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BOURCET et al.(10) **Pub. No.: US 2017/0294591 A1**(43) **Pub. Date: Oct. 12, 2017**(54) **COMPOUND, COMPOSITION AND
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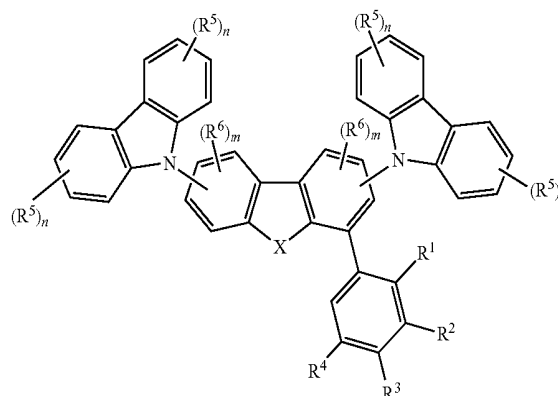
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(2013.01)(57) **ABSTRACT**

A compound of formula (I) wherein: X is O , S, NR^{11} , CR^{11}_2 or SiR^{11}_2 wherein R^{11} in each occurrence is independently a substituent; R^1 is a substituent; R^2 , R^3 , and R^4 are each independently H or a substituent; R^5 and R^6 independently in each occurrence is a substituent; m independently in each occurrence is 0, 1 or 2; and n independently in each occurrence is 0, 1, 2, 3 or 4. The compound may be used as a host for a phosphorescent light-emitting material in an organic light-emitting device.

(I)



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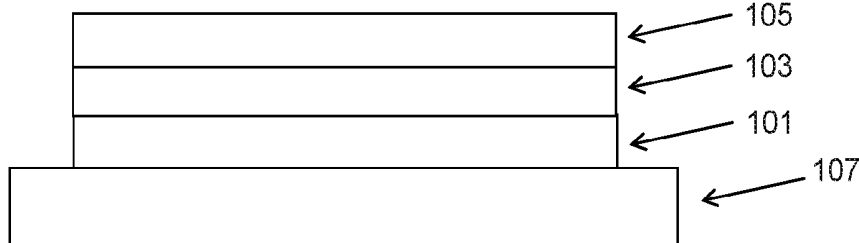
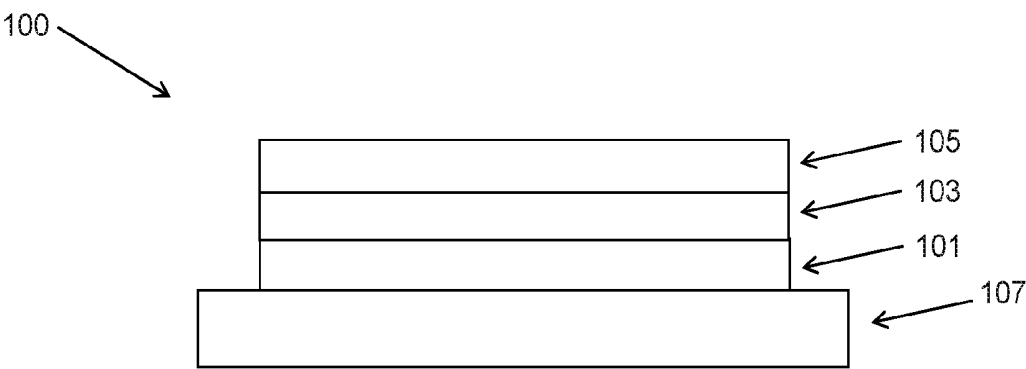


FIGURE 1



COMPOUND, COMPOSITION AND ORGANIC LIGHT-EMITTING DEVICE

BACKGROUND OF THE INVENTION

[0001] 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.

[0002] An OLED may comprise a substrate carrying an anode, a cathode and one or more organic light-emitting layers between the anode and cathode.

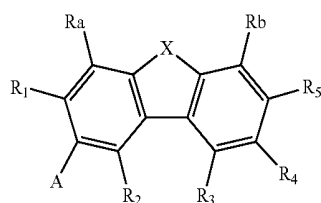
[0003] Holes are injected into the device through the anode and electrons are injected through the cathode during operation of the device. Holes in the highest occupied molecular orbital (HOMO) and electrons in the lowest unoccupied molecular orbital (LUMO) of a light-emitting material combine to form an exciton that releases its energy as light.

[0004] Light-emitting materials include small molecule, polymeric and dendrimeric materials. Light-emitting polymers include poly(arylene vinylenes) such as poly(p-phenylene vinylenes) and polymers containing arylene repeat units, such as fluorene repeat units.

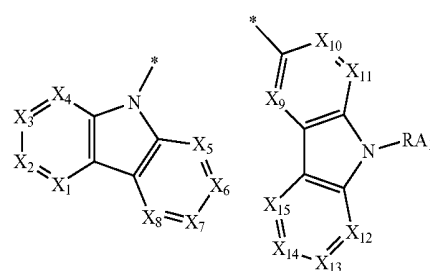
[0005] A light emitting layer may comprise a host material and a light-emitting dopant wherein energy is transferred from the host material to the light-emitting dopant. For example, J. Appl. Phys. 65, 3610, 1989 discloses a host material doped with a fluorescent light-emitting dopant (that is, a light-emitting material in which light is emitted via decay of a singlet exciton).

[0006] Phosphorescent dopants are also known (that is, a light-emitting dopant in which light is emitted via decay of a triplet exciton).

[0007] JP 2013/016717 discloses compounds of formula (1):



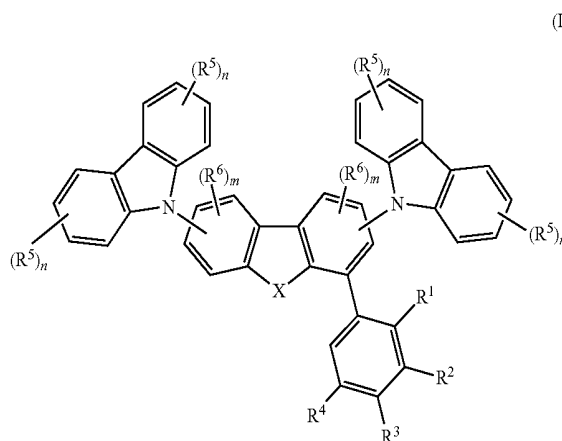
[0008] wherein R_1 - R_5 , Ra and Rb are H or a substituent, X is O, S, NR^8 , $Si(R^8)_2$ or CR^9R^{10} and A is a group of formula (II):



[0009] wherein X_1 - X_{15} is N or CR and RA_1 is H or a substituent.

