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(54) Title: METHOD FOR PREPARING AN ORGANIC SEMICONDUCTING LAYER

(57) Abstract: A method for preparing an organic electronic device comprising at least an anode layer, a hole transporting interlayer, a light emitting layer, and a cathode layer, the method comprising the steps of:(i) depositing a hole transporting interlayer from a solution comprising a specific molecular architecture; and (ii) annealing said deposited layer by heating to a temperature of 160°C or below and exposing the deposited layer to UV radiation.

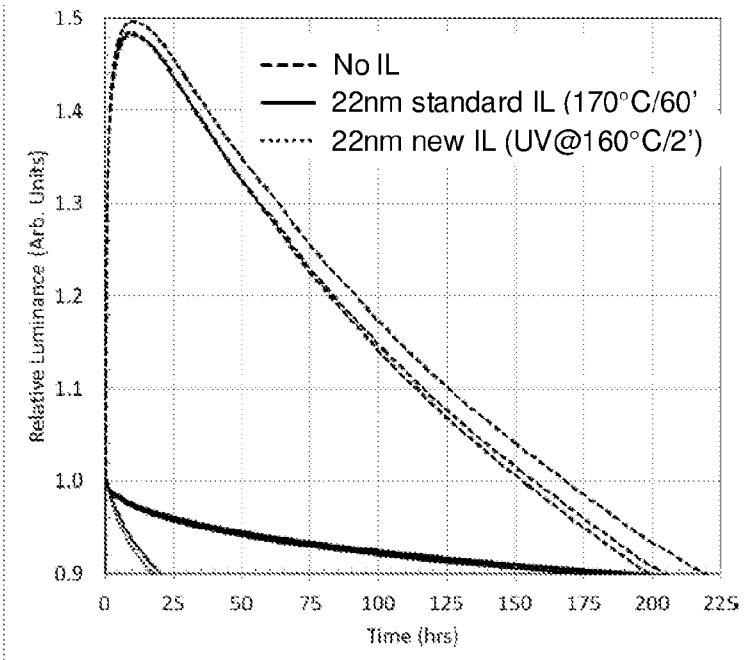

Fig.2

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METHOD FOR PREPARING AN ORGANIC SEMICONDUCTING LAYER

FIELD OF THE INVENTION

The present invention relates to a method for preparing an organic electronic device comprising the formation of a hole transporting interlayer using monomers which comprise polar groups. The invention is also concerned with polymers suitable for the formation of such interlayers as well as with organic electronic devices, in particular organic light emitting diodes, obtainable by the method of the invention.

BACKGROUND

In recent years, organic electronic devices were developed in large scale for various commercial applications, including innovative thin mobile devices, high-resolution displays, and photovoltaic cells. The new generation of devices must fulfil the requirements of being low-cost, lightweight and even flexible. It is also desired that said devices perform functions traditionally accomplished with much more expensive components based on conventional semiconductor materials, such as silicon.

Organic electronic devices are based on small molecules and/or polymers, and include, for example, organic light-emitting devices (OLEDs), organic thin film transistors (OTFT), organic photovoltaic (OPV) devices and thermoelectric (TE) generators.

There has been considerable interest in light emitting organic materials, such as conjugated polymers, for a number of years. Light emitting polymers possess a delocalised pi-electron system along the polymer backbone. The delocalised pi-electron system confers semiconducting properties to the polymer to provide the ability to support positive and negative charge carriers with high mobilities along the polymer chain.

Thin films of these conjugated polymers can be used in the preparation of OLEDs. These devices have numerous advantages over devices prepared using conventional semiconducting materials, including the possibility of wide area displays, low DC working voltages and simplicity of manufacture. Devices of this type are described in, for example, WO-A-90/13148, U.S. Pat. No. 5,512,654 and WO-A-95/06400.

Great efforts have been dedicated to the realization of a full-colour, all plastic screen. The major challenges to achieve this goal are: (1) access to conjugated polymers emitting light of the three basic colours red, green and blue; and (2) the

conjugated polymers must be easy to process and fabricate into full-colour display structures. OLEDs are effective in meeting the first requirement, since manipulation of the emission colour can be achieved by changing the chemical structure of the organic emissive compound.

However, while modulation of the chemical nature of the emissive layer is often relatively easy and inexpensive on the lab scale it can be an expensive and complicated process on the industrial scale. The second requirement of the easy processability and build-up of full colour matrix devices raises the question of how to micro-pattern fine multicolour pixels and how to achieve full-colour emission. Inkjet printing, hybrid inkjet printing technology and spin coating are examples of suitable technologies that can be adopted to apply the polymer solutions in the desired pattern.

At their most basic, organic electroluminescent devices generally comprise an organic light emitting material which is positioned between a hole injecting electrode and an electron injecting electrode. The hole injecting electrode (i.e. the anode) is typically a transparent tin-doped indium oxide (ITO)-coated glass substrate. The material commonly used for the electron injecting electrode (cathode) is a low work function metal such as calcium or aluminium.

Typical device architectures are disclosed in, for example, WO-A-90/13148; U.S. Pat. No. 5,512,654; WO-A-95/06400; R. F. Service, Science 1998, 279, 1135; Wudl et al., Appl. Phys. Lett. 1998, 73, 2561; J. Bharathan, Y. Yang, Appl. Phys. Lett. 1998, 72, 2660; T. R. Hebner, C. C. Wu, D. Marcy, M. L. Lu, J. Sturm, Appl. Phys. Lett. 1998, 72, 519); and WO 99/48160.

The injection of holes from the hole injecting layer such as ITO into the organic emissive layer is controlled by the energy difference between the hole injecting layer work function and the highest occupied molecular orbital (HOMO) of the emissive material, and the chemical interaction at the interface between the hole injecting layer and the emissive material. The deposition of high work function organic materials on the hole injecting layer, such as poly (styrene sulfonate)-doped poly (3,4-ethylene dioxythiophene) (PEDOT/PSS), N,N′-diphenyl-N,N′-(2-naphthyl)-(1,1′-phenyl)-4,4′-diamine (NBP) and N,N′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD), provides hole transporting interlayers (HTILs) which facilitate the hole injection into the light emitting layer, transport holes stably from the hole injecting electrode and obstruct electrons. These layers are effective in increasing the number of holes introduced into the light emitting layer. However, the surface of ITO is not well defined and the chemistry at the interface with these conventional hole transport materials is hard to control.

