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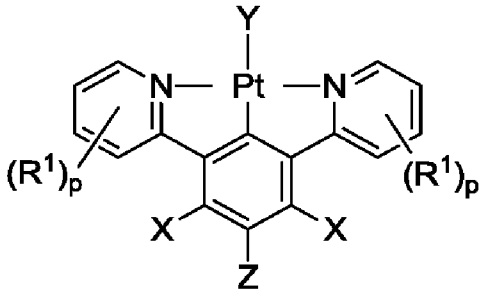
(54) Title: LIGHT-EMITTING COMPOUND



(I)

(57) Abstract: A compound of formula (I): wherein: X is an electron withdrawing group, and each X is independently selected; Y is ligand; Z is selected from the group consisting of cyano, C_{1-10} perfluoroalkyl and –C(=O)OR wherein R is a hydrocarbyl; each R^1 is independently a substituent; and p in each occurrence is independently 0, 1, 2, 3 or 4.

Light-Emitting Compound

Field of the Invention

The present invention relates to light-emitting compounds, in particular phosphorescent light-emitting compounds; compositions, formulations and light-emitting devices comprising said light-emitting compounds; and methods of making said light-emitting devices.

Background of the Invention

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

An OLED device may comprise a substrate carrying an anode, a cathode and one or more organic light-emitting layers between the anode and cathode.

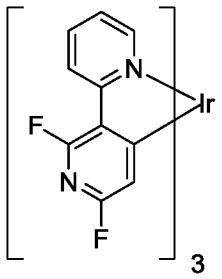
Holes are injected into the OLED device through the anode and electrons are injected through the cathode during operation of the device. Holes in the highest occupied molecular orbital (HOMO) and electrons in the lowest unoccupied molecular orbital (LUMO) of a light-emitting material present within the OLED device combine to form an exciton that releases its energy as light.

Suitable light-emitting materials developed to date include small molecule, polymeric and dendrimeric materials. Suitable light-emitting polymers include poly(arylene vinylenes) such as poly(p-phenylene vinylenes) and polyarylenes such as polyfluorenes.

Within an OLED device, the light-emitting material may be used as a dopant within a light emitting layer. The light-emitting layer may comprise a semiconducting host material and the light-emitting dopant, and energy will be transferred from the host

material to the light-emitting dopant. For example, J. Appl. Phys. 65, 3610, 1989 discloses a host material doped with a fluorescent light-emitting dopant (that is, a light-emitting material in which light is emitted via decay of singlet excitons).

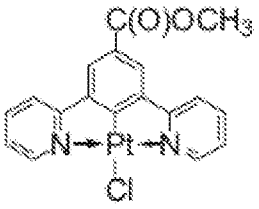
As well as fluorescent light-emitting dopants, phosphorescent dopants are also known (that is, a light-emitting dopant in which light is emitted via decay of triplet excitons). Known phosphorescent dopants include complexes of heavy transition metals. For example, Lee et al, Inorganic Chemistry 48(3), 2009, 1030-1037 discloses the following blue light-emitting compound:



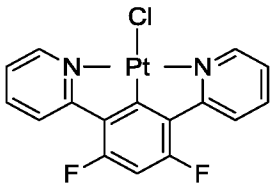
Platinum-containing complexes are known to be used as phosphorescent dopants. For example, US 2006/0098475 discloses platinum complexes for light-emitting devices. Organo-metallic platinum complexes for electroluminescent devices are also disclosed in US 2005/0123788 and organo-platinum luminophores are disclosed in US 2010/0317851.

Dopants such as the platinum-containing complexes described above can be used in combination with other compounds to produce white phosphorescent OLEDs. Yang et al, Appl. Phys. Lett. 2008, 93, 193305 and Kalinowski et al, Chemical Physics 2010, 278, 47-57 both disclose a white phosphorescent OLED containing the blue-emitting complex platinum (II) [1,3-difluoro-di(2-pyridinyl)benzene] chloride.

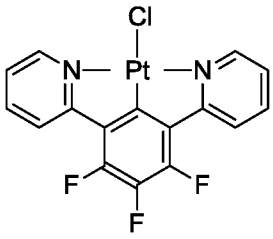
Kalinowski et al, Adv. Mater. 2007, 19, 4000-40005 discloses a further white phosphorescent OLED containing the following blue light-emitting material:



It is an object of the invention to provide blue phosphorescent light-emitting compounds, including deep blue phosphorescent light-emitting compounds. Murphy et al, "Blue-shifting the monomer and excimer phosphorescence of tridentate cyclometallated platinum (II) complexes for optimal white-light OLEDs" Chem. Commun. 2012 DOI: 10.1039/c2cc31330h discloses the following compound:



Wang et al, "Facile Synthesis and Characterisation of Phosphorescent Pt(N-C-N)X Complexes", Inorg. Chem., 2010, 49(24), 11276-11286 discloses the following compound:

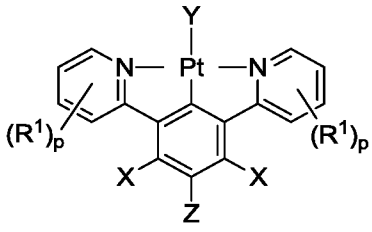


Summary of the Invention

The present invention provides blue light-emitting platinum complexes.

Phosphorescent compounds

The present invention relates to a compound of formula (I):



(I)

wherein:

X is an electron withdrawing group, and each X is independently selected;

Y is ligand;

Z is selected from the group consisting of cyano, C_{1-10} perfluoroalkyl and –C(=O)OR wherein R is a hydrocarbyl;

each R^1 is independently a substituent; and

p in each occurrence is independently 0, 1 , 2, 3 or 4.

The tridentate ligand of this compound contains two pyridine outer rings. The two outer rings are co-ordinated to the central metal ion through N atoms, and the central ring of the tridentate ligand is co-ordinated through a C atom.

The present inventors have found that the presence of one or more bulky substituents R^1 in the compound of formula (I) provides steric hindrance around the present electron withdrawing group such that the phosphorescent emission of the metal complex is shifted to a shorter wavelength. The compound of formula (I) may have a photoluminescent emission peak in the blue region of the visible spectrum and, if excimers are formed, a peak in the red region of the visible spectrum. Shifting excimer emission to a shorter peak wavelength may reduce the quantity of excimer emission in the invisible infra-red region of the spectrum. One or more substituents R^1 on one or both of the outer rings of the complex may be provided.

Where Z is –C(=O)OR, R may be a bulky group which may aid in increasing luminescent efficiency of compounds of the invention.

Substitutents X, Z and R^1 may be selected according to their effect on colour of emission of the metal complex, and colour of emission may be tuned by selection of X, Z and R^1.

Substituent X

One or two electron-withdrawing substituents X may cause emission of the metal complex to shift to a shorter wavelength as compared to a complex in which substituents X are not present. Conversely, one or two electron-donating substituents X may cause

emission of the metal complex to shift to a longer wavelength as compared to a complex in which substituents X are not present.

Electron withdrawing substituents X may be substituents having a positive Hammett constant.

In one embodiment of the present invention, each X may independently be a halogen. The inclusion of one or two halogens in the complexes of the invention may lead to a blue shift in emission. The halogens may be fluorine, chlorine, bromine, iodine and astatine. Preferably, one or more X is fluorine, and each X may be fluorine.

Substituent Z

Substituent Z is selected from the group consisting of cyano, C_{1-10} perfluoroalkyl and –C(=O)OR wherein R is a hydrocarbyl. In a preferred embodiment Z is –C(=O)OR wherein R is a hydrocarbyl. In a further preferred embodiment Z is $–CF_3$.

Substituent R

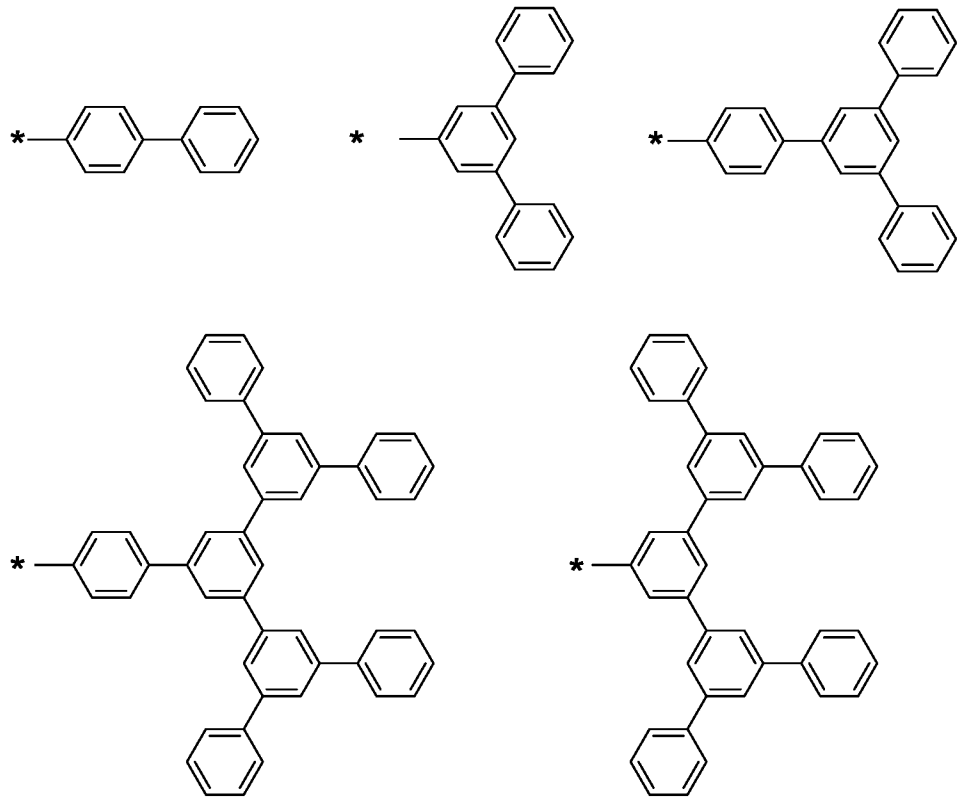
In one embodiment, R may be selected from the group consisting of linear, branched or cyclic alkyl, an aryl that may be unsubstituted or substituted with one or more alkyl groups, or a branched or unbranched chain of aryl groups wherein each aryl group may independently be unsubstituted or substituted with one or more alkyl groups.

Exemplary hydrocarbyl substituents R include the following:

- C_{1-20} alkyl (e.g. C_1 alkyl, C_2 alkyl, C_3 alkyl, C_4 alkyl, C_5 alkyl, C_6 alkyl, C_7 alkyl, C_8 alkyl, C_9 alkyl, C_{10} alkyl, C_{11} alkyl, C_{12} alkyl, C_{13} alkyl, C_{14} alkyl, C_{15} alkyl, C_{16} alkyl, C_{17} alkyl, C_{18} alkyl, C_{19} alkyl or C_{20} alkyl);
- C_{6-20} aryl, preferably phenyl, that may be unsubstituted or substituted with one or more C_{1-20} alkyl groups (e.g. C_1 alkyl, C_2 alkyl, C_3 alkyl, C_4 alkyl, C_5 alkyl, C_6 alkyl, C_7 alkyl, C_8 alkyl, C_9 alkyl, C_{10} alkyl, C_{11} alkyl, C_{12} alkyl, C_{13} alkyl, C_{14} alkyl, C_{15} alkyl, C_{16} alkyl, C_{17} alkyl, C_{18} alkyl, C_{19} alkyl or C_{20} alkyl);
- A branched or linear chain of two or more phenyl rings, each of which ring may be unsubstituted or substituted with one or more C_{1-20} (e.g. C_1 alkyl, C_2 alkyl, C_3 alkyl, C_4 alkyl, C_5 alkyl, C_6 alkyl, C_7 alkyl, C_8 alkyl, C_9 alkyl, C_{10}

alkyl, C_{11} alkyl, C_{12} alkyl, C_{13} alkyl, C_{14} alkyl, C_{15} alkyl, C_{16} alkyl, C_{17} alkyl, C_{18} alkyl, C_{19} alkyl or C_{20} alkyl) alkyl groups.

Exemplary substituents having branched or linear phenyl chains include the following, each of which may be substituted with one or more C_{1-20} (e.g. C_1 alkyl, C_2 alkyl, C_3 alkyl, C_4 alkyl, C_5 alkyl, C_6 alkyl, C_7 alkyl, C_8 alkyl, C_9 alkyl, C_{10} alkyl, C_{11} alkyl, C_{12} alkyl, C_{13} alkyl, C_{14} alkyl, C_{15} alkyl, C_{16} alkyl, C_{17} alkyl, C_{18} alkyl, C_{19} alkyl or C_{20} alkyl) alkyl groups:



wherein * represents a point of attachment of the substituent to the metal complex.

A bulky substituent R may allow control of formation of excimers, in particular at relatively high concentrations of the compound of the invention. Exemplary bulky substituents for use within compounds of the invention include substituents containing a secondary or tertiary carbon atom, for example 2-ethylhexyl or tert-butyl groups and substituents containing one or more phenyl groups.

Hydrocarbyl substituents R may improve solubility of a compound of the invention in common organic solvents, for example mono- or poly-alkyl benzenes, as compared to a compound of the invention in which such hydrocarbyl substituents are absent.