SUMMARY OF THE INVENTION

[0010] In a first aspect the invention provides a compound of formula (I):



[0011] wherein:

[0012] X is O, S, NR^{11} , CR^{11}_2 or SiR^{11}_2 wherein R^{11} in each occurrence is independently a substituent;

[0013] R^1 is a substituent;

[0014] R^2 , R^3 , and R^4 are each independently H or a substituent;

[0015] R^5 and R^6 independently in each occurrence is a substituent;

[0016] m independently in each occurrence is 0, 1 or 2; and

[0017] n independently in each occurrence is 0, 1, 2, 3 or 4.

[0018] In a second aspect the invention provides a composition comprising a compound according to the first aspect and at least one light-emitting dopant.

[0019] In a third aspect the invention provides a formulation comprising a compound according to the first aspect or a composition according to the second aspect and at least one solvent.

[0020] In a fourth aspect the invention provides an organic light-emitting device comprising an anode, a cathode and one or more organic layers between the anode and cathode including a light-emitting layer wherein at least one of the one or more organic layers comprises a compound according to the first aspect.

[0021] In a fifth aspect the invention provides a method of forming an organic light-emitting device according to the fourth aspect, the method comprising the step of forming the light-emitting layer over one of the anode and the cathode and forming the other of the anode and the cathode over the light-emitting layer.

DESCRIPTION OF THE DRAWINGS

[0022] The invention will now be described in more detail with reference to the drawings in which:

[0023] FIG. 1 illustrates an OLED according to an embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0024] FIG. 1 illustrates an OLED 100 according to an embodiment of the invention comprising an anode 101, a cathode 105 and a light-emitting layer 103 between the anode and cathode. The device 100 is supported on a substrate 107, for example a glass or plastic substrate.

[0025] One or more further layers may be provided between the anode 101 and cathode 105, for example hole-transporting layers, electron transporting layers, hole blocking layers and electron blocking layers. The device may contain more than one light-emitting layer.

[0026] Preferred device structures include:

[0027] Anode/Hole-injection layer/Light-emitting layer/Cathode

[0028] Anode/Hole transporting layer/Light-emitting layer/Cathode

[0029] Anode/Hole-injection layer/Hole-transporting layer/Light-emitting layer/Cathode

[0030] Anode/Hole-injection layer/Hole-transporting layer/Light-emitting layer/Electron-transporting layer/Cathode.

[0031] Preferably, at least one of a hole-transporting layer and hole injection layer is present.

[0032] Preferably, both a hole injection layer and hole-transporting layer are present.

[0033] Light-emitting materials include red, green and blue light-emitting materials.

[0034] A blue emitting material may have a photoluminescent spectrum with a peak in the range of 400-490 nm, optionally 420-490 nm.

[0035] A green emitting material may have a photoluminescent spectrum with a peak in the range of more than 490 nm up to 580 nm, optionally more than 490 nm up to 540 nm

[0036] A red emitting material may optionally have a peak in its photoluminescent spectrum of more than 580 nm up to 630 nm, optionally 585-625 nm.

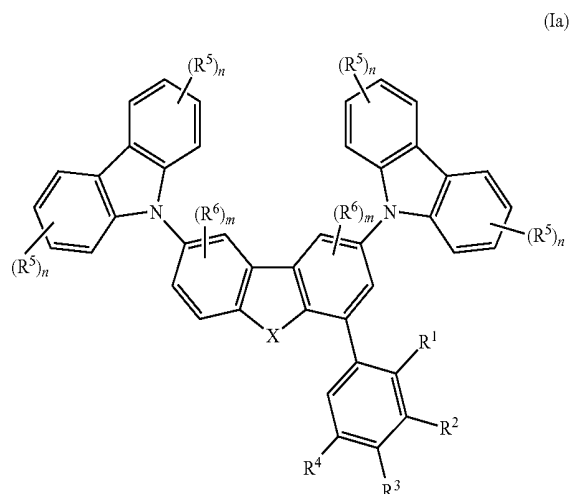
[0037] Light-emitting layer 103 may contain a compound of formula (I) doped with one or more luminescent dopants. The light-emitting layer 103 may consist essentially of these materials or may contain one or more further materials, for example one or more charge-transporting materials or one or more further light-emitting materials. When used as a host material for one or more light-emitting dopants, the lowest excited stated singlet (S^1) or the lowest excited state triplet (T^1) energy level of the host material is preferably no more than 0.1 eV below that of the light-emitting material, and is more preferably about the same as or higher than that of the light-emitting material in order to avoid quenching of luminescence from the light-emitting dopant.

[0038] In the case where the luminescent dopant is a phosphorescent dopant, the compound of formula (I) preferably has a T^1 of greater than 2.8 eV, preferably greater than 3.0 eV.

[0039] Triplet energy levels of compounds of formula (I) may be measured from the energy onset of the phosphorescence spectrum measured by low temperature phosphorescence spectroscopy (Y. V. Romaovskii et al, Physical Review Letters, 2000, 85 (5), p 1027, A. van Dijken et al, Journal of the American Chemical Society, 2004, 126, p 7718). The triplet energy level of a phosphorescent material may be measured from its phosphorescence spectrum.

[0040] In a preferred embodiment, light-emitting layer 103 contains a compound of formula (I) and at least one of green and blue phosphorescent light-emitting materials.

[0041] The compound of formula (I) may have formula (Ia):



[0042] R^1 may be selected from the group consisting of:

[0043] 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 $-COO-$, and one or more H atoms may be replaced with F; and

[0044] $-(Ar^1)_p$ wherein Ar^1 independently in each occurrence is an aryl or heteroaryl group that may be unsubstituted or substituted with one or more substituents, preferably unsubstituted phenyl or phenyl substituted with one or more C_{1-10} alkyl groups, and p is at least 1, optionally 1, 2 or 3.

[0045] Preferably, R^1 is a C_{1-30} hydrocarbyl group, more preferably C_{1-20} alkyl, phenyl or biphenyl which may be unsubstituted or substituted with one or more C_{1-10} alkyl groups.