In the prior art, hole transporting interlayers are known which are based on polymers which do contain olefinic crosslinking components attached to the polymeric backbone which comprise an active double bond, in combination with compounds such as benzocyclobutene derivatives. After depositing a polymer film comprising such units thermal crosslinking treatments are applied, usually at temperatures of about 170°C or more for 60 minutes or more. In case of employing benzocyclobutene derivatives, the cyclobutene rings thereby open to result in the formation of highly reactive dienes which then may react with the neighbouring olefin units in a Diels Alder [4+2] cycloaddition reaction. The obtained crosslinked polymer becomes insoluble, provides the desired interlayer function and allows for further deposition of the remaining layers to form the desired organic electronic device without any detrimental effect on teh interlayer.

However, such crosslinking reactions occur at relatively high temperatures above 170°C, and require long annealing times, typically at least 60 minutes, which makes integration into roll-to-roll fabrication on flexible organic electronic devices on light weight plastic substrates difficult.

In view of the above, there is a need for an improved material suitable for the formation of interlayers, overcoming the scale-up problems associates with the methods known in the art as well as overcoming the temperature restrictions associated with the prior art technologies discussed above. Namely, such new materials should allow the use of solution based technologies for their deposition, while allowing for processes for rendering the material insoluble which do not interfere with the other layers already present. These new materials for the interlayers should however not interfere with the required functionality and allow integration into standard manufacturing processes of organic electronic devices. Preferably the new materials should allow for a solution based process and maintain the satisfactory interlayer function known from the interlayers based on olefinic crosslinking reactions mentioned above. This would allow for a more cost and time efficient production of organic electronic devices. There is also a need for organic electronic devices employing such materials as well as processes for producing organic electronic devices employing such nes interlayer materials.

SUMMARY OF INVENTION

Based on evaluations of known interlayer polymers which do comprise repeating units providing crosslinking functionalities by thermal treatment, i.e. the olefinic moieties and the cyclobutene moieties, the present invention provides a polymer material suitable for interlayer formation which is characterized in that it comprises a repeating unit with polar groups provided on side chains. These polar groups allow for the preparation of polymeric materials, suitable for interlayer preparation, which may be crosslinked by a process requiring lower temperatures, compared with the prior art materials discussed above while still providing teh desired interlayer functionality. The polymer is specified in claim 1.

The present invention also provides a method for preparing an organic electronic device utilizing such interlayer materials, typically comprising at least an anode layer, a hole transporting interlayer, a light emitting layer, and a cathode layer, the method comprising the steps of:

(i) depositing a hole transporting interlayer from a solution comprising repeating units which comprise polar groups on side chains; and

(ii) annealing said deposited layer by heating to a temperature of 160°C or below and exposing the deposited layer to UV radiation.

The present invention also provides an organic electronic device comprising at least an anode layer, a hole transporting interlayer, a light emitting layer, and a cathode layer, said organic electronic device obtainable by the method of the present invention.

Preferred embodiments are set forth in the sub-claims and the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates the external quantum efficiency of a device in accordance with the present invention compared with two control devices representing the prior art.

Figure 2 illustrates the operational lifetime of a device in accordance with the present invention compared with two control devices representing the prior art.

DEFINITIONS

As used herein the term "semiconductor" refers to a compound that can act as either an electrical conductor or insulator depending upon the voltage applied to it. The term "semiconducting layer" refers to a continuous film of material that is semiconducting. The semiconducting layer formed in the present invention comprises a mixture or blend of polymeric and non-polymeric semiconductor. Preferably the polymeric semiconductor forms a matrix in which the non-polymeric semiconductor is dispersed.

As used herein the term "polymeric semiconductor" refers to polymeric compounds comprising repeating units that are semiconductors. Polymers usually have a polydispersity of greater than 1.

As used herein the term "non-polymeric semiconductor" refers to small molecule compounds that are semiconductors. The term includes dendrimeric and oligomeric compounds (e.g. dimers, trimers, tetramers and pentamers) that have a polydispersity of 1. Preferred non-polymeric semiconductors are crystalline.

As used herein the term "lateral distribution" refers to a distribution of non-polymeric semiconductor crystals which extend substantially the entire length of the channel between the source and the drain electrodes as well as over the source and drain electrodes, in a direction parallel to the surface of the electrodes.

As used herein the term "aromatic solvent" refers to solvents comprising one or more compounds that comprise a planar ring that has 4n+2 pi electrons, wherein n is a non-negative integer.

As used herein the term "boiling point" refers to the temperature at which boiling occurs at 1 atmosphere of pressure.

As used herein the term "alkyl" refers to saturated, straight chained, branched or cyclic groups. Alkyl groups may be substituted or unsubstituted.

As used herein the term "alkenyl" refers to unsaturated straight chained, branched or cyclic groups. Alkenyl groups may be substituted or unsubstituted.

As used herein the term "alkoxy" refers to O-alkyl groups, wherein alkyl is as defined above.

As used herein the term "amino" refers to primary (i.e. NH_2), secondary (NHR) and tertiary amino groups (NR_2) wherein R is alkyl as defined above.

As used herein the term "amido" refers to groups of the formulae –NHCOR and –NRCOR wherein each R, which may the same or different, is alkyl as defined above.

As used herein the term "silyl" refers to groups of the formulae –A-SiR'R''R''' wherein A is optionally present and is a saturated or unsaturated group selected from

C_{1-8} alkylene, C_{1-8} alkenylene or C_{1-8} alkynylene and each of R', R'' and R''' is H or alkyl as defined above.

As used herein the term "stannyl" refers to groups of the formulae $-Sn(R')_r$ wherein r is 1, 2 or 3 and each R' is H or alkyl as defined above.

As used herein the term "halogen" encompasses atoms selected from the group consisting of F, Cl, Br and I.

As used herein the term "aryl" includes single and multiple ring compounds, including multiple ring compounds that contain separate or fused rings. As used herein the term "heteroaryl" refers to aryl groups comprising a heteroatom selected from N, O and S. An example of an aryl group is phenyl, i.e. C_6H_5. Phenyl groups may be substituted or unsubstituted. An example of a heteroaryl group is thiophene, i.e. C_4H_4S. It may be substituted or unsubstituted.

If not defined otherwise herein all compositional ratios and % refer to the weight (i.e. define the wt.-% of a given component in a copolymer or blend).

DESCRIPTION OF THE INVENTION

Polymeric materials suitable for interlayer formation, i.e. for the preparation in particular of hole transporting interlayers, typically do comprise repeating units responsible for hole transport, repeating units responsible for proving conjugation and/or conjugation break along the polymer backbone, and repeating units responsible for the post deposition crosslinking, in order to allow insolubilization of the deposited polymer layer. Repeating units known for providing hole transport are aromatic repeating units comprising tri-aryl amine groups. Repeating units proving conjugation and/or conjugation break known to the skilled person are repeating units based on aromatic compounds, preferably fluorine based compounds. Repeating units known in the art for providing functionalities for the post deposition crosslinking reactions are aromatic repeating units comprising cyclobutene units and aromatic units comprising side chains with (preferable terminal) olefinic moieties. While these materials have been used for the preparation of the respective layers in light emitting devices, the functionalities employed for post deposition crosslinking require the above described long treatment times and high temperatures.