Substituent R^1

One or more electron-donating substituents R^1 may cause emission of the metal complex to shift to a shorter wavelength as compared to a complex in which substituents R^1 are not present. Conversely, one or more electron-withdrawing substituents R^1 may cause emission of the metal complex to shift to a longer wavelength as compared to a complex in which substituents R^1 are not present.

Where present, there may be 1, 2, 3 or 4 R^1 groups per pyridine ring. Preferably there is only one group R^1 group per pyridine ring.

Where more than one R^1 substituent is present within the compound of the invention, each R^1 substituent is independently selected such that each R^1 substituent may be the same or different.

Where present, R^1 groups may be positioned at one or more of positions 2, 3, 4 and 5. Preferably, R^1 is substituted at the 4-position of the pyridine ring they are bound to.

If present, each R^1 substituent is preferably an electron donating group. Electron donating substituents may be substituents having a negative Hammett constant.

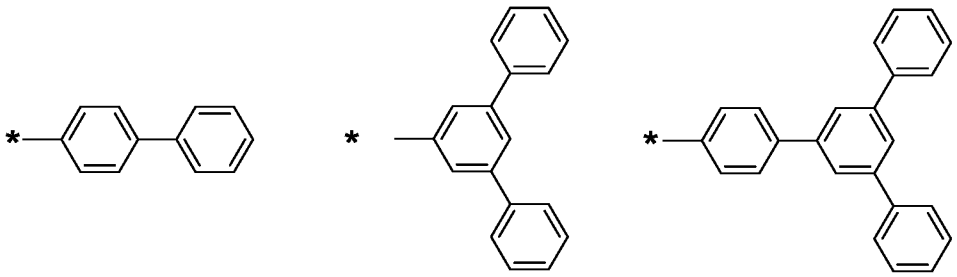
Exemplary electron-donating substituents include hydrocarbyl groups, optionally C_{1-60} or C_{1-30} hydrocarbyl,, $-OR^{12}$, $-NR^{12}$ and groups of formula $*-BR^{12}_2$, wherein * represents a point of attachment of the boron atom to the metal complex; and R^{12} independently in each occurrence is a hydrocarbyl, optionally C_{1-30} hydrocarbyl, optionally C_{1-20} alkyl or phenyl substituted with one or more C_{1-20} alkyl groups.

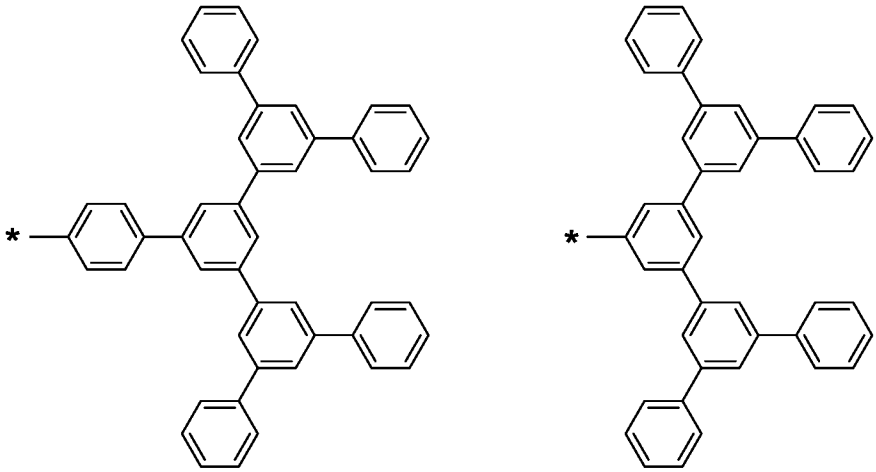
In one embodiment, each R^1 may be independently selected from the group consisting of linear, branched or cyclic alkyl, an aryl that may be unsubstituted or substituted with one or more alkyl groups, or a branched or unbranched chain of aryl groups wherein each aryl group may independently be unsubstituted or substituted with one or more alkyl groups.

Exemplary hydrocarbyl substituents R^1 include the following:

- C_{1-20} alkyl (e.g. C_1 alkyl, C_2 alkyl, C_3 alkyl, C_4 alkyl, C_5 alkyl, C_6 alkyl, C_7 alkyl, C_8 alkyl, C_9 alkyl, C_{10} alkyl, C_{11} alkyl, C_{12} alkyl, C_{13} alkyl, C_{14} alkyl, C_{15} alkyl, C_{16} alkyl, C_{17} alkyl, C_{18} alkyl, C_{19} alkyl or C_{20} alkyl);
- C_{6-20} aryl, preferably phenyl, that may be unsubstituted or substituted with one or more C_{1-20} alkyl groups (e.g. C_1 alkyl, C_2 alkyl, C_3 alkyl, C_4 alkyl, C_5 alkyl, C_6 alkyl, C_7 alkyl, C_8 alkyl, C_9 alkyl, C_{10} alkyl, C_{11} alkyl, C_{12} alkyl, C_{13} alkyl, C_{14} alkyl, C_{15} alkyl, C_{16} alkyl, C_{17} alkyl, C_{18} alkyl, C_{19} alkyl or C_{20} alkyl);
- A branched or linear chain of two or more phenyl rings, each of which ring may be unsubstituted or substituted with one or more C_{1-20} (e.g. C_1 alkyl, C_2 alkyl, C_3 alkyl, C_4 alkyl, C_5 alkyl, C_6 alkyl, C_7 alkyl, C_8 alkyl, C_9 alkyl, C_{10} alkyl, C_{11} alkyl, C_{12} alkyl, C_{13} alkyl, C_{14} alkyl, C_{15} alkyl, C_{16} alkyl, C_{17} alkyl, C_{18} alkyl, C_{19} alkyl or C_{20} alkyl) alkyl groups.

Exemplary substituents having branched or linear phenyl chains include the following, each of which may be substituted with one or more C_{1-20} (e.g. C_1 alkyl, C_2 alkyl, C_3 alkyl, C_4 alkyl, C_5 alkyl, C_6 alkyl, C_7 alkyl, C_8 alkyl, C_9 alkyl, C_{10} alkyl, C_{11} alkyl, C_{12} alkyl, C_{13} alkyl, C_{14} alkyl, C_{15} alkyl, C_{16} alkyl, C_{17} alkyl, C_{18} alkyl, C_{19} alkyl or C_{20} alkyl) alkyl groups:





wherein * represents a point of attachment of the substituent to the metal complex.

Bulky substituents R^1 may provide control over formation of excimers, in particular at relatively high concentrations of the compound of the invention. Exemplary bulky substituents for use within compounds of the invention include substituents containing a tertiary carbon atom, for example a tert-butyl group, and substituents containing one or more phenyl groups.

Hydrocarbyl substituents R^1 may improve solubility of a compound of the invention in common organic solvents, for example mono- or poly-alkyl benzenes, as compared to a compound of the invention in which such hydrocarbyl substituents are absent. The presence of one or more hydrocarbyl substituents R^1 is therefore preferred.

Where present, substituents R^1 are preferably provided para- to the N atom of the pyridine ring they are bound to.

The two outer pyridine rings of the compound of formula (I) may differ in one or more of: value of p; identity of R^1; and substitution position of R^1. In one embodiment, p of one pyridine ring is 0 and p of the other pyridine ring is at least 1.

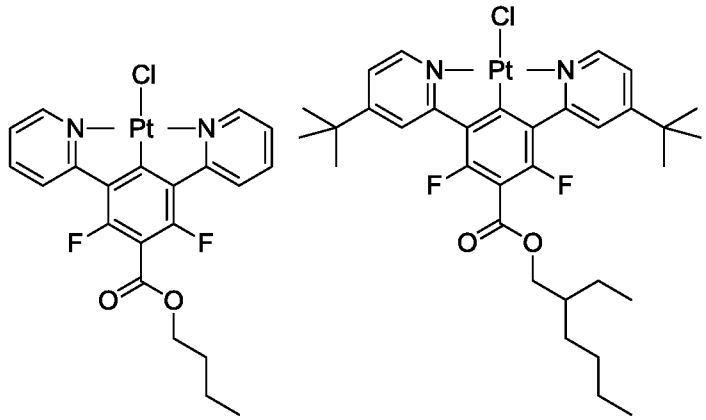
Ligand Y

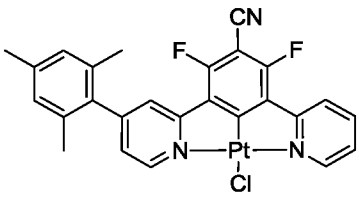
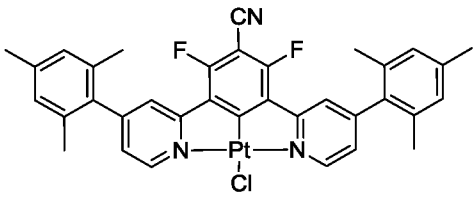
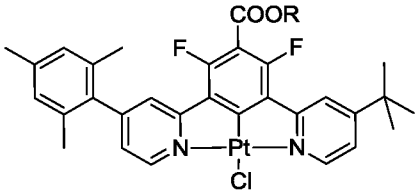
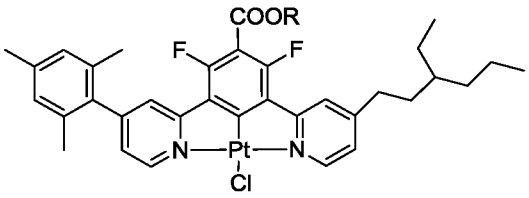
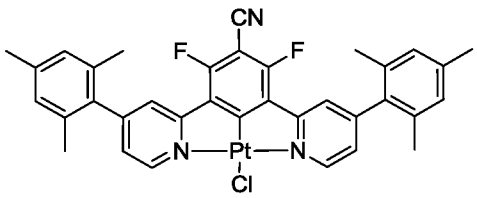
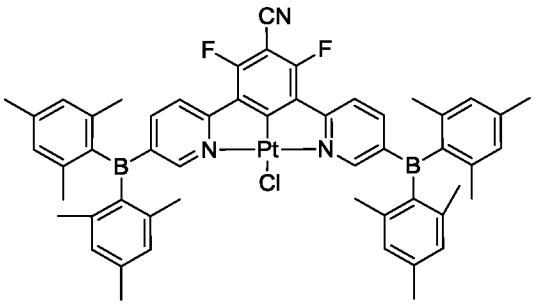
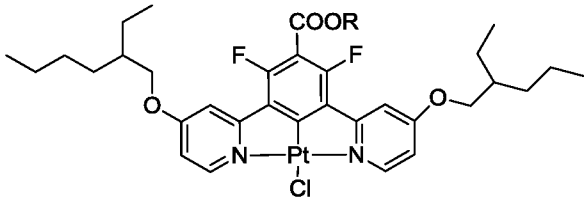
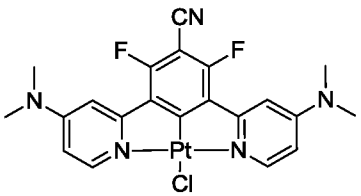
In one embodiment, substituent Y may be selected from the group consisting of a halogen, cyano, acetylenic or phenoxy group. Phenoxy ligand Y may be unsubstituted or

substituted with one or more substituents, optionally one or more C_{1-20} alkyl groups. The use of an electron withdrawing group at position Y is thought to shift the wavelength of emission towards the blue. Here, the halogen may be selected from the group consisting of fluorine, chlorine, bromine, iodine and astatine. Preferably substituent Y is chlorine.

Specific Examples of compounds

Specific examples of compounds according to the invention include the following:



Compound properties

The compound of the invention may emit blue light, and may have a photoluminescence spectrum with a peak of less than 480 nm, preferably less than 470 nm, optionally a peak in the range of 420-470 nm.

The compound of the invention may have a CIE y co-ordinate of less than 0.4.

Compositions & formulations

In one embodiment, the present invention includes a composition comprising a charge-transporting host material and a compound according to the invention. The compound of the invention may be provided in an amount of at least 1% by weight relative to the host

material, optionally in the range of 1-15% by weight. Preferably the compound of the invention will be present in an amount of greater than 1% by weight. In the case of a polymer host material, the molar % of the compound of the invention is the molar % relative to the total number of moles of repeat units of the polymer.

The composition of the invention may be a white light emitting composition comprising the compound of the invention. The emitted white light may have a CIE x coordinate equivalent to that emitted by a black body at a temperature in the range of 2500-9000K and a CIE y coordinate within 0.05 or 0.025 of the CIE y co-ordinate of said light emitted by a black body, optionally a CIE x coordinate equivalent to that emitted by a black body at a temperature in the range of 2700-4500K.

White light may be formed of blue emission from a compound of the invention, and one or more fluorescent or phosphorescent materials emitting at longer wavelengths that, together with emission of the compound of the invention, provide white light.

In a further embodiment ,the compound of the invention may be the only light emitting material in the white light emitting composition of the invention.

A compound of the invention may be dispersed or dissolved in a solvent or mixture of two or more solvents to form a formulation that may be used to form a layer containing the compound by depositing the formulation and evaporating the solvent or solvents. The formulation may contain one or more further materials in addition to a compound of the invention, for example the formulation may contain a host material. All of the components of the formulation may be dissolved in the solvent or solvent mixture, in which case the formulation is a solution, or one or more components may be dispersed in the solvent or solvent mixture, in which case the formulation is a suspension. Exemplary solvents for use alone or in a solvent mixture include aromatic compounds, preferably, benzene, that may be unsubstituted or substituted. Preferably, substituents are selected from halogen (preferably chlorine), C1-10 alkyl and C1-10 alkoxy. Exemplary solvents are toluene, xylene, chlorobenzen and anisole.