[0046] A biphenyl group R^1 may be 1,2-, 1,3- or 1,4-linked biphenyl group.

[0047] R^2, R^3 and R^4 independently may be selected from the group consisting of:

[0048] H;

[0049] CN;

[0050] 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 $-COO-$, and one or more H atoms may be replaced with F; and

[0051] aryl and heteroaryl groups that may be unsubstituted or substituted with one or more substituents, preferably unsubstituted phenyl or phenyl substituted with one or more C_{1-20} alkyl groups.

[0052] Each R^5 and R^6 , where present, may independently in each occurrence be selected from the group consisting of 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 $-COO-$, and one or more H atoms may be replaced with F; aryl and heteroaryl groups that may be unsubstituted or substituted with one or more substituents, preferably phenyl substituted with one or more C_{1-20} alkyl groups; F; CN and NO_2 .

[0053] Preferably, each m is 0.

[0054] Preferably, each n is 0.

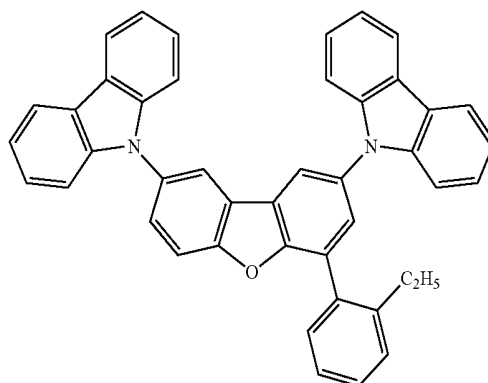
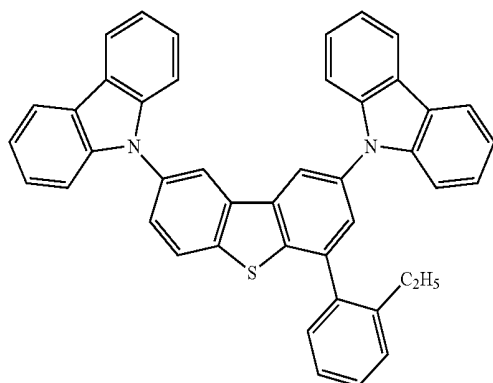
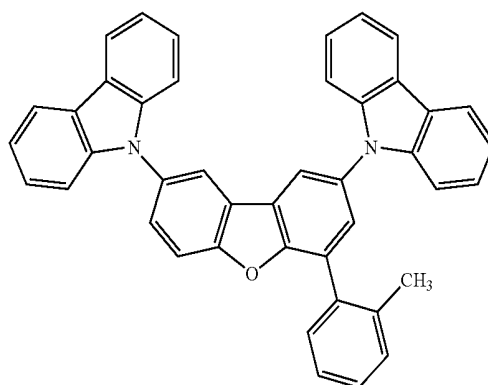
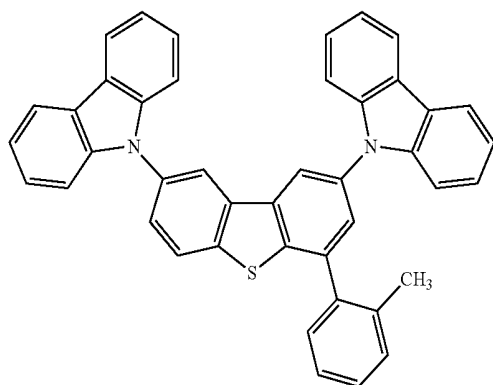
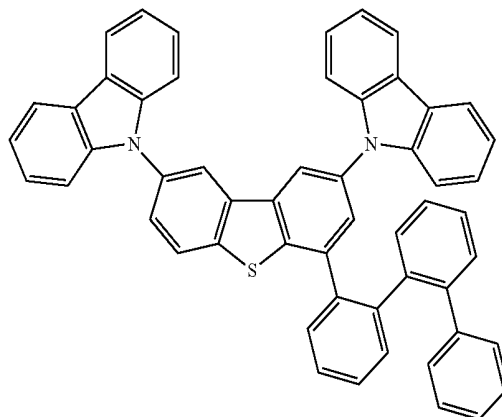
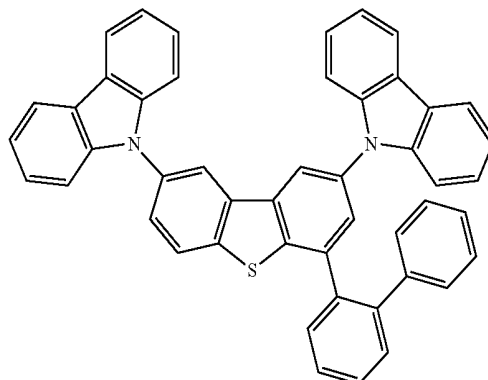
[0055] Preferably, each of R^2 , R^3 and R^4 is H.

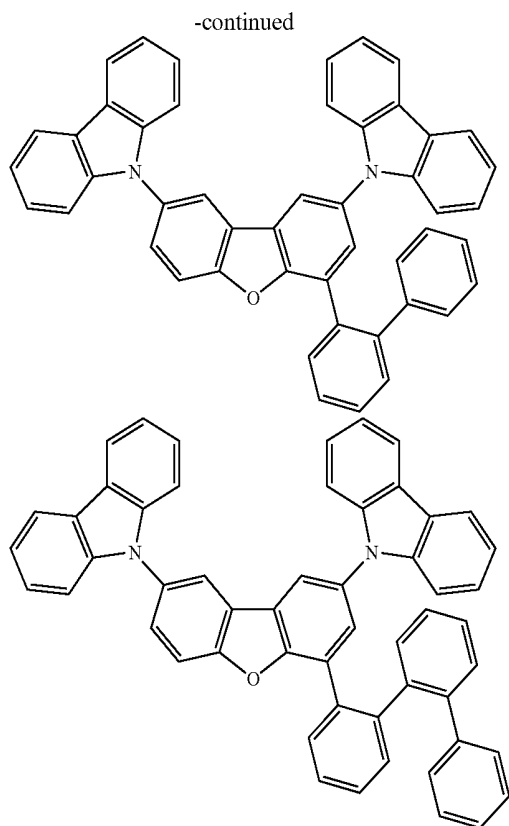
[0056] Where present, R^{11} is preferably a C_{1-40} hydrocarbyl group, optionally a C_{1-20} alkyl group or phenyl that may be unsubstituted or substituted with one or more C_{1-20} alkyl groups.

