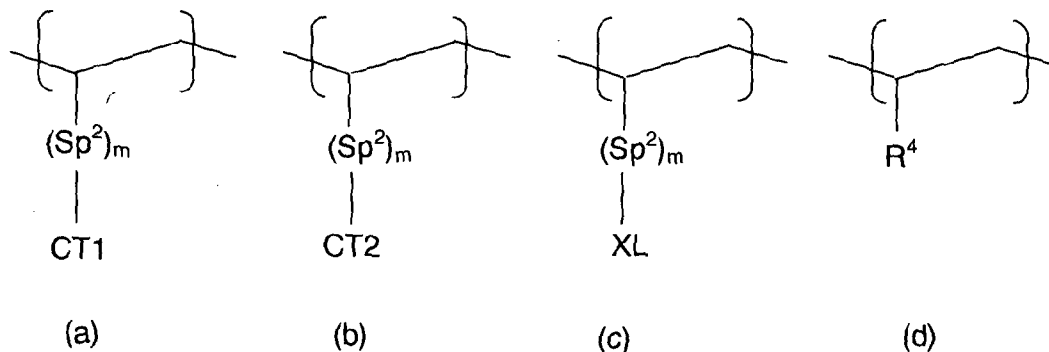
wherein Bind represents a binding group; Sp^1 in each occurrence independently represents a spacer group; CT in each occurrence independently represents a charge-transporting group; EWG is an electron-withdrawing group; m in each occurrence is independently 0 or 1; p is 0 or 1; and q is 0 or an integer.

- 6) A method according to claim 5 wherein Bind comprises a phosphonic acid group.
- 7) A method according to claim 5 or 6 wherein Sp^1 is an optionally substituted alkyl group.
- 8) A method according to claim 5, 6 or 7 wherein CT comprises a group of formula (V):



wherein Ar^1 and Ar^2 in each occurrence are independently selected from optionally substituted aryl or heteroaryl groups; R in each occurrence is independently H, a substituent or $-(\text{Sp})_m\text{-Bind}$, preferably a substituent or $-(\text{Sp})_m\text{-Bind}$; n is greater than or equal to 1, preferably 1 or 2; x and y are each independently 1, 2 or 3; and wherein any of the aryl or heteroaryl groups of the group of formula (V) may be linked by a direct bond or a divalent linking group.

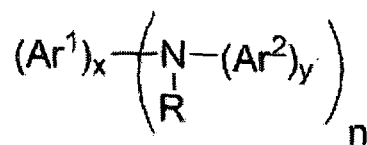
- 9) A method according to any of claims 1-7 wherein CT comprises an optionally substituted carbazole or an optionally substituted phenoxazine.
- 10) A method according to claim 8 wherein CT comprises an optionally substituted fused thiophene, preferably optionally substituted thieno[3,2-b]thiophene or thienobenzothiophene.
- 11) A method according to any preceding claim wherein the charge transporting material is a polymer.
- 12) A method according to claim 11 wherein the polymer comprises a polymer backbone with charge transporting groups pendant from the backbone.
- 13) A method according to claim 12 wherein the polymer comprises at least two different charge transporting groups pendant from the backbone.
- 14) A method according to any of claims 11-13 wherein a backbone of the polymer comprises repeat units of formula a and optionally comprises repeat units of formulae b, c and / or d:



wherein CT1 is a first charge transporting group; CT2 is a second charge transporting group; XL is a crosslinkable group; each Sp^2 is independently a spacer group; R^4 in each occurrence is independently H or a substituent; and each m is independently 0 or 1.

- 15) A method according to claim 14 wherein Sp^2 in each occurrence is selected from the group consisting of optionally substituted alkyl, optionally substituted arylalkyl and optionally substituted heteroarylalkyl.

- 16) A method according to claim 14 or 15 wherein CT1 and / or, where present, CT2 comprises a group of formula (Va)



(Va)

wherein Ar¹ and Ar² in each occurrence are independently selected from optionally substituted aryl or heteroaryl groups; R in each occurrence is independently H, a substituent, a direct bond to the polymer backbone or a bond to Sp²; n is greater than or equal to 1, preferably 1 or 2; x and y are each independently 1, 2 or 3; and wherein any of the aryl or heteroaryl groups of the group of formula (Va) may be linked by a direct bond or a divalent linking group.