Techniques for forming layers from a formulation include printing and coating techniques such spin-coating, dip-coating, roll printing, screen printing and inkjet printing.

Host Material

The charge transporting host material utilised in the compositions and formulations described above may have a triplet excited state energy level (T_1) that is preferably no more than 0.1 lower than, and preferably at least the same as or higher than, triplet excited state energy level of the phosphorescent compound of the invention. This allows for transfer of triplet excitons from the host material to the phosphorescent compounds of the invention.

The triplet excited state energy levels of the host material and the phosphorescent compound of the invention may be determined from their respective phosphorescence spectra.

The host material may be a polymer or a non-polymeric compound.

The compound of the invention may be mixed with the host material or may be bound to the host material. In the case where the host material is a polymer, the metal complex of the invention may be provided as a main chain unit, a side group or an end group of the polymer.

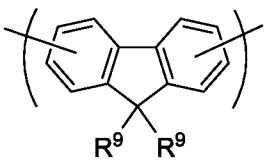
In the case where the compound of the invention is provided as a side group, the metal complex may be directly bound to a main chain of the polymer or spaced apart from the main chain by a spacer group. Exemplary spacer groups include C_{1-20} alkyl groups, aryl-C_{1-20} alkyl groups and C_{1-20} alkoxy groups. The polymer main chain or spacer group may be bound to the tridentate ligand of the compound of the invention.

If the compound of the invention is bound to a polymer comprising conjugated repeat units then it may be bound to the polymer such that there is no conjugation between the conjugated repeat units and the compound of the invention, or such that the extent of conjugation between the conjugated repeat units and the compound of the invention is limited.

Exemplary host material polymers include polymers having a non-conjugated backbone with charge-transporting groups pendant from the non-conjugated backbone, for example poly(vinylcarbazole), and polymers comprising conjugated repeat units in the backbone of the polymer. If the backbone of the polymer comprises conjugated repeat units then the extent of conjugation between repeat units in the polymer backbone may be limited in order to maintain a triplet energy level of the polymer that is no lower than that of the phosphorescent compound of the invention.

Exemplary repeat units of a conjugated polymer include optionally substituted monocyclic and polycyclic arylene repeat units as disclosed in for example, Adv. Mater. 2000 12(23) 1737-1750 and include: 1,2-, 1,3- and 1,4-phenylene repeat units as disclosed in J. Appl. Phys. 1996, 79, 934; 2,7-fluorene repeat units as disclosed in EP 0842208; indenofluorene repeat units as disclosed in, for example, Macromolecules 2000, 33(6), 2016-2020; and spirofluorene repeat units as disclosed in, for example EP 0707020. Each of these repeat units is optionally substituted. Examples of substituents include solubilising groups such as C_{1-20} alkyl or alkoxy; electron withdrawing groups such as fluorine, nitro or cyano; and substituents for increasing glass transition temperature (Tg) of the polymer.

One exemplary class of arylene repeat units is optionally substituted fluorene repeat units, such as repeat units of formula IV:



(IV)

wherein R^9 in each occurrence is the same or different and is H or a substituent, and wherein the two groups R^9 may be linked to form a ring.

Each R^9 is preferably a substituent, and each R^9 may independently be selected from the group consisting of:

- optionally substituted alkyl, optionally C_{1-20} alkyl, wherein one or more non-adjacent C atoms may be replaced with optionally substituted aryl or heteroaryl, O, S, substituted N, C=O or -COO-;
- optionally substituted aryl or heteroaryl;
- a linear or branched chain of aryl or heteroaryl, each of which groups may independently be substituted, for example a group of formula $-(Ar^6)_r$ as described below with reference to formula (VII); and
- a crosslinkable-group, for example a group comprising a double bond such and a vinyl or acrylate group, or a benzocyclobutane group.

In the case where R^9 comprises aryl or heteroaryl ring system, or a linear or branched chain of aryl or heteroaryl ring systems, the or each aryl or heteroaryl ring system may be substituted with one or more substituents R^3 selected from the group consisting of:

alkyl, for example C_{1-20} alkyl, wherein one or more non-adjacent C atoms may be replaced with O, S, substituted N, C=O and -COO- and one or more H atoms of the alkyl group may be replaced with F or aryl or heteroaryl optionally substituted with one or more groups R^4,

aryl or heteroaryl optionally substituted with one or more groups R^4,

NR^5_2, OR^5, SR^5, and

fluorine, nitro and cyano;

wherein each R^4 is independently alkyl, for example C_{1-20} alkyl, in which one or more non-adjacent C atoms may be replaced with O, S, substituted N, C=O and -COO- and one or more H atoms of the alkyl group may be replaced with F, and each R^5 is independently selected from the group consisting of alkyl and aryl or heteroaryl optionally substituted with one or more alkyl groups.

Optional substituents for one or more of the aromatic carbon atoms of the fluorene unit are preferably selected from the group consisting of alkyl, for example C_{1-20} alkyl, wherein one or more non-adjacent C atoms may be replaced with O, S, NH or substituted N, C=O and -COO-, optionally substituted aryl, optionally substituted heteroaryl, alkoxy,

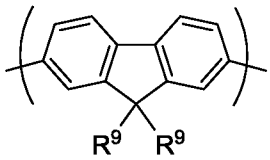
alkylthio, fluorine, cyano and arylalkyl. Particularly preferred substituents include C_{1-20} alkyl and substituted or unsubstituted aryl, for example phenyl. Optional substituents for the aryl include one or more C_{1-20} alkyl groups.

Where present, substituted N may independently in each occurrence be NR^6 wherein R^6 is alkyl, optionally C_{1-20} alkyl, or optionally substituted aryl or heteroaryl. Optional substituents for aryl or heteroaryl R^6 may be selected from R^4 or R^5.

Preferably, each R^9 is selected from the group consisting of C_{1-20} alkyl and optionally substituted phenyl. Optional substituents for phenyl include one or more C_{1-20} alkyl groups.

If the compound of the invention is provided as a side-chain of the polymer then at least one R^9 may comprise a compound of the invention that is either bound directly to the 9-position of a fluorene unit of formula (IV) or spaced apart from the 9-position by a spacer group.

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

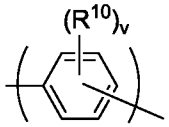


(IVa)

Optionally, the repeat unit of formula (IVa) is not substituted in a position adjacent to the 2- or 7- positions.

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

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



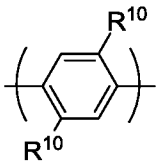
(V)

wherein v is 0, 1, 2, 3 or 4, optionally 1 or 2, and R^{10} independently in each occurrence is a substituent, optionally a substituent R^9 as described above with reference to formula (IV), for example C_{1-20} alkyl, and phenyl that is unsubstituted or substituted with one or more C_{1-20} alkyl groups.

The repeat unit of formula (V) may be 1,4- linked, 1,2-linked or 1,3-linked.

If the repeat unit of formula (V) is 1,4-linked and if v is 0 then the extent of conjugation of repeat unit of formula (V) to one or both adjacent repeat units may be relatively high.

If v is at least 1, and / or the repeat unit is 1,2- or 1,3 linked, then the extent of conjugation of repeat unit of formula (V) to one or both adjacent repeat units may be relatively low. In one preferred arrangement, the repeat unit of formula (V) is 1,3-linked and v is 0, 1, 2 or 3. In another preferred arrangement, the repeat unit of formula (V) has formula (Va):



(Va)

A host polymer may comprise charge-transporting units CT that may be hole-transporting units or electron transporting units.

A hole transporting unit may have a low electron affinity (2 eV or lower) and low ionisation potential (5.8 eV or lower, preferably 5.7 eV or lower, more preferred 5.6 eV or lower).

An electron-transporting unit may have a high electron affinity (1.8 eV or higher, preferably 2 eV or higher, even more preferred 2.2 eV or higher) and high ionisation

potential (5.8 eV or higher) Suitable electron transport groups include groups disclosed in, for example, Shirota and Kageyama, Chem. Rev. 2007, 107, 953-1010.

Electron affinities and ionisation potentials may be measured by cyclic voltammetry (CV) wherein the working electrode potential is ramped linearly versus time.

When cyclic voltammetry reaches a set potential the working electrode's potential ramp is inverted. This inversion can happen multiple times during a single experiment. The current at the working electrode is plotted versus the applied voltage to give the cyclic voltammogram trace.

HOMO or LUMO energy levels may be measured by any method known in the art. Apparatus to measure HOMO or LUMO energy levels by CV may comprise a cell containing a tert-butyl ammonium perchlorate/ or tertbutyl ammonium hexafluorophosphate solution in acetonitrile, a glassy carbon working electrode where the sample is coated as a film, a platinium counter electrode (donor or acceptor of electrons) and a reference glass electrode no leak Ag/AgCl. Ferrocene is added in the cell at the end of the experiment for calculation purposes. (Measurement of the difference of potential between Ag/AgCl/ferrocene and sample/ferrocene).

Method and settings:

3mm diameter glassy carbon working electrode

Ag/AgCl/no leak reference electrode

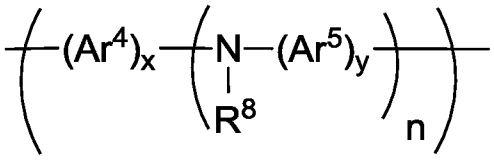
Pt wire auxiliary electrode

0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile

LUMO = 4.8 - ferrocene (peak to peak maximum average) + onset

Sample: 1 drop of 5mg/mL in toluene spun at 3000rpm LUMO (reduction) measurement: A good reversible reduction event is typically observed for thick films measured at 200 mV/s and a switching potential of -2.5V. The reduction events should be measured and compared over 10 cycles, usually measurements are taken on the 3rd cycle. The onset is taken at the intersection of lines of best fit at the steepest part of the reduction event and the baseline.

Exemplary hole-transporting units CT include optionally substituted (hetero)arylamine repeat units, for example repeat units of formula (VI):



(VI)

wherein Ar^4 and Ar^5 in each occurrence are independently selected from optionally substituted aryl or heteroaryl, n is greater than or equal to 1, preferably 1 or 2, R^8 is H or a substituent, preferably a substituent, and x and y are each independently 1, 2 or 3.

Ar^4 and Ar^5 may each independently be a monocyclic or fused ring system.

R^8, which may be the same or different in each occurrence when n > 1, is preferably selected from the group consisting of alkyl, for example C_{1-20} alkyl, Ar^6, a branched or linear chain of Ar^6 groups, or a crosslinkable unit that is bound directly to the N atom of formula (VI) or spaced apart therefrom by a spacer group, wherein Ar^6 in each occurrence is independently optionally substituted aryl or heteroaryl. Exemplary spacer groups are as described above, for example C_{1-20} alkyl, phenyl and phenyl-C_{1-20} alkyl.

Ar^6 groups may be substituted with one or more substituents as described below. An exemplary branched or linear chain of Ar^6 groups may have formula $-(Ar^6)_r$, wherein Ar^6 in each occurrence is independently selected from aryl or heteroaryl and r is at least 1, optionally 1, 2 or 3. An exemplary branched chain of Ar^6 groups is 3,5-diphenylbenzene.

Any of Ar^4, Ar^5 and Ar^6 may independently be substituted with one or more substituents. Preferred substituents are selected from the group R^{11} consisting of:

alkyl, for example C_{1-20} alkyl, wherein one or more non-adjacent C atoms may be replaced with O, S, substituted N, C=O and -COO- and one or more H atoms of the alkyl group may be replaced with F or aryl or heteroaryl optionally substituted with one or more groups R^4,

aryl or heteroaryl optionally substituted with one or more groups R^4,

NR^5_2, OR^5, SR^5,

fluorine, nitro and cyano;

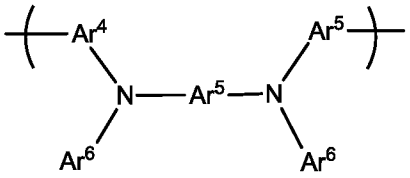
wherein each R^4 is independently alkyl, for example C_{1-20} alkyl, in which one or more non-adjacent C atoms may be replaced with O, S, substituted N, C=O and -COO- and one or more H atoms of the alkyl group may be replaced with F, and each R^5 is independently selected from the group consisting of alkyl and aryl or heteroaryl optionally substituted with one or more alkyl groups.

Any two of Ar^4, Ar^5 and, if present, Ar^6 in the repeat unit of Formula (VI) that are directly linked to a common N atom 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.

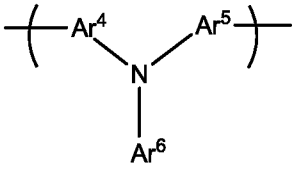
Where present, substituted N or substituted C of R^{11}, R^4 or of the divalent linking group may independently in each occurrence be NR^6 or CR^6_2 respectively wherein R^6 is alkyl or optionally substituted aryl or heteroaryl. Optional substituents for aryl or heteroaryl R^6 are C_{1-20} alkyl.

In one preferred arrangement, R^8 is Ar^6 and each of Ar^4, Ar^5 and Ar^6 are independently and optionally substituted with one or more C_{1-20} alkyl groups.