[0057] Preferably, X is S or O.

[0058] Exemplary compounds of formula (I) include the following:

-continued





[0059] Light-Emitting Compounds

[0060] A preferred use of compounds of formula (I) is as the host material for a light-emitting material in a light-emitting layer of an OLED.

[0061] Suitable light-emitting materials for a light-emitting layer include polymeric, small molecule and dendritic light-emitting materials, each of which may be fluorescent or phosphorescent.

[0062] A light-emitting layer of an OLED may be unpatterned, or may be patterned to form discrete pixels. Each pixel may be further divided into subpixels. The light-emitting layer may contain a single light-emitting material, for example for a monochrome display or other monochrome device, or may contain materials emitting different colours, in particular red, green and blue light-emitting materials for a full-colour display.

[0063] A light-emitting layer may contain more than one light-emitting material, for example a mixture of light-emitting materials that together provide white light emission.

[0064] A white-emitting OLED may contain a single, white-emitting layer or may contain two or more layers that emit different colours which, in combination, produce white light. The light emitted from a white-emitting OLED may have 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 2700-6000K.

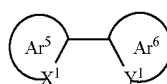
[0065] Exemplary phosphorescent light-emitting materials include metal complexes comprising substituted or unsubstituted complexes of formula (IX):



[0066] wherein M is a metal; each of L^1 , L^2 and L^3 is a coordinating group; q is a positive integer; r and s are each independently 0 or a positive integer; and the sum of (a. q)+(b. r)+(c. s) is equal to the number of coordination sites available on M, wherein a is the number of coordination sites on L^1 , b is the number of coordination sites on L^2 and c is the number of coordination sites on L^3 . a, b and c are preferably each independently 1, 2 or 3. Preferably, a, b and c are each a bidentate ligand (a, b and c are each 2). In an embodiment, q is 3 and s is 0. In another embodiment, q is 1 or 2, r is 1 and s is 0 or 1.

[0067] Heavy elements M induce strong spin-orbit coupling to allow rapid intersystem crossing and emission from triplet or higher states. Suitable heavy metals M include d-block metals, in particular those in rows 2 and 3 i.e. elements 39 to 48 and 72 to 80, in particular ruthenium, rhodium, palladium, rhenium, osmium, iridium, platinum and gold. Iridium is particularly preferred.

[0068] Exemplary ligands L^1 , L^2 and L^3 include carbon or nitrogen donors such as porphyrin or bidentate ligands of formula (X):



(X)

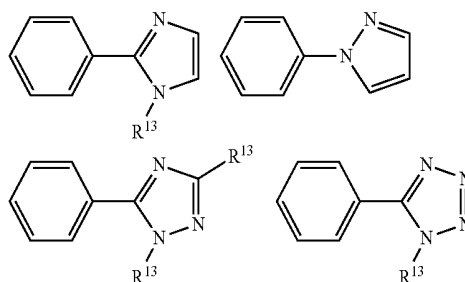
[0069] wherein Ar^5 and Ar^6 may be the same or different and are independently selected from substituted or unsubstituted aryl or heteroaryl; X^1 and Y^1 may be the same or different and are independently selected from carbon or nitrogen; and Ar^5 and Ar^6 may be fused together. Ligands wherein X^1 is carbon and Y^1 is nitrogen are preferred, in particular ligands in which Ar^5 is a single ring or fused heteroaromatic of N and C atoms only, for example pyridyl or isoquinoline, and Ar^6 is a single ring or fused aromatic, for example phenyl or naphthyl.

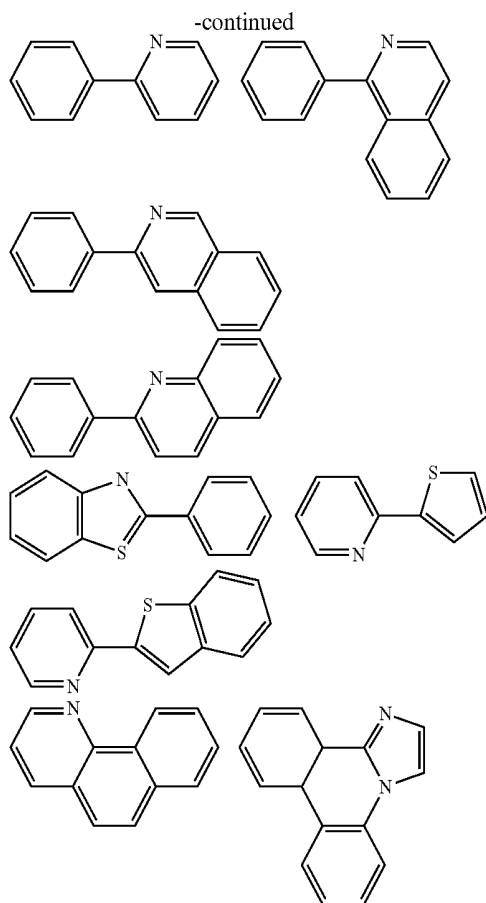
[0070] To achieve red emission, Ar^5 may be selected from phenyl, fluorene, naphthyl and Ar^6 are selected from quinoline, isoquinoline, thiophene and benzothiophene.

[0071] To achieve green emission, Ar^5 may be selected from phenyl or fluorene and Ar^6 may be pyridine.

[0072] To achieve blue emission, Ar^5 may be selected from phenyl and Ar^6 may be selected from imidazole, pyrazole, triazole and tetrazole.

[0073] Examples of bidentate ligands are illustrated below:





[0074] Each of Ar^5 and Ar^6 may carry one or more substituents. Two or more of these substituents may be linked to form a ring, for example an aromatic ring.

[0075] Other ligands suitable for use with d-block elements include diketones, in particular acetylacetonate (acac), tetrakis-(pyrazol-1-yl)borate, 2-carboxypyridyl, tri-arylphosphines and pyridine, each of which may be substituted.

