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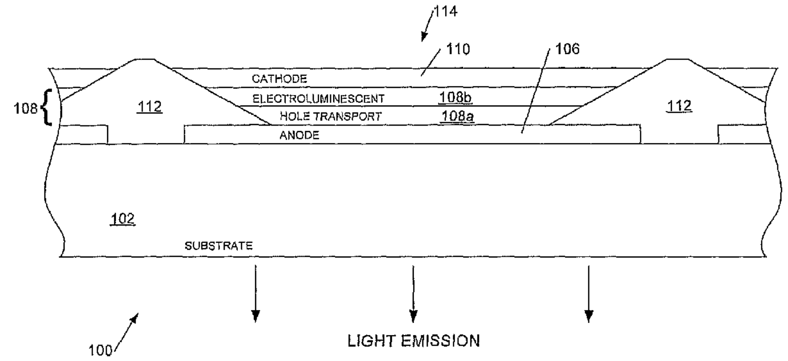
(54) Title: METHODS OF MANUFACTURING OPTO-ELECTRICAL DEVICES



(57) Abstract: A method of fabricating an opto-electrical device, the method comprising the steps: depositing, on a substrate comprising a first electrode for injecting charge carriers of a first polarity, a composition comprising a conductive or semi-conductive organic material, a solvent, and a first additive; and, depositing a second electrode for injecting charge carriers of a second polarity opposite to the first polarity, wherein the first additive is a basic additive.

METHODS OF MANUFACTURING OPTO-ELECTRICAL DEVICES

Field of Invention

This invention relates to a method of fabricating an opto-electrical device, and the use of compositions in methods of manufacturing opto-electrical devices.

Background of Invention

One class of opto-electrical devices is that using an organic material for light emission (or detection in the case of photovoltaic cells and the like). The basic structure of these devices is a light emissive organic layer, for instance a film of a poly (p-phenylenevinylene) ("PPV") or polyfluorene, sandwiched between a cathode for injecting negative charge carriers (electrons) and an anode for injecting positive charge carriers (holes) into the organic layer. The electrons and holes combine in the organic layer generating excitons which then undergoes radiative decay to give light (in light detecting devices this process essentially runs in reverse). In WO90/13148 the organic light- emissive material is a polymer. In US 4,539,507 the organic light-emissive material is of the class known as small molecule materials, such as (8-hydroxyquinoline) aluminium ("Alq3"). In a practical device one of the electrodes is transparent, to allow the photons to escape the device.

A typical organic light-emissive device ("OLED") is fabricated on a glass or plastic substrate coated with a transparent anode such as indium-tin-oxide ("ITO"). A layer of a thin film of at least one electroluminescent organic material (which here includes organometallic material) covers the first electrode. Finally, a cathode covers the layer of electroluminescent organic material. The cathode is typically a metal or alloy and may comprise a single layer, such as aluminium, or a plurality of layers such as calcium and aluminium.

A multicoloured display may be constructed using groups of red, green, and blue emitting pixels. So-called active matrix displays have a memory element, typically a storage capacitor and a transistor, associated with each pixel whilst passive matrix displays have no such memory element and instead are repetitively scanned to give the impression of a steady image.

Figure 1 shows a vertical cross section through an example of an OLED device 100. In an active matrix display, part of the area of a pixel is occupied by associated drive circuitry (not shown in Figure 1). The structure of the device is somewhat simplified for the purposes of illustration.

The OLED 100 comprises a substrate 102, typically 0.7 mm or 1.1 mm glass but optionally clear plastic, on which an anode layer 106 has been deposited. The anode layer typically comprises around 150 nm thickness of ITO (indium tin oxide), over which is provided a metal contact layer, typically around 500nm of aluminium, sometimes referred to as anode metal. Glass substrates coated with ITO and contact metal may be purchased from Corning, USA. The contact metal (and optionally the ITO) is patterned as desired so that it does not obscure the display, by a conventional process of photolithography followed by etching.

A substantially transparent hole injection layer 108a is provided over the anode metal, followed by an electroluminescent layer 108b. Banks 112 may be formed on the substrate, for example from positive or negative photoresist material, to define wells 114 into which these active organic layers may be selectively deposited, for example by a droplet deposition or inkjet printing technique. The wells thus define light emitting areas or pixels of the display.

A cathode layer 110 is then applied by, say, physical vapour deposition. The cathode layer typically comprises a low work function metal such as calcium or barium covered with a thicker, capping layer of aluminium and optionally including an additional layer immediately adjacent the electroluminescent layer, such as a layer of lithium fluoride, for improved electron energy level matching. The cathode may be transparent. This is particularly preferred for active matrix devices wherein emission through the substrate is partially blocked by drive circuitry located underneath the emissive pixels. In the case of a transparent cathode device, it will be appreciated that the anode is not necessarily transparent. In the case of passive matrix displays, mutual electrical isolation of cathode lines may achieved through the use of cathode separators (element 302 of Figure 3b). Typically a number of displays are fabricated on a single substrate and at the end of the fabrication process the substrate is scribed, and the displays separated. An encapsulant such as a glass sheet or a metal can is utilized to inhibit oxidation and moisture ingress.

Organic LEDs of this general type may be fabricated using a range of materials including polymers, dendrimers, and so-called small molecules, to emit over a range of wavelengths at varying drive voltages and efficiencies. Examples of polymer-based OLED materials are described in WO90/13148, WO95/06400 and WO99/48160; examples of dendrimer-based materials are described in WO 99/21935 and WO 02/067343; and examples of small molecule OLED materials are described in US 4,539,507. The aforementioned polymers, dendrimers and small molecules emit light by radiative decay of singlet excitons (fluorescence). However, up to 75% of excitons are triplet excitons which normally undergo non-radiative decay. Electroluminescence by radiative decay of triplet excitons (phosphorescence) is disclosed in, for example, "Very high-efficiency green organic light-emitting devices based on electrophosphorescence" M.A. Baldo, S. Lamansky, P.E. Burrows, M.E. Thompson, and S.R. Forrest *Applied Physics Letters*, Vol. 75(1) pp.4-6, July 5, 1999. In the case of a polymer-based OLED, layers 108 comprise a hole injection layer 108a and a light emitting polymer (LEP) electroluminescent layer 108b. The electroluminescent layer may comprise, for example, around 70nm (dry) thickness of PPV (poly(p-phenylenevinylene)) and the hole injection layer, which helps match the hole energy levels of the anode layer and of the electroluminescent layer, may comprise, for example, around 50-200 nm, preferably around 150 nm (dry) thickness of PEDOT:PSS (polystyrene-sulphonate-doped polyethylene-dioxythiophene).

The deposition of material for organic light emitting diodes (OLEDs) using ink jet printing techniques are described in a number of documents including, for example: EP 0880303 and "Ink-Jet Printing of Polymer Light-Emitting Devices", Paul C. Duineveld, Margreet M. de Kok, Michael Buechel, Aad H. Sempel, Kees A.H. Mutsaers, Peter van de Weijer, Ivo G.J. Camps, Ton J.M. van den Biggelaar, Jan-Eric

J.M. Rubingh and Eliav I. Haskal, Organic Light-Emitting Materials and Devices V, Zakya H. Kafafi, Editor, Proceedings of SPIE Vol. 4464 (2002). Ink jet techniques can be used to deposit materials for any form of soluble organic material, including both small molecule and polymer LEDs.

Figure 2 shows a view from above (that is, not through the substrate) of a portion of a three-colour active matrix pixellated OLED display 200 after deposition of one of the active colour layers. The figure shows an array of banks 112 and wells 114 defining pixels of the display.

Figure 3a shows a view from above of a substrate 300 for inkjet printing a passive matrix OLED display. Figure 3b shows a cross-section through the substrate of figure 3a along line Y-Y'.

Referring to figures 3a and 3b, the substrate is provided with a plurality of cathode undercut separators 302 to separate adjacent cathode lines (which will be deposited in regions 304). A plurality of wells 308 is defined by banks 310, constructed around the perimeter of each well 308 and leaving an anode layer 306 exposed at the base of the well. The edges or faces of the banks are tapered onto the surface of the substrate as shown, heretofore at an angle of between 10 and 40 degrees. The banks present a hydrophobic surface in order that they are not wetted by the solution of deposited organic material and thus assist in containing the deposited material within a well. This is achieved by treatment of a bank material such as polyimide with an O_2/CF_4 plasma as disclosed in EP 0989778. Alternatively, the plasma treatment step may be avoided by use of a fluorinated material such as a fluorinated polyimide as disclosed in WO 03/083960.