Particularly preferred units satisfying Formula (VI) include units of Formulae 1-4:



1



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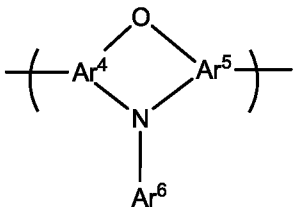

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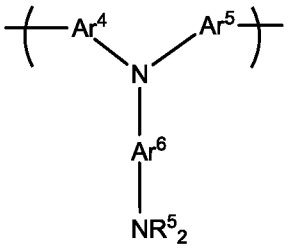


4

Where present, preferred substituents for Ar^6 include substituents as described forAr^4 and Ar^5, in particular alkyl and alkoxy groups.

Ar^4, Ar^5 and Ar^6 are preferably phenyl, each of which may independently be unsubstituted or substituted with one or more substituents as described above.

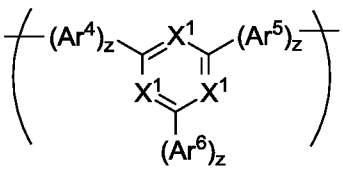
In another preferred arrangement, Ar^4, Ar^5 and Ar^6 are phenyl, each of which may be unsubstituted or substituted with one or more C_{1-20} alkyl groups, and r = 1.

In another preferred arrangement, Ar^4 and Ar^5 are phenyl, each of which may be unsubstituted or substituted with one or more C_{1-20} alkyl groups, and R^8 is 3,5-diphenylbenzene wherein each phenyl of R^8 may be unsubstituted or substituted with one or more C_{1-20} alkyl groups.

In another preferred arrangement, n, x and y are each 1 and Ar^4 and Ar^5 are phenyl linked by an oxygen atom to form a phenoxazine ring, and R^8 is phenyl or 3,5-diphenylbenzene that is unsubstituted or substituted with one or more C_{1-20} alkyl groups.

Triazines form an exemplary class of electron-transporting units, for example optionally substituted di-or tri-(hetero)aryltriazine attached as a side group through one of the (hetero)aryl groups. Other exemplary electron-transporting units are pyrimidines and pyridines; sulfoxides and phosphine oxides; benzophenones; and boranes, each of which may be unsubstituted or substituted with one or more substituents, for example one or more C_{1-20} alkyl groups.

Exemplary electron-transporting units CT have formula (VII):



(VII)

wherein Ar^4, Ar^5 and Ar^6 are as described with reference to formula (VI) above, and may each independently be substituted with one or more substituents described with reference to Ar^4, Ar^5 and Ar^6, and z in each occurrence is independently at least 1, optionally 1, 2 or 3 and X^1 is N or CR^7, wherein R^7 is H or a substituent, preferably H or C_{1-10} alkyl..

Preferably, Ar^4, Ar^5 and Ar^6 of formula (VII) are each phenyl, each phenyl being optionally and independently substituted with one or more C_{1-20} alkyl groups.

In one preferred embodiment, all 3 groups X^1 are N.

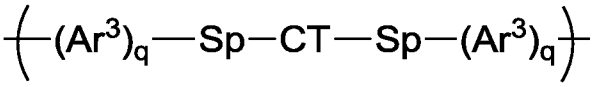
If all 3 groups X^1 are CR^7 then at least one of Ar^1, Ar^2 and Ar^3 is preferably a heteroaromatic group comprising N.

Each of Ar^4, Ar^5 and Ar^6 may independently be substituted with one or more substituents. In one arrangement, Ar^4, Ar^5 and Ar^6 are phenyl in each occurrence. Exemplary substituents include R^{11} as described above with reference to formula (VI), for example C_{1-20} alkyl or alkoxy.

Ar^6 of formula (VII) is preferably phenyl, and is optionally substituted with one or more C_{1-20} alkyl groups or a crosslinkable unit. The crosslinkable unit may or may not be a unit of formulae (I)-(III) bound directly to Ar^6 or spaced apart from Ar^6 by a spacer group.

A preferred repeat unit of formula (VII) is 2,4-6-triphenyl-1,3,5-triazine wherein the phenyl groups are unsubstituted or substituted with one or more C_{1-20} alkyl groups.

The charge-transporting units CT may be provided as distinct repeat units formed by polymerising a corresponding monomer. Alternatively, the one or more CT units may form part of a larger repeat unit, for example a repeat unit of formula (VIII):



(VIII)

wherein CT represents a conjugated charge-transporting group; each Ar^3 independently represents an unsubstituted or substituted aryl or heteroaryl; q is at least 1, optionally 1, 2 or 3; and each Sp independently represents a spacer group forming a break in conjugation between Ar^3 and CT.

Sp is preferably a branched, linear or cyclic C_{1-20} alkyl group.

Exemplary CT groups may be units of formula (VI) or (VII) described above.

Ar^3 is preferably an unsubstituted or substituted aryl, optionally an unsubstituted or substituted phenyl or fluorene. Optional substituents for Ar^3 may be selected from R^3 as described above, and are preferably selected from one or more C_{1-20} alkyl substituents.

q is preferably 1.

The polymer may comprise repeat units that block or reduce conjugation along the polymer chain and thereby increase the polymer bandgap. For example, the polymer may comprise units that are twisted out of the plane of the polymer backbone, reducing conjugation along the polymer backbone, or units that do not provide any conjugation path along the polymer backbone. Exemplary repeat units that reduce conjugation along the polymer backbone are substituted or unsubstituted 1,3-substituted phenylene repeat units, and 1,4-phenylene repeat substituted with a C_{1-20} alkyl group in the 2- and / or 5-position, as described above with reference to formula (V).

The molar percentage of charge transporting repeat units in the polymer, for example repeat units of formula (VI), (VII) or (VIII), may be in the range of up to 75 mol %, optionally in the range of up to 50 mol % of the total number of repeat units of the polymer.

Preferred methods for preparation of conjugated polymers, such as polymers comprising one or more of repeat units of formulae (IV), (V), (VI), (VII) and (VIII) as described above, 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 pi-Conjugated Poly(arylene)s Prepared by Organometallic Processes", 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 reactive 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 one reactive group is a halogen and the other reactive group is a boron derivative group. Alternatively, block or regioregular 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 sulfonic acids and sulfonic acid esters such as tosylate, mesylate and triflate.

Organic light-emitting devices (OLEDs)

In one embodiment, the present invention includes an organic light-emitting device (OLED) comprising an anode, a cathode and a light-emitting layer between the anode and the cathode, wherein the light-emitting layer comprises a compound or a composition according to the invention.

Figure 1, which is not drawn to any scale, illustrates schematically an OLED according to an embodiment of the invention. The OLED is carried on substrate 1 and comprises an anode (2), a cathode (4) and a light-emitting layer (3) between the anode and the cathode.

Within the scope of the invention, further layers (not shown) may be provided between the anode and the cathode including, without limitation, charge-transporting layers, charge-blocking layers and charge injection layers.

The device may contain more than one (e.g. 2 or 3) light-emitting layers.

Exemplary OLED structures including one or more further layers include the following:

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

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

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

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

In one preferred embodiment, the OLED comprises at least one, optionally both, of a hole injection layer and a hole transporting layer.

The light-emitting layer (3) may contain a host material and a phosphorescent compound of the invention. The light-emitting layer may contain further light-emitting compounds, for example further phosphorescent or fluorescent light-emitting materials having a colour of emission differing from that of the compound of the invention. The host material may combine holes injected from the anode and electrons injected from the cathode to form singlet and triplet excitons. The triplet excitons at least may be transferred to the phosphorescent compound, and decay from a triplet excited state of the phosphorescent compound to produce phosphorescence.

Producing light-emitting layer(s) for an OLED

Multiple organic layers of an OLED may be formed by deposition of formulations containing the active materials for each layer.

During OLED formation, a layer of the device may be crosslinked to prevent it from partially or completely dissolving in the solvent or solvents used to deposit an overlying layer. Layers that may be cross-linked include a hole-transporting layer prior to formation by solution processing of an overlying light-emitting layer, or crosslinking of one light-emitting layer prior to formation by solution processing of another, overlying light-emitting layer.

Suitable cross-linkable groups include groups comprising a reactive double bond such as a vinyl or acrylate group, or a benzocyclobutane group. Where a layer to be cross-linked contains a polymer, the crosslinkable groups may be provided as substituents of repeat units of the polymer.

Techniques for forming layers from a formulation include printing and coating techniques such spin-coating, dip-coating, roll printing, screen printing and inkjet printing.

Coating methods such as spin-coating are particularly suitable for devices wherein patterning of the light-emitting layer is unnecessary e.g. for lighting applications or simple monochrome segmented displays.

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

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

White OLEDs

An OLED containing a compound of the invention may emit white light.

The emitted white light may have a CIE x coordinate equivalent to that emitted by a black body at a temperature in the range of 2500-9000K and a CIE y coordinate within 0.05 or 0.025 of the CIE y co-ordinate of said light emitted by a black body, optionally a CIE x coordinate equivalent to that emitted by a black body at a temperature in the range of 2700-4500K.

White light may be formed of blue emission from a compound of the invention, and one or more fluorescent or phosphorescent materials emitting at longer wavelengths that, together with emission of the compound of formulae of the invention, provide white light. White light may be provided by blue emission and longer wavelength excimer

emission from a compound of the invention, in which case the compound of the invention may be the only light-emitting material of a white light emitting composition.

A white-emitting OLED may have a single light-emitting layer emitting white light, or may contain two or more light-emitting layers wherein the light emitted from the two or more layers combine to provide white light.

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 and the light-emitting layer or layers of an OLED to improve 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 polyacid such as polystyrene sulfonate (PSS) as disclosed in EP 0901176 and EP 0947123, polyacrylic acid or a fluorinated sulfonic acid, for example Nafion ®; polyaniline as disclosed in US 5723873 and US 5798170; and optionally substituted polythiophene or poly(thienothiophene). Examples of conductive inorganic materials include transition metal oxides such as VOx, MoOx and RuOx as disclosed in Journal of Physics D: Applied Physics (1996), 29(11), 2750-2753.

Charge transporting and charge blocking layers

A hole transporting layer may be provided between the anode and the light-emitting layer or layers. Likewise, an electron transporting layer may be provided between the cathode and the light-emitting layer or layers.

Similarly, an electron blocking layer may be provided between the anode and the light-emitting layer and a hole blocking layer may be provided between the cathode and the light-emitting 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.

A charge-transporting layer or charge-blocking layer may be crosslinked, particularly if a layer overlying that charge-transporting or charge-blocking layer is deposited from a solution. The crosslinkable group used for this crosslinking may be a crosslinkable group comprising a reactive double bond such as a vinyl or acrylate group, or a benzocyclobutane group.

If present, a hole transporting layer located between the anode and the light-emitting layers preferably has a HOMO level of less than or equal to 5.5 eV, more preferably around 4.8-5.5 eV as measured by cyclic voltammetry. The HOMO level of the hole transport layer may be selected so as to be within 0.2 eV, optionally within 0.1 eV, of an adjacent layer (such as a light-emitting layer) in order to provide a small barrier to hole transport between these layers.

If present, an electron transporting layer located between the light-emitting layers and cathode preferably has a LUMO level of around 3-3.5 eV as measured by square wave cyclic voltammetry. For example, a layer of a silicon monoxide or silicon dioxide or other thin dielectric layer having thickness in the range of 0.2-2nm may be provided between the light-emitting layer nearest the cathode and the cathode. HOMO and LUMO levels may be measured using cyclic voltammetry.

A hole transporting layer may contain a hole-transporting (hetero)arylamine, such as a homopolymer or copolymer comprising hole transporting repeat units of formula (VI). Exemplary copolymers comprise repeat units of formula (VI) and optionally substituted (hetero)arylene co-repeat units, such as phenyl, fluorene or indenofluorene repeat units as described above, wherein each of said (hetero)arylene repeat units may optionally be substituted with one or more substituents such as alkyl or alkoxy groups. Specific co-repeat units include fluorene repeat units of formula (IV) and optionally substituted phenylene repeat units of formula (V) as described above.

If a charge-transporting layer is provided adjacent to a light-emitting layer containing a compound of the invention then the triplet energy level of the material or materials of the charge transporting layer are preferably at least the same as or higher than that of the compound of the invention

An electron transporting layer may contain a polymer comprising a chain of optionally substituted arylene repeat units, such as a chain of fluorene repeat units.

Cathode

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

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

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

Organic optoelectronic 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 one or more plastic layers, for example a substrate of alternating plastic and dielectric barrier layers or a laminate of thin glass and plastic.

The device may be 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 or an airtight container. 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.

The present invention encompasses a method of forming an organic light-emitting device according to the invention. The method comprises the step of forming the light-emitting layer over one of the anode or cathode, and forming the other of the anode or cathode over the light-emitting layer.

Within this method, the light-emitting layer may be formed by depositing a formulation according to the invention and evaporating the solvent.

The invention will now be described by means of example only by reference to the following Examples and Figures.