The novel polymer usable for the formation of hole transporting interlayers comprises repeating units responsible for hole transport as well as repeating units for providing conjugation and/or conjugation break, but does not comprise conventional repeating units responsible in the prior art for crosslinking of the polymer. These

repeating units therefore do not comprise cycloalkene moieties and/or other olefinic moieties. Instead the novel materials provided by the present invention do comprise repeating units allowing for post deposition crosslinking selected among aromatic repeating units with side chains, preferably alkylene side chains, which do show a terminal polar group. Such polar groups as further defined herein do allow for post deposition crosslinking (by UV irradiation and temperature increase, requiring shorter treatment times and typically also lower treatment temperatures).

The side chains on which the polar group as identified herein is provided are preferably alkylene side chains with 2 to 10, preferably 2 to 6, more preferably 2 to 4 carbon atoms. Preferably the side chain is a non-branched alkylene side chain.

The polar groups used in accordance with the present invention may be selected among the group comprising amino groups, alkyl- or aryl amino groups, di-alkyl or di-aryl amino groups, mixed alkyl aryl amino groups, glycol groups, including polyethylene (PEG) and polypropylene glycol groups, ether and polyether groups, ketone and aldehyde moieties, carboxyl groups as well as carboxylic ester groups. A suitable aryl group to be used for the polar groups as defined herein is in particular a phenyl group, with further examples being aromatic units with two or more aromatic rings, which may be fused or connected in any other manner, such as naphthyl, fluorenyl, etc. Typically these aryl groups do not show any further substituents, although it is possible for these aryl groups to have alkyl substituents, preferably with from 1 to 10, more preferably from 1 to 4 carbon atoms. Any group as identified above comprising an alkyl moiety, preferably comprises an alkyl moiety with from 1 to 10 carbon atoms, preferably 1 to 5 carbon atoms. Examples are methyl, ethyl, propyl, iso-propyl, butyl, tert-butyl and pentyl groups. Examples of such polar groups are di-methyl or di-isopropyl amino groups, carboxylic acid ester groups (-COOR) with the R residue being an alkyl group as exemplified above, as well as ketone groups (-COR) with the R residue again being an alkyl group as illustrated above. Preferred are (terminal) amino, alkyl amino, and di-alkyl amino groups. Such a material may be prepared using standard polymerization techniques known in the art, yielding a polymeric material which, after synthesis and work-up still is soluble, can be deposited using solution based methods while allowing for a post deposition crosslinking requiring lower temperatures and reduced crosslinking processing time.

In a preferred embodiment the polymeric material provided by the present invention comprises repeating units responsible for hole transport, conjugation and/or conjugation break as well as for the crosslinking which are fluorine based repeating units. For such repeating units polymerization technologies are known to the skilled

person, allowing for the synthesis of the novel polymeric materials in a manner readily available to the skilled person, such as polymerization using metal catalysts. Suitable examples for such repeating units and respective monomers are illustrated in the examples.

As identified above, the repeating unit employed for the purpose of providing post deposition crosslinking is an aromatic repeating unit, preferable a fluorine based repeating unit, which does comprise side chains, preferable aliphatic side chains comprising terminal polar groups. The aliphatic side chains typically are alkylene side chains with 2 to 10, preferable 2 to 4 carbon atoms. Preferably each repeating unit comprises at least two of these side chain polar groups. The polar groups preferably are selected among dialkyl amino groups, wherein the alkyl groups have from 1 to 6 carbon atoms, preferable from 1 to 4 carbon atoms. A particularly preferred amino group is the dimethyl amino group.

The amount of a repeating unit as described herein with side chains with (terminal) polar groups may be employed in the polymer in amounts of from 0.5 to 10 %, preferable 1 to 5 %.

Surprisingly it has been found that using such a molecular architecture (i.e. a polymer comprising repeating units responsible for hole transport, repeating units responsible for conjugation and/or conjugation break and repeating units as defined herein for providing the functionality of post deposition crosslinking, but nor comprising conventional olefin and cyclobutene based repeating units) allows the formation of a polymeric material which may be processed from solution and allows the formation of an insoluble layer (with hole transport functionality) requiring less detrimental crosslinking reactions. Namely, the polymeric material as defined herein may be crosslinked by a combination of a temperature treatment at temperatures not exceeding 170°C with UV irradiation. It has been found that crosslinking may be achieved with treatment times as short as 5 to 10 minutes, so that compared to the prior art conditions (thermal treatment of at least 170°C for 60 minutes or more) faster processing is achieved at lower overall temperatures.

By using the molecular architecture as outlined above it is furthermore possible to integrate a hole transport interlayer formation into the existing processes for the preparation of organic electronic devices, yielding devices with the desired functionally while being less demanding in relation to temperature induces problems due to the lower crosslinking temperatures and faster processing times enabled by the present invention.

In accordance therewith the present invention also provides the following.

The present invention provides a method for preparing an organic electronic device comprising at least an anode layer, a hole transporting interlayer, a light emitting layer, and a cathode layer, the method comprising the steps of:

(i) depositing a hole transporting interlayer from a solution comprising a polymeric material as described above; and

(ii) annealing said deposited layer by heating to a temperature of 160°C or below and exposing the deposited layer to UV radiation.

Advantageously, with the method of the present invention, a hole transporting interlayer of an organic electronic device is formed very fast with low annealing temperatures while allowing for similar initial device performance as compared to devices comprising standard interlayers known in the art.

The annealing step of the deposited hole transporting interlayer in accordance with the present invention is advantageously carried out at a temperature of 160°C or below, preferably at a temperature of 150°C or below, and more preferably at a temperature of 140°C or below. In order to provide complete annealing, the annealing temperature is preferably at least 100°C, more preferably at least 120°C. For comparison, in the prior art, typical annealing temperatures are well above 170°C and are generally around 200°C.

The annealing step of the deposited hole transporting interlayer in accordance with the present invention is preferably carried out for a time of less than 30 minutes, preferably 5 minutes or less, more preferably for a time of 4 minutes or less, and even more preferably for a time of 3 minutes or less. In order to provide complete annealing, the annealing time is preferably at least 1 minute, more preferably at least 2 minutes. For comparison, in the prior art, typical annealing times are typically 60 minutes and may at times be even longer.