[0076] Exemplary substituents include groups R^{13} as described below with reference to Formula (VII). Particularly preferred substituents include fluorine or trifluoromethyl which may be used to blue-shift the emission of the complex, for example as disclosed in WO 02/45466, WO 02/44189, US 2002-117662 and US 2002-182441; alkyl or alkoxy groups, for example C_{1-20} alkyl or alkoxy, which may be as disclosed in JP 2002-324679; carbazole which may be used to assist hole transport to the complex when used as an emissive material, for example as disclosed in WO 02/81448; phenyl or biphenyl which may be unsubstituted or substituted with one or more C_{1-10} alkyl groups; and dendrons which may be used to obtain or enhance solution processability of the metal complex, for example as disclosed in WO 02/66552.

[0077] One or more of L^1 , L^2 and L^3 may comprise a carbene group.

[0078] A light-emitting dendrimer comprises a light-emitting core bound to one or more dendrons, wherein each dendron comprises a branching point and two or more dendritic branches. Preferably, the dendron is at least partially conjugated, and at least one of the branching points

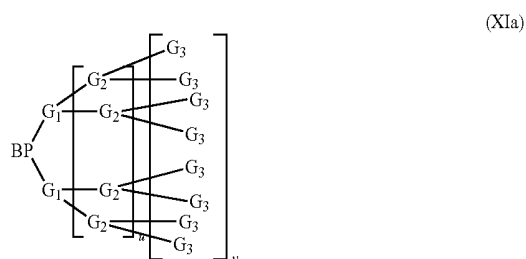
and dendritic branches comprises an aryl or heteroaryl group, for example a phenyl group. In one arrangement, the branching point group and the branching groups are all phenyl, and each phenyl may independently be substituted with one or more substituents, for example alkyl or alkoxy.

[0079] A dendron may have optionally substituted formula (XI)



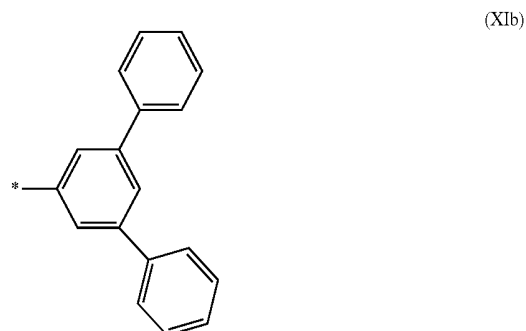
[0080] wherein BP represents a branching point for attachment to a core and G_1 represents first generation branching groups.

[0081] The dendron may be a first, second, third or higher generation dendron. G_1 may be substituted with two or more second generation branching groups G_2 , and so on, as in optionally substituted formula (XIa):



[0082] wherein u is 0 or 1; v is 0 if u is 0 or may be 0 or 1 if u is 1; BP represents a branching point for attachment to a core and G_1 , G_2 and G_3 represent first, second and third generation dendron branching groups. In one preferred embodiment, each of BP and G_1 , $G_2 \dots G_n$ is phenyl, and each phenyl BP, G_1 , $G_2 \dots G_{n-1}$ is a 3,5-linked phenyl.

[0083] A preferred dendron is a substituted or unsubstituted dendron of formula (XIb):



[0084] wherein * represents an attachment point of the dendron to a core.

[0085] BP and/or any group G may be substituted with one or more substituents, for example one or more C_{1-20} alkyl or alkoxy groups.

[0086] Light-emitting material(s) in a composition comprising the compound of formula (I) and one or more light-emitting materials may make up about 0.05 wt % up to about 50 wt %, optionally about 1-40 wt % of the composition.

[0087] Charge Transporting and Charge Blocking Layers

[0088] A device containing a light-emitting layer containing a compound of formula (I) may have charge-transporting and/or charge blocking layers.

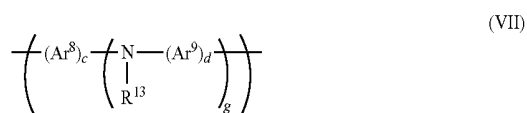
[0089] A hole transporting layer may be provided between the anode and the light-emitting layer or layers of an OLED. An electron transporting layer may be provided between the cathode and the light-emitting layer or layers.

[0090] An electron blocking layer may be provided between the anode and the light-emitting layer(s) and a hole blocking layer may be provided between the cathode and the light-emitting layer(s). Charge-transporting and charge-blocking layers may be used in combination. Depending on the HOMO and LUMO levels of the material or materials in a layer, a single layer may both transport one of holes and electrons and block the other of holes and electrons.

[0091] If present, a hole transporting layer located between the anode and the light-emitting layer(s) preferably has a material having a HOMO level of less than or equal to 5.5 eV, more preferably around 4.8-5.5 eV or 4.9-5.3 eV as measured by cyclic voltammetry. The HOMO level of the material in the hole transport layer may be selected so as to be within 0.2 eV, optionally within 0.1 eV of the light-emitting material of the light-emitting layer.

[0092] A hole-transporting layer may contain polymeric or non-polymeric charge-transporting materials. Exemplary hole-transporting materials contain arylamine groups.

[0093] A hole transporting layer may contain a homopolymer or copolymer comprising a repeat unit of formula (VII):



[0094] wherein Ar⁸ and Ar⁹ in each occurrence are independently selected from substituted or unsubstituted aryl or heteroaryl, g is greater than or equal to 1, preferably 1 or 2, R¹³ is H or a substituent, preferably a substituent, and c and d are each independently 1, 2 or 3.

[0095] R¹³, which may be the same or different in each occurrence when g>1, is preferably selected from the group consisting of alkyl, for example C₁₋₂₀ alkyl, Ar¹⁰, a branched or linear chain of Al¹⁰ groups, or a crosslinkable unit that is bound directly to the N atom of formula (VIII) or spaced apart therefrom by a spacer group, wherein Al¹⁰ in each occurrence is independently optionally substituted aryl or heteroaryl. Exemplary spacer groups are C₁₋₂₀ alkyl, phenyl and phenyl-C₁₋₂₀ alkyl.

[0096] Any of Ar⁸, Ar⁹ and, if present, Al¹⁰ in the repeat unit of Formula (VII) may be linked by a direct bond or a divalent linking atom or group to another of Ar⁸, Ar⁹ and Ar¹⁰. Preferred divalent linking atoms and groups include O, S; substituted N; and substituted C.

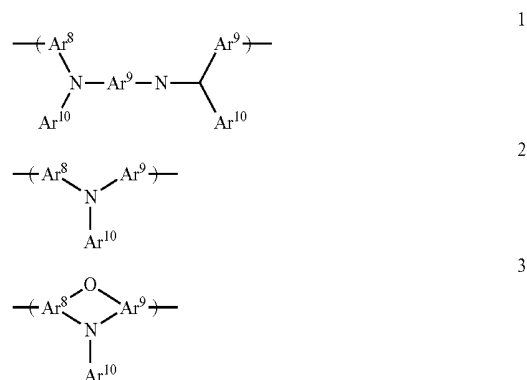
[0097] Any of Ar⁸, Ar⁹ and, if present, Ar¹⁰ may be substituted with one or more substituents. Exemplary sub-

stituents are substituents R¹⁰, wherein each R¹⁰ may independently be selected from the group consisting of:

[0098] substituted or unsubstituted alkyl, optionally C₁₋₂₀ 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— and one or more H atoms may be replaced with F; and

[0099] a crosslinkable group attached directly to Ar⁸, Ar⁹ or Ar¹⁰ or spaced apart therefrom by a spacer group, for example a group comprising a double bond such and a vinyl or acrylate group, or a benzocyclobutane group

[0100] Preferred repeat units of formula (VII) have formulae 1-3:



[0101] In one preferred arrangement, R¹³ is Ar¹⁰ and each of Ar⁸, Ar⁹ and Ar¹⁰ are independently and optionally substituted with one or more C₁₋₂₀ alkyl groups. Ar⁸, Ar⁹ and Ar¹⁰ are preferably phenyl.

[0102] In another preferred arrangement, the central Ar⁹ group of formula (1) linked to two N atoms is a polycyclic aromatic that may be unsubstituted or substituted with one or more substituents R¹⁰. Exemplary polycyclic aromatic groups are naphthalene, perylene, anthracene and fluorene.

[0103] In another preferred arrangement, Ar⁸ and Ar⁹ are phenyl, each of which may be substituted with one or more C₁₋₂₀ alkyl groups, and R¹³ is —(Ar¹⁰), wherein r is at least 2 and wherein the group —(Ar¹⁰), forms a linear or branched chain of aromatic or heteroaromatic groups, for example 3,5-diphenylbenzene wherein each phenyl may be substituted with one or more C₁₋₂₀ alkyl groups. In another preferred arrangement, c, d and g are each 1 and Ar⁸ and Ar⁹ are phenyl linked by an oxygen atom to form a phenoxazine ring.

[0104] A hole-transporting polymer containing repeat units of formula (VII) may be a copolymer containing one or more further repeat units. Exemplary further repeat units include arylene repeat units, each of which may be unsubstituted or substituted with one or more substituents.

[0105] Exemplary arylene repeat units include without limitation, fluorene, phenylene, naphthalene, anthracene, indenofluorene, phenanthrene and dihydrophenanthrene repeat units, each of which may be unsubstituted or substituted with one or more substituents.

[0106] Substituents of arylene repeat units, if present, may be selected from C₁₋₄₀ hydrocarbyl, preferably C₁₋₂₀ alkyl; phenyl which may be unsubstituted or substituted with one or more

[0107] C_{1-10} alkyl groups; and crosslinkable hydrocarbyl groups, for example C_{1-40} hydrocarbyl groups comprising benzocyclobutene or vinylene groups.

[0108] Phenylene repeat units may be 1,4-linked phenylene repeat units that may be unsubstituted or substituted with 1, 2, 3 or 4 substituents. Fluorene repeat units may be 2,7-linked fluorene repeat units.

[0109] Fluorene repeat units preferably have two substituents in the 9-position thereof. Aromatic carbon atoms of fluorene repeat units may each independently be unsubstituted or substituted with a substituent.

[0110] If present, an electron transporting layer located between the light-emitting layers and cathode preferably has a LUMO level of around 1.8-2.7 eV as measured by cyclic voltammetry. An electron-transporting layer may have a thickness in the range of about 5-50 nm.

[0111] 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. The crosslinkable group may be provided as a substituent of, or may be mixed with, a charge-transporting or charge-blocking material used to form the charge-transporting or charge-blocking layer.

[0112] A charge-transporting layer adjacent to a light-emitting layer containing a phosphorescent light-emitting material preferably contains a charge-transporting material having a lowest triplet excited state (T_1) excited state that is no more than 0.1 eV lower than, preferably the same as or higher than, the T_1 excited state energy level of the phosphorescent light-emitting material(s) in order to avoid quenching of triplet excitons.

[0113] The polystyrene-equivalent number-average molecular weight (M_n) measured by gel permeation chromatography of the polymers described herein may be in the range of about 1×10^3 to 1×10^8 , and preferably 1×10^4 to 5×10^6 . The polystyrene-equivalent weight-average molecular weight (M_w) of the polymers described herein may be 1×10^3 to 1×10^8 , and preferably 1×10^4 to 1×10^7 .

[0114] Polymers as described herein are suitably amorphous.

[0115] Hole Injection Layers

[0116] A conductive hole injection layer, which may be formed from a conductive organic or inorganic material, may be provided between the anode 101 and the light-emitting layer 103 of an OLED as illustrated in FIG. 1 to assist hole injection from the anode into the layer or layers of semiconducting polymer. Examples of doped organic hole injection materials include optionally substituted, doped poly(ethylene dioxythiophene) (PEDOT), in particular PEDOT 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 U.S. Pat. No. 5,723,873 and U.S. Pat. No. 5,798,170; and optionally substituted polythiophene or poly(thienothiophene). Examples of conductive inorganic materials include transition metal oxides such as VOx, MoOx and RuOx as disclosed in Journal of Physics D: Applied Physics (1996), 29(11), 2750-2753.

[0117] Cathode

[0118] The cathode 105 is selected from materials that have a workfunction allowing injection of electrons into the light-emitting layer of the OLED. 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 conductive materials such as metals, for example a bilayer of a low workfunction material and a high workfunction material such as calcium and aluminium, for example as disclosed in WO 98/10621. The cathode may comprise elemental barium, for example as disclosed in WO 98/57381, Appl. Phys. Lett. 2002, 81(4), 634 and WO 02/84759. The cathode may comprise a thin (e.g. 1-5 nm) layer of metal compound, in particular an oxide or fluoride of an alkali or alkali earth metal, between the organic layers of the device and one or more conductive cathode layers to assist electron injection, for example lithium fluoride as disclosed in WO 00/48258; barium fluoride as disclosed in Appl. Phys. Lett. 2001, 79(5), 2001; and barium oxide. In order to provide efficient injection of electrons into the device, the cathode preferably has a workfunction of less than 3.5 eV, more preferably less than 3.2 eV, most preferably less than 3 eV. Work functions of metals can be found in, for example, Michaelson, J. Appl. Phys. 48(11), 4729, 1977.

[0119] 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.

[0120] 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.

[0121] Encapsulation

[0122] 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.

[0123] 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.

[0124] Formulation Processing

[0125] A formulation suitable for forming a charge-transporting or light-emitting layer may be formed from a compound of formula (I), any further components of the layer such as light-emitting dopants, and one or more suitable solvents.

[0126] The formulation may be a solution of the compound of formula (I) and any other components in the one or more solvents, or may be a dispersion in the one or more solvents in which one or more components are not dissolved. Preferably, the formulation is a solution.

[0127] Solvents suitable for dissolving compounds of formula (I) are solvents comprising alkyl substituents for example benzenes substituted with one or more C_{1-10} alkyl or C_{1-10} alkoxy groups, for example toluene, xylenes and methylanisoles.

[0128] Particularly preferred solution deposition techniques including printing and coating techniques such as spin-coating, inkjet printing and slot-die coating.

[0129] Spin-coating is particularly suitable for devices wherein patterning of the light-emitting layer is unnecessary—for example for lighting applications or simple monochrome segmented displays.

[0130] Inkjet printing is particularly suitable for high information content displays, in particular full colour displays. A device may be inkjet printed by providing a patterned layer over the first electrode and defining wells for printing of one colour (in the case of a monochrome device) or multiple colours (in the case of a multicolour, in particular full colour device). The patterned layer is typically a layer of photoresist that is patterned to define wells as described in, for example, EP 0880303.

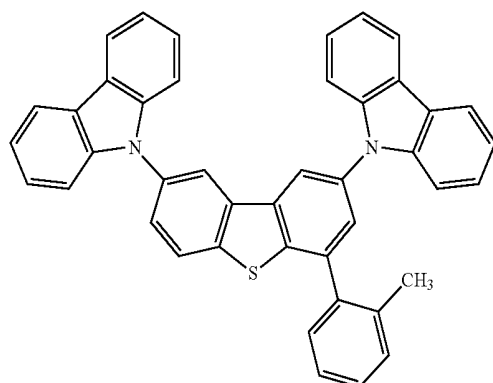
[0131] As an alternative to wells, the ink may be printed into channels defined within a patterned layer. In particular, the photoresist may be patterned to form channels which, unlike wells, extend over a plurality of pixels and which may be closed or open at the channel ends.

[0132] Other solution deposition techniques include dip-coating, roll printing and screen printing.

EXAMPLES

Example 1

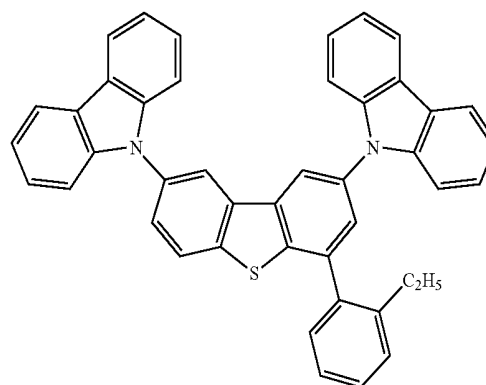
[0133]



[0134] (2,8-di(9H-carbazol-9-yl)dibenzo[b,d]thiophen-4-yl)boronic acid pinacol ester (3.5 g, 5.5 mmol) and 2-bromotoluene (0.73 ml, 6.0 mmol) were dissolved in toluene (50 ml). The solution was purged with nitrogen for 30 minutes. At the same time a solution of tetraethylammonium hydroxide (20 wt % in water, 16 ml, 21.9 mmol) was also purged with nitrogen for 30 minutes. SPhos (49 mg, 0.11 mmol) and tri(dibenzylidene)dipalladium (50 mg, 0.06 mmol) were added to the toluene solution and the mixture was purged with nitrogen while being heated up to 105° C. The base was added to the toluene solution and the mixture was stirred at 105° C. for 20 hrs. After cooling, the layers were separated and the aqueous layer was extracted 1× with toluene. The combine organics were washed 5× with water, dried with $MgSO_4$, filtered and concentrated under reduced pressure. The resulting solid was dissolved in a mixture of hexane:dichloromethane (7:3) and filtered through a silica/florisil plug (sinter funnel packed with a layer of florisil on top of a layer of silica), eluted with a mixture of hexane:dichloromethane (7:3). Filtrate was concentrated under reduced pressure. The solid was recrystallised 1× from toluene/hexane and 1× from toluene/methanol to give the product as a white solid at 99.8% purity by HPLC. The material was then precipitated 4× from a dichloromethane solution into methanol, then stirred into refluxing methanol for 2 hrs, cooled down and filtered. It was dried in vacuum oven at 60° C. to give 1.56 g of Example 1 at 99.8% HPLC purity, 47% yield. The material could be purified further by sublimation.

Example 2

[0135]

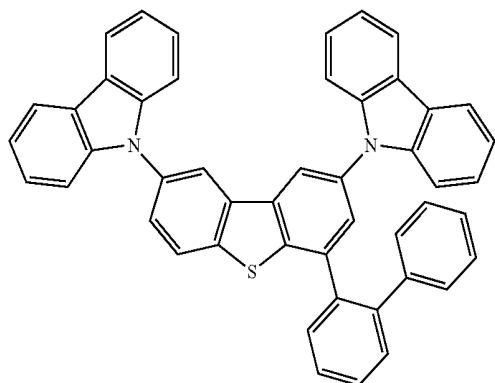


[0136] (2,8-di(9H-carbazol-9-yl)dibenzo[b,d]thiophen-4-yl)boronic acid (10 g, 17.9 mmol), 2-ethylbromobenzene (3.3 g, 17.9 mmol) and SPhos (130 mg, 0.32 mmol) were dissolved in a mixture of toluene (115 mL) and ethanol (15 mL). The solution was purged with nitrogen for 1 h. At the same time a solution of tetraethylammonium hydroxide (20 wt % in water, 28 mL) was also purged with nitrogen for 1 h. The base was added to the toluene/ethanol solution along with tri(dibenzylidene)dipalladium (150 mg, 0.16 mmol) and the mixture was stirred at 100° C. overnight. After cooling the reaction mixture was filtered into a separating funnel. The layers were separated and the aqueous layer was extracted with toluene. The combine organics were washed with hot water (5×50 mL), dried with $MgSO_4$, filtered and concentrated. The solid recrystallised from toluene/acetoni-

trile four times to give the product as a white solid at 99.9% purity by HPLC. The material could be purified further by sublimation.

Example 3

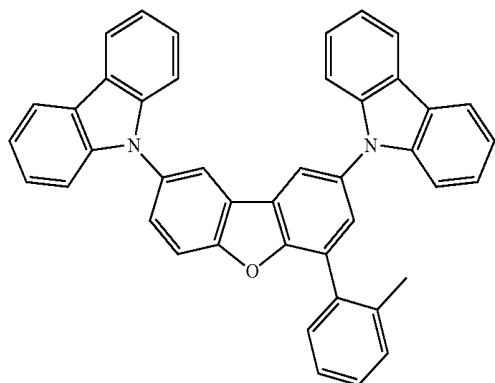
[0137]



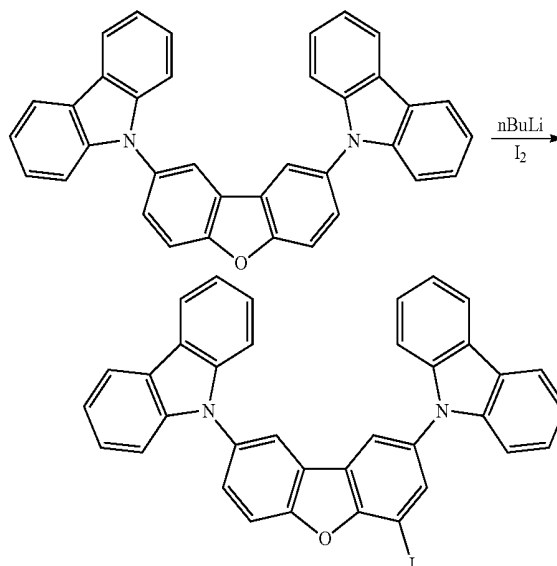
[0138] 9,9'-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzothiophene-2,8-diyl)bis(N-carbazole) (5 g, 7.8 mmol), 2-bromobiphenyl (1.9 g, 8.2 mmol) and SPhos (66 mg, 0.16 mmol) were dissolved in a mixture of toluene (50 mL) and ethanol (20 mL). The solution was purged with nitrogen for 1 h. At the same time a solution of tetraethylammonium hydroxide (20 wt % in water, 12 mL) was also purged with nitrogen for 1 h. The base was added to the toluene/ethanol solution along with tri(dibenzylidene)dipalladium (70 mg, 0.08 mmol) and the mixture was stirred at 95° C. overnight. After cooling the reaction mixture was filtered into a separating funnel. The layers were separated and the aqueous layer was extracted with toluene. The combine organics were washed with hot water (5x50 mL), dried with MgSO₄, filtered and concentrated. The solid was taken up in DCM and precipitated into acetonitrile. The filtered solid was columned on silica eluting with a gradient of 5-25% ethyl acetate in heptane. The product-containing fractions were combined and recrystallised from toluene/acetonitrile three times followed by recrystallisation from toluene/heptanes to give the product as a white solid at 99.9% purity by HPLC. The material could be purified further by sublimation.

Example 4

[0139]

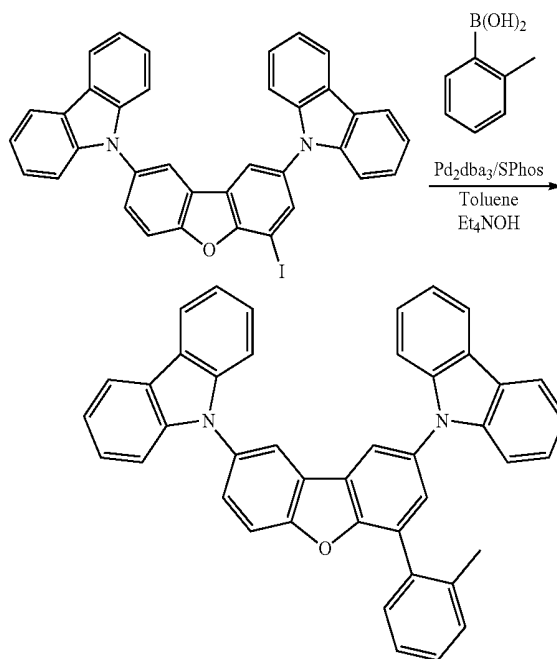


[0140] Stage 1



[0141] 2,8-di((H-carbazol-9-yl)dibenzo[b,d]furan) (80 g, 161 mmol) was dissolved in dry THF and cooled to -40° C. nButyllithium (100 mL, 1.6 M, 161 mmol) was added slowly and then the mixture was stirred at 50° C. for 18 h. The mixture was cooled to -78° C. and iodine (40.6 g 161 mmol) in dry THF (800 mL) was added slowly. The mixture was allowed to reach r.t. and stirred for 16 h before being quenched with 1.5 N HCl. The organics were extracted with 500 mL ethyl acetate, washed with water, dried with sodium sulfate, filtered and concentrated. The residue was purified by trituration in hot toluene followed by column chromatography on silica eluting with ethyl acetate in hexanes. The product was used without further purification.

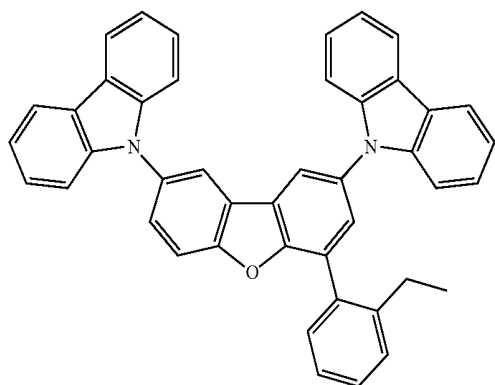
[0142] Stage 2