Description of the Drawings

Figure 1 illustrates an OLED according to an embodiment of the invention;

Figure 2 is the normalized photoluminescence spectra (10 % emitter by weight in polyvinylcarbazole) of two compositions according to embodiments of the invention (Example 1 and Example 2) and a comparative composition (Comparative Emitter 1);

Figure 3 is a CIE chart of emission from two compositions according to embodiments of the invention containing Emitter Example 1 and polyvinylcarbazole, one composition containing 5 weight % of Emitter Example 1 and the other containing 10 weight % of Emitter Example 1;

Figure 4 is a CIE chart of chart of emission at 1 , 5 and 10 emitter weight % from a composition according to another embodiment of the invention containing Emitter Example 2 in polyvinylcarbazole;

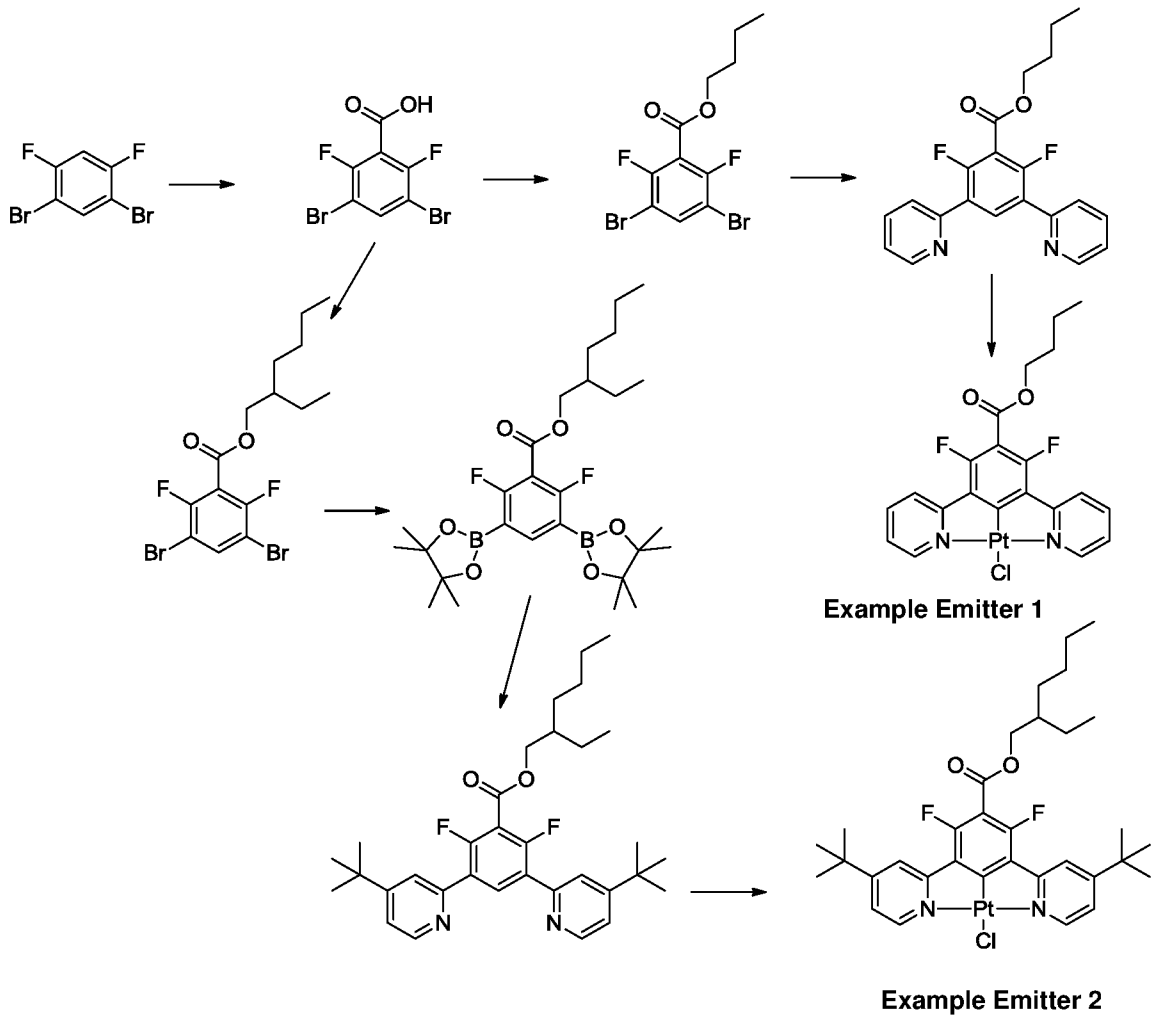
Figure 5 is a CIE chart of emission at 1, 5 and 10 emitter weight % from acomparative composition of Comparative Emitter 1 in polyvinylcarbazole; and

Figure 6 is a CIE chart of emission from OLEDs according to embodiments of the invention containing Emitter Example 1 and a comparative OLED containing Comparative Emitter 2.

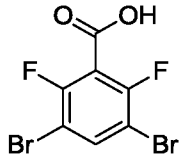
Examples

Preparation of emitters

Example Emitters 1 and 2 were prepared according to the following reaction scheme:

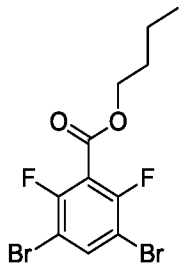


3,5-dibromo-2,6-difluorobenzoic acid



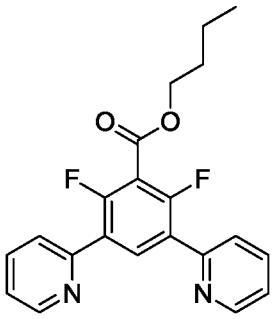
A cooled (-78 ^{0}C) solution of diisopropylamine (2.25 mL, 16 mmol) in dry THF (10 mL) was treated with n-BuLi (10 mL, 16 mmol, 1.6 M) and then allowed to warm to room temperature. This LDA solution was added drop wise to a solution of 1,5-dibromo-2,4-difluorobenzene (3.50 g, 13 mmol) in dry THF (20 mL) at -78 ^{0}C. The solution was stirred at -78 ^{0}C for 20 minutes, dry $CO_{2(g)}$ was bubbled through it, it was warmed to room temperature and dil HCl (10 mL) was added, extracted to DCM, dried ($MgSO_4$) and evaporated. Yield (2.73 g, 67 %) as a pale white solid. ^{1}H NMR ($CDCl_3$): δ 8.35 (1H, t, J=9 Hz).

n-butyl 3,5-dibromo-2,6-difluorobenzoate



A mixture of 3,5-dibromo-2,6-difluorobenzoic acid (1.08 g, 3.41 mmol) and $SOCl_2$ (10 mL) was heated under reflux for 3 hours. All volatiles were removed by rotary evaporation. Butan-1-ol (20 mL) was added and the mixture was stirred at 50-60°C for 3 hours. The mixture was then evaporated to dryness to give the pure ester. Yield (1.26 g, 99%). ^{1}H NMR ($CDCl_3$): δ 7.83 (1H, t, J= 9 Hz), 4.35 (2H, t, J=9 Hz, OCH_2), 1.67 (2H, quintet, J=7 Hz, CH_2), 1.35 (2H, m, CH_2), 0.95 (3H, t J=7 Hz, CH_3).

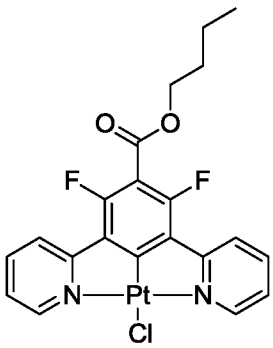
n-butyl 2,6-difluoro-3,5-di(2-pyridyl) benzoate



A solution of butyl 1,5-dibromo-2,4-difluoro benzoate (1.21g, 3.2 mmols), 2-tributylstanyl pyridine (2.31 g, 6.4 mmols) in dry DMF was degassed by bubbling

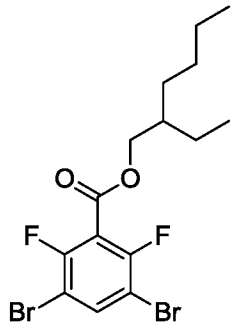
nitriogen through the mixture for 10 minutes. $Pd(PPh_3)_4$ (0.2 g) was added and the mixture was heated at 115 °C for 15 hours. The reaction mixture was evaporated to dryness. The product was purified by column chromatography using silica gel and a mixture of petrolium ether/EtOAc: 1:1 as an eluent. Yield (0.44 g , 36%). ^1H NMR ($CDCl_3$) δ 8.75 (2H, dd), 8.73 (2H, t J=7.2 Hz), 7.74 (4H, m), 7.23 (2H,m), 4.32 (2H, t J=7.1 Hz), 1.70 (2H, quintet, J= 5 Hz), 1.40 (2H, m), 0.95 (3H, t, J=7 Hz).

Preparation of Example Emitter 1



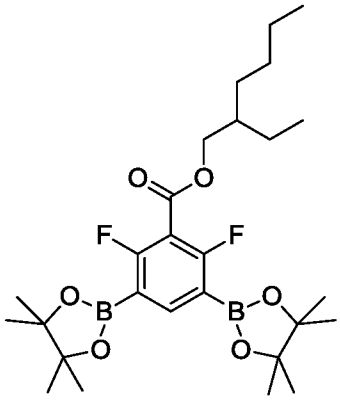
To a solution of the butyl 4,6-difluoro-1,3-(2-dipyridyl)benzoate (0.2 g, 5 mmol) in glacial acetic acid 50 (mL), potassium tetrachloroplatinate (0.2g, 5 mmols) was added. The mixture was heated under reflux with vigorous stirring for 24 hours. The resulting mixture was evaporated to dryness, DCM (50 mL) was added and the mixture was filtered through sintered glass filter (porosity 3). To the filtrate, ethanol (5 mL) was added and the mixture was evaporated to a volume of approximately 6-8 mL. At this point most of the product has precipitated. The solid was filtered off, washed thoroughly with ethanol and dried. Yield 105 mg. ^1H NMR ($CDCl_3$): δ 9.31 (2H, dd J=6 and 1 Hz, $J(^{195}Pt)$=36 Hz, H_6), 7.96 (4H, m, H_5, H_4), 7.35 (2H, td J=4 and 1 Hz, H_3), 4.40 (2H, t J=9 Hz, CH_2O), 1.85(2H, quintet J=5 Hz, CH_2), 1.53 (2H, m, CH_2), 1.01 (3H, t J=9.3 Hz, CH_3).

2-Ethylhexyl 3,5-dibromo-2,6-difluorobenzoate



A mixture of 3,5-dibromo-2,6-difluorobenzoic acid (0.62 g, 1.91 mmols) and $SOCl_2$ (10 mL) was heated under reflux for 3 hours. Excess of thionyl chloride was evaporated and 2-ethyl-1-hexanol (20 mL) was added. The mixture was stirred at 60°C for 3 hours. Evaporation of the excess in vacuum afforded pure product. Yield (0.82 g, 97 %). ^1H NMR ($CDCl_3$): δ 7.85 (1H, t J=7.1 Hz, ArH), 4.28 (2H, d, J=5.6, OCH_2), 1.67 (1H, m, CH), 1.23-1.43 (8H, m, CH_2x4), 0.87-0.98 (6H, m, CH_3x2).

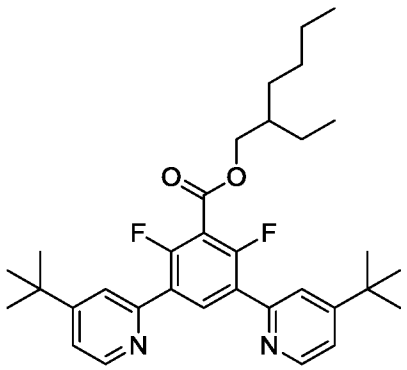
2-Ethylhexyl 2,6-difluoro-3,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)benzoate



A mixture of 1,5-dibromoderivative (2.8 g, 6.54 mmol), bispinacolatodiboron (4.3 g, 17.0 mmol), potassium acetate (3.7 g, 45 mmol), $dppfPdCl_2$ (320 mg, 6% mol) and dry dioxane (60 cm^3) was degassed by bubbling argon through the mixture for 10 minutes. The reaction mixture was stirred at 100°C for 30 min and then at 85°C for an additional 15 hours. The solvent was removed by rotary evaporation. The residue was treated with hexane (50 mL) and filtered. The filtrate was evaporated to dryness and the product was purified by column chromatography (silica gel, ethyl acetate/hexane ½). Yield is 3 g. NMR showed the product as well as about 30% of the product of deboronation. This

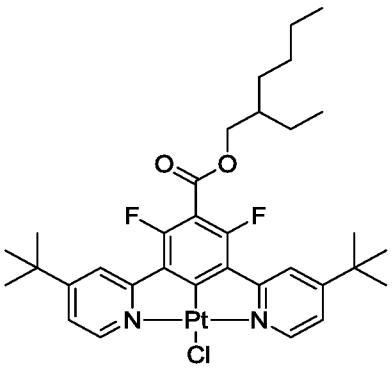
mixture was used in the next step. ^{1}H NMR ($CDCl_3$): δ 8.18 (1H, t, J= 7.1 Hz, ArH), 4.26 (2H, d, J=5.6, OCH_2), 1.7 (1H, m, CH), 1.4 (s, 24H, CH_3x8), 1.23-1.43 (8H, m, CH_2x4), 0.87-0.98 (6H, m, CH_3x2).