Due to the annealing step of the hole transporting interlayer being carried out at comparatively low temperatures and for a short amount of time in the presence of UV radiation, integration into roll-to-roll fabrication on flexible organic electronic devices on light weight plastic substrates is achieved in a simple and cost effective manner.

The solution for deposition of the hole transporting interlayer comprises a polymeric material as outlined above in a suitable solvent. Suitable solvents are known to the skilled person.

Since the formation of the hole transporting interlayer is based on the presence of repeating units which comprise polar groups, the annealing step of the method of the present invention can be carried out at lower temperatures and for shorter time periods

in the presence of UV radiation. It has been found that a conventional annealing step, i.e. without UV irradiation does not provide the required insolubilisation. The repeating units comprising the above polar groups also result in the advantage of the film formation not requiring any kind of crosslinking agent or crosslinking component, said crosslinking agent generally being required in the art and demanding higher annealing temperatures and annealing times. Thus, the solution for the deposition of the hole transporting layer does not comprise any crosslinking components which comprise non-aromatic double bonds. The solution for the deposition of the hole transporting layer does also not comprise any other components such as benzocyclobutene derivatives typically employed for the prior art crosslinking reactions.

In a further embodiment, the present invention provides an organic electronic device comprising at least an anode layer, a hole transporting interlayer, a light emitting layer, and a cathode layer, said organic electronic device obtainable by the above method. Preferably, the organic electronic device is an organic light emitting diode.

A typical OLED geometry in accordance with the present invention includes

- a transparent conductive oxide anode (for example an ITO anode),
- optionally a hole injection layer,
- a hole transporting interlayer,
- a light emitting layer,
- a cathode.

Efficient hole injection into the light emitting layer requires the band offset between the hole transporting interlayer and the light emitting to be small. As a consequence of this requirement, in the case of deep-HOMO materials employed in the light emitting layer, the hole transporting interlayer also needs to display a high ionisation potential (i.e. a deep-HOMO level). In order to enable hole injection from the anode into deep-HOMO hole transporting interlayer materials, the work function (WF) of the anode needs to be increased from around about 5.0 eV for native ITO to match the HOMO level in the hole transporting interlayer material. In order to match the WF of the ITO anode to the HOMO level in the hole transporting interlayer material, the surface of the ITO anode may preferably be covered with a thin layer of a p-doped conjugated polymer.

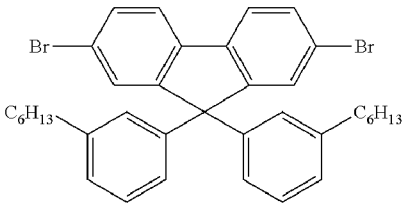
HOMO and LUMO energy level values may generally be calculated by any method known to the skilled person in order to determine the energy levels required. A suitable measurement method is photoelectron spectroscopy using AC-2 apparatus available from RK Instruments Inc. Measurements may alternatively be made using

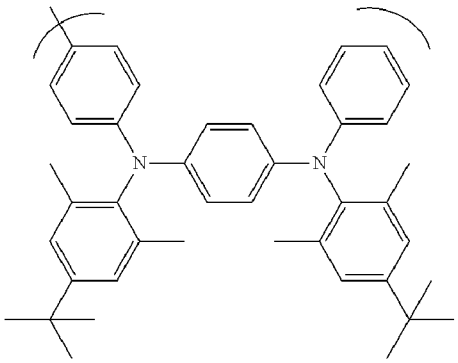
ultraviolet photoelectron spectroscopy measurements performed in a vacuum system, by irradiating the sample surface with ultraviolet light of a fixed wavelength. This measurement results in plots of the Photoelectron Intensity as a function of Kinetic Energy, which are 1:1-projections of the Density-Of-State in the sample substrate. HOMO levels of various organic compounds can also be found in, for example, Dekker, Handbook of Photophysics, 2nd Edition, 1993.

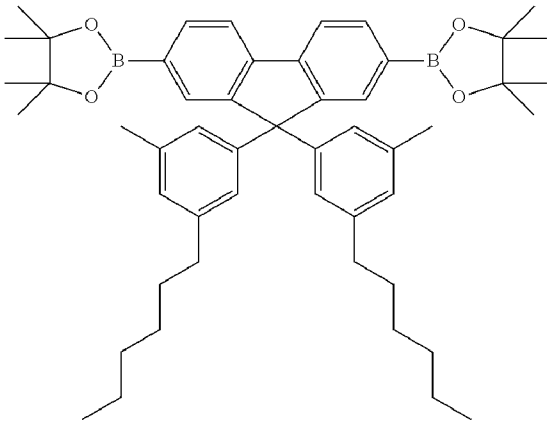
In a more preferred embodiment, the method of the present invention comprises the following further steps:

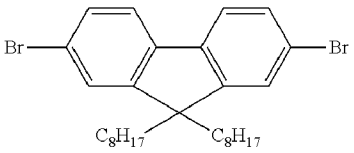
- depositing a solution of a light emitting polymer on the top of the hole transporting interlayer;
- drying said layer of light emitting polymer to give a light emitting polymer layer; and
- thermally evaporating a material such as a low work function metal onto the light emitting polymer layer formed in the afore-mentioned step to form a cathode, thus giving the desired organic light emitting device;

Preferably, the light emitting polymer is formed from the following monomers:







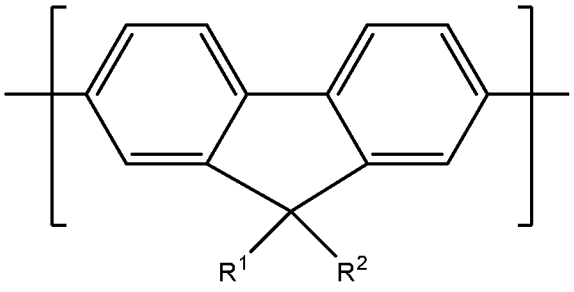


Also preferred is the low work function metal forming the cathode being a bi-layer or tri-layer structure of metals or compounds selected from sodium fluoride, aluminium, calcium and silver.

Deposition of the hole transporting interlayer is generally carried out from a solution. Any conventional solution-based processing method may be used. Representative examples of solution-based processing methods include spin coating, dip coating, slot die coating, doctor blade coating and ink-jet printing. In preferred methods of the invention, however, depositing is carried out by spin coating. The parameters used for spin coating the semiconductor film such as spin coating speed,

acceleration and time are selected on the basis of the target thickness for the semiconducting layer. Typical target thicknesses are in the range of 20 to 60 nm. Preferably the spin coating is carried out in a single phase spin. Preferably the spin speed is 300 to 1000 rpm, more preferably 400 to 900 rpm and still more preferably 500 to 750 rpm. Preferably the spin time is 5 to 180 seconds, more preferably 10 to 60 seconds and still more preferably 20 to 40 seconds. Preferably the acceleration time from rest is less than 3 seconds, preferably less than 2 seconds and still more preferably less than 1 second. Any conventional spin coating apparatus may be used. The apparatus is used in a conventional manner.

