Composition comprising a fluorescent light-emitting material and a triplet-accepting unit comprising an optionally substituted compound of formula (I): The composition may be used in an organic light-emitting device; the optionally substituted compound of formula (I) may be blended with or attached to the fluorescent light emitting material; and the composition may be deposited by solution deposition.
FIG. 1

\[ S_{IE} \rightarrow T_{IE} \rightarrow T_{IA} \rightarrow S_{OE} \]

Quench

FIG. 2

\[ S_{IE} \rightarrow S_{BE} \rightarrow T_{IE} \rightarrow T_{IA} + T_{IA} \]

\[ S_{OE} \rightarrow S_{OA} \rightarrow S_{OA} \]
FIG. 3

FIG. 4
FIG. 7

![Luminance vs Time Graph](image)

*Example vs Comparative Example*

FIG. 8

![Current Density vs Voltage Graph](image)

*Comparative Example vs Example*
**FIG. 9**

**EQE vs Voltage**

- **Example**
- **Comparative Example**

Voltage (V)

EQE
ORGANIC LIGHT-EMITTING COMPOSITION COMPRISING ANTHRANTHENE DERIVATIVES AND DEVICE AND METHOD USING THE SAME

[0001] This application claims priority from UK patent application no. 1010741.5 filed on Jun. 25, 2010, UK patent application no. 1010742.3 filed on Jun. 25, 2010, UK patent application no. 1010745.6 filed on Jun. 25, 2010, UK patent application no. 1010743.1 filed on Jun. 25, 2010 and UK patent application no. 1101642.5 filed on Jun. 31, 2011. The contents of each aforementioned priority-forming application are incorporated herein in their entirety by reference.

SUMMARY OF THE INVENTION

[0002] This invention relates to organic light emitting compositions, organic light-emitting devices comprising the same, and methods of making said devices.

BACKGROUND OF THE INVENTION

[0003] Electronic devices comprising active organic materials are attracting increasing attention for use in devices such as organic light emitting diodes, organic photovoltaic devices, organic photosensors, organic transistors and memory array devices. Devices comprising organic materials offer benefits such as low weight, low power consumption and flexibility. Moreover, use of soluble organic materials allows use of solution processing in device manufacture, for example inkjet printing or spin-coating.

[0004] 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 is provided over the first electrode. Finally, a cathode is provided over the layer of electroluminescent organic material. Charge transporting, charge injecting or charge blocking layers may be provided between the anode and the electroluminescent layer and/or between the cathode and the electroluminescent layer.

[0005] In operation, holes are injected into the device through the anode and electrons are injected into the device through the cathode. The holes and electrons combine in the organic electroluminescent layer to form an exciton which then undergoes radiative decay to give light.

[0006] In WO98/13148 the organic light-emissive material is a conjugated polymer such as poly(phenylenevinylene). In U.S. Pat. No. 4,539,507 the organic light-emissive material is of the class known as small molecule materials, such as tris-(8-hydroxyquinoline) aluminium ("Alq3"). These materials are used to emit light by radiative decay of singlet excitons (fluorescence) however spin statistics dictate that up to 75% of excitons are triplet excitons which undergo non-radiative decay, i.e. quantum efficiency may be as low as 25% for fluorescent OLEDs—see, for example, Chem. Phys. Lett., 1993, 210, 61, Nature (London), 2001, 409, 494, Synth. Met., 2002, 125, 55 and references therein.

[0007] It has been postulated that the presence of triplet excitons, which may have relatively long-lived triplet excited states, can be detrimental to OLED lifetime as a result of triplet-triplet or triplet-singlet interactions ("lifetime" as used herein in the context of OLED lifetime means the length of time taken for the luminescence of the OLED at constant current to fall by 50% from an initial luminance value, and "lifetime" as used herein in the context of lifetime of a triplet excited state means the half-life of a triplet exciton). US 2007/145886 discloses an OLED comprising a triplet-quenching material to prevent or reduce triplet-triplet or triplet-singlet interactions.


[0009] OLEDs have great potential for display and lighting applications. However, there remains a need to improve performance of these devices.

SUMMARY OF THE INVENTION

[0010] In a first aspect, the invention provides a composition comprising a fluorescent light-emitting material and a triplet-accepting unit comprising an optionally substituted compound of formula (I):

![Formula (I)](image)

[0011] Optionally, the fluorescent light-emitting material is a polymer comprising fluorescent light-emitting repeat units.

[0012] Optionally, the compound of formula (I) is substituted with one or more substituents selected from the group consisting of:

- alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, substituted N, C=O and —COO— and wherein one or more H atoms may be replaced with F; or

- aryl, heteroaryl, aryalkyl or heteroaryalkyl, each of which may optionally be substituted with halogen, cyano, or alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, substituted N, C=O and —COO—.

[0015] Optionally, the compound of formula (I) comprises formula (Ia):

![Formula (Ia)](image)

wherein each R3 is independently selected from H and a substituent selected from the group of claim 3, and at least one R2 is not H.

[0016] Optionally, a substituent R1 that is not H is present in the 2 and/or 8- positions of the compound of formula (I).
 Optionally, the composition comprises a physical mixture of the light-emitting material and the compound of formula (I).

 Optionally, the triplet-accepting unit is chemically bound to the fluorescent light-emitting material.

 Optionally, the triplet-accepting unit is bound in the main chain of the polymer or bound as a side group or end group of the polymer.

 Optionally, the triplet accepting unit is bound in the main chain of the polymer through its 1- and 8-positions or is bound as a side-group or end-group of the polymer through its 2- or 8-position.

 Optionally, the light-emitting material comprises an amine.

 Optionally, the light-emitting material is a polymer comprising amine repeat units.

 Optionally, the triplet-accepting unit is present in an amount of at least 0.1 mol % relative to the light-emitting material.

 In a second aspect the invention provides a solution comprising a solvent and a composition according to any preceding claim.