- 17) A method according to claim 14 or 15 wherein CT1 and / or, where present, CT2 comprises an optionally substituted fused thiophene, preferably optionally substituted thieno[3,2-b]thiophene or thienobenzothiophene.
- 18) A method according to any of claims 14-17 wherein XL comprises a polymerisable double bond.
- 19) A method according to any preceding claim wherein the device is an organic light-emitting device; the organic semiconductor is a light-emitting material; and the organic semiconductor energy level is a HOMO level or a LUMO level.
- 20) A method according to claim 19 wherein the organic semiconductor energy level is a HOMO level that is separated from the workfunction of the anode by at least 0.2 eV, optionally at least 0.35 eV, optionally at least 0.5 eV.
- 21) A method according to claim 19 or 20 wherein the first electrode is an anode, preferably indium tin oxide, the second electrode is a cathode; the charge-transporting material is a hole transporting material; the organic semiconductor energy level is a HOMO level; the energy level of the charge transporting layer is a HOMO level; the charge transporting group of the self-assembling monolayer is a hole-transporting group; the energy level of the charge transporting group of the

self-assembling monolayer is a HOMO level; and the charge-transporting layer is a hole transporting layer.

- 22) A method of forming an organic electronic device comprising the steps of:
- forming a self-assembled monolayer on a first electrode by bringing at least one self-assembling material into contact with the first electrode;
 - forming a charge-transporting layer by depositing at least one charge transporting polymer onto the self-assembled monolayer
 - forming an organic semiconductor layer comprising an organic semiconductor over the self-assembled monolayer; and
 - forming a cathode over the organic semiconductor layer, wherein:
 - the first electrode has a work function value;
 - the organic semiconductor has an organic semiconductor energy level;
 - the charge-transporting polymer provides the charge transporting layer with at least one energy level falling between the work function value of the first electrode and the organic semiconductor energy level; and
 - the at least one self-assembling material provides the self-assembled monolayer with at least one energy level falling between the work function value of the first electrode and the organic semiconductor energy level.
- 23) A method according to claim 22 wherein the charge-transporting polymer is deposited onto the self-assembled monolayer from a solution in a solvent.
- 24) A method according to claim 22 or 23 wherein the charge-transporting polymer comprises a crosslinkable group and wherein the crosslinkable group is crosslinked following deposition of the charge transporting polymer.
- 25) A method according to claim 24 wherein the organic semiconductor layer is formed by depositing a formulation comprising a solvent and the organic semiconductor and evaporating the solvent.

- 26) An organic light-emitting device comprising an anode; a self-assembled monolayer on the anode; a hole-transporting layer on the self-assembled monolayer; an organic light-emitting layer over the hole-transporting layer; and a cathode over the organic light-emitting layer; wherein the organic light-emitting layer comprises a material having a photoluminescent CIE(y) value of no greater than 0.1.
- 27) An organic light-emitting device according to claim 26 wherein the material of the organic light-emitting layer emits light when the device is in operation.
- 28) An organic light-emitting device according to claim 26 or 27 wherein the material of the organic light-emitting layer is a host material for a light-emitting dopant that emits light when the device is in operation.
- 29) An organic light-emitting device according to claim 26, 27 or 28 wherein the anode carrying the self-assembled monolayer has a workfunction that is further from vacuum level than the anode without the self-assembled monolayer.
- 30) An organic light-emitting device according to any one of claims 26-29 wherein the SAM is formed from a self-assembly material comprising a phosphonic acid and wherein the anode is indium-tin oxide.
- 31) An organic light-emitting device according to any of claims 26-30 wherein the SAM has at least one HOMO level; the charge transporting layer has at least one HOMO level; said HOMO levels both falling between a workfunction of the anode and a HOMO level of the material of the light-emitting layer.
- 32) An organic electronic device comprising a first electrode; a second electrode; an organic semiconducting layer comprising an organic semiconductor between the first and second electrodes; a self-assembled monolayer on the first electrode; and a charge-transporting layer between the self-assembled monolayer and the organic semiconducting layer, wherein:
the first electrode has a work function value;
the organic semiconductor has an organic semiconductor energy level;

the charge-transporting layer comprises at least one charge-transporting material providing the charge transporting layer with at least one energy level falling between the work function value of the first electrode and the organic semiconductor energy level;

the self-assembled monolayer comprises at least one self-assembled material providing the self-assembled monolayer with at least one energy level falling between the work function value of the first electrode and the organic semiconductor energy level; and

wherein at least one of the at least one charge-transporting material and the at least one self-assembled material provide their respective layers with at least two energy levels falling between the work function value of the first electrode and the organic semiconductor energy level.