2-Ethylhexyl 2,6-difluoro-3,5-di(4-tertbutylpyridine2-yl)benzoate



A mixture of 2-chloro-4-tert-butylpyridine (1.95 g, 11.5 mmol), 1,3-diboronic acid dipinacol ester derivative (3g, 5.7 mmol), aqueous K_3PO_4 (3M, 11 mL, 33 mmol) and 1,4-dioxane (60 ml) was degassed by bubbling nitrogen through the mixture for 15 minutes. $Pd(PPh_3)_4$ (600 mg) was added and the mixture was degassed for additional 10 minutes. The reaction mixture was then stirred at 90-95°C for 14 hours under nitrogen atmosphere. 1,4-Dioxane was removed by rotary evaporation. The product was extracted with 1/1 mixture of petrol ether and ethyl acetate. Organic layer was washed with brine, dried over $MgSO_4$ filtered and evaporated to dryness. The product was purified by column chromatography (silicagel, ethyl acetate/hexane, 1/3 vol). ^{1}H NMR ($CDCl_3$): δ 8.61 (br.d, J = 5.2 Hz, pyH), 8.6 (1H, t J= 8.7 Hz, ArH), 7.75 (1H, br.s., pyH), 7.27 (2H, dd, J= 5.2, 1.2 Hz, pyH), 4.33 (2H, d, J=5.6, OCH_2), 1.72 (1H, m, CH), 1.23-1.43 (8H, m, CH_2x4), 1.32 (18H, s, t-Bu), 0.87-0.98 (6H, m, CH_3x2).

Preparation of Example Emitter 2



A mixture of the proligand (99 mg, 0.18 mmol), potassium tetrachloroplatinate (77 mg, 0.18 mmol) and glacial acetic acid 50 (mL) was heated under reflux with vigorous stirring for 23 hours. The resulted mixture was evaporated to dryness. The product was then purified by column chromatography using silicagel and dichloromethane. Yield 85 mg, 61%. ^{1}H NMR ($CDCl_3$): δ 9.23 (2H, d, J=6.2 Hz, J(^{195}Pt)=36 Hz), 7.97 (2H, d, J = 1.2 Hz), 7.30 (2H, dd, J= 6.2, 1.2 Hz), 4.32 (2H, d, J=5.6, OCH_2), 1.75 (1H, m, CH), 1.23-1.43 (8H, m, CH_2x4), 1.40 (18H, s, t-Bu), 0.87-0.98 (6H, m, CH_3x2).

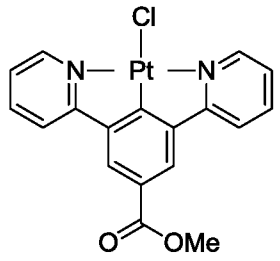
Preparation of triaryl ligands by diborylation of dibromobenzene and Suzuki-Miyaura coupling is disclosed by Avitia et al, Tetrahedron Letters 2011, 52, 1631-1634.

The substituents on the outer pyridine rings of emitter E220 are both the same, however it will be appreciated that attachment of the two outer pyridine rings to the central benzene ring in separate steps allows for synthesis of emitters with different (asymmetric) substitutions of the outer pyridine rings, including emitters in which the two outer pyridine rings are substituted with different substituents; substituted in different positions; and where one outer pyridine is substituted with one or more substituents and the other outer pyridine ring is unsubstituted.

Comparison of emission properties

An ester-substituted Comparative Emitter 1 is disclosed by Kalinowski et al, Adv. Mater. 2007, 19, 4000-40005. A difluoro-substituted Comparative Emitter 2 is disclosed by Yang et al., Appl. Phys. Lett. 2008, 93, 193305 and Kalinowski et al, Chemical Physics

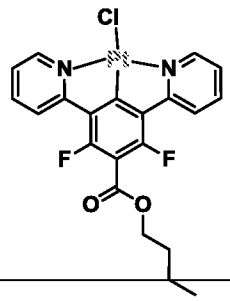
2010, 278, 47-57. These two comparative emitters have been analysed here for comparison.

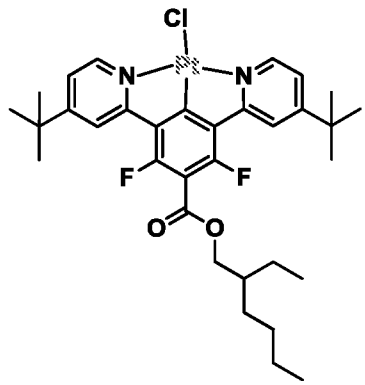
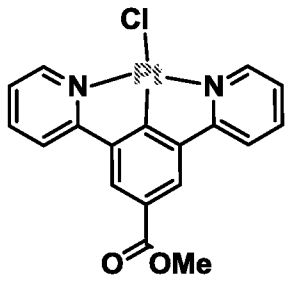
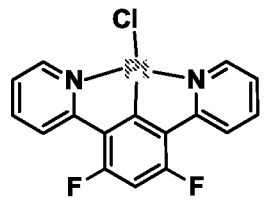


Comparative Emitter 1

Calculated energy levels and triplet levels of Examples 1-3 and Comparative Emitter 1 are provided in Table 1. For the ground state geometry optimisation, the density functional theory (DFT) with the level of B3LYP is used (Gaussian 03 software). Based on these results, the HOMO and LUMO energy are calculated. Then, the time dependent density functional theory with the level of B3LYP is used for the calculation of triplet (T1) energy. For all DFT and TDDFT calculations, 6-31g* is used as the basis, but when 6-31g* is unavailable, LANL2DZ is used instead. (e.g., 6-31g* for C, N and H, but LANL2DZ for Pt.)

Table 1 – Calculated energy and triplet levels

Emitter	**HOMO (eV)**	**LUMO (eV)**	**Peak wavelength (nm)**
Emitter 1 	-5.89	-2.17	464

Emitter 2 	-5.73	-1.96	446
Comparative Emitter 1 	-5.67	-2.06	485
Comparative Emitter 2 	-5.73	-2.05	471

Comparative Emitter 1 is disclosed in Williams et al, Adv. Mater, 2007, 19, 4000.

Comparative Emitter 2 is disclosed in Appl. Phys. Lett. 93, 2008, 193305.

Emitter Examples 1 and 2 both have a shorter peak wavelength than Comparative Emitters 1 and 2. Without wishing to be bound by any theory, it is believed that the blue shift of Emitter Example 1 as compared to Comparative Emitters 1 and 2 is due to the central ring of Emitter Example 1 being electron deficient relative to the central ring of Comparative Emitters 1 and 2.

As shown in the modelling data, the electron donating alkyl groups of Emitter Example 2 causes a blue shift relative to Emitter Example 1. Without wishing to be bound by any theory, it is believed that electron-donating groups present on the outer rings of the tridentate ligand of Emitter Example 2 cause a blue shift.

Within the scope of the present invention, the substituents on the central and outer rings may be selected so as to tune the colour of emission of the metal complex. A shift to a longer peak wavelength may be achieved by substitution of one or both of the outer rings with one or more electron-withdrawing substituents. A shift to a shorter peak wavelength may be achieved by substitution of one or both of the outer rings with one or more electron-donating substituents.

Compositions

A composition of Emitter 1 and poly(9-vinylcarbazole) (PVK) was dissolved in anisole, and the solution was deposited onto a glass substrate by spin-coating to form a film of the composition. Films having an emitter concentration of 1 wt % and 10 wt % relative to weight of polyvinylcarbazole were prepared.

For the purpose of comparison, the same compositions were prepared using Comparative Emitter 1, disclosed by Kalinowski et al., Adv. Mater. 2007, 19, 4000-4005 and described above in place of Emitter 1 and Emitter 2.

Photoluminescent quantum yield (PLQY) and CIE (x, y) co-ordinates for these compositions were measured and are presented in Table 2.

Table 2 – PLQY & CIE coordinates of emitters

Composition Number	**Composition:** emitter concentration (wt %)	**PLQY (%)**	**CIE X**	**CIE Y**
1	1% Comparative Emitter 1	79	0.190	0.470
2	1%: Emitter Example 1	71	0.170	0.320
3	1% Emitter Example 2	75	0.180	0.300
4	10% Comparative Emitter 1	55	0.260	0.490
5	10%: Emitter Example 1	46	0.370	0.350
6	10% Emitter Example 2	76	0.350	0.340

At high concentration (10 %), efficiency is higher for Emitter Example 2 than for Comparative Emitter 1. Without wishing to be bound by any theory, it is believed that the bulky substituents of Emitter Example 2 may prevent concentration quenching effects at high concentrations. The CIE y value is lower for Emitter 1 and Emitter 2 as compared to Comparative Emitter 1 at both 1 and 10 weight %.

Figure 2 shows the photoluminescent spectra of the 10 weight % compositions 4-6 above. The peak emission of Emitters 1 and 2 (Compositions 4 and 5) in the blue region are at a shorter wavelength than for Comparative Emitter 1 (Composition 6). Furthermore, blue-shifting has the effect of blue-shifting excimer emission, resulting in less excimer emission occurring in the infra-red region of the spectrum. In addition, an unexpectedly strong excimer emission of Emitters 1 and 2 is achieved in the red region of the spectrum compared to the emission of the Comparative Emitter 1 in this region.

With reference to Figures 3 and 4, which show CIE charts for compositions containing Emitter Examples 1 and 2 respectively, it can be seen that white emission that is close to black body radiation can be obtained by selection of the emitter concentration and control of excimer emission.

With reference to Figure 5, it can be seen that it is not possible to obtain emission close to black body radiation from compositions of Comparative Emitter 1.

Device example

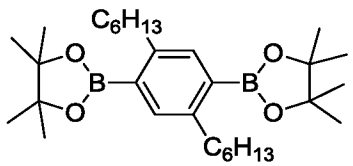
An organic light-emitting device having the following structure was prepared:

ITO / HIL / HTL / LE / Cathode

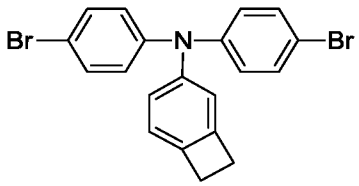
Wherein ITO is an indium-tin oxide anode; HIL is a hole-injecting layer comprising a hole-injecting material, HTL is a hole-transporting layer, LE is a light-emitting layer formed by spin-coating Polymer Example 1; and the cathode comprises a layer of metal fluoride in contact with the light-emitting layer and a layer of aluminium formed over the layer of metal fluoride.

A substrate carrying ITO was cleaned using UV / Ozone. The hole injection layer was formed by spin-coating an aqueous formulation of a hole-injection material available from Plextronics, Inc. A hole transporting layer was formed to a thickness of 20 nm by spin-coating a hole-transporting polymer and crosslinking the polymer by heating. A light-emitting layer was formed by depositing a light-emitting composition to a thickness of 75 nm by spin-coating. A cathode was formed by evaporation of a first layer of a metal fluoride to a thickness of about 2 nm, a second layer of aluminium to a thickness of about 200 nm and an optional third layer of silver.

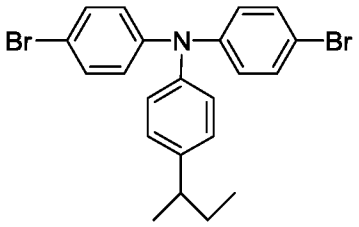
The hole transporting polymer was formed by Suzuki polymerisation as described in WO 00/53656 of the following monomers:



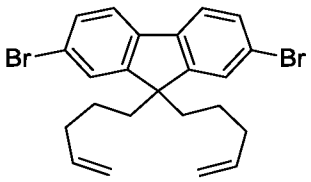
50 mol %



10 mol %



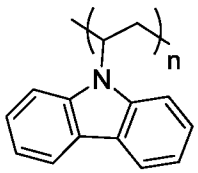
35 mol %



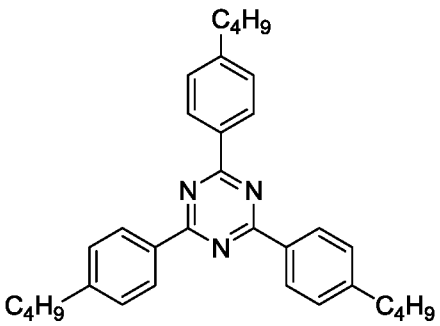
5 mol %

The hole transport polymer has the following molecular weight characteristics (GPC relative to polystyrene standard, in Dalton): Mw 350,000, Mp 264,000, Mn 42,000, Pd 8.24.

For the light-emitting layer, a blend of PVK, ET1 and emitter was spun from o-xylene. The structures of PVK, ET1 and Comparative Emitter 2 are shown below.



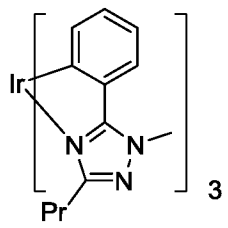
PVK (polyvinylcarbazole)



ET1

PVK (Sigma-Aldrich, average M_w 1,100,000 Dalton) was further purified by precipitation from chlorobenzene into methanol. ET1 was synthesised following the general procedure disclosed in WO 2008/025997.

Comparative Emitter 2 was prepared as described in US 7,659,010B2.



Comparative Emitter 2

The composition of the emissive layer and device results are shown in Table 3. White emission was obtained from Emitter Example 1 (see Figure 6). In particular, at 10 weight % of Emitter Example 1, near-pure white light is obtained whereas the device containing Comparative Emitter 2 does not produce white light.