 In a third aspect the invention provides an organic light-emitting device comprising an anode, a cathode and a light-emitting layer between the anode and cathode, wherein the light-emitting layer comprises a composition according to the first aspect.

 In a fourth aspect the invention provides a method of forming an organic light-emitting device according to the third aspect comprising the steps of depositing the solution according to the second aspect and evaporating the solvent.

 In a fifth aspect the invention provides use of an optionally substituted unit of formula (I) for acceptance of triplet excitons generated by a light-emitting material in a composition comprising the triplet-accepting unit and the light-emitting material.

 Optionally according to the fifth aspect the composition comprises a physical mixture of the light-emitting material and a compound of formula (I).

 Optionally according to the fifth aspect the unit of formula (I) is chemically bound to the fluorescent light-emitting material.

 Optionally according to the fifth aspect the light-emitting material is a polymer and the unit of formula (I) is bound in the main chain of the polymer or bound as a side group or end group of the polymer.

 Optionally according to the fifth aspect the unit of formula (I) quenches triplet excitons generated by the light-emitting material.

 Optionally according to the fifth aspect the unit of formula (I) mediates triplet-triplet annihilation of triplet excitons transferred from the light emitting polymer to the triplet-accepting unit.

 In a sixth aspect the invention provides a light-emitting composition comprising a polymer and an optionally substituted light emitting unit of formula (I):

 In a seventh aspect the invention provides a compound of formula (I):

 where the compound is substituted with at least one solubilising group. Optionally, the solubilising group is selected from alkyl and arylalkyl.

 It will be appreciated that the invention in its first aspect relates to a composition wherein the triplet-accepting unit of formula (I) emits substantially no light. The excited singlet state energy level (S1) of the light-emitting material is no higher than, and preferably lower than, the corresponding energy level of triplet-accepting unit in order to prevent any substantial transfer of singlet excitons from the S1 energy level of the light-emitting material to the S1 level of the triplet-accepting material.

 The opposite is the case in the second aspect of the invention, wherein the unit of formula (I) is the light-emitting material.

 “Aryl” and “heteroaryl” as used herein includes both fused and unfused aryl and heteroaryl groups respectively.

 “Triplet accepting unit” as used herein means a unit capable of receiving triplet excitons from the light emitting unit. In order to function efficiently, the triplet accepting unit has a triplet excited state energy level T1 that is lower in energy than that of the light-emitting unit, preferably lower by at least kT to prevent back-transfer of triplet excitons from the triplet accepting unit to the light-emitting unit.

 BRIEF DESCRIPTION OF THE DRAWINGS

 FIG. 1 is a schematic illustration of triplet quenching by a compound of formula (I);

 FIG. 2 is a schematic illustration of a first triplet-triplet annihilation mechanism involving a by a compound of formula (I);

 FIG. 3 illustrates a second triplet-triplet annihilation mechanism involving a compound of formula (I);

 FIG. 4 illustrates an organic light-emitting device according to an embodiment of the invention;
FIG. 5 illustrates the electroluminescent spectrum of an exemplary OLED of the invention compared to the electroluminescent spectrum of a comparative device;

FIG. 6 illustrates the lifetime of 4 exemplary OLEDs of the invention compared to the electroluminescent spectrum of a comparative device;

FIG. 7 illustrates the $T_{1,4}$ lifetime (i.e., time for decay to 30% of initial luminescence) of 4 exemplary OLEDs of the invention compared to the electroluminescent spectrum of a comparative device;

FIG. 8 illustrates current density vs. voltage for an exemplary device and a comparative device; and

FIG. 9 illustrates external quantum efficiency vs. voltage for an exemplary device and a comparative device.

**DETAILED DESCRIPTION OF THE INVENTION**

The invention is described in detail hereinafter with respect to (A) compositions wherein the compound of formula (I) is a triplet-accepting material, and (B) compositions wherein the compound of formula (I) is a light-emitting material.

A. Anthanthrene as a Triplet-Accepting Material.

The present inventors have identified a number of pathways by which triplet excitons may be caused to undergo decay in order to reduce or eliminate decay by pathways that cause a drop in device lifetime. Some of these pathways allow for radiative exciton decay by delayed fluorescence that can provide for better device efficiency as compared to non-radiative decay pathways.

Without wishing to be bound by any theory, the mechanisms of triplet quenching and delayed fluorescence believed to occur are described below.

**Triplet Quenching**

FIG. 1 illustrates a first energy transfer mechanism for an exemplary OLED. For the avoidance of any doubt energy level diagrams herein, including FIG. 1, are not drawn to any scale. FIG. 1 illustrates energy transfer for an OLED provided with a light emitting material having a singlet excited state energy level $S_{1,4}$ and a singlet ground state energy level $S_{0,4}$. Singlet excitons having energy $S_{1,4}$ decay by emission of fluorescent light hv, illustrated by the solid arrow between $S_{1,4}$ and $S_{0,4}$ in FIG. 1. Triplet-triplet exciton interactions or triplet-singlet exciton interactions may create “super-excited” states on the light-emitting material. Without wishing to be bound by any theory, it is believed that formation of these highly energetic “super-excited” states on the light emitting material may be detrimental to operational lifetime of the material. However, by providing a triplet accepting unit having an excited triplet state energy level $T_{1,4}$ that is lower than $T_{1,4}$, it is possible for triplet excitons to be transferred for non-radiative quenching to the triplet accepting unit, the alternative of radiative decay from $T_{1,4}$ to $S_{0,4}$, illustrated by a dotted line in FIG. 1, being a spin-forbidden process. $S_{1,4}$ and $T_{1,4}$ levels can be measured from the fluorescence and phosphorescence spectra respectively.