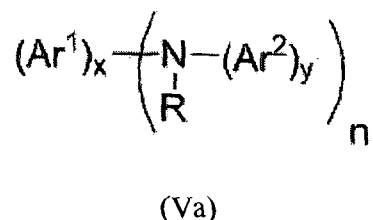
- 33) A self-assembling material comprising a binding group, a first charge-transporting group having a first energy level and at least one further charge transporting group having at least one further energy level wherein the first and at least one further energy levels are different.
- 34) A self-assembling material according to claim 33 wherein the first charge-transporting group and the at least one further charge-transporting group are spaced apart by a spacer group that breaks any conjugation path between the first charge-transporting group and the at least one further charge-transporting group
- 35) A self-assembling material according to claim 33 or 34 wherein the first and at least one further energy levels are HOMO levels.
- 36) A self-assembling material according to any of claims 33-35, the material having optionally substituted formula (I):



(I)

- 37) wherein Bind represents a binding group; Sp^1 in each occurrence independently represents the spacer group; CT in a first occurrence represents the first charge-transporting group; CT in each further occurrence represents the at least one

further charge transporting group; EWG is an electron-withdrawing group; m in each occurrence is independently 0 or 1; p is 0 or 1; and q is at least 2. A self-assembling material according to any of claims 33-36 wherein one or more of the first charge transporting group and the at least one further charge-transporting group comprises a group of formula (Va)



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

- 38) A method according to claim 37 wherein one or more of the first charge transporting group and the at least one further charge-transporting group is selected from optionally substituted carbazole and optionally substituted phenoxazine.
- 39) A method according to any of claims 33-38 wherein one or more of the first charge transporting group and the at least one further charge-transporting group is an optionally substituted fused thiophene, preferably optionally substituted thieno[3,2-b]thiophene or thienobenzothiophene.
- 40) A self-assembling material according to any of claims 33-39 wherein the binding group comprises a phosphonic acid group.
- 41) A self-assembling material according to any of claims 34-40 wherein the spacer group is an optionally substituted alkyl group.
- 42) An organic electronic device comprising an electrode layer carrying a self-assembled monolayer comprising the self assembling material according to any of

claims 33-41, the self-assembling material being bound to the electrode layer through the binding group

- 43) An organic electronic device according to claim 42 wherein the device is an organic light-emitting device and the electrode is an anode, the device further comprising a cathode and a light-emitting layer between the self-assembled monolayer and the cathode.
- 44) An organic electronic device according to claim 43 wherein a hole-transporting layer is provided between the self-assembled monolayer and the light-emitting layer.
- 45) An organic electronic device according to claim 43 or 44 wherein the anode layer comprises indium-tin oxide.
- 46) A method of forming an organic electronic device according to any of claims 42-45, the method comprising the steps of:

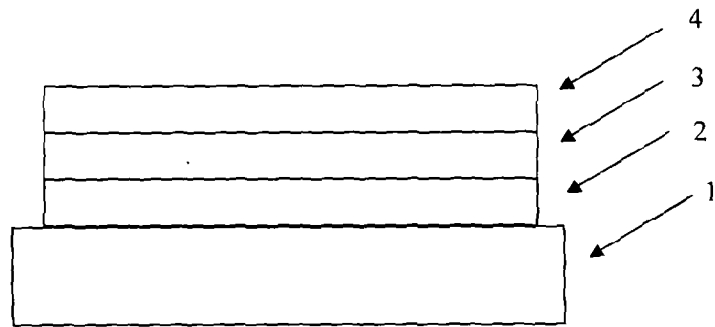
forming the self-assembled monolayer on the anode layer by bringing the self-assembling material into contact with the anode layer;

forming the organic light-emitting layer by depositing an organic light-emitting material over the self-assembled monolayer; and

forming a cathode over the organic light-emitting layer.
- 47) A method according to claim 46 comprising the further step of forming a hole-transporting layer between the self-assembled monolayer and the light-emitting layer by depositing a hole-transporting material over the self-assembled monolayer.