Table 3 – Device data

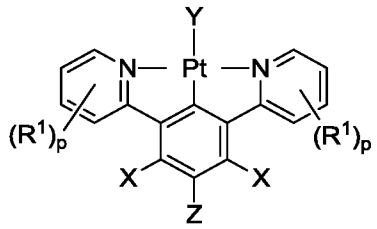
Emissive layer			**CIE coordinates at 400 cd/m2**		**Median at 1000Cd/m2**				
Emitter (% by weight)	**PVK (% by weight)**	**ET1 (% by weight)**	**CIE x**	**CIE y**	**V**	**J**	**Efficiency (Lm/W)**	**Efficiency (Cd/A)**	**EQE (%)**
Comparative Emitter 2 (10)	70	20	0.154	0.232	9.98	6.2	5.04	16.03	9.76
Emitter Example 1 (10)	70	20	0.32	0.336	13.02	78.5	0.31	1.27	1.21
Emitter Example 1 (5)	72.5	22.5	0.204	0.321	10.98	31	0.92	3.22	2.15
Emitter Example 1 (1)	74.5	24.5	0.154	0.31	9.4	15	2.23	6.69	3.77

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

combinations of features disclosed herein will be apparent to those skilled in the art without departing from the scope of the invention as set forth in the following claims.

CLAIMS

1. A compound of formula (I):



(I)

wherein:

X is an electron withdrawing group, and each X is independently selected;

Y is ligand;

Z is selected from the group consisting of cyano, C_{1-10} perfluoroalkyl and –C(=O)OR wherein R is a hydrocarbyl;

each R^1 is independently a substituent; and

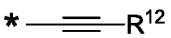
p in each occurrence is independently 0, 1 , 2, 3 or 4.

2. The compound of claim 1, wherein Z is –C(=O)OR.

3. The compound of claim 1 or claim 2, wherein each X is independently a halogen.

4. The compound of claim 3, wherein one or more X is fluorine.

5. The compound of claim 4, wherein each X is fluorine.

6. The compound of any preceding claim wherein Y is selected from the group consisting of a halogen, cyano, unsubstituted or substituted phenoxy and a group of formula: 

wherein R^{12} is a hydrocarbyl, optionally C_{1-30} hydrocarbyl, optionally C_{1-20} alkyl or phenyl substituted with one or more C_{1-20} alkyl groups.

7. The compound of claim 6, wherein Y is chlorine.

8. The compound of any of claims 2-7, wherein R is a C_{1-60} hydrocarbyl.

9. The compound of claim 8, wherein R is selected from the group consisting of linear, branched or cyclic alkyl; aryl that may be unsubstituted or substituted with one or more alkyl groups; and a branched or unbranched chain of aryl groups

wherein each aryl group may independently be unsubstituted or substituted with one or more alkyl groups.

10. The compound of claim 9 wherein R is a branched C_{1-20} alkyl.

11. The compound of any preceding claim, wherein each R^1 is independently a C_{1-60} hydrocarbyl, *–OR^{12}, *–NR^{12} or *–BR^{12}_2, wherein * represents a point of attachment to the metal complex and R^{12} independently in each occurrence is a hydrocarbyl, optionally C_{1-30} hydrocarbyl, optionally C_{1-20} alkyl or phenyl substituted with one or more C_{1-20} alkyl groups and wherein two R^{12} groups linked to the same N or B atom may be linked to form a ring.

12. The compound of claim 11, wherein each R^1 is independently selected from the group consisting of linear, branched or cyclic alkyl; aryl that may be unsubstituted or substituted with one or more alkyl groups; and a branched or unbranched chain of aryl groups wherein each aryl group may independently be unsubstituted or substituted with one or more alkyl groups.

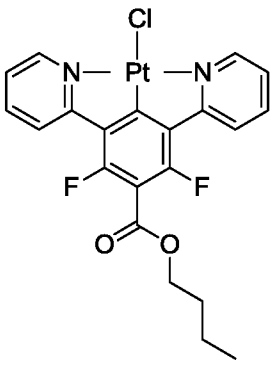
13. The compound of claim 12, wherein at least one R^1 comprises a tertiary carbon atom.

14. The compound of claim 13, wherein at least one R^1 is a tert-butyl group.

15. The compound of any of claims 1-10, wherein each p is 0.

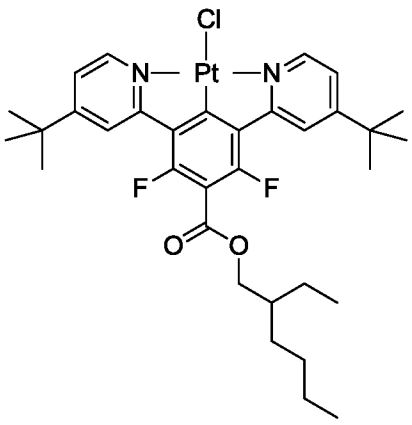
16. The compound of any of claims 1-14, wherein at least one p, optionally each p, is 1.

17. A compound of formula (II):



(II)

18. A compound of formula (III):



(III)

19. A compound according to any preceding claim wherein a photoluminsecent spectrum of the compound has a peak at a wavelength of less than 480 nm, preferably less than 470 nm.

20. A composition comprising a charge-transporting host material and a compound according to any preceding claim.

21. The composition of claim 20, wherein the compound according to any preceding claim is present in an amount of greater than 1% by weight, preferably up to 15% by weight.

22. A white light emitting composition comprising the compound of any one of claims 1-19.

23. The white light emitting composition according to claim 22 wherein the composition comprises one or more light emitting materials in addition to the compound of any one of claims 1-19.

24. The white light emitting composition according to claim 22, wherein the compound of any one of claims 1-19 is the only light emitting material in the composition.

25. A formulation comprising a composition according to any one of claims 20-24 and at least one solvent.

26. An organic light-emitting device comprising an anode, a cathode and a light-emitting layer between the anode and the cathode, wherein the light-emitting layer comprises a compound according to any of claims 1-19.

27. The organic light-emitting device according to claim 26 wherein the light-emitting layer comprises a composition according to any one of claims 20-24.

28. A method of forming an organic light-emitting device of claim 26 or claim 27, the method comprising the step of forming the light-emitting layer over one of the anode or cathode, and forming the other of the anode or cathode over the light-emitting layer.

29. The method of claim 28, wherein the light-emitting layer is formed by depositing the formulation according to claim 25 and evaporating the solvent.

FIGURE 1

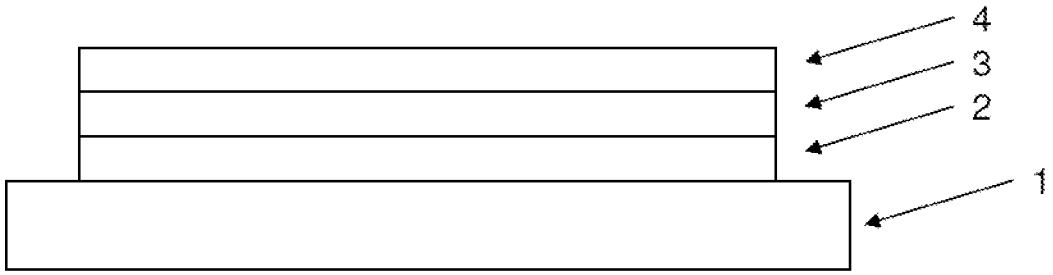


FIGURE 2

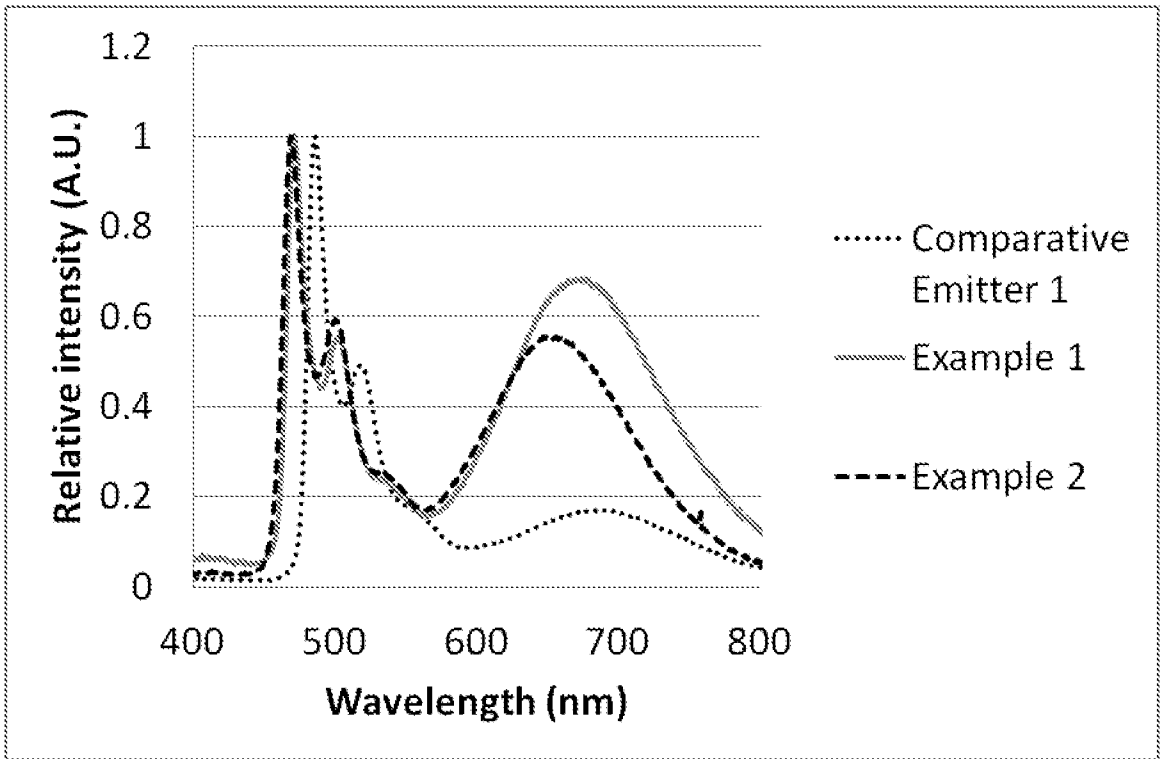
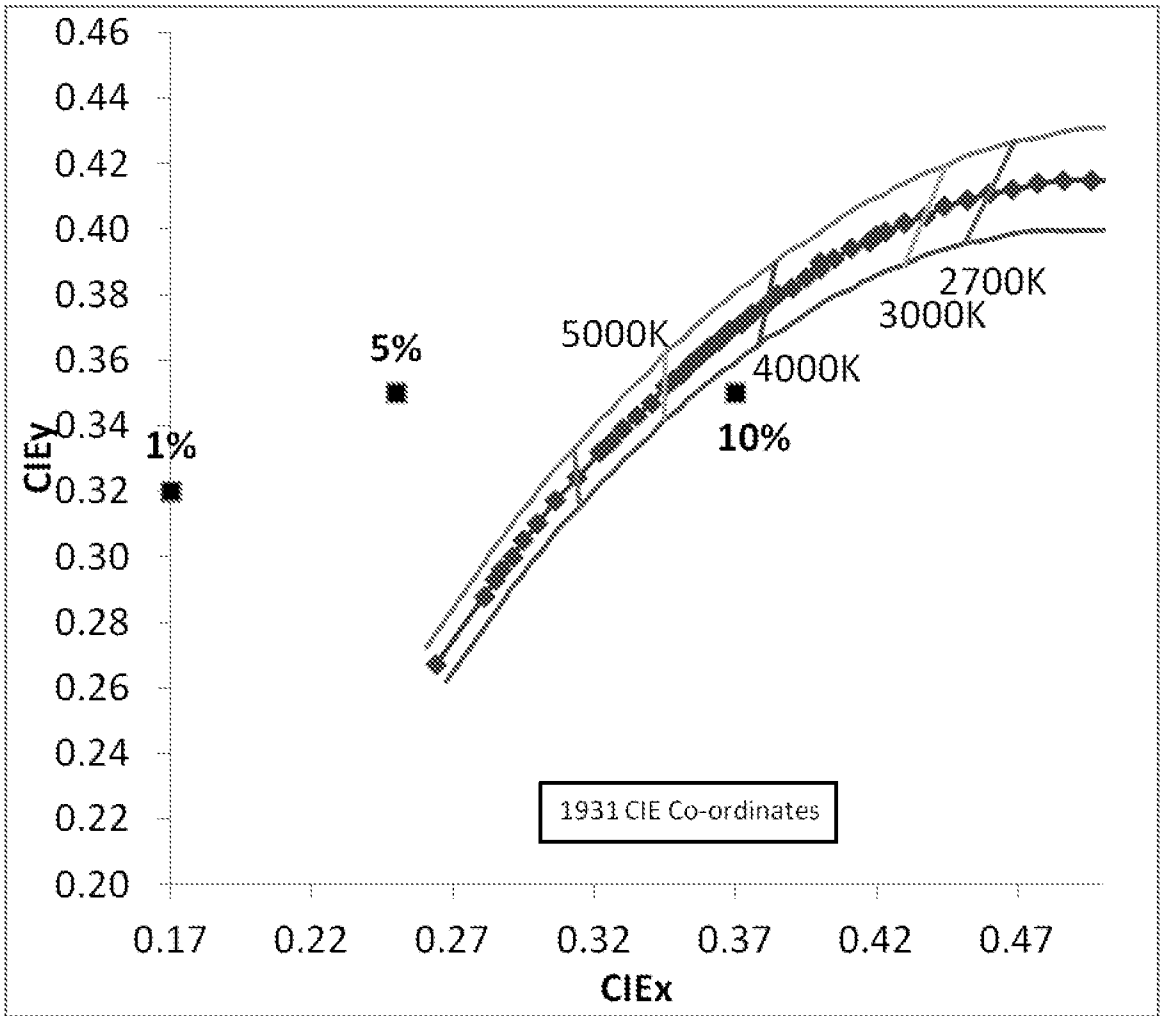