As previously mentioned, the bank and separator structures may be formed from resist material, for example using a positive (or negative) resist for the banks and a negative (or positive) resist for the separators; both these resists may be based upon polyimide and spin coated onto the substrate, or a fluorinated or fluorinated-like photoresist may be employed. In the example shown the cathode separators are around 5 μm in height and approximately 20 μm wide. Banks are generally between 20 μm and 100 μm in width and in the example shown have a 4 μm taper at each edge (so that the banks are around 1 μm in height). The pixels of Figure 3a are approximately 300 μm square but, as described later, the size of a pixel can vary considerably, depending upon the intended application.

These devices have great potential for displays and lighting. However, there are several significant problems. One is to make the device efficient, particularly as measured by its external power efficiency and its external quantum efficiency. Another is to optimise (e.g. to reduce) the voltage at which peak efficiency is obtained. Another is to stabilise the voltage characteristics of the device over time. Another is to increase the lifetime of the device.

To this end, numerous modifications have been made to the basic device structure described above in order to solve one or more of these problems.

One such modification is the provision of a layer of conductive polymer between the light-emissive organic layer and one of the electrodes. It has been found that the provision of such a conductive polymer layer can improve the turn-on voltage, the brightness of the device at low voltage, the efficiency, the lifetime and the stability of the device. Examples of such conductive polymers include polythiophene derivatives such as poly(ethylene dioxythiophene), or polyaniline derivatives. It may be advantageous in some device arrangements to not have too high a conductivity of the conductive polymer. For example, if a plurality of electrodes are provided in a device but only one continuous layer of conductive polymer extending over all the electrodes, then too high a conductivity can lead to lateral conduction (known as "cross-talk"). Furthermore, if the conductive polymer is not covered by the overlying layer(s) of organic material between the conductive polymer and the cathode then there is a risk of shorting between the conductive polymer and the cathode.

The conductive polymer layer may also be selected to have a suitable workfunction so as to aid in hole or electron injection and/or to block holes or electrons. There are thus two key electrical features: the overall conductivity of the conductive polymer composition; and the workfunction of the conductive polymer composition. The stability of the composition and reactivity with other components in a device will also be critical in providing an acceptable lifetime for a practical device. The processability of the composition will be critical for ease of manufacture.

Conductive polymer formulations are discussed in the applicant's earlier application WO2006/123167. There is an ongoing need to optimise the organic formulations used in these devices both in the light emitting layer and the conductive polymer layer, in particular to improve inkjet performance and wetting properties of these compositions.

Furthermore, devices comprising acidic conductive polymers such as PEDOT / PSS suffer from corrosion of layers adjacent to PEDOT / PSS, in particular the anode layer.

A problem associated with ink jet printing of materials for organic opto-electrical devices is that the printing process involves printing stripes (or swathes) of ink (corresponding to the ink jet head width) which results in an inbuilt asymmetry in the drying environment. Specifically, at a swathe edge more drying occurs on the unprinted side since the solvent concentration in the atmosphere above the substrate is less than the printed side. With more evaporation taking place on the unprinted side more solute is deposited on this side and the film profile becomes asymmetric, resulting in visible non-uniformities in the resultant display.

Another problem associated with ink jet printing of organic opto-electrical devices such as those discussed above is that in the resultant device, the organic hole injecting layer can extend beyond the overlying organic semi-conductive layer providing a shorting path between the cathode and the anode at an edge of the well. This problem is exacerbated if the contact angle of the conductive organic composition with the bank material is too low. This problem is further exacerbated if the conductivity of the organic hole injecting layer is too high. One solution to this problem is to modify the bank structure. However, providing a more complex bank structure is expensive and increases the complexity of the manufacturing method for the device.

In addition to the aforementioned problems of depositing prior art compositions using ink jet printing, it has also been found that some compositions comprising conductive and semi-conductive organic material are also difficult, or indeed impossible, to deposit by other methods such as spin-coating. As such, it is an aim of the present invention to provide compositions which are easier to deposit by any solution processing method including, for example, spin-coating as well as ink jet printing.

The present applicant seeks to solve, or at least reduce, the problems outlined above by adapting compositions, in particular compositions for ink jet printing, comprising conductive or semi-conductive organic material. These adapted compositions are of particular use in the manufacture of light-emissive devices.

WO 2004/029128 discloses compositions of PEDOT with counterions such as fluorinated polyacids as an alternative to counterions such as PSS, and teaches that the pH of these formulations may be modified using an ion-exchange resin. pH of formulations modified in this way may be further modified by addition of aqueous basic salts such as sodium hydroxide. Example 21 of this publication teaches that modification of pH of PEDOT / PSS using an ion exchange resin significantly degrades device performance.

WO 2005/034261 discloses a method for preserving an acidic organic material having a 2wt % concentration by increasing its pH.

WO 2004/063277 discloses addition of co-solvents to aqueous PEDOT / PSS in order to increase the conductivity of films formed from the aqueous solution.

Summary of the present invention

According to a first aspect of the present invention there is provided a method of fabricating an opto-electrical device, the method comprising the steps: depositing, on a substrate comprising a first electrode for injecting charge carriers of a first polarity, a composition comprising a conductive or semi-conductive organic material, a solvent, and a first additive; and depositing a second electrode for injecting charge carriers of a second polarity opposite to the first polarity, wherein the first additive is a basic additive.

The solvent may dissolve the conductive or semiconductive organic material, or the solvent and conductive or semi-conductive organic material may together form a dispersion. For example, an aqueous composition of PEDOT/PSS is in the form of a dispersion. Preferably, the composition is a dispersion. Preferably, the solvent is an aqueous solvent. Preferably, the organic material is conductive.

In the case where the composition comprises a conductive organic material, this material preferably comprises a polycation and a charge balancing polyanion, for example PEDOT with a polyanion such as PSS. Another example is polythienothiophene with a polyanion.

It has surprisingly been found that the addition of a basic additive to a composition comprising a conductive or semi-conductive organic material in a solvent, in particular an acidic composition, results in a composition that forms much smoother films as compared to compositions without a basic additive.

It has also been found that a basic additive can be used to tune the conductivity of a film formed from the composition. For example, the base can form a salt with an acidic conductive organic material, in particular a conductive organic material comprising a polyacid such as poly(styrene sulfonic acid), neutralizing acid groups and increasing resistivity. Neutralisation of acidic compositions in this way has the added benefit of making the composition less hazardous, and also less likely to corrode an inkjet head during inkjet printing. Thus, the organic material preferably comprises acidic groups, and the composition according to the invention preferably has a pH greater than or equal to 7, more preferably greater than or equal to 8, most preferably in the range 8-10.

It has further been found that a formulation comprising a basic additive is much less corrosive than formulations without such an additive. Without wishing to be bound by any theory, this effect is attributed to the higher pH of formulations comprising a basic additive. Thus, corrosion of metal tracking for electrodes such as gold tracking or MoCr stacks is significantly or completely reduced. Moreover, in the case of inkjet printed devices, the present inventors have found that the formulations according to the invention do not corrode the nozzle plate of the inkjet head, unlike the higher pH formulations of the prior art.

It will be appreciated that any basic additive will serve to neutralise acidic compositions. However, not all basic additives result in an increase in resistivity of a film formed from the composition. In particular, unsubstituted primary amines, in particular primary alkylamines such as ethylamine and ethylenediamine, have been found to give a large increase in resistivity. In contrast, basic additives comprising hydroxy substituents, for example hydroxy amines such as ethanolamine, tend to either reduce or have little effect on resistivity. Thus, appropriate choice of basic additives and mixtures thereof can be used to tune the resistivity of the compositions.

Preferably, the basic additive can be evaporated from the formulation upon drying. It will therefore be appreciated that the additive is preferably not an ionic base such as sodium hydroxide or similar salts. Preferably, the additive is a non-ionic organic base. The provision of a basic additive, in particular a basic additive with a high boiling point, can increase the drying time of the composition. Thus, during ink jet printing, the amount of evaporation occurring in the time between deposition of adjacent swathes is reduced leading to a greater uniformity of drying and a more symmetric film formation around a swathe join.

The basic additive may also serve to solubilise the conductive or semiconductive organic material.

Typically, there will only be a few seconds until the next swathe is printed when ink jet printing. However, due to the high surface to volume ratio of an ink, drying times are in the order of seconds. As a result significant drying can occur prior to deposition of an adjacent swathe.

As explained above, a basic additive can serve to neutralise an acidic composition. The inventors have found that the amount of amine required for this purpose is very low, and can be less than 2% or even less than 1% by volume. The inventors have also found that high boiling point amines can be used in excess of the amount required to neutralise the composition. By using basic additives, the amount of evaporation occurring in this time can be reduced. Once adjacent swathes have been deposited the drying environment becomes symmetrical resulting in symmetric layer profiles around the swathe join.