The triplet accepting unit has a singlet excited state energy level $S_{1,4}$ that is higher than the singlet excited state energy level $S_{1,4}$ in order to substantially or completely prevent transfer of singlet excitons from $S_{1,4}$ to $S_{1,4}$. Preferably, $S_{1,4}$ is at least kT higher in energy than $S_{1,4}$ in order to prevent any substantial back-transfer of excitons. Likewise, $T_{1,4}$ is preferably at least kT higher in energy than $T_{1,4}$.

**Triplet-Triplet Annihilation**

FIG. 2 illustrates a second energy transfer mechanism for an exemplary OLED.

According to this embodiment, triplet-triplet annihilation (TTA), caused by an interaction between two triplet-accepting units, results in a triplet-triplet annihilation singlet exciton having an energy of up to 2$kT_{1,4}$, wherein $T_{1,4}$ represents the triplet excited state energy level of the triplet-accepting material. This singlet exciton, formed on the first of the two triplet-accepting units, has energy level $S_{2,4}$ that is higher in energy than $S_{1,4}$ and $S_{2,4}$ and so it may transfer to $S_{1,4}$ and then to $S_{1,4}$ from which light hv may be emitted as delayed fluorescence. The triplet exciton on the second of the two triplet-accepting units may decay to the ground state $S_{0,4}$.

Initially, the triplet exciton formed at $T_{1,4}$ is transferred to $T_{1,4}$. By providing a triplet-accepting material having energy level $T_{1,4}$ that is lower than $T_{1,4}$, rapid transfer of excitons from $T_{1,4}$ to $T_{1,4}$ may occur. This transfer is relatively rapid compared to the rate of decay of triplet excitons from $T_{1,4}$ to $S_{0,4}$, illustrated by a dotted arrow in FIG. 1, which is a spin-forbidden process. The energy gap between $T_{1,4}$ and $T_{1,4}$ is preferably greater than kT in order to avoid back-transfer of excitons from $S_{1,4}$ to $S_{1,4}$. Likewise, the energy gap between $S_{1,4}$ and $S_{1,4}$ is preferably greater than kT in order to avoid back-transfer of excitons from $S_{1,4}$ to $S_{1,4}$.

A pathway for decay of the triplet exciton on $T_{1,4}$ in competition with triplet-triplet annihilation is the non-radiative (quenching) pathway to $S_{1,4}$, described above with reference to FIG. 1. A number of measures may be taken to maximise the probability of TTA rather than decay to $S_{1,4}$, in particular:

i) The triplet-absorbing material may be selected such that triplet excitons on $T_{1,4}$ have a relatively long lifetime $\tau_{ex}$. A relatively long lifetime not only means that the rate of decay to $S_{1,4}$ is relatively slow but also that the likelihood of TTA is relatively high.

ii) The concentration of triplet-absorbing material in the light-emitting layer may be relatively high, for example greater than 1 mol %, for example in the range of 1-10 mol %.

iii) Two or more triplet-accepting materials may be provided in close proximity, for example as described above with reference to units of formula (II).

Each of these measures may be used alone or in combination.

FIG. 3 illustrates a third energy transfer mechanism for an exemplary OLED.

In this case, triplet-triplet annihilation occurs between the triplet exciton of energy $T_{1,4}$ located on the triplet accepting triplet-accepting unit and the triplet exciton of energy $T_{1,4}$ located on the light-emitting material. It will be appreciated that this results in a triplet-triplet annihilation singlet exciton (TTAS) having an energy of up to $T_{1,4}$.

This singlet exciton’s energy level of $S_{1,4}$ is higher than that of $S_{1,4}$ and so it may transfer its energy to $S_{1,4}$ and from there to $S_{1,4}$ from which light hv may be emitted as delayed fluorescence. Without wishing to be bound by any theory, it is believed that avoiding formation of super-excited states on the light-emitting polymer formed during OLED driving may improve device lifetime. Moreover, by utilising TTA to produce stable delayed fluorescence it is possible to improve efficiency as compared to a device in which all triplet excitons are quenched (as illustrated in FIG. 1) or as compared to a device in which there is no triplet accepting unit wherein intensity of delayed fluorescence may drop sharply following initial OLED driving.

It will be appreciated that it is possible for two or all three of the triplet-quenching mechanism and the two TTA
mechanisms described above to occur within the same device, and that the amount of delayed fluorescence from each of the TTA two mechanisms will depend on factors such as the concentration of light emitting material, the concentration of triplet accepting units, the rate constants of competing processes and the excited state lifetime of triplet excitons on the light emitting unit and the triplet accepting unit. Measures described above with reference to FIG. 2 may be employed to increase the probability of TTA.

[0066] The rate constant for transfer of triplet excitons from the light-emitting material to the triplet-accepting material may be selected so as to be greater than the rate constant for quenching of triplet excitons.

Triplet-Accepting Material

[0067] The triplet-accepting anthanthrene may be blended with the light-emitting material, and the light-emitting composition may comprise one or more further components, for example one or more charge transporting materials, in particular one or more hole transporting or electron transporting materials. Alternatively, the triplet-accepting anthanthrene may be bound to the light-emitting material, or to any of the aforementioned other components, where present.

[0068] In the case where the anthanthrene is blended with the light-emitting material, the anthanthrene is optionally substituted with solubilising groups. Anthanthrene compounds may have formula (Ia):

\[
\begin{align*}
\text{wherein each } R^2 & \text{ is independently selected from } H \text{ or a substituent, and at least one } R^2 \text{ is not } H. \text{ Preferred substituents } R^2 \text{ are alkyl and optionally substituted aryl or heteroaryl, in particular optionally substituted phenyl.} \\
\text{[0069]} & \text{ In the case where } R^2 \text{ is alkyl, one or more } H \text{ atoms may be replaced by } F \text{ and one or more non-adjacent } C \text{ atoms may be replaced with } O, \text{ substituted } N, \text{ C} = \text{O and } \text{—COO—. Particularly preferred alkyl groups are } n\text{-butyl, } t\text{-butyl, } n\text{-hexyl} \text{ and } n\text{-octyl.} \\
\text{[0070]} & \text{ Substitution of } R^2 \text{ in the 2- and/or 8- positions of the anthanthrene ring is particularly preferred.} \\
\text{[0071]} & \text{ In the case where } R^2 \text{ is aryl or heteroaryl, preferred substituents include alkyl and alkoxy groups. Exemplary compounds of formula (Ia) include the following:}
\end{align*}
\]

wherein Ak is alkyl, in particular branched or straight chain C$_{1-10}$ alkyl.