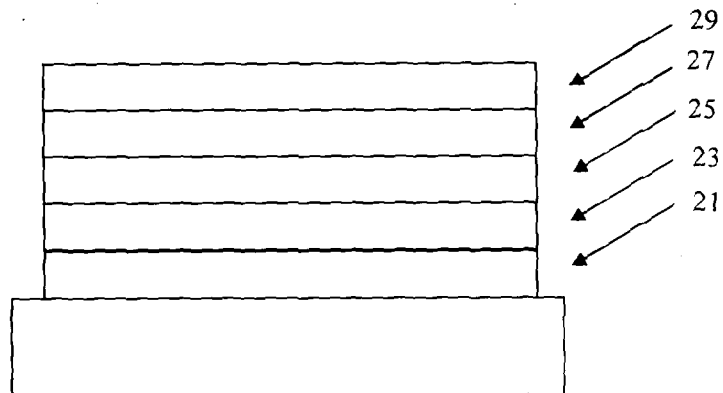
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FIGURE 1

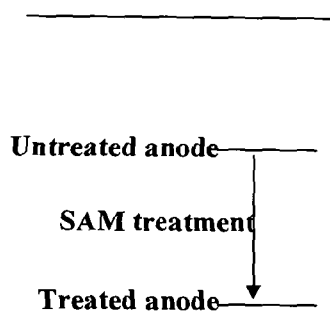
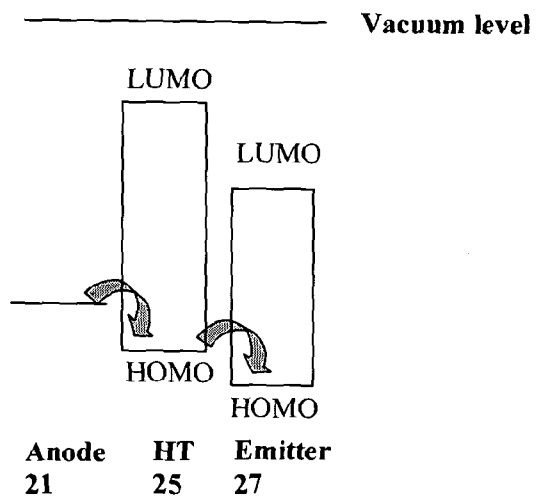
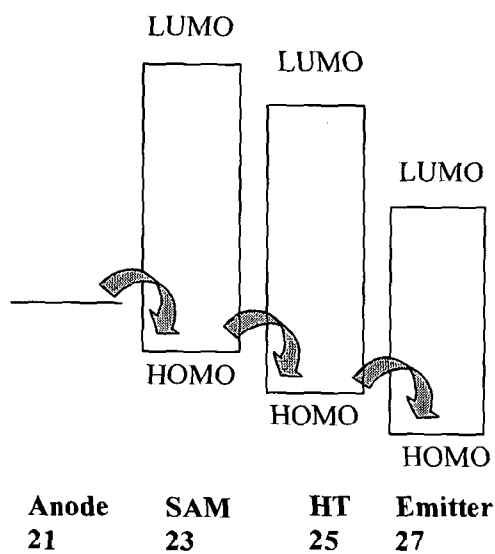


PRIOR ART

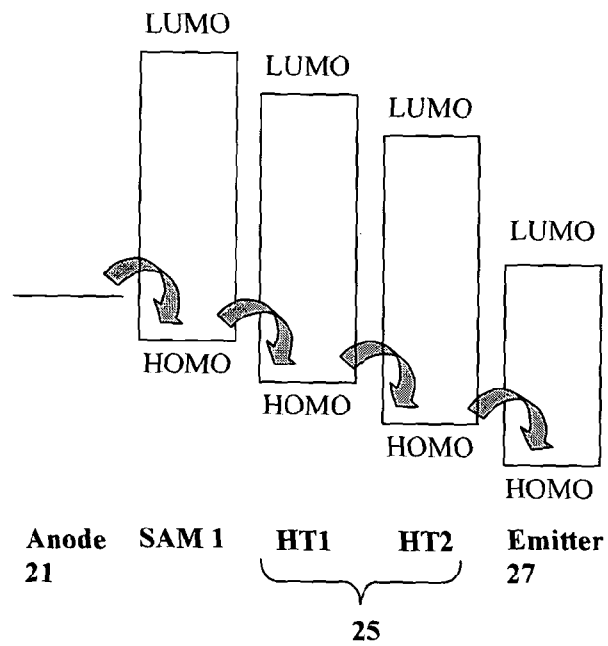
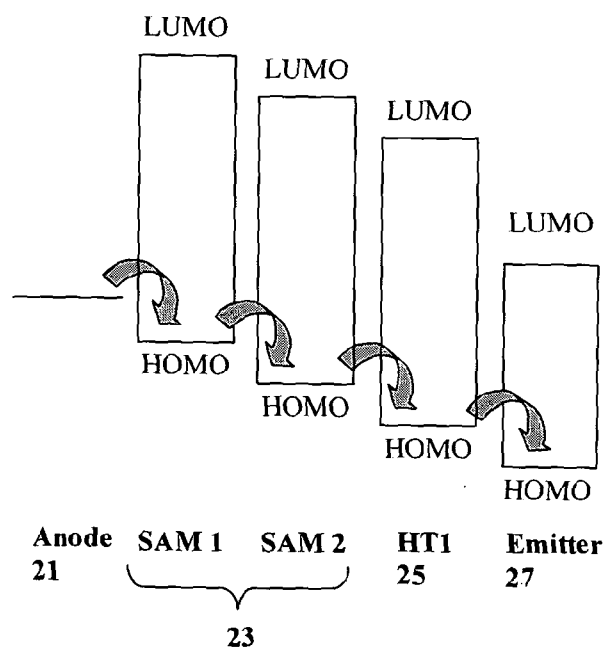
FIGURE 2