The amount and type of basic additive to be added to a composition will be dependent on how much of a reduction in drying time is desired. This will be dependent on the time taken to print adjacent swathes. Thus, for slower printing times, a slower drying composition is desirable and a larger volume and/or higher boiling point basic additive will be required.

The basic additive may be added to a composition from a solution in a solvent, however in the case of non-ionic organic bases, it is preferred that the additive is added in neat form to avoid unnecessary dilution of the composition.

The addition of a basic additive is preferably the primary means, preferably the only means, by which the pH of a composition is modified.

The amount and/or type of solvent to be used will depend on the speed of ink jet printing (how much time it takes to print successive swathes). The amount and/or type of solvent will also depend on the surface to volume ratio of the ink droplet. For larger ink droplets, evaporation will be slower and for a given print speed, a lower boiling point basic additive may be required when compared to an arrangement utilizing smaller droplets. One key feature of embodiments of the present invention is that the print speed, the droplet size/well size, and the boiling point of the basic additive are selected such that when a first swathe and a second swathe are successively printed adjacent to each other, the print rate is such that the first swathe does not significantly dry prior to completing printing of the second swathe.

One problem found with adding high boiling point solvents such as glycerol is that there is a large increase in the conductivity of the composition resulting in problems due to shorting between electrodes. Accordingly, it is required to add a conductivity modifier in order to reduce the conductivity of the composition. The conductivity modifier may be, for example, a large excess of PSS in a PEDOT:PSS formulation. However, a problem with this is that the composition becomes very acidic and device lifetime may be poor. In contrast, as the basic additives of the present invention do not produce a large increase in conductivity, no conductivity modifier such as excess PSS is required, thus improving device lifetime.

Following on from the above, a particular problem in organic opto-electrical devices is that the conductive organic hole injecting layer may extend beyond the overlying organic semi-conductive layer providing a shorting path between the cathode deposited thereover and the underlying anode. This problem is exacerbated if the conductivity of the organic hole injecting layer is high, which can be the case when using high boiling point solvents such as glycerol. In contrast, compositions comprising a basic additive have lower conductivity thus reducing the shorting problem.

Asymmetric drying at the swathe join can also lead to shorting paths being created at the swathe join. Accordingly, the use of a basic additive which alleviates asymmetric drying will also reduce the shorting problem caused by poor film morphologies. The present applicant has found that in some cases addition of a high boiling point solvent increases shorting at the swathe joins. This has been found to be due to an increase in the conductivity of the conductive polymer film. This problem is avoided by using a basic additive.

The base in the additive may remain in a film formed using the composition or may be volatile and evaporate from the film during fabrication. In either case, the base may affect the charge balance in the film or act as a surface modifier in order to increase the lifetime of a device.

Preferably, the basic additive has a boiling point greater than 100°C. In some instances, vacuum drying and baking is believed to break down any salt formed by the base and the organic material releasing the base and acid groups on the organic material.

Preferably, the basic additive is an amine, most preferably an organic amine. It has been found that amines provide particularly good compositions for use in fabricating organic opto-electrical devices. Examples of classes of amines include primary, secondary and tertiary alkyl amines; primary or secondary aryl amines; diamines; pyridines; pyrimidines and quinolines. The amine may optionally be substituted. In particular, alkylamines may be substituted with one or more hydroxy, thio or amino groups. Specific examples of substituted amines include alkylamines with one or more hydroxy groups such as triethanolamine, diethanolamine, ethanolamine, ethylamine, 4-amino-1-butanol, 4-amino-2-butanol, 6-amino-1-hexanol, 5-amino-1-pentanol, and ethylenediamine.

Because little or none of the amine additive may remain in the resultant film formed by compositions of the present invention if a volatile amine is utilized, the additive can be provided in the composition in relatively large amounts or as a minor additive component in the composition. Preferably, the additive is provided in an amount in the range 1 to 40% by volume, more preferably 5 to 30%, most preferably 10-20%. If the additive is provided at lower or higher concentrations, the solution processability of the composition is not as good. In the case where an acidic conductive organic material is used, up to about 2% v/v, such as around 0.1-2 or 1-2% v/v of the basic additive is typically required for neutralisation of the conductive organic material.

The solubility, processability and functional properties of the organic material may be very sensitive to changes in solvent. Accordingly, it is advantageous to retain a portion of solvent in which the organic material is stable. Water may be a suitable solvent for some organic materials, particularly charged conductive organic materials such as doped PEDOT, which forms a dispersion with water. As such, the solvent will typically be the usual solvent used for the organic material for achieving good solubility, processability and conductance characteristics.

Suitable solvents for non-polar organic materials include mono- or poly-alkylated benzenes, for example xylene.

The solid content of the composition may be between 0.5% and 6%, 1% and 4%, 1.5% and 3%, and in some cases is preferably 2%. The solid content also affects the form of the film after drying. If the solid content is too high then the film forms a dome shape whereas if the solid content is too low then an excessive coffee ring effect occurs. It has been found that the provision of a basic additive allows the use of a higher solid content when compared with high boiling point additives such as glycerol, which allows an increase in film thickness over previous compositions.

A light-emitting layer may be deposited as a composition comprising a semi-conductive organic material in a composition according to the present invention. Preferably, the organic material comprises a polymer and most preferably the polymer is either fully or partially conjugated.

A charge injecting layer may be deposited as a composition comprising a conductive organic material in a composition according to the present invention. Preferably, the organic material comprises a polymer and most preferably the organic material comprises PEDOT with a suitable polyanion, for example PSS.

Embodiments of the present invention relate to new PEDOT ink formulations for improved film uniformity within pixels and across swathe joins. Slower drying inks have been formulated which do not compromise other aspects of the inks performance. This provides an alternative to interlacing which is very slow.

The present applicant has found that the problem of film non-uniformity in PEDOT is very important to device performance. The device performance may not be directly affected significantly by the thickness of the PEDOT film. However, the uniformity of the PEDOT film affects the uniformity of the overlying electroluminescent layer. The EL layer is very sensitive to changes in thickness. Accordingly, the present applicant has found that it is paramount that uniform films of PEDOT profiles are achieved in order to achieve uniform EL profiles.

Organic amines such as ethanolamine, when added to PEDOT compositions act to neutralise acid groups on PEDOT/PSS giving a large increase in resistivity. Thus amine salts are formed with $-SO_3H$ groups on the PSS polymer. Vacuum drying and baking is believed to break down the salt releasing volatile amine and free $-SO_3H$ groups.

When added in excess of the amount required to neutralise the conductive organic material (>~1% - >20%) the amine acts as a high boiling point solvent reducing evaporation rate of the composition on drying and eliminating (physical) swath joins. A solids content of 2% allows an increase in film thickness as compared to a formulation not comprising a basic additive. The result is an ink jet printing formulation that has the correct resistivity to avoid electrical swath joins and a component that reduces evaporation rate thus eliminating physical swaths.

In the case where the composition of the invention is inkjet printed, it preferably has a surface tension of at least 35 mN m to avoid leakage of the composition from the inkjet print head.

The quantity of counterion present in a PEDOT:counterion composition is at least sufficient to balance the charge on PEDOT, and the PEDOT:counterion ratio may be in the range 1:10 to 1:30, more preferably in the range 1:15 to 1:20. Preferably, the counterion is a polymeric acid such as a polysulfonic acid (for example PSS or Nafion) or poly acrylic acid. Most preferably, the counterion is PSS.

The compositions of the present invention may be deposited by any solution processing method, for example ink-jet printing, spin-coating, dip-coating, roll-printing, flexographic printing or screen printing. The viscosity of the composition for inkjet printing is preferably in the range 2 to 30 mPa, 2 to 20 mPa, 4 to 12 mPa, more preferably 6 to 8 mPa, and most preferably approximately 8 mPa, at 20 degrees centigrade. Higher viscosities may be suitable for other solution processing methods.

It will be appreciated from the above that the basic additive can provide a number of advantages including film smoothness, improved jettability, resistivity modification, pH control and improved device performance.

The compositions of the present invention may comprise more than one basic additive in order to optimise the properties of the composition. For example, a high-boiling basic additive such as triethanolamine may be used to improve jetting characteristics, whereas a low boiling basic additive such as ethylamine may be used to enhance resistivity. Similarly, more than one basic additive may be used to tune the resistivity of the composition.

Other additives may also be included, for example alcohol ether additives such as butoxyethanol that may serve to improve jetting properties and wetting of the composition; sufoxides such as dimethylsulfoxide; and amides such and dimethylformamide.