[0072] In the case where the light-emitting material is a polymer, the anthanthrene may be provided in the form of repeat units in the main chain of the polymer. These repeat units may correspond to compounds of formula (Ia) wherein two R$_2$ groups are replaced with a bond to an adjacent repeat unit. Linking through the 2- and/or 8- positions allows for linkage to adjacent aromatic repeat units without significant change in the HOMO-LUMO gap of the material due to the relatively low electron density at these positions as compared to the 4- and/or 10- positions, resulting in little or no conjugation to adjacent aromatic repeat units.

[0073] Exemplary repeat units include the following:
wherein * denotes the linking points for linking the repeat unit into the polymer chain, and Ak is as described above.

[0074] The anthanthrene group may be bound into the main chain of a light-emitting polymer by polymerising a monomer comprising the repeat unit illustrated above substituted with a leaving group capable of participating in a metal-catalysed cross-coupling reaction. Exemplary leaving groups include halogen and boronic acid or ester groups for use in Suzuki or Yamamoto polymerisation reactions. These reactions are described in more detail below.

[0075] Alternatively, or additionally, in the case where the light-emitting material is a polymer the anthanthrene may be provided in the form of polymer end groups or side-groups pendant from the polymer main chain. In this case, exemplary side-groups or end-groups include the following optionally substituted repeat units:

[0076] As described above, linkage through the 2- or 8-positions results in little or no conjugation to adjacent aromatic groups.

[0077] The anthanthrene side-group or end-group may be formed by reacting an anthanthrene compound substituted with a suitable leaving group capable of participating in a metal-catalysed cross-coupling reaction, such as a halogen or boronic acid or ester, with a leaving group on the polymer.

[0078] Alternatively, an anthanthrene side-group may be incorporated into a light-emitting polymer by providing it as a substituent of a monomer as illustrated below:

\[
\text{Anthanthrene-Spacer-Anthanthrene (II)}
\]

wherein PG represents a polymerisable group such as a leaving group as described above, or a polymerisable double bond.

[0079] In order to increase the probability of TTA and delayed fluorescence as described above, a plurality of triplet-accepting anthanthrene units may be provided in close proximity. For example, two anthanthrene groups may be provided in an optionally substituted compound having the formula (II):

\[
\text{Anthanthrene-Spacer-Anthanthrene (II)}
\]
wherein “Anthanthrene” represents a compound of formula (I) and “Spacer” is a conjugated or non-conjugated spacer group. The spacer group separates the two triplet-accepting anthanthrene groups, and preferably separates their electronic characteristics (for example the HOMO and LUMO). Depending on the precise nature of the conjugation and orbital overlap, Sp could optionally comprise one or more arylene or heteroarylene groups such as substituted phenyl, biphenyl or fluorene. Alternatively, Sp could optionally comprise a non-conjugated linking group such as alkyl, or another molecular link that does not provide a conjugation path between the anthanthrenes.

The unit of formula (II) may be a separate compound physically mixed with the light-emitting material or it may be bound to the light-emitting material. In the case where the light-emitting material is a polymer, the unit of formula (II) may be bound as a main-chain repeat unit, a side group or an end-group as described above.

Alternatively or additionally, the triplet-accepting unit may be an oligomer or polymer, or a component of an oligomer or polymer, comprising a repeat structure of formula (IIb):

$$\text{[Anthanthrene Spacer]}_m$$

wherein m is at least 2. This oligomer or polymer may be mixed with the light-emitting material or may be provided within the polymer backbone.

Although binding of the triplet-accepting unit to the light-emitting polymer is described above, it will be appreciated that the triplet-accepting unit may be bound to any other component of the composition, where present, in the same way.

The concentration of the triplet-accepting unit of formula (I) is optionally at least 0.1 mol% or at least 1 mol%, for example in the range of 1-10 mol%. A higher concentration of the triplet-accepting material increases the probability of TTA.

In order to increase the probability of TTA, the lifetime of excited state triplets residing on the triplet accepting material is optionally at least 1 microsecond. The lifetime of a triplet exciton is its half-life, which may be measured by flash photolysis to measure monomolecular triplet lifetime as described in Handbook of Photochemistry, 2nd Edition, Steven L. Murov, Ian Carmichael and Gordon L Hug and references therein, the contents of which are incorporated herein by reference.

Anthanthrene has a $T_1$ level of 850 nm and a $S_1$ level of 430 nm. By comparison, anthracene has a $T_1$ level of 670 nm and a $S_1$ level of 375 nm. The lower energy $T_1$ level of anthanthrene means that it can be used as a triplet absorber with a wider variety of light-emitting materials than anthracene.

It will be appreciated that, unlike phosphorescent dopants, the triplet-accepting material does not provide an energetically favourable pathway for absorbed triplets to undergo radiative decay, and as a result substantially none of the energy of the triplet exciton absorbed by the triplet-accepting material is lost from the triplet-accepting material in the form of light emission from the triplet-accepting material.

The dynamics of singlet and triplet excitons may be studied using time resolved electroluminescence as well as quasi-continuous wave (quasi-cw) and time resolved excited state absorption. The density of triplet excitons on a light-emitting material, for example on the polymer backbone of a conjugated light-emitting polymer, may be measured using quasi-cw excited state absorption.