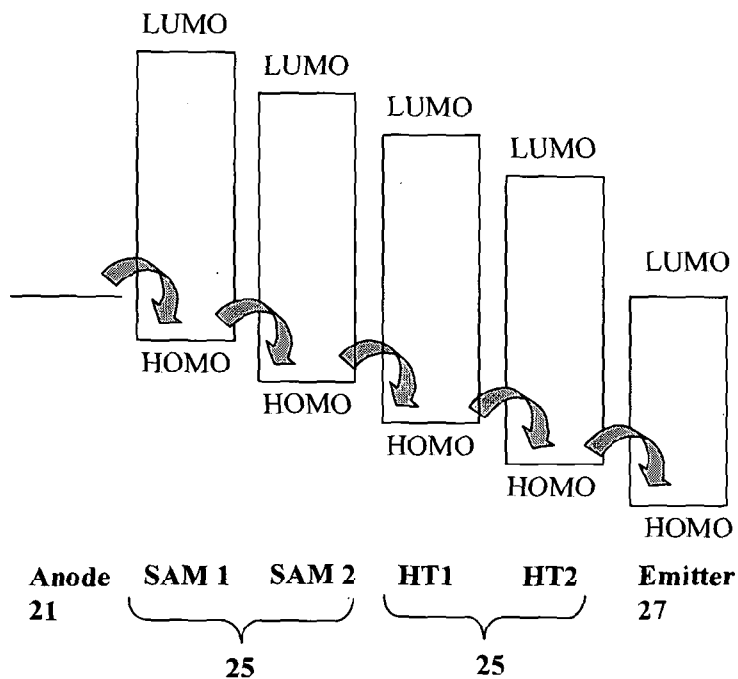
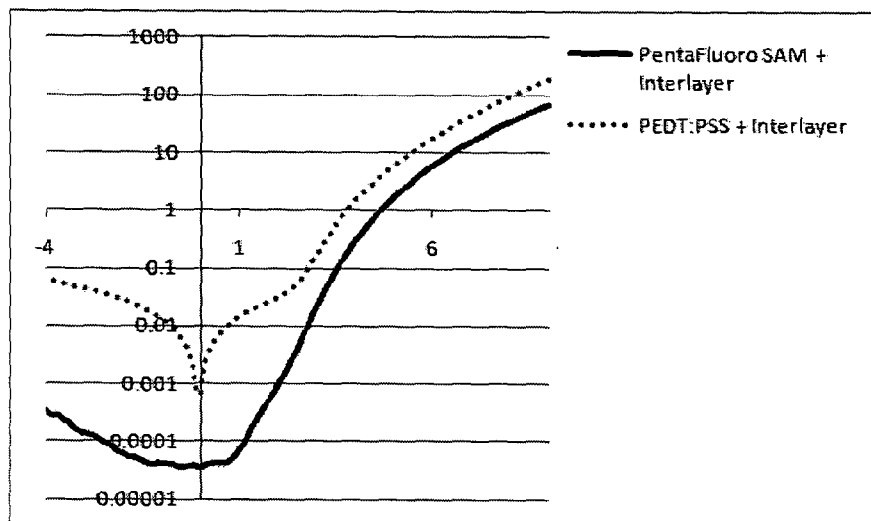
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FIGURE 3**FIGURE 4****FIGURE 5**