Furthermore, the basic additive of the present invention may be used in combination with other, non-basic, additives in order to tune the properties of the composition. Examples of other additives include polyacids, for example a polysulfonic acid such as PSS or Nafion ®, or poly acrylic acid; and alcohols, in particular polyols such as ethylene glycol.

According to one embodiment of the present invention there is provided a method of manufacturing an organic light-emissive display comprising: providing a substrate comprising a first electrode layer and a bank structure defining a plurality of wells; depositing a conductive polymer layer over the first electrode; depositing an organic light-emissive layer over the conductive polymer layer; and depositing a second electrode over the organic light-emissive layer, wherein at least one of the conductive polymer layer and the organic light-emissive layer is deposited by ink jet printing a composition as described herein into the plurality of wells.

Brief Summary of the Drawings

Embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 shows a vertical cross section through an example of an OLED device;

Figure 2 shows a view from above of a portion of a three colour pixelated OLED display;

Figures 3a and 3b show a view from above and a cross-sectional view respectively of a passive matrix OLED display;

Figure 4 shows a titration curve for a composition according to the invention.

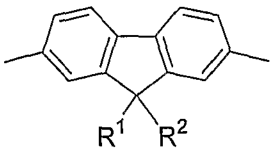
Detailed Description of Preferred Embodiments

The general device architecture is illustrated in Figure 1 and has been described previously.

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 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. 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.

Suitable polymers for charge transport and emission may comprise a first repeat unit selected from arylene repeat units, in particular: 1,4-phenylene repeat units as disclosed in J. Appl. Phys. 1996, 79, 934; fluorene repeat units as disclosed in EP 0842208; indenofluorene repeat units as disclosed in, for example, Macromolecules 2000, 33(6), 2016-2020; and spirofluorene repeat units as disclosed in, for example EP 0707020. Each of these repeat units is optionally substituted. Examples of substituents include solubilising groups such as C_{1-20} alkyl or alkoxy; electron withdrawing groups such as fluorine, nitro or cyano; and substituents for increasing glass transition temperature (Tg) of the polymer.

Particularly preferred polymers comprise optionally substituted, 2,7-linked fluorenes, most preferably first repeat units of formula:

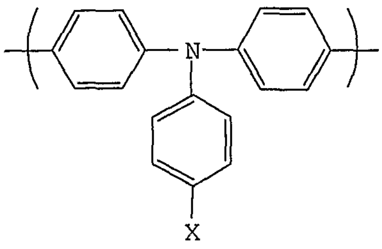


wherein R^1 and R^2 are independently selected from hydrogen or optionally substituted alkyl, alkoxy, aryl, arylalkyl, heteroaryl and heteroarylalkyl. More preferably, at least one of R^1 and R^2 comprises an optionally substituted C_4-C_{20} alkyl or aryl group.

A polymer comprising the first repeat unit may provide one or more of the functions of hole transport, electron transport and emission depending on which layer of the device it is used in and the nature of co-repeat units.

In particular:
- a homopolymer of the first repeat unit, such as a homopolymer of 9,9-dialkylfluoren-2,7-diyl, may be utilised to provide electron transport;
- a copolymer comprising a first repeat unit and a triarylamine repeat unit utilised to provide hole transport and / or emission; or
- a copolymer comprising a first repeat unit and heteroarylene repeat unit may be utilised for charge transport or emission.

Particularly preferred triarylamine repeat units are selected from optionally substituted repeat units of formulae 1-6:



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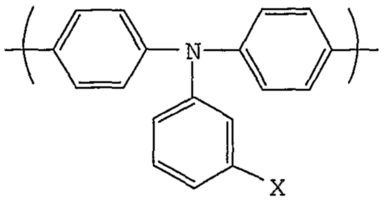

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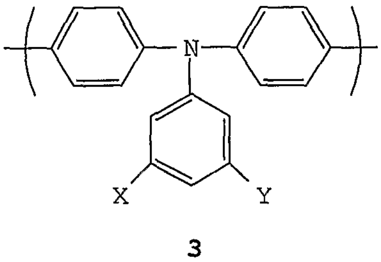

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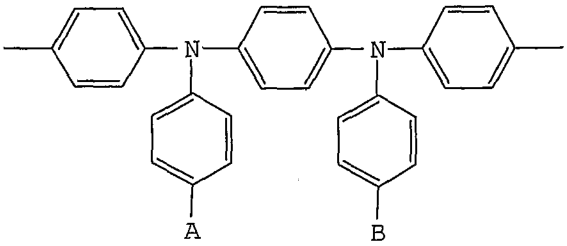

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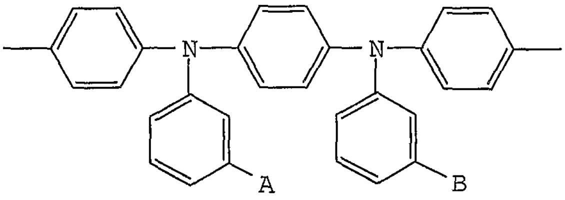

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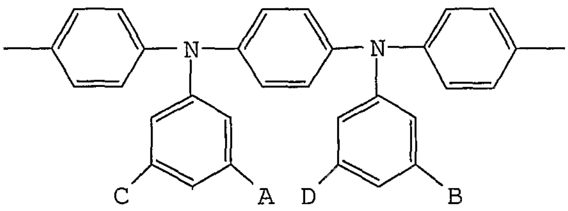
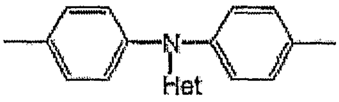


6

wherein X, Y, A, B, C and D are independently selected from H or a substituent group. More preferably, one or more of X, Y, A, B, C and D is independently selected from the group consisting of optionally substituted, branched or linear alkyl, aryl, perfluoroalkyl, thioalkyl, cyano, alkoxy, heteroaryl, alkylaryl and arylalkyl groups. Most preferably, X, Y, A and B are C_{1-10} alkyl. The aromatic rings in the backbone of the polymer may be linked by a direct bond or a bridging group or bridging atom, in particular a bridging heteroatom such as oxygen.

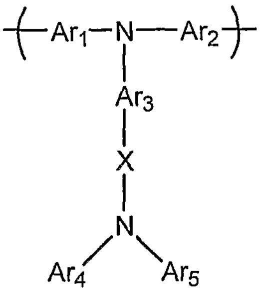
Also particularly preferred as the triarylamine repeat unit is an optionally substituted repeat unit of formula 6a:



6a

wherein Het represents a heteroaryl group.

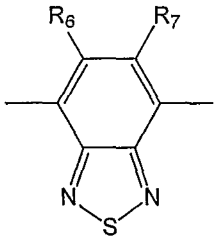
Another preferred hole transporting material comprises the repeat unit of general formula (6aa):



(6aa)

where Ar_1, Ar_2, Ar_3, Ar_4 and Ar_5 each independently represent an aryl or heteroaryl ring or a fused derivative thereof; and X represents an optional spacer group.

Preferred heteroarylene repeat units are selected from formulae 7-21:



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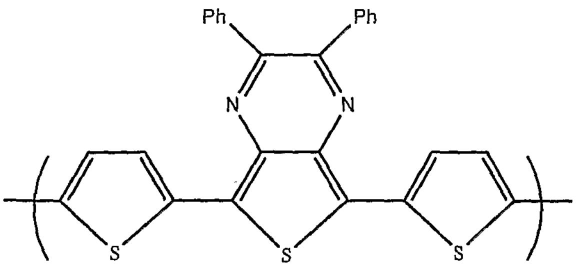
wherein R_6 and R_7 are the same or different and are each independently hydrogen or a substituent group, preferably alkyl, aryl, perfluoroalkyl, thioalkyl, cyano, alkoxy, heteroaryl, alkylaryl or arylalkyl. For ease of manufacture, R_6 and R_7 are preferably the same. More preferably, they are the same and are each a phenyl group.