For example, the triplet state of polyfluorenes has been well characterised with these techniques with a strong excited state absorption feature peaking at 780 nm attributed to the triplet state (King, S., Rothe, C. & Monkman, A. Triplet build in and decay of isolated polystyrenefluorene chains in dilute solution. J. Chem. Phys. 121, 10803-10808 (2004) and Rothe, C., King, S. M., Dias, F. & Monkman, A. P. Triplet excitation state and related phenomena in the beta-phase of poly(9,9-dioctyl)fluorene. Physical Review B 70, (2004)).

Accordingly, probes of triplet population of a polyfluorene may be performed at 780 nm, and the skilled person will understand how to modify this probe for other light-emitting materials based on the excited state absorption features of those materials.

FIG. 4 illustrates the structure of an OLED according to an embodiment of the invention. The OLED comprises a transparent glass or plastic substrate 1, an anode 2, a cathode 4 and a light-emitting layer 3 provided between anode 2 and the cathode 4. Further layers may be located between anode 2 and the cathode, such as charge transporting, charge injecting or charge blocking layers.

Light Emitting Material

Suitable light-emitting materials for use in layer 3 include small molecule, polymeric and dendrimeric materials, and compositions thereof. Suitable light-emitting polymers for use in layer 3 include poly(arylene vinylenes) and polyarylenes such as: polystyrenes, particularly 2,7-linked 9,9 diiodyl polystyrenes or 2,7-linked 9,9 diaryl polyfluorenes; polystyrenefluorenes, particularly 2,7-linked poly-9,9'-spirofluorene; polyindeno[2,3-b]thiophenes, particularly 2,7-linked polypyrrolenefluorenes; polyphenylene, particularly alkyl or alkoy substituted pol-1,4-phenylene. Such polymers as disclosed in, for example, Adv. Mater. 2000 12(23) 1737-1750 and references therein.

A suitable light-emitting polymer may be a light-emitting homopolymer comprising light-emitting repeat units, or it may be a copolymer comprising light-emitting repeat units and further repeat units such as hole transporting and/or electron transporting repeat units as disclosed in, for example, WO00/55927. Each repeat unit may be provided in a main chain or side chain of the polymer.

Polymers for use as light-emitting materials in devices according to the present invention preferably comprise a repeat unit selected from arylene repeat units as disclosed in, for example, Adv. Mater. 2000 12(23) 1737-1750 and references therein. Exemplary first repeat units include: 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 (T$_g$) of the polymer.

[0095] Particularly preferred polymers comprise optionally substituted, 2,7-linked fluorenes, most preferably repeat units of formula IV:

![Formula IV](image)

wherein R$^1$ and R$^2$ are independently H or a substituent and wherein R$^1$ and R$^2$ may be linked to form a ring. R$^1$ and R$^2$ are preferably selected from the group consisting of hydrogen; optionally substituted alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, substituted N, C=O and —COO—; optionally substituted aryl or heteroaryl; and optionally substituted arylalkyl or heteroarylalkyl. More preferably, at least one of R$^1$ and R$^2$ comprises an optionally substituted C$_4$-C$_{20}$ alkyl or aryl group.

[0096] In the case where R$^1$ or R$^2$ is aryl or heteroaryl, preferred optional substituents include alkyl groups wherein one or more non-adjacent C atoms may be replaced with O, S, substituted N, C=O and —COO—.

[0097] Optional substituents for the fluorene unit, other than substituents R$^1$ and R$^2$, are preferably selected from the group consisting of alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, substituted N, C=O and —COO—, optionally substituted aryl, optionally substituted heteroaryl, alkoxy, alkylthio, fluorene, cyano and arylalkyl.

[0098] Preferably, the polymer comprises an arylene repeat unit as described above and an arylamine repeat unit, in particular a repeat unit V:

![Formula V](image)

wherein Ar$^1$ and Ar$^2$ are optionally substituted aryl or heteroaryl groups, n is greater than or equal to 1, preferably 1 or 2, and R is H or a substituent, preferably a substituent. R is preferably alkyl or aryl or heteroaryl, most preferably aryl or heteroaryl, in particular phenyl. Any of the aryl or heteroaryl groups in the unit of formula I, including the case where R is aryl or heteroaryl, may be substituted. Preferred substituents are selected from alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, substituted N, C=O and —COO—, optionally substituted aryl, optionally substituted heteroaryl, alkoxy, alkylthio, fluorene, cyano and arylalkyl. Preferred substituents include alkyl and alkoxyl groups. Any of the aryl or heteroaryl groups in the repeat unit of formula I may be linked by a direct bond or a divalent linking atom or group. Preferred divalent linking atoms and groups include O, S; substituted N; and substituted C.

[0099] Particularly preferred units satisfying formula 1 include units of formulae I-3:

![Diagram](image)

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

[0100] The arylamine repeat units are preferably present in an amount up to 30 mol%, preferably up to 20 mol%. These percentages apply to the total number of arylamine units present in the polymer in the case where more than one type of repeat unit of formula (V) is used.

[0101] The polymer may comprise heteroarylene repeat units for charge transport or emission.

[0102] Binding the anthanthrene to the light-emitting material may result in more efficient triplet acceptance as compared to mixing of the anthanthrene with the light-emitting material because this binding may provide intramolecular triplet acceptance pathways unavailable to a corresponding mixed system. In the case where a light-emitting polymer is used, the anthanthrene may be bound to a light-emitting repeat unit of the polymer and/or to any other repeat unit of the polymer that may be present, for example an electron transporting repeat unit and/or a hole transporting repeat unit.

[0103] Moreover, binding may be beneficial for processing reasons. For example, if the anthanthrene has low solubility then binding it to a soluble light-emitting material, in particular a light-emitting polymer, allows the anthanthrene unit to be carried in solution by the light-emitting material, enabling device fabrication using solution processing techniques. Finally, binding the anthanthrene unit to the light-emitting material may prevent phase separation effects in solution-processed devices that may be detrimental to device performance.