Preferably the material for the light emitting layer is a polymer, more preferably a conjugated polymer. Preferably the polymer is a polymeric semiconductor and comprises a repeat unit of formula (IIIa)



(IIIa)

wherein R^1 and R^2 are the same or different and each is selected from the group consisting of hydrogen, an alkyl group having from 1 to 16 carbon atoms, an aryl group having from 5 to 14 carbon atoms and a 5- to 7-membered heteroaryl group containing from 1 to 3 sulfur atoms, oxygen atoms and/or nitrogen atoms, said aryl group or heteroaryl group being unsubstituted or substituted with one or more substituents selected from an alkyl group having from 1 to 16 carbon atoms and an alkoxy group having from 1 to 16 carbon atoms.

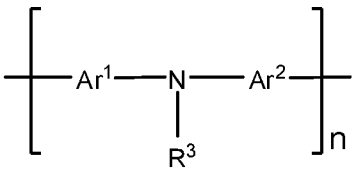
Examples of alkyl groups include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl or decyl. Examples of aryl groups include phenyl, indenyl, naphthyl, phenanthrenyl and anthracenyl groups. Examples of 5- to 7- membered heteroaryl groups include furyl, thienyl, pyrrolyl, azepinyl, pyrazolyl, imidazolyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, 1,2,3-oxadiazolyl, triazolyl, tetrazolyl, thiadiazolyl, pyranyl, pyridyl, pyridazinyl, pyrimidinyl and pyrazinyl groups. Examples of alkoxy groups include methoxy, ethoxy, propoxy, isopropoxy and butoxy.

In preferred polymeric semiconductors R^1 and R^2 are the same.

Preferred polymers comprise a repeat unit of formula (IIIa) wherein, wherein R^1 and R^2 are each selected from the group consisting of hydrogen, an alkyl group having from 1 to 12 carbon atoms and a phenyl group, said phenyl group being unsubstituted

or substituted with one or more substituents selected from an alkyl group having from 1 to 12 carbon atoms and an alkoxy group having from 1 to 12 carbon atoms. Still more preferred polymeric semiconductors comprise a repeat unit of formula (IIIa) wherein R^1 and R^2 are each selected from the group consisting of an alkyl group having from 4 to 12 carbon atoms and a phenyl group, said phenyl group being unsubstituted or substituted with one or more substituents selected from an alkyl group having from 4 to 8 carbon atoms and an alkoxy group having from 4 to 8 carbon atoms. Yet further preferred polymeric semiconductors comprise a repeat unit of formula (IIIa) wherein R^1 and R^2 are each selected from the group consisting of an alkyl group having from 4 to 12 carbon atoms, preferably butyl, pentyl, hexyl, heptyl, octyl, nonyl or decyl, particularly octyl, e.g. n-ocytyl.

Further preferred polymers comprise a repeat unit of formula (IIIb):



(IIIb)

wherein Ar^1 and Ar^2 are the same or different and each is selected from an aryl group having from 5 to 14 carbon atoms and a 5- to 7-membered heteroaryl group containing from 1 to 3 sulfur atoms, oxygen atoms and/or nitrogen atoms, said aryl group or heteroaryl group being unsubstituted or substituted with one or more substituents selected from an alkyl group having from 1 to 16 carbon atoms and an alkoxy group having from 1 to 16 carbon atoms;

R^3 is an alkyl group having from 1 to 8 carbon atoms or a phenyl group which may be unsubstituted or substituted with an alkyl group having from 1 to 8 carbon atoms;

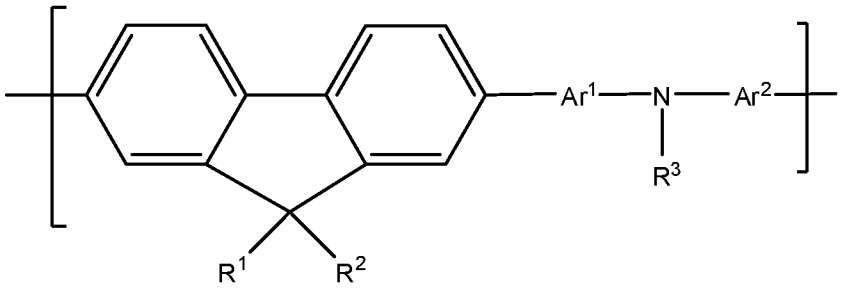
and n is an integer greater than or equal to 1, preferably 1 or 2.

Examples of aryl groups include phenyl, indenyl, naphthyl, phenanthrenyl and anthracenyl groups. Examples of 5- to 7- membered heteroaryl groups include furyl, thienyl, pyrrolyl, azepinyl, pyrazolyl, imidazolyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, 1,2,3-oxadiazolyl, triazolyl, tetrazolyl, thiadiazolyl, pyranyl, pyridyl, pyridazinyl, pyrimidinyl and pyrazinyl groups. Examples of alkyl groups include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl or decyl. Examples of alkoxy groups include methoxy, ethoxy, propoxy, isopropoxy and butoxy.

In preferred polymers comprising a repeat unit of formula (IIIb) Ar^1 and Ar^2 are the same. Particularly preferably each of Ar^1 and Ar^2 is a phenyl group, preferably an unsubstituted phenyl group.

In further preferred polymers comprising a repeat unit of formula (IIIb) R^3 is an alkyl group having from 1 to 8 carbon atoms or a phenyl group which may be unsubstituted or substituted with an alkyl group having from 1 to 8 carbon atoms. Particularly preferably R^3 is alkyl group, especially an alkyl group comprising 2 to 5 carbon atoms, e.g. ethyl, propyl, butyl, pentyl. Still more preferably R^3 is a phenyl group substituted with an alkyl group having from 1 to 8 carbon atoms, e. g. ethyl, propyl, butyl, pentyl.

Still more preferably the polymer comprises a repeat unit of formula (IIIa) and a repeat unit of formula (IIIb). Preferably the ratio of repeat unit of formula (I) to formula (II) is in the range 3:1 to 1:3, more preferably 2:1 to 1:2 and still more preferably about 1:1. Particularly preferably the polymeric semiconductor comprises a repeat unit of formula (IIIc):



(IIIc)

wherein R^1, R^2, Ar^1, Ar^2 and R^3 are as defined above in relation to formulae (IIIa) and (IIIb).

Yet more preferably the polymer is TFB [9,9'-dioctylfluorene-co-N-(4-butylphenyl)-diphenylamine]n, wherein n is greater than 100.