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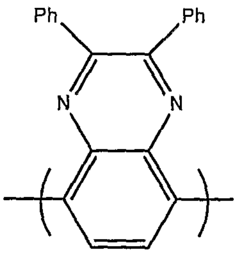

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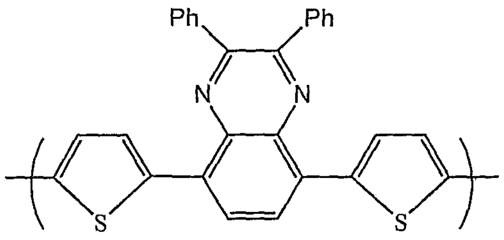

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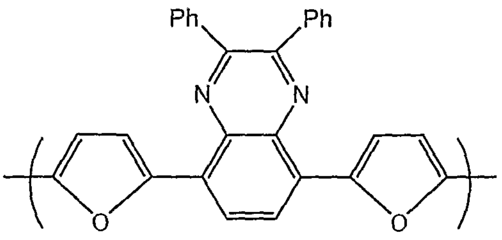

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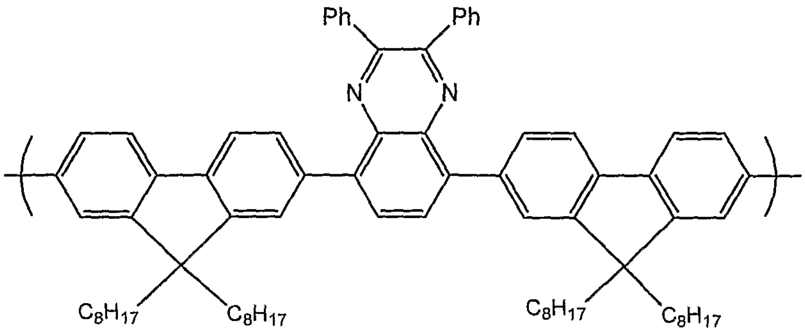

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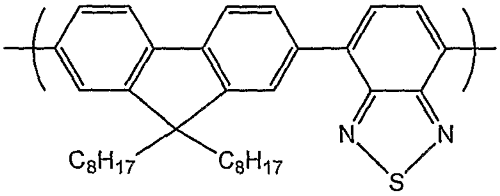

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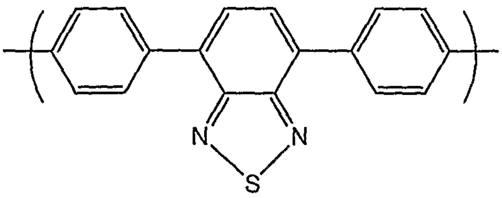

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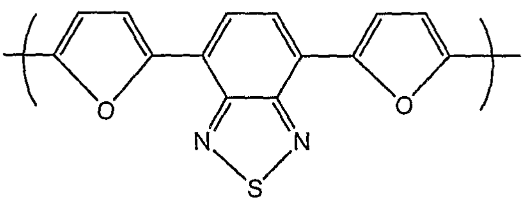

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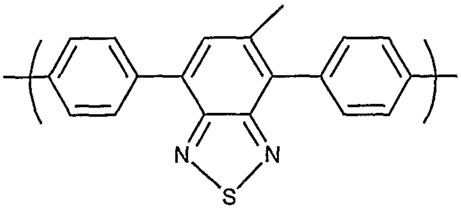

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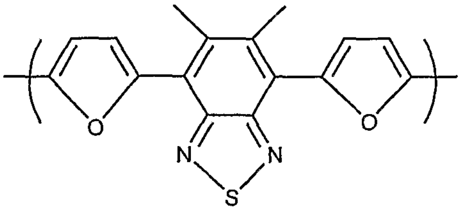

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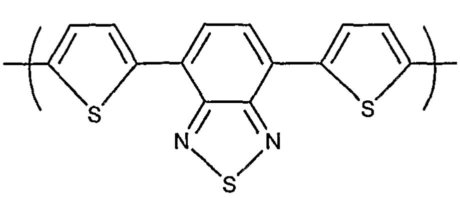

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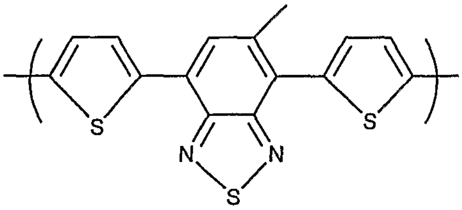

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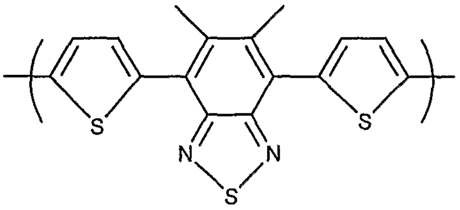

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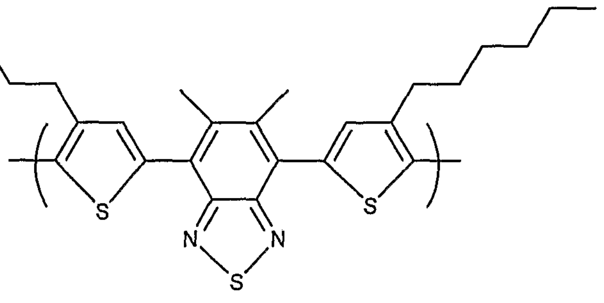


21

Electroluminescent copolymers may comprise an electroluminescent region and at least one of a hole transporting region and an electron transporting region as disclosed in, for example, WO 00/55927 and US 6353083. If only one of a hole transporting region and electron transporting region is provided then the electroluminescent region may also provide the other of hole transport and electron transport functionality.

The different regions within such a polymer may be provided along the polymer backbone, as per US 6353083, or as groups pendant from the polymer backbone as per WO 01/62869.

Preferred methods for preparation of these polymers are Suzuki polymerisation as described in, for example, WO 00/53656 and Yamamoto polymerisation as described in, for example, T. Yamamoto, "Electrically Conducting And Thermally Stable π - Conjugated Poly(arylene)s Prepared by Organometallic Processes", Progress in Polymer Science 1993, 17, 1153-1205. These polymerisation techniques both operate via a "metal insertion" wherein the metal atom of a metal complex catalyst is inserted between an aryl group and a leaving group of a monomer. In the case of Yamamoto polymerisation, a nickel complex catalyst is used; in the case of Suzuki polymerisation, a palladium complex catalyst is used.

For example, in the synthesis of a linear polymer by Yamamoto polymerisation, a monomer having two reactive halogen groups is used. Similarly, according to the method of Suzuki polymerisation, at least one reactive group is a boron derivative group such as a boronic acid or boronic ester and the other reactive group is a halogen. Preferred halogens are chlorine, bromine and iodine, most preferably bromine.

It will therefore be appreciated that repeat units and end groups comprising aryl groups as illustrated throughout this application may be derived from a monomer carrying a suitable leaving group.

Suzuki polymerisation may be used to prepare regioregular, block and random copolymers. In particular, homopolymers or random copolymers may be prepared when one reactive group is a halogen and the other reactive group is a boron derivative group. Alternatively, block or regioregular, in particular AB, copolymers may be prepared when both reactive groups of a first monomer are boron and both reactive groups of a second monomer are halogen.

As alternatives to halides, other leaving groups capable of participating in metal insertion include groups include tosylate, mesylate and triflate.

A single polymer or a plurality of polymers may be deposited from solution to form layer 5. Suitable solvents for polyarylenes, in particular polyfluorenes, include mono- or poly-alkylbenzenes such as toluene and xylene. Particularly preferred solution deposition techniques are spin-coating and inkjet printing.

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

Inkjet printing is particularly suitable for high information content displays, in particular full colour displays. Inkjet printing of OLEDs is described in, for example, EP 0880303.

In some cases, distinct layers of the device may be formed by different methods, for example a hole injection and / or transport layer may be formed by spin-coating and an emissive layer may be deposited by inkjet printing.

If multiple layers of the device are formed by solution processing then the skilled person will be aware of techniques to prevent intermixing of adjacent layers, for example by crosslinking of one layer before deposition of a subsequent layer or selection of materials for adjacent layers such that the material from which the first of these layers is formed is not soluble in the solvent used to deposit the second layer.

Numerous hosts are described in the prior art including "small molecule" hosts such as 4,4'-bis(carbazol-9-yl)biphenyl), known as CBP, and (4,4',4''-tris(carbazol-9-yl)triphenylamine), known as TCTA, disclosed in Ikai et al. (Appl. Phys. Lett., 79 no. 2, 2001, 156); and triarylamines such as tris-4-(N-3-methylphenyl-N-phenyl)phenylamine, known as MTDATA. Polymers are also known as hosts, in particular homopolymers such as poly(vinyl carbazole) disclosed in, for example, Appl. Phys. Lett. 2000, 77(15), 2280; polyfluorenes in Synth. Met. 2001, 116, 379, Phys. Rev. B 2001, 63, 235206 and Appl. Phys. Lett. 2003, 82(7), 1006; poly[4-(N-4-vinylbenzyloxyethyl, N-methylamino)-N-(2,5-di-tert-butylphenylnapthalimide] in Adv. Mater. 1999, 11(4), 285; and poly(para-phenylenes) in J. Mater. Chem. 2003, 13, 50-55. Copolymers are also known as hosts.