[0104] Where the light-emitting material is a conjugated polymer comprising light-emitting repeat units and further repeat units, for example light-emitting amine repeat units of formula (V) and fluorene repeat units of formula (IV), conjugation of the anthanthrene unit into the polymer main chain (for example by conjugation with fluorene repeat units) may reduce the T$_1$ energy level of the anthanthrene unit, thus increasing the energetic favourability of triplet excitation transfer from the emitter unit to the anthanthrene unit. This reduction in T$_1$ energy level of the anthanthrene unit may also enable use of the anthanthrene unit with light-emitting materials with T$_1$ levels that are too low for use with an anthanthrene unit that is not conjugated in this way.

[0105] Preferred methods for preparation of conjugated light-emitting polymers comprise a "metal insertion" wherein the metal atom of a metal complex catalyst is inserted
between an aryl or heteroaryl group and a leaving group of a monomer. Exemplary metal insertion methods 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) Prepared by Organometallic Process", Progress in Polymer Science 1993, 17, 1153-1205. 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 group is a halogen. Preferred halogens are chlorine, bromine and iodine, most preferably bromine.

It will therefore be appreciated that repeat units illustrated throughout this application may be derived from a monomer carrying suitable leaving groups. Likewise, an end group or side group may be bound to the polymer by reaction of 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 only 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.

Light-emitting layer 3 may consist of the light-emitting polymer and the triplet accepting unit alone, alone or may comprise these materials in combination with one or more further materials. In particular, the light-emitting polymer may be blended with hole and/or electron transporting materials or alternatively may be covalently bound to hole and/or electron transporting materials as disclosed in, for example, WO 99/48160.

Light-emitting copolymers may comprise a light-emitting region and at least one of a hole transporting region and an electron transporting region as disclosed in, for example, WO 00/55927 and U.S. Pat. No. 6,353,083. If only one of a hole transporting region and electron transporting region is provided then the electroluminescent region may also provide the other of hole transport and electron transport functionality—for example, an amine unit as described above may provide both hole transport and light-emission functionality. A light-emitting copolymer comprising light-emitting repeat units and one or both of a hole transporting repeat units and electron transporting repeat units may provide said units in a polymer main-chain, as per U.S. Pat. No. 6,353,083, or in polymer side-groups pendant from the polymer backbone.

The light-emitting material may emit light of any colour provided that its S1 and T1 energy levels relative to the anthanthrene unit are as described above, however the light-emitting material is preferably a blue light-emitting material, in particular a material having photoluminescent light emission with a peak wavelength in the range of from 400 to 500 nm, preferably 430 to 500 nm.

Light-emitting layer 3 may be patterned or unpatterned. A device comprising an unpatterned layer may be used an illumination source, for example. A white light emitting device is particularly suitable for this purpose. A device comprising a patterned layer may be, for example, an active matrix display or a passive matrix display. In the case of an active matrix display, a patterned electroluminescent layer is typically used in combination with a patterned anode layer and an unpatterned cathode. In the case of a passive matrix display, the anode layer is formed of parallel stripes of anode material, and parallel stripes of electroluminescent material and cathode material arranged perpendicular to the anode material wherein the stripes of electroluminescent material and cathode material are typically separated by stripes of insulating material ("cathode separators") formed by photolithography.

B. Anthanthrene as a Light-Emitting Material

In the case where an anthanthrene compound is used as a light-emitting material, the S1 level of the anthanthrene compound is lower than that of the host material from which it receives singlet excitons.

Preferably, the unit of formula (I) emits blue light.

The unit of formula (I) may be a compound that is physically mixed with, and not chemically bound to, its polymer host material. Alternatively, the unit of formula (I) may be chemically bound to its host material, in which case the unit of formula (I) may be provided as a repeat unit in the polymer main chain or bound to the polymer as a side group or end group. Suitable light-emitting compounds, repeat units, side groups and end groups of formula (I) are as described above with respect to triplet-accepting materials.

Surprisingly, the present inventors have found that incorporation of an anthanthrene unit into a conjugated polymer, in particular by incorporation of the unit into a conjugated polymer main chain, does not result in significant red shifting of the colour of emission of the resulting polymer, in particular when the unit is linked through its 2- and 8- positions. In particular, this red-shift is typically no more than 10 nm or even 5 nm.

Colour shifting of an anthanthrene following substitution with solubilising substituents may be avoided by selection of the position of solubilising substituents.

A suitable host material in this case includes fluorene homopolymer or a copolymer comprising fluorene units and one or more co-repeat units having an S1 level higher than that of the anthanthrene emitter.

Exemplary materials, processes and device architectures of the OLED are described in more detail below. It will be appreciated that these materials, processes and device architectures are applicable to any OLED comprising a unit of formula (I), regardless of whether that unit is functioning as an emitter unit or a substantially non-emissive triplet-accepting unit.

Hole Injection Layers

A conductive hole injection layer, which may be formed from a conductive organic or inorganic material, may be provided between the anode 2 and the electroluminescent layer 3 to assist hole injection from the anode into the layer or layers of semiconducting polymer. Examples of doped organic hole injection materials include optionally substituted, doped poly(ethylene dioxythiophene) (PEDT), in particular PEDT doped with a charge-balancing polycacid such as polystyrene sulfonate (PSS) as disclosed in EP 0901176 and EP 0947123, polycrylic acid or a fluorinated sulfonic acid, for example Naflon® polyaniline as disclosed in U.S. Pat. No. 5,723,873 and U.S. Pat. No. 5,798,170, and optionally substituted polythiophene or poly(thienothiophene). Examples of conductive inorganic materials include transi-
tion metal oxides such as VO\textsubscript{X}, MoO\textsubscript{X}, and RuO\textsubscript{X} as disclosed in Journal of Physics D: Applied Physics (1996), 29(11), 2750-2753.

Charge Transporting Layers

0121 A hole transporting layer may be provided between the anode and the electroluminescent layer. Likewise, an electron transporting layer may be provided between the cathode and the electroluminescent layer.