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FIGURE 6**FIGURE 7**

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FIGURE 8**FIGURE 9**

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FIGURE 10a

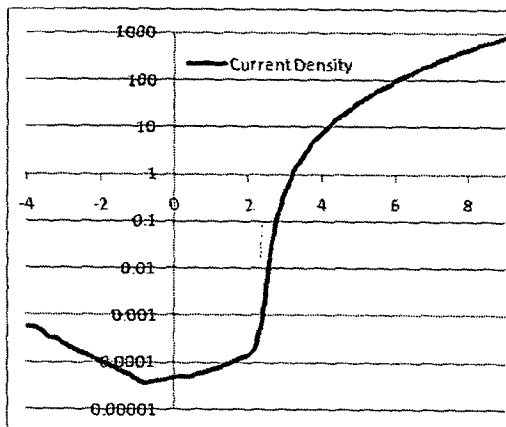
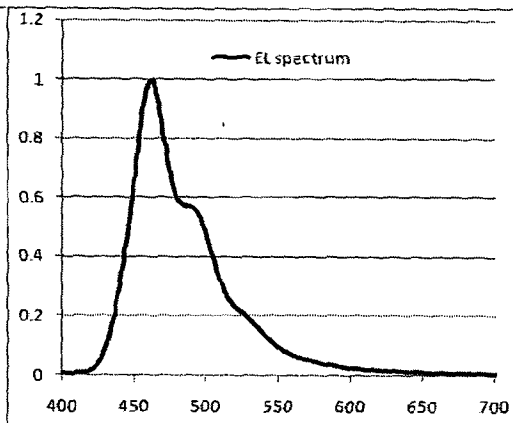


FIGURE 10b



INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2012/000540

A. CLASSIFICATION OF SUBJECT MATTER
 INV. 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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JAEMIN LEE ET AL: "Modification of an ITO anode with a hole-transporting SAM for improved OLED device characteristics", JOURNAL OF MATERIALS CHEMISTRY, THE ROYAL SOCIETY OF CHEMISTRY, CAMBRIDGE, GB, vol. 12, no. 12, 4 October 2002 (2002-10-04), pages 3494-3498, XP002507277, ISSN: 0959-9428, DOI: 10.1039/B206939C [retrieved on 2002-10-04]	1,2,4,5, 8,19-31
Y	Sections "Device fabrication" and "Results and discussion"; figures 1,4; table 1 ----- -/-	7,9-12



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

21 September 2012

Date of mailing of the international search report

02/10/2012

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040,
 Fax: (+31-70) 340-3016

Authorized officer

Bakos, Tamás

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2012/000540

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	XU X ET AL: "Electrode modification in organic light-emitting diodes", DISPLAYS DEVICES, DEMP A PUBLICATIONS, TOKYO, JP, vol. 27, no. 1, 1 January 2006 (2006-01-01), pages 24-34, XP027950052, ISSN: 0141-9382 [retrieved on 2006-01-01] page 29, column 1, paragraph 2 - page 30, column 1, paragraph 1; figures 4,5 -----	1,5,6,8, 19,20
X	HO P K H ET AL: "ULTRATHIN SELF-ASSEMBLED LAYERS AT THE ITO INTERFACE TO CONTROL CHARGE INJECTION AND ELECTROLUMINESCENCE EFFICIENCY IN POLYMER LIGHT-EMITTING DIODES", ADVANCED MATERIALS, WILEY VCH VERLAG, DE, vol. 10, no. 10, 9 July 1998 (1998-07-09), pages 769-774, XP000774680, ISSN: 0935-9648, DOI: 10.1002/(SICI)1521-4095(199807)10:10<769::AID-ADMA769>3.3.CO;2-V -----	33,35, 36,42-47
A	page 769, column 2, paragraph 3 - page 770, column 1, paragraph 1; figure 1; table 1 -----	3,13-18, 34,37-41
Y	US 7 811 624 B1 (WANG HAILIANG [US]) 12 October 2010 (2010-10-12) column 2, line 1 - column 3, line 6; figures 1,2 -----	7,9-12
A	PETER K H HO ET AL: "Molecular-scale interface engineering for polymer light-emitting diodes", NATURE: INTERNATIONAL WEEKLY JOURNAL OF SCIENCE, NATURE PUBLISHING GROUP, UNITED KINGDOM, vol. 404, 30 March 2000 (2000-03-30), pages 481-484, XP007908914, ISSN: 0028-0836, DOI: 10.1038/35006610 page 481, column 1, paragraph bottom - page 482, column 1, paragraph 2; figures 1,2 -----	32

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2012/000540

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 7811624	B1	12-10-2010	NONE