The emissive species may be metal complexes. The metal complexes may comprise optionally substituted complexes of formula (22):

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

(22)

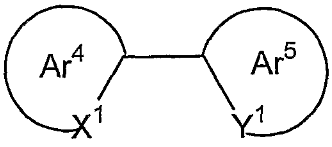
wherein M is a metal; each of L^1, L^2 and L^3 is a coordinating group; q is an integer; r and s are each independently 0 or an integer; and the sum of (a. q) + (b. r) + (c.s) is equal to the number of coordination sites available on M, wherein a is the number of coordination sites on L^1, b is the number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

Heavy elements M induce strong spin-orbit coupling to allow rapid intersystem crossing and emission from triplet states (phosphorescence). Suitable heavy metals M include:

- lanthanide metals such as cerium, samarium, europium, terbium, dysprosium, thulium, erbium and neodymium; and
- d-block metals, in particular those in rows 2 and 3 i.e. elements 39 to 48 and 72 to 80, in particular ruthenium, rhodium, pallaidum, rhenium, osmium, iridium, platinum and gold.

Suitable coordinating groups for the f-block metals include oxygen or nitrogen donor systems such as carboxylic acids, 1,3-diketonates, hydroxy carboxylic acids, Schiff bases including acyl phenols and iminoacyl groups. As is known, luminescent lanthanide metal complexes require sensitizing group(s) which have the triplet excited energy level higher than the first excited state of the metal ion. Emission is from an f-f transition of the metal and so the emission colour is determined by the choice of the metal. The sharp emission is generally narrow, resulting in a pure colour emission useful for display applications.

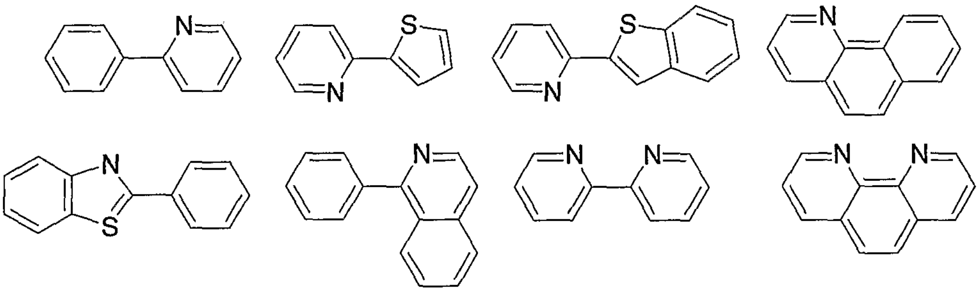
The d-block metals form organometallic complexes with carbon or nitrogen donors such as porphyrin or bidentate ligands of formula (VI):



(VI)

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

Examples of bidentate ligands are illustrated below:



Each of Ar^4 and Ar^5 may carry one or more substituents. Particularly preferred substituents include fluorine or trifluoromethyl which may be used to blue-shift the emission of the complex as disclosed in WO 02/45466, WO 02/44189, US 2002-117662 and US 2002-182441; alkyl or alkoxy groups as disclosed in JP 2002-324679; carbazole which may be used to assist hole transport to the complex when used as an emissive material as disclosed in WO 02/81448; bromine, chlorine or iodine which can serve to functionalise the ligand for attachment of further groups as disclosed in WO 02/68435 and EP 1245659; and dendrons which may be used to obtain or enhance solution processability of the metal complex as disclosed in WO 02/66552. Other ligands suitable for use with d-block elements include diketonates, in particular acetylacetonate (acac); triarylphosphines and pyridine, each of which may be substituted.

Main group metal complexes show ligand based, or charge transfer emission. For these complexes, the emission colour is determined by the choice of ligand as well as the metal.

The host material and metal complex may be combined in the form of a physical blend. Alternatively, the metal complex may be chemically bound to the host material. In the case of a polymeric host, the metal complex may be chemically bound as a substituent attached to the polymer backbone, incorporated as a repeat unit in the polymer backbone or provided as an end-group of the polymer as disclosed in, for example, EP 1245659, WO 02/31896, WO 03/18653 and WO 03/22908.

A wide range of fluorescent low molecular weight metal complexes are known and have been demonstrated in organic light emitting devices [see, e. g., Macromol. Sym. 125 (1997) 1-48, US-A 5,150,006, US-A 6,083,634 and US-A 5,432,014].. Suitable ligands for di or trivalent metals include: oxinoids, e. g. with oxygen-nitrogen or oxygen-oxygen donating atoms, generally a ring nitrogen atom with a substituent oxygen atom, or a substituent nitrogen atom or oxygen atom with a substituent oxygen atom such as 8-hydroxyquinolate and hydroxyquinoxalinol-10-hydroxybenzo (h) quinolinato (II), benzazoles (III), schiff bases, azoindoles, chromone derivatives, 3-hydroxyflavone, and carboxylic acids such as salicylato amino carboxylates and ester carboxylates. Optional substituents include halogen, alkyl, alkoxy, haloalkyl, cyano, amino, amido, sulfonyl, carbonyl, aryl or heteroaryl on the (hetero) aromatic rings which may modify the emission colour.

Composition formation procedure

The composition used in the method according to the invention may be prepared by simply blending the basic additive with the conductive or semi-conductive organic material.

In the case of doped PEDOT, the basic additive may be blended with a commercially available aqueous dispersion of doped PEDOT, for example PEDOT:PSS sold under the name Baytron P ® by H C Starck of Leverkusen, Germany. Further solvents and /

or additives may also be added in order to optimise the properties of the dispersion such as its jettability, drying characteristics and resistivity, and / or in order to improve the performance of the end device. Exemplary further additives include polymeric acids, for example excess PSS, and exemplary further solvents include alcohols, in particular polyols such as ethylene glycol.

An exemplary composition according to the present invention comprises commercially available Baytron P VP AI4083 to which is added extra PSS, ethylene glycol and a basic amine to give a formulation having a pH of 8.

Device manufacturing procedure

The procedure follows the steps outlined below:

1) Depositing a PEDT/PSS composition according to the first aspect of the invention onto indium tin oxide supported on a glass substrate (available from Applied Films, Colorado, USA) by spin coating.

2) Depositing a layer of hole transporting polymer by spin coating from xylene solution having a concentration of 2 % w/v.

3) Heating the layer of hole transport material in an inert (nitrogen) environment.

4) Optionally spin-rinsing the substrate in xylene to remove any remaining soluble hole transport material.

5) Depositing an organic light-emissive material by spin-coating from xylene solution.

6) Depositing a metal compound/conductive material bi-layer cathode over the organic light-emissive material and encapsulating the device using an airtight metal enclosure available from Saes Getters SpA.

Full colour display manufacturing procedure

A full colour display can be formed according to the process described in EP 0880303 by forming wells for red, green and blue subpixels using standard lithographical techniques; inkjet printing PEDT/PSS into each subpixel well; inkjet printing hole transport material; and inkjet printing red, green and blue electroluminescent materials into wells for red, green and blue subpixels respectively.

Sample Experimental Results

1. Conductivity

PEDOT:PSS compositions comprising several different amines were formulated and tested for their influence on resistivity. The conductivity measurements were taken by spinning a film of PEDOT-PSS onto an inter-digitated test structure to a thickness of 10 microns (as measured using DekTak apparatus).and using a modified four-point probe in order to record the lateral resistivity across the bottom of the PEDOT film. The resistivity of the bulk PEDOT film is assumed to be the same.

Additive	**Resistivity (ohm.cm)**
Ethylamine	8.769E+06
Ethylenediamine	1.836E+07
Ethanolamine	4.990E+04
None (comparison)	5.207E+04

It can be seen that, unlike high boiling point additives such as glycerol, the compositions do not shown a large increase in conductivity when compared with a control composition with no additive. The PEDOT:PSS composition comprising ethanol amine has a resistivity closest to the control composition and has a favourable boiling point to act as a high boiling point solvent. As such, this amine is preferred.

2. Composition pH

Figure 4 shows a titration curve for ethylenediamine added to PEDOT / PSS. The pH increases sharply between around pH 2-7. The present inventors have found that compositions in this pH range are not processable because the solids present in the dispersion aggregate. However, the dispersion is processable outside this pH range at around pH 8 and above.

3. Film profiles

The above composition comprising ethanolamine was ink-jet printed onto a pixellated substrate comprising ink wells and film thickness profiles were measured for each pixel across a row of the substrate using a Zygo white light interferometer. Results indicated that the films had a similar profile across the row, even at a swath join.