A non-polymeric material for the light emitting layer may be any small molecule semiconductor suitable for the purpose, e.g. those known to the skilled person skilled as described in the prior such as those small molecule semiconductors described in WO2010/061176. Suitable non-polymeric materials are commercially available. Typical examples include pentacene derivatives and thiophene derivatives.

Advantageously, with the method of the present invention, hole transporting interlayer using monomers which comprise polar groups can be formed for organic electronic devices. The polar groups are attached to the monomers via flexible spacers and allow for the omission of crosslinking agents with active double bonds or

other compounds with similar purpose such as benzocyclobutene derivatives. The improved process is solution-based, overcoming the scale-up problems associates with the methods known in the art so far, and allows for a more cost and time efficient production of organic electronic devices.

In the following, the invention will be further illustrated on the basis of examples.

EXAMPLES

Example 1

Performances were compared for spin-coated Blue OLED pixels (1) without a hole transporting interlayer, (2) with 22 nm of a standard thermally crosslinked hole transporting interlayer (60 min at 170°C), and (3) with 22 nm of a hole transporting interlayer according to the invention, which was crosslinked in a UV- assisted annealing step for 2 minutes (UVGL-58 Lamp; 254nm, 6W).

The following OLED device structures were used:

Standard blue-emitting devices fabricated by spin-coating in a glove box, with:

ITO anode/ 35 nm hole injection layer (HIL) / x nm IL / 65nm LEP (blue Light Emitting Polymer) / standard NaF-Al-Ag cathode

x nm IL = no IL; 22 nm interlayer polymer 3 (170°C / 60 min); and 22 nm interlayer polymer 4 (UV at 160°C / 2 min).

The interlayers used in the experiment were formed as follows:

1) Standard interlayer polymer 3: Conjugation-broken IL

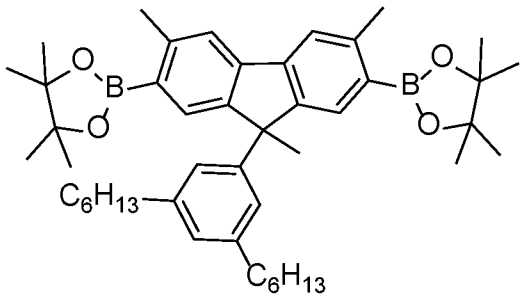
50% monomer 1	40% monomer 2 + <u>5% monomer 3 + 5% monomer 4</u>

UV-crosslinked interlayer polymer 4: Conjugated IL

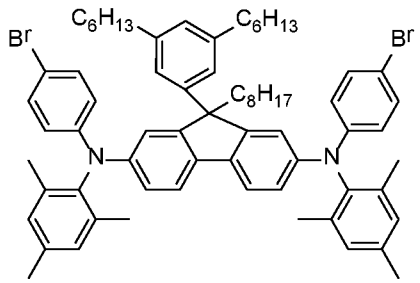
50% monomer 5	17.5% monomer 5 + 30% monomer 6 + 2.5% monomer 7

Monomers used in the ILs:

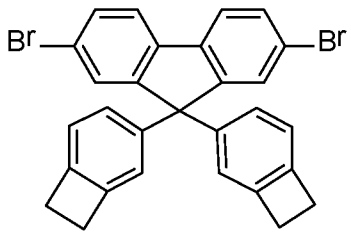
- monomer 1:



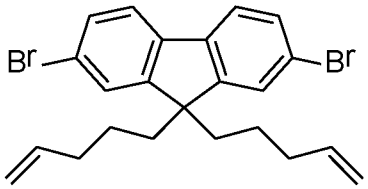
- monomer 2: Amine Hole Transport Unit



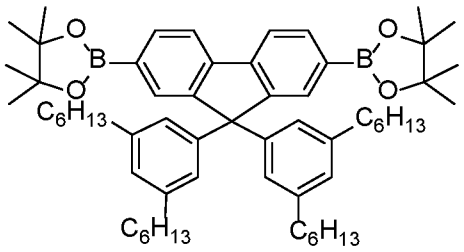
- monomer 3: BCB component



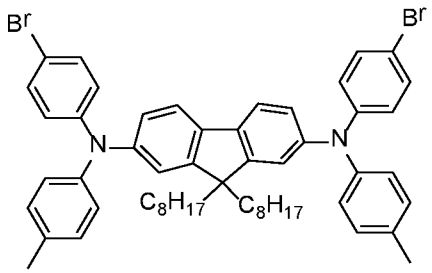
- monomer 4: Olefin component



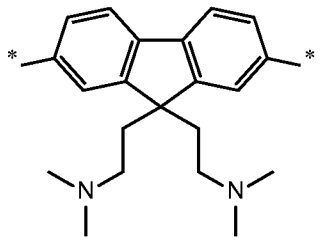
- monomer 5: Fluorene backbone monomer



- monomer 6: Amine Hole Transport Unit



- monomer 7: Fluorene with Dimethylamino groups



- External Quantum Efficiency

As illustrated in Figure 1, the control devices with 22nm of standard interlayer polymer 3 hole transporting interlayer (crosslinked at 170°C/60 min) display a maximum averaged EQE of just below 10%, whereas the averaged maximum EQE of blue devices without a hole transporting interlayer is very low, at around 1%.

The external quantum efficiency is the ratio of electrons collected from a device to the number of photons incident on the device. Absolute values for the external quantum efficiency were measured with a calibrated integrating sphere.

By contrast, introducing the new interlayer polymer 4 (crosslinked for 2 minutes under UV-illumination at 160°C) in accordance with the present invention results in a maximum averaged EQE of around 7%.

The experiment shows that OLEDs produced with a fast-cured hole transporting interlayer in accordance with the present invention display much better EQEs than hole transporting interlayer free devices.

- Operational Lifetime

As illustrated in Figure 2, lifetime traces for hole transporting interlayer free devices are shown and compared to devices with standard interlayer polymer 3 and hole transporting interlayers in accordance with the present invention, all normalised at t = 6 min. The control devices with 22nm of standard interlayer polymer 3 (crosslinked at 170°C/60 min) display T90% lifetimes of approx. 180 hrs, when driven from 500Cd/m^2 initial luminance, with a standard decay shape. In stark contrast to this, the hole transporting interlayer free devices display massive “bright waving”, i.e. a fast initial luminance increase during the first hours of lifetime testing. Once the maximum of the bright wave is reached, the rate of decay then becomes much faster than in the control devices, resulting in T90% lifetimes of 258.6 hrs.