FIGURE 3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0.42
0.40
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0.20
CIEy
0.17
0.22
0.27
0.32
0.37
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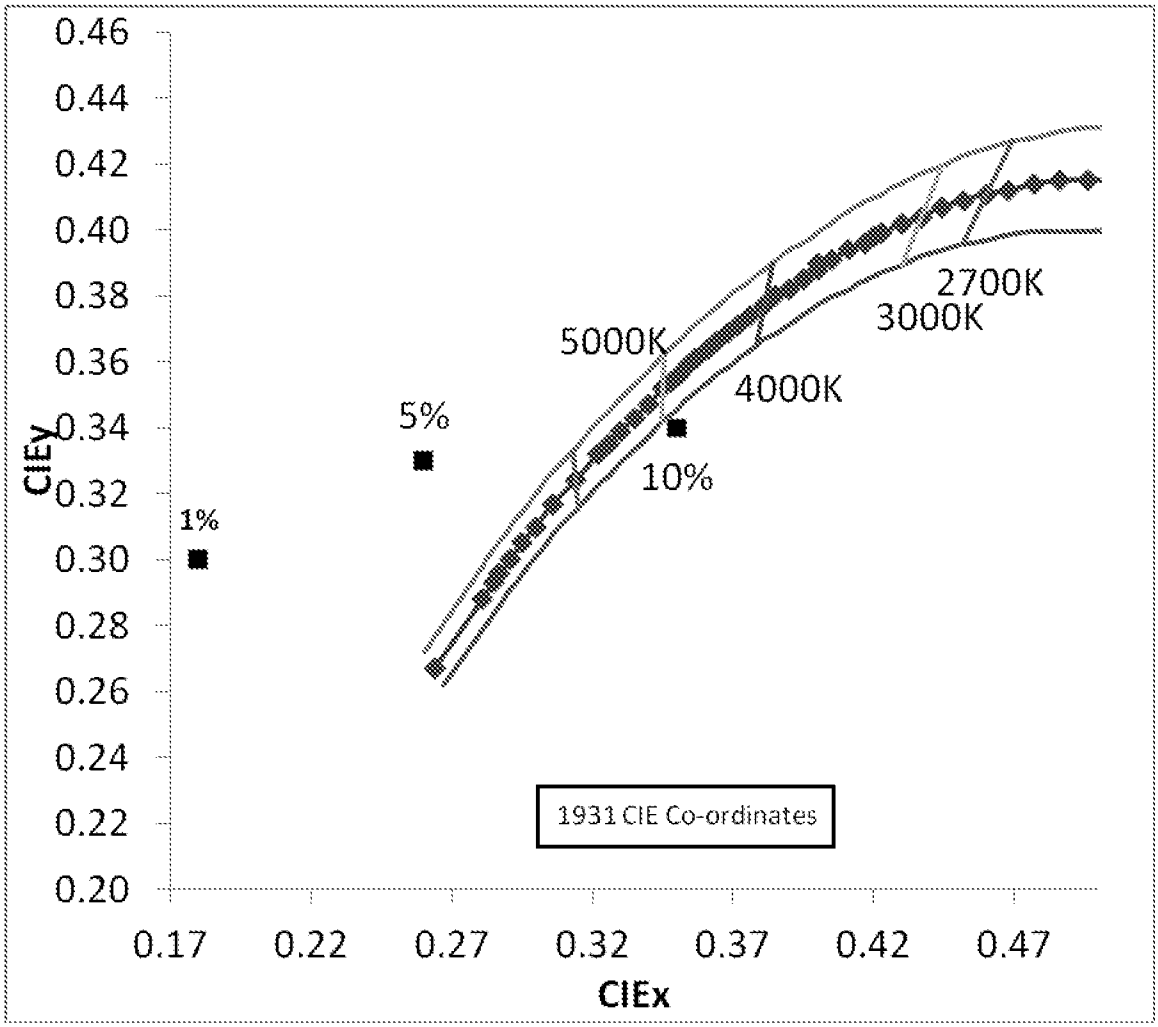
CIEx
1%
5%
10%
5000K
4000K
3000K
2700K
1931 CIE Co-ordinates

FIGURE 4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CIEy
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0.32
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CIEx
1%
5%
10%
2700K
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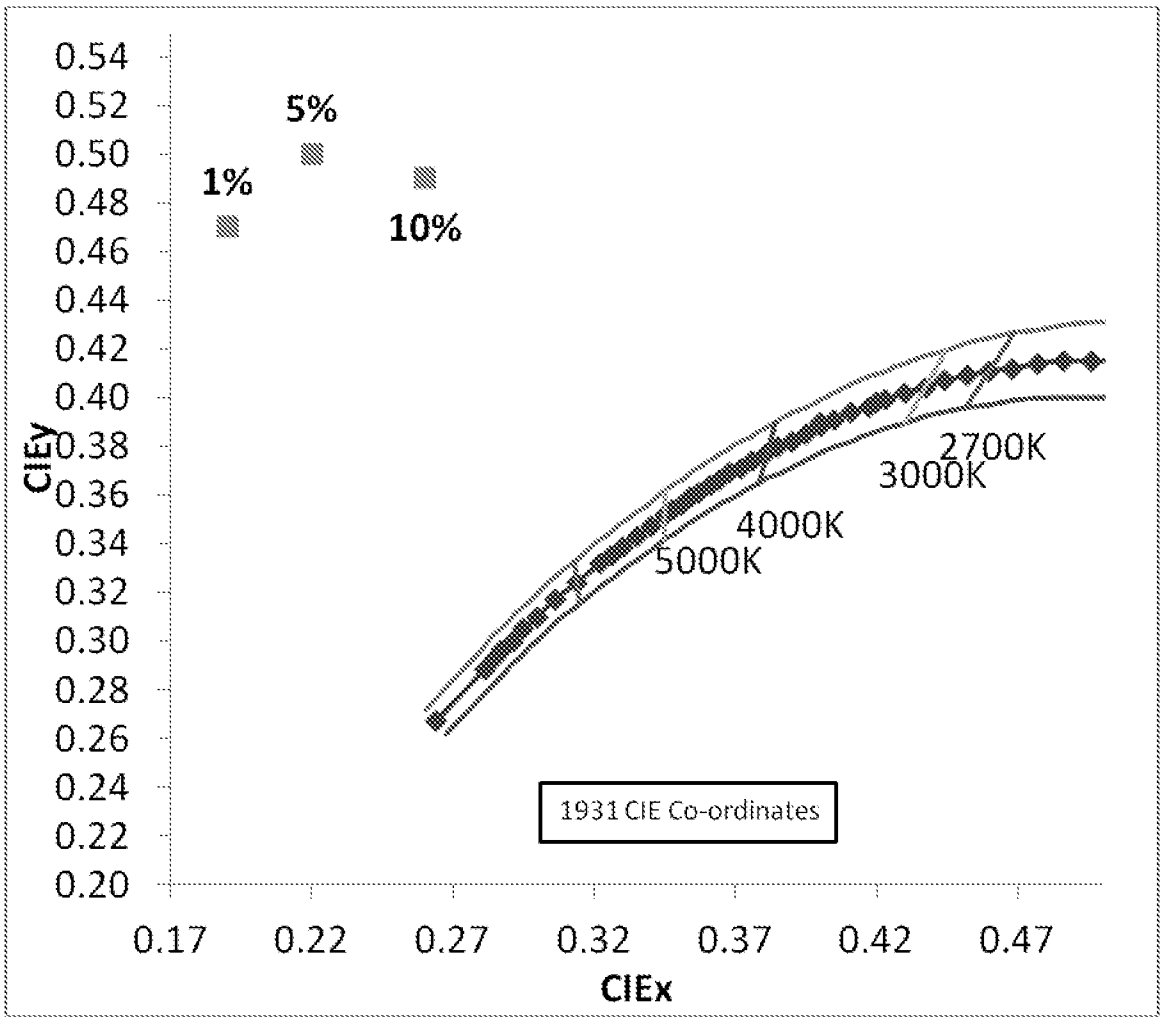
5000K
1931 CIE Co-ordinates

FIGURE 5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CIEy
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1%
10%
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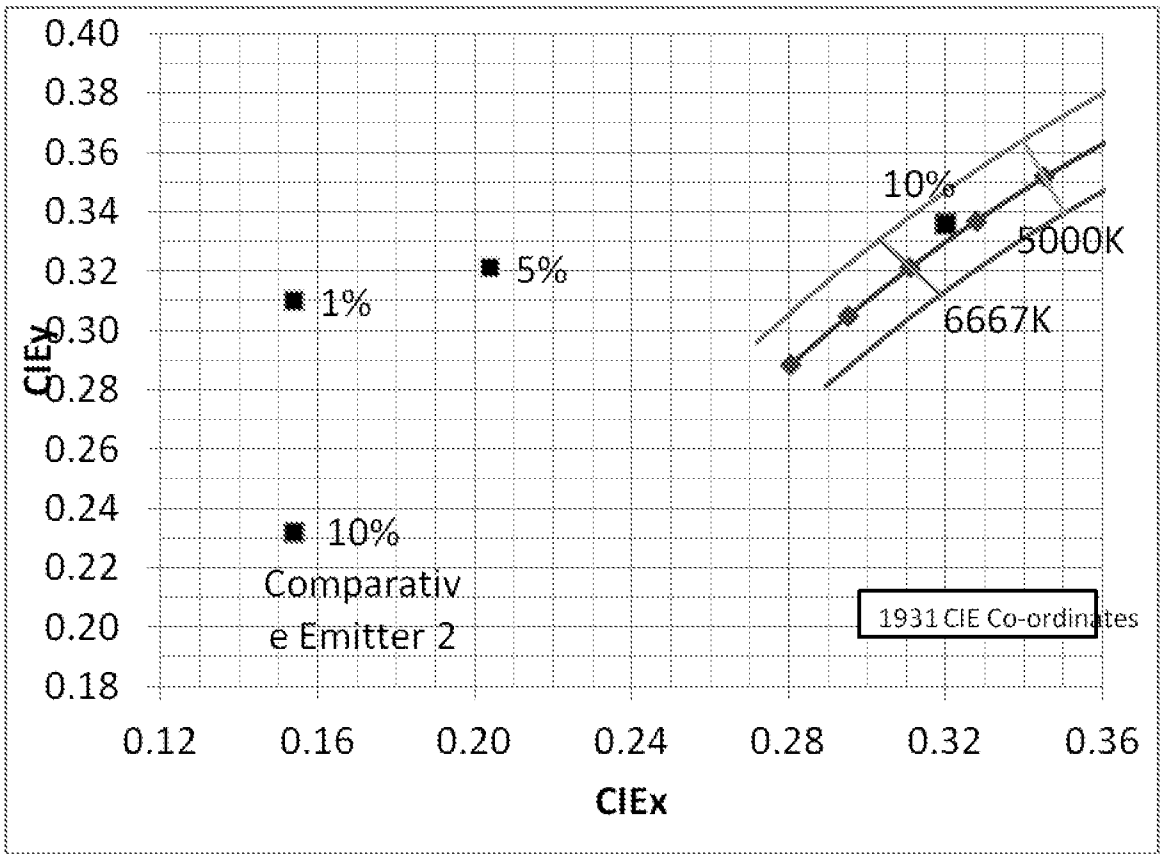
CIEx

FIGURE 6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0.24
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0.32
0.36
CIEx
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5%
10%
Comparativ
e Emitter 2
10%
5000K
6667K
1931 CIE Co-ordinates

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2013/051814

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07F15/00 C09K11/06 H01L51/00 H05B33/14
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)
C07F H05B C09K

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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZIXING WANG ET AL: "Facile Synthesis and Characterization of Phosphorescent Pt(N [and] C [and] N)X Complexes", INORGANIC CHEMISTRY, vol. 49, no. 24, 20 December 2010 (2010-12-20), pages 11276-11286, XP055078100, ISSN: 0020-1669, DOI: 10.1021/ic100740e cited in the application	1-29
Y	compounds Pt-5, Pt-6 paragraph [Introduction]	2,6, 11-14
X	WO 2009/040551 A1 (UNIV YORK [GB]; BRUCE DUNCAN W [GB]; KOZHEVNIKOV VALEY [GB]) 2 April 2009 (2009-04-02)	1-29
Y	examples 8-22 claim 1	2,6, 11-14

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

☒ See patent family annex.

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"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

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"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
11 September 2013	19/09/2013

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	Eberhard, Michael

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2013/051814

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009040551 A1	02-04-2009	EP 2207784 A1	21-07-2010
		JP 2011508723 A	17-03-2011
		US 2010317851 A1	16-12-2010
		US 2012157681 A1	21-06-2012
		WO 2009040551 A1	02-04-2009