The absence or presence of a change in film profile at a swath join is demonstrated by plotting the centroid position of the dry film profile in each pixel across the swath join as shown in Figure 6. Figure 6 indicates how the centroid position varies for a number of different PEDOT:PSS compositions. It can be seen that many of the compositions have a large variation in the centroid position around the swath position which is located at pixel numbers 30/31. The composition comprising a basic additive (ethanolamine) is labelled PC43 in Figure 6. It can be seen that there is little variation in the centroid position indicating that film formation is substantially uniform across the substrate, even at the swath position.

The film profile measurements were measured using a Zygo interferometer. This can be used to scan either width or lengthways over a pixel and the layer thickness recorded.

4. Device results

Organic electroluminencent devices were manufactured according to the previously described process. Devices were manufactured with and without a basic additive in the PEDOT:PSS composition.

Lifetime (in hours) of devices comprising an additive according to the present invention are shown in the table below.

	PEDOT:PSS (1:16)	PEDOT:PSS (1:40) + glycerol	PEDOT:PSS (1:16) + glycerol + basic additive
Red	250	255	363

	(4000 cd/m2)		
Green	250 (6000 cd/m2)	138	248
Blue	130 (1800 cd/m2)	80	142

As can be seen, lifetime is improved as compared to devices comprising no additive or the non-basic additive glycerol. Moreover, device results such as drive voltage and luminescence are comparable to controls indicating that the doped PEDOT:PSS structure is unaffected as a result of neutralisation by the base or is regenerated after baking. As such, compositions according to the present invention improve film formation without detrimentally affecting the opto-electrical properties of the device. Furthermore, swath joins are eliminated, shorts are reduced and lifetime of the devices is improved.

It has also surprisingly been found that the composition of the invention provides a smoother film than a composition that does not comprise a basic additive.
For example, inkjet printing of PEDOT / PSS with added amine gave a film with a +/- 2nm variation in thickness (measured as root mean square variation), whereas printing of PEDOT / PSS without added amine gave a film with +/- 5 nm variation

The compositions of the present invention has been described for use in organic light emitting diodes, however it will be appreciated that these compositions may similarly be applied to other devices, for example organic photoresponsive devices (including photodetectors and photovoltaic devices such as solar cells); in organic switching devices, in particular organic thin film transistors; and other plastic electronic devices.

Claims

1. A method of fabricating an opto-electrical device, the method comprising the steps:

depositing, on a substrate comprising a first electrode for injecting charge carriers of a first polarity, a composition comprising a conductive or semi-conductive organic material, a solvent, and a first additive; and

depositing a second electrode for injecting charge carriers of a second polarity opposite to the first polarity, wherein the first additive is a basic additive.

2. A method according to claim 1, wherein the composition is a dispersion.

3. A method according to claim 1, wherein the composition is a solution.

4. A method according to any preceding claim, wherein the basic additive is an amine.

5. A method according to claim 4, wherein the amine is an organic amine.

6. A method according to claim 5, wherein the organic amine is selected from triethanolamine, diethanolamine, ethanolamine, ethylamine, 4-amino-1-butanol, 4-amino-2-butanol, 6-amino-1-hexanol, 5-amino-1-pentanol, and ethylenediamine.

7. A method according to any preceding claim, wherein the basic additive has a boiling point greater than 100°C.

8. A method according to any preceding claim, wherein the basic additive is provided in an amount in the range 1 to 40% by volume, more preferably 5 to 30%, most preferably 10-20% by volume.

9. A method according to any preceding claim, wherein composition is an aqueous composition.

10. A method according to any preceding claim, wherein the organic material is polymeric.

11. A method according to any preceding claim wherein the composition comprises a conductive organic material.

12. A method according to any preceding claim wherein the organic material comprises acidic groups.

13. A method according to any preceding claim wherein the composition has a pH of at least 8.

14. A method according to any preceding claim, wherein the organic material comprises a hole injecting material.

15. A method according to claim 14, wherein the hole injecting material comprises PEDOT with a charge-balancing counterion.

16. A method according to claim 15, wherein the ratio of PEDOT:counterion is between 1:6 and 1:30.

17. A method according to 15 or 16, wherein the counterion is PSS.

18. A method according to any preceding claim, wherein the composition is deposited by ink-jet printing

19. A method according to any preceding claim, wherein a composition comprising a conductive organic material is deposited over the first electrode and a composition comprising a semi-conductive organic material is deposited thereover, at least one of the conductive and semi-conductive compositions comprising the basic additive.

20. A method according to any preceding claim, wherein the substrate comprises a bank structure defining a plurality of wells and the composition is deposited into the plurality of wells by ink jet printing to form a display.

21. A method according to claim 20, wherein the display is printed in swathes.

22. A method according to claim 21, wherein a first swathe and a second swathe are successively printed adjacent to each other, the print rate being such that the first swathe does not significantly dry prior to completing printing of the second swathe.

23. Use of a composition comprising a conductive or semi-conductive organic material, a solvent, and a basic additive in a method of fabricating an opto-electrical device.

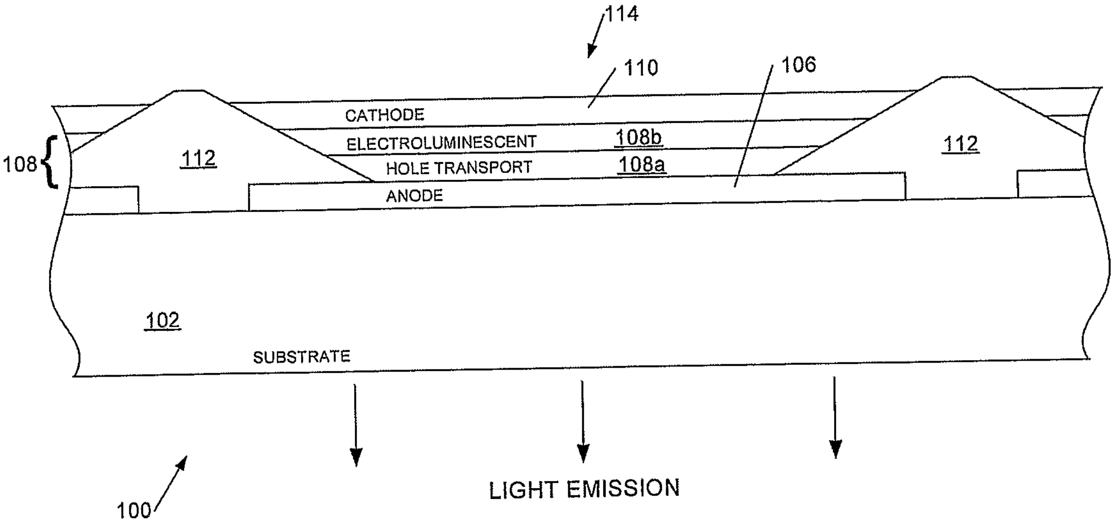


Figure 1
(PRIOR ART)