In addition, due to their very low EQEs, the hole transporting interlayer free devices in the above experiment were driven from just 100Cd/m^2 initial luminance. Assuming a quadratic dependence of the lifetime on initial luminance, T90% lifetimes of just 10.3 hrs would be expected for the hypothetical case of driving the hole transporting interlayer free devices from 500Cd/m^2 initial luminance as for the control devices.

The hole transporting interlayer in accordance with the present invention (crosslinked for 2 minutes under UV-illumination at 160°C) results in T90% lifetimes of approximately 19.5 hrs, when driven from 1000Cd/m^2 initial luminance. Again assuming a quadratic dependence of the lifetime on initial luminance, T90% lifetimes of

around 78 hrs would be expected for the hypothetical case of driving devices with hole transporting interlayers in accordance with the present invention from 500Cd/m^2 initial luminance as for the control devices.

	T90% (h)	Initial Luminance L_0 (Cd/m2)	Luminance-correction: T90% (h) x $[L_0/L_0(Contr)]^2$	**Initial luminance-corrected T90% as % of control**
No IL	**207.0**	100.0	8.3	**4.5**
22nm standard IL (170°C/60') [control]	**185.0**	500.0	185.0	**100.0**
22nm new IL (UV@160°C/2')	**19.5**	1000.0	78.0	**42.2**

This experiment shows that for the same initial luminance conditions, OLEDs with fast-cured IL600 are expected to display much better lifetimes than IL-free devices.

The present invention provides an improved process which is solution-based, overcoming the scale-up problems associates with the methods known in the art so far, and allows for a more cost and time efficient production of organic electronic device being formed very fast with low annealing temperatures while allowing for similar initial device performance as compared to devices comprising standard interlayers known in the art.

CLAIMS

1. A polymer usable for the formation of hole transporting interlayers comprising repeating units responsible for hole transport as well as repeating units for providing conjugation and/or conjugation break, and comprising repeating units allowing for post deposition crosslinking selected among aromatic repeating units with side chains, preferably alkylene side chains, which side chains have a terminal polar group selected from the group consisting of: amino groups, alkyl- or aryl amino groups, di-alkyl or di-aryl amino groups, mixed alkyl aryl amino groups, polyether groups, ketone and aldehyde moieties, and carboxyl groups.

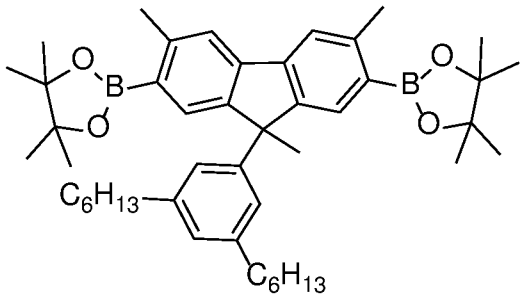
2. A polymer according to claim 1, not comprising aromatic repeating units comprising cyclobutene units and aromatic units comprising side chains with (preferable terminal) olefinic moieties.

3. A polymer according to claim 1 or claim 2, wherein the repeating units responsible for hole transport as well as repeating units for providing conjugation and/or conjugation break are fluorene based repeating units.

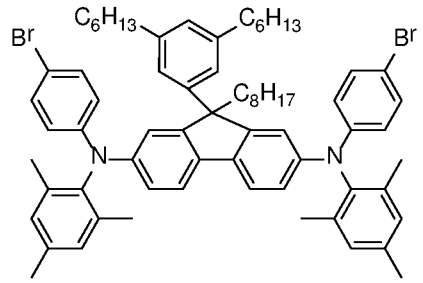
4. A polymer according to any one of claims 1 to 3, wherein the repeating units allowing for post deposition crosslinking are fluorene based repeating units.

5. Polymer according to any one of claims 1 to 4, comprising repeating units based upon any one of the following structures:

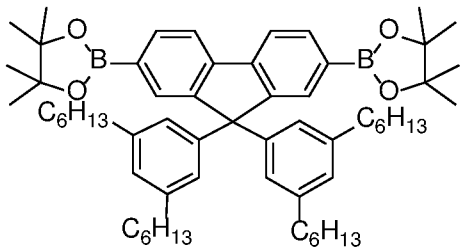
Fluorene backbone (conjugation break)



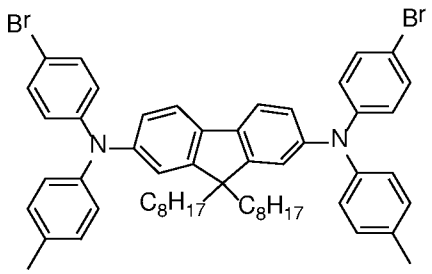
Amine Hole Transport Unit



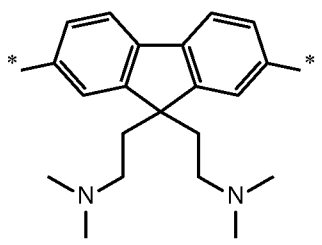
Fluorene backbone monomer (conjugated)



Amine Hole Transport Unit



Fluorene with Dimethylamino groups



6. A method for preparing an organic electronic device comprising at least an anode layer, a hole transporting interlayer, a light emitting layer, and a cathode layer, the method comprising the steps of:

(i) depositing a hole transporting interlayer from a solution comprising a polymeric material as defined in any of the preceding claims; and

(ii) annealing said deposited layer by heating to a temperature of 160°C or below and exposing the deposited layer to UV radiation.

7. The method of claim 6, wherein the annealing step of the deposited layer is carried out at a temperature of 150°C or below.

8. The method of claim 6 or 7, wherein the annealing step is carried out for a time period of 5 minutes or less.

9. The method of any of claims 6 to 8, wherein the annealing step is carried out for a time period of 3 minutes or less.

10. An organic electronic device comprising at least an anode layer, a hole transporting layer, a light emitting layer, and a cathode layer, the hole transport layer consisting of or including a polymeric material according to any one of claim 1 to 5.

11. The organic electronic device of claim 10, wherein said organic electronic device is an organic light emitting diode.