0122 Similarly, an electron blocking layer may be provided between the anode and the electroluminescent layer and a hole blocking layer may be provided between the cathode and the electroluminescent layer. Transporting and blocking layers may be used in combination. Depending on its HOMO and LUMO levels, a single layer may both transport one of holes and electrons and block the other of holes and electrons.

0123 If present, a hole transporting layer located between anode 2 and electroluminescent layer 3 preferably has a HOMO level of less than or equal to 5.5 eV, more preferably around 4.8-5.5 eV. HOMO levels may be measured by cyclic voltammetry, for example.

0124 If present, an electron transporting layer located between electroluminescent layer 3 and cathode 4 preferably has a LUMO level of around 3.3-5.5 eV. For example, a layer of a silicon monoxide or silicon dioxide or other thin dielectric layer having thickness in the range of 0.2-2 nm is provided between electroluminescent layer 3 and layer 4.

0125 Polymers for use as charge transporting materials may comprise arylene units, such as fluorene units of formula (IV) and other units described above.

0126 A hole-transporting polymer may comprise arylene repeat units, in particular repeat units of formula (V), such as repeat units of formulae 1-3, described above. This polymer may be a homopolymer or it may be a copolymer comprising arylene repeat units in an amount up to 95 mol %, preferably up to 70 mol %. These percentages apply to the total number of arylene units present in the polymer in the case where more than one type of repeat unit of formula (V) is used.

0127 Charge transporting units may be provided in a polymer main-chain or polymer side-chain.

Cathode

0128 Cathode 4 is selected from materials that have a workfunction allowing injection of electrons into the electroluminescent layer. Other factors influence the selection of the cathode such as the possibility of adverse interactions between the cathode and the electroluminescent material. The cathode may consist of a single material such as a layer of aluminium. Alternatively, it may comprise a plurality of metals, for example a bilayer of a low workfunction material and a high workfunction material such as calcium and aluminium as disclosed in WO 98/10621; elemental barium as disclosed in WO 98/57381, Appl. Phys. Lett. 2002, 81(4), 634 and WO 02/84759; or a thin layer of metal compound, in particular an oxide or fluoride of an alkali or alkali earth metal, to assist electron injection, for example lithium fluoride as disclosed in WO 00/48258; barium fluoride as disclosed in Appl. Phys. Lett. 2001, 79(5), 2001; and barium oxide. In order to provide efficient injection of electrons into the device, the cathode preferably has a workfunction of less than 3.5 eV, more preferably less than 3.2 eV, most preferably less than 3 eV. Work functions of metals can be found in, for example, Michaelson, J. Appl. Phys. 48(11), 4729, 1977.

0129 The cathode may be opaque or transparent. Transparent cathodes are particularly advantageous for active matrix devices because emission through a transparent anode in such devices is at least partially blocked by drive circuitry located underneath the emissive pixels. A transparent cathode will comprise a layer of an electron injecting material that is sufficiently thin to be transparent. Typically, the lateral conductivity of this layer will be low as a result of its thinness. In this case, the layer of electron injecting material is used in combination with a thicker layer of transparent conducting material such as indium tin oxide.

0130 It will be appreciated that a transparent cathode device need not have a transparent anode (unless, of course, a fully transparent device is desired), and so the transparent anode used for bottom-emitting devices may be replaced or supplemented with a layer of reflective material such as a layer of aluminium. Examples of transparent cathode devices are disclosed in, for example, GB 2348316.

Encapsulation

0131 Optical devices tend to be sensitive to moisture and oxygen. Accordingly, the substrate preferably has good barrier properties for prevention of ingress of moisture and oxygen into the device. The substrate is commonly glass, however alternative substrates may be used, in particular where flexibility of the device is desirable. For example, the substrate may comprise a plastic as in U.S. Pat. No. 6,268,695 which discloses a substrate of alternating plastic and barrier layers or a laminate of thin glass and plastic as disclosed in EP 0949850.

0132 The device is preferably encapsulated with an encapsulant (not shown) to prevent ingress of moisture and oxygen. Suitable encapsulants include a sheet of glass, films having suitable barrier properties such as silicon dioxide, silicon monoxide, silicon nitride or alternating stacks of polymer and dielectric as disclosed in, for example, WO 01/81649 or an airtight container as disclosed in, for example, WO 01/19142. In the case of a transparent cathode device, a transparent encapsulating layer such as silicon monoxide or silicon dioxide may be deposited to micron levels of thickness, although in one preferred embodiment the thickness of such a layer is in the range of 20-300 nm. A getter material for absorption of any atmospheric moisture and/or oxygen that may permeate through the substrate or encapsulant may be disposed between the substrate and the encapsulant.

Solution Processing

0133 Light-emitting layer 3 may be deposited by any process, including vacuum evaporation and deposition from a solution in a solvent. In the case where the light emitting layer comprises a polyarylene, such as a polyfluorene, suitable solvents for solution deposition include mono- or poly-alkylbenzenes such as toluene and xylene. Particularly preferred solution deposition techniques include printing and coating techniques, preferably spin-coating and inkjet printing.

0134 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.

0135 Inkjet printing is particularly suitable for high information content displays, in particular full colour displays. A device may be inkjet printed by providing a patterned layer over the first electrode and defining wells for printing of one colour (in the case of a monochrome device) or multiple colours (in the case of a multicolour, in particular full colour
The patterned layer is typically a layer of photoresist that is patterned to define wells as described in, for example, EP 0880303.

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

Other solution deposition techniques include dip-coating, roll printing, nozzle printing, and screen printing.

If multiple layers of an OLED 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.

Material Examples 1 and 2

Anthanthrene compounds 1 and 2 were prepared according to the following synthetic method:

This synthesis illustrates substitution at the 2 and 8 positions. Analogous substitution may be provided at the 6,12 and/or 4,10-positions as illustrated below.