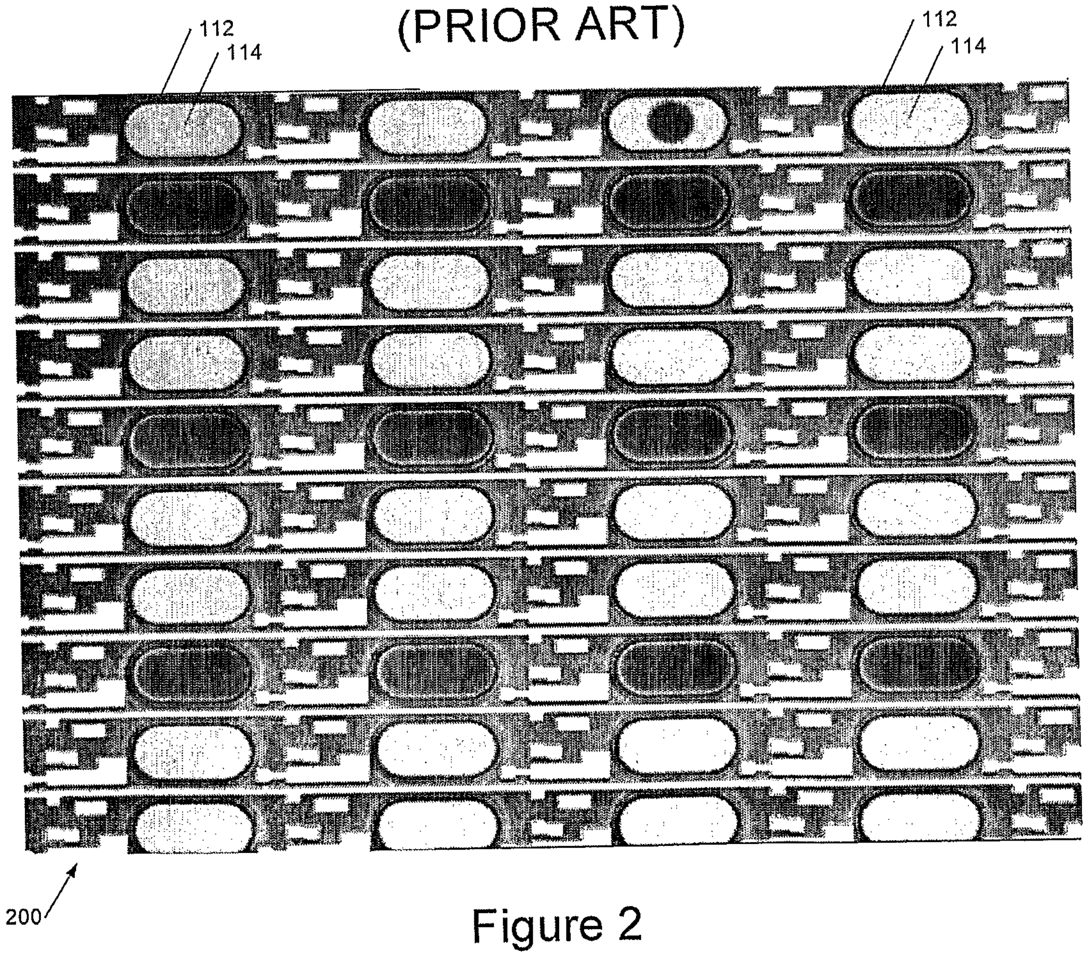


Figure 2

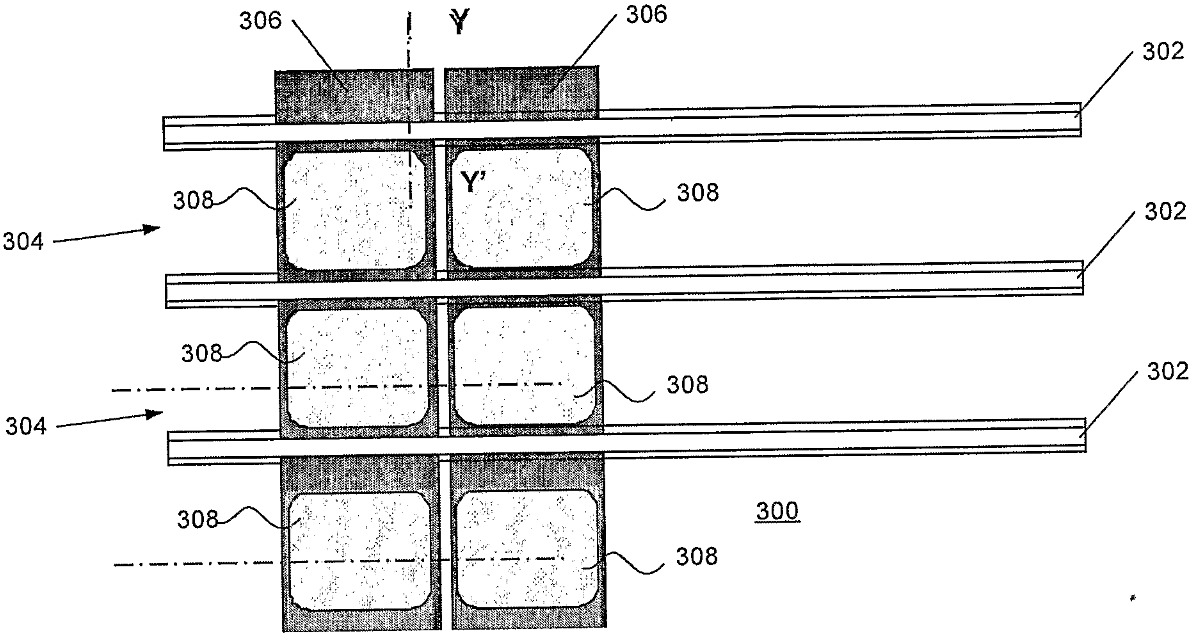


Figure 3a

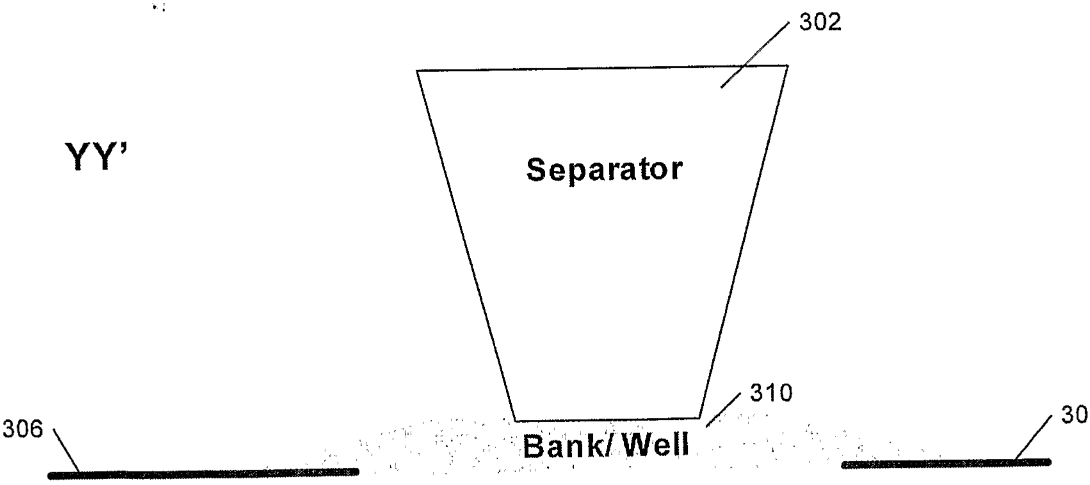


Figure 3b

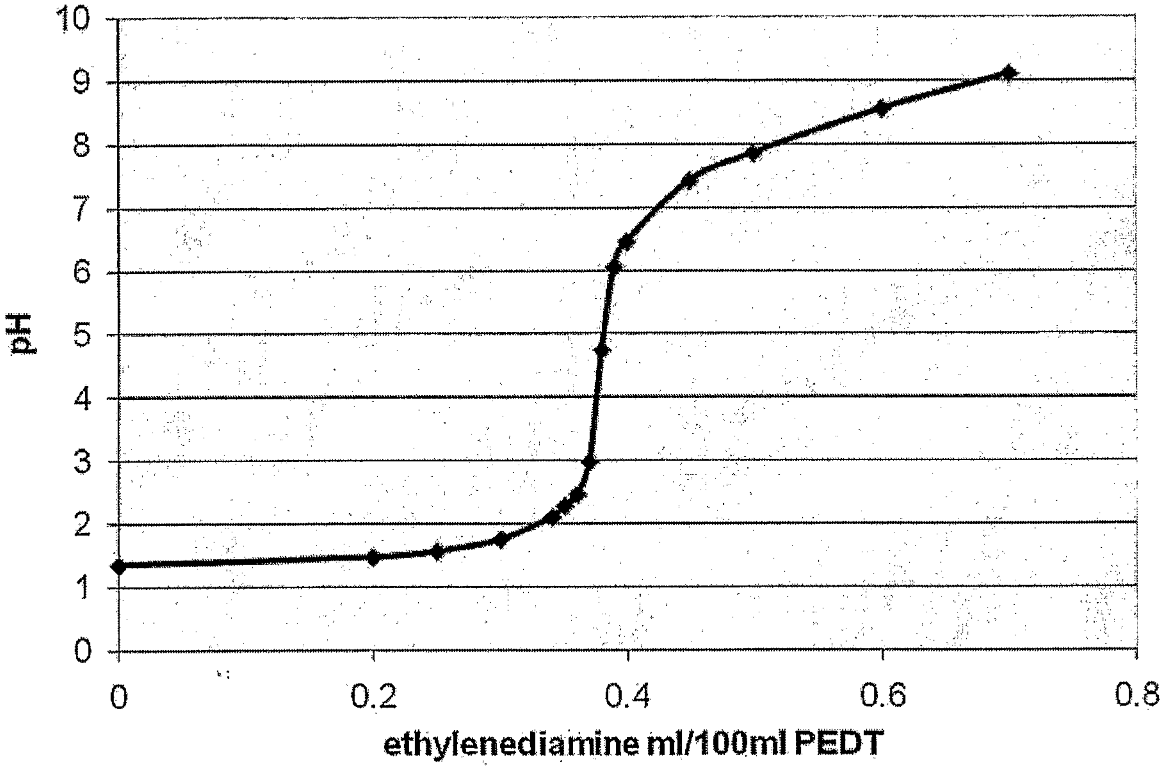


Figure 4