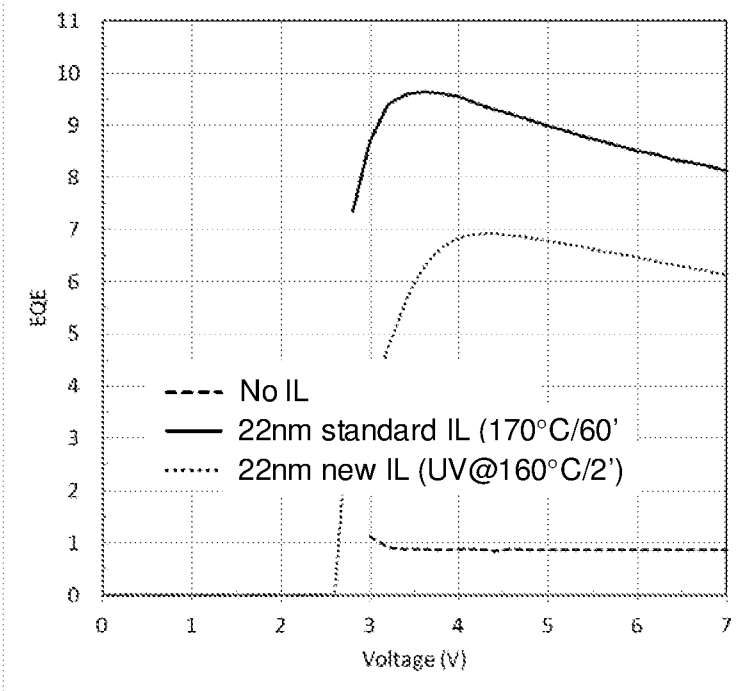

EQE
Voltage (V)
No IL
22nm standard IL (170°C/60'
22nm new IL (UV@160°C/2')

Fig.1

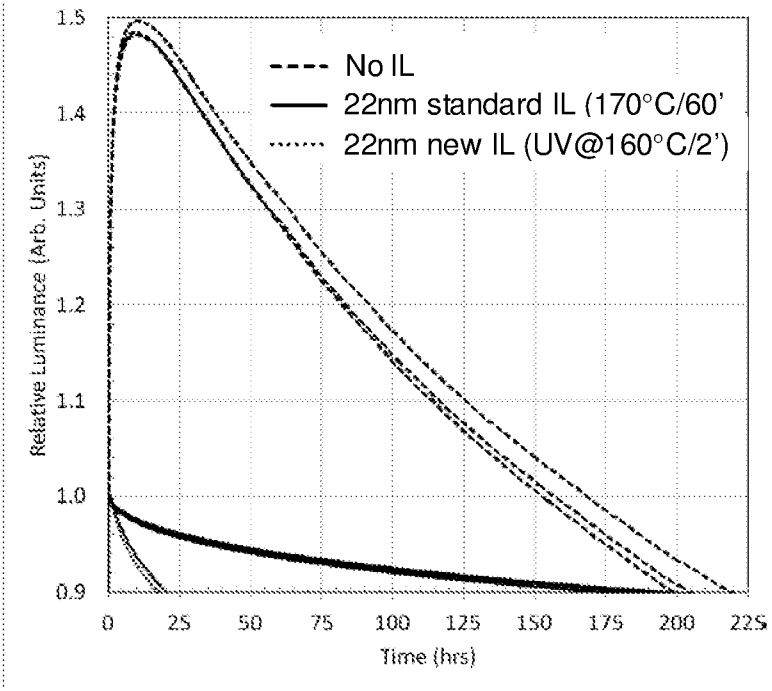

Relative Luminance (Arb. Units)
Time (hrs)
No IL
22nm standard IL (170°C/60'
22nm new IL (UV@160°C/2')

Fig.2

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2016/051848

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G61/00 H01L51/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G 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	WO 2010/079330 A1 (CAMBRIDGE DISPLAY TECH [GB]; GODDARD SIMON [GB]; WALLACE PAUL [GB]; TE) 15 July 2010 (2010-07-15) examples page 18 f.; Table 1	1-11
X	WO 2014/102543 A2 (CAMBRIDGE DISPLAY TECH [GB]; SUMITOMO CHEMICAL CO [JP]) 3 July 2014 (2014-07-03) claims 1, 5, 7, 9, 18; examples page 26 f.	1-11
X	WO 2013/013754 A1 (MERCK PATENT GMBH [DE]; PAN JUNYOU [DE]; SCHULTE NIELS [DE]) 31 January 2013 (2013-01-31) working examples page 71 f.	1-11

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"E" earlier application or patent but published on or after the international filing date

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

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 September 2016	13/10/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Kositza, Matthias

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2016/051848

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/049689 A2 (DOW GLOBAL TECHNOLOGIES INC [US]; INBASEKARAN MICHAEL [US]; YU WANGLIN) 2 June 2005 (2005-06-02) claims 1-12; examples 1 and 2	1-11
X	WO 2005/052027 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; GAYNOR SCOTT [US]; INBASEKARAN MICHA) 9 June 2005 (2005-06-09) claims 9 and 11; examples 1-6	1-11

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2016/051848

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010079330 A1	15-07-2010	GB 2466842 A	14-07-2010
		TW 201033300 A	16-09-2010
		WO 2010079330 A1	15-07-2010
WO 2014102543 A2	03-07-2014	CN 104870414 A	26-08-2015
		EP 2935182 A2	28-10-2015
		JP 2016503087 A	01-02-2016
		KR 20150100866 A	02-09-2015
		US 2015333262 A1	19-11-2015
		WO 2014102543 A2	03-07-2014
WO 2013013754 A1	31-01-2013	EP 2737553 A1	04-06-2014
		JP 2014527290 A	09-10-2014
		US 2014175420 A1	26-06-2014
		WO 2013013754 A1	31-01-2013
WO 2005049689 A2	02-06-2005	CN 1882632 A	20-12-2006
		CN 102585172 A	18-07-2012
		DE 112004002221 T5	18-01-2007
		GB 2424896 A	11-10-2006
		JP 4714153 B2	29-06-2011
		JP 5398955 B2	29-01-2014
		JP 2007514654 A	07-06-2007
		JP 2007528916 A	18-10-2007
		JP 2013014770 A	24-01-2013
		KR 20060127853 A	13-12-2006
		KR 20120001810 A	04-01-2012
		TW I364447 B	21-05-2012
		TW I382078 B	11-01-2013
		TW 201229002 A	16-07-2012
		US 2007063191 A1	22-03-2007
		US 2007102695 A1	10-05-2007
		US 2011105711 A1	05-05-2011
		WO 2005049548 A1	02-06-2005
		WO 2005049689 A2	02-06-2005
WO 2005052027 A1	09-06-2005	CN 1886443 A	27-12-2006
		CN 102796260 A	28-11-2012
		DE 112004002204 T5	26-10-2006
		GB 2424897 A	11-10-2006
		JP 5209207 B2	12-06-2013
		JP 5209763 B2	12-06-2013
		JP 2007511636 A	10-05-2007
		JP 2011251984 A	15-12-2011
		KR 20060100415 A	20-09-2006
		KR 20110121729 A	08-11-2011
		KR 20120101163 A	12-09-2012
		TW 201219350 A	16-05-2012
		US 2007096082 A1	03-05-2007
		US 2013085258 A1	04-04-2013
		WO 2005052027 A1	09-06-2005