Material Example 3

Anthanthrene compound 3 was prepared according to the following synthetic method, starting from commercially available anthanthrene:
Device Example

[0142] A device having the following structure was formed:

![Device Diagram](image)

ITO/HIL/HTL/EL/MF/Al

[0143] wherein ITO represents an indium-tin oxide anode; HIL is a hole-injection layer formed from Plectronics Inc; HTL is a hole-transport layer of a polymer comprising fluorene repeat units of formula (IV) and amine repeat units of formula (V); EL is an electroluminescent layer comprising fluorene repeat units of formula (IV) and amine repeat units of formula (V) blended with 1 mol% of anthanthrene compound 3; MF is a metal fluoride; and the bilayer of MF/Al forms a cathode for the device.

[0144] As shown in FIG. 5 this device has an electroluminescent spectrum that is virtually identical to that of a comparative device wherein no anthanthrene compound is present, indicating that the S1 energy level of the anthanthrene compound is higher than that of the light-emitting unit of the polymer.

[0145] As shown in FIG. 6, the T_{50} lifetime (that is, the time taken for the device brightness to fall to 50% of its original brightness at constant current) is approximately the same as that of the comparative device, however the decay curve is considerably flatter. In particular, as shown in more detail in FIG. 7, the T_{50} lifetime is much longer for the exemplary device as compared to the comparative device.

[0146] FIGS. 8 and 9 illustrate that there is little change in current density vs. voltage or external quantum efficiency vs. voltage in the exemplary device as compared to the comparative device.

[0147] Although the present invention has been described in terms of specific exemplary embodiments, it will be appreciated that various modifications, alterations and/or combinations of features disclosed herein will be apparent to those skilled in the art without departing from the scope of the invention as set forth in the following claims.

1. A composition comprising a fluorescent light-emitting material and a triplet-accepting unit comprising an optionally substituted compound of formula (I):

2. A composition according to claim 1 wherein the fluorescent light-emitting material is a polymer comprising fluorescent light-emitting repeat units.

3. A composition according to claim 1 wherein the compound of formula (I) is substituted with one or more substituents selected from the group consisting of: alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, substituted N, C—O and —COO—and wherein one or more H atoms may be replaced with F; or aryl, heteroaryl, arylalkyl or hetarylalkyl, each of which may optionally be substituted with halogen, cyano, or alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, substituted N, C—O and —COO—.

4. A composition according to claim 1 wherein the compound of formula (I) comprises formula (Ia):

![Formula Diagram](image)

wherein each R^3 is independently selected from H and a substituent selected from the group consisting of alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, substituted N, C—O and —COO—and wherein one or more H atoms may be replaced with F; or aryl, heteroaryl, arylalkyl or hetarylalkyl, each of which may optionally be substituted with halogen, cyano, or alkyl wherein one or more non-adjacent C atoms may be replaced with O, S, substituted N, C—O and —COO—, and at least one R^3 is not H.

5. A composition according to claim 1 wherein a substituent R^4 that is not H is present in the 2- and/or 8- positions of the compound of formula (I).

6. A composition according to claim 1 where the composition comprises a mixture of the light-emitting material and the compound of formula (I).

7. A composition according to claim 1 wherein the triplet-accepting unit is chemically bound to the fluorescent light-emitting material or, if present, to another component of the light-emitting composition.

8. A composition according to claim 2 wherein the triplet-accepting unit is bound in the main chain of the polymer or bound as a side group or end group of the polymer.

9. A composition according to claim 8 wherein the triplet-accepting unit is bound in the main chain of the polymer.
through its 2- and 8-positions or is bound as a side-group or end-group of the polymer through its 2- or 8-position.

10. A composition according to claim 1 wherein the light-emitting material comprises an amine.

11. A composition according to claim 2 wherein the light-emitting material is a polymer comprising amine repeat units.

12. A composition according to claim 1 wherein the triplet-accepting unit is present in an amount of at least 0.1 mol % relative to the light-emitting material.

13. A solution comprising a solvent and a composition according to claim 1.

14. An organic light-emitting device comprising an anode, a cathode and a light-emitting layer between the anode and cathode, wherein the light-emitting layer comprises a composition according to claim 1.

15. A method of forming an organic light-emitting device according to claim 14 comprising the steps of depositing a solution comprising a solvent and a composition comprising a fluorescent light-emitting material and a triplet-accepting unit comprising an optionally substituted compound of formula (I):

and evaporating the solvent.

16. Use of an optionally substituted unit of formula (I) for acceptance of triplet excitons generated by a light-emitting material in a composition comprising the triplet-accepting unit and the light-emitting material:

17. Use according to claim 16 wherein the composition comprises a physical mixture of the light-emitting material and a compound of formula (I).

18. Use according to claim 16 wherein the unit of formula (I) is chemically bound to the fluorescent light-emitting material.

19. Use according to claim 18 wherein the light-emitting material is a polymer and the unit of formula (I) is bound in the main chain of the polymer or bound as a side group or end group of the polymer.

20. Use according to claim 16 wherein the unit of formula (I) quenches triplet excitons generated by the light-emitting material.

21. Use according to claim 16 wherein the unit of formula (I) mediates triplet-triplet annihilation of triplet excitons transferred from the light-emitting material to the triplet-accepting unit.

22. A light-emitting composition comprising a polymer and an optionally substituted light emitting unit of formula (I):

23. A light-emitting composition according to claim 22 wherein the composition comprises a blend of the polymer and a compound of formula (I).

24. A composition according to claim 22 wherein the unit of formula (I) is bound in the main chain of the polymer or bound as a side group of the polymer.

25. A compound of formula (I):

26. A compound according to claim 25 wherein the solubilising group.

wherein the compound is substituted with at least one solubilising group.

27. A compound according to claim 25 wherein the solubilising group is selected from alkyl and arylalkyl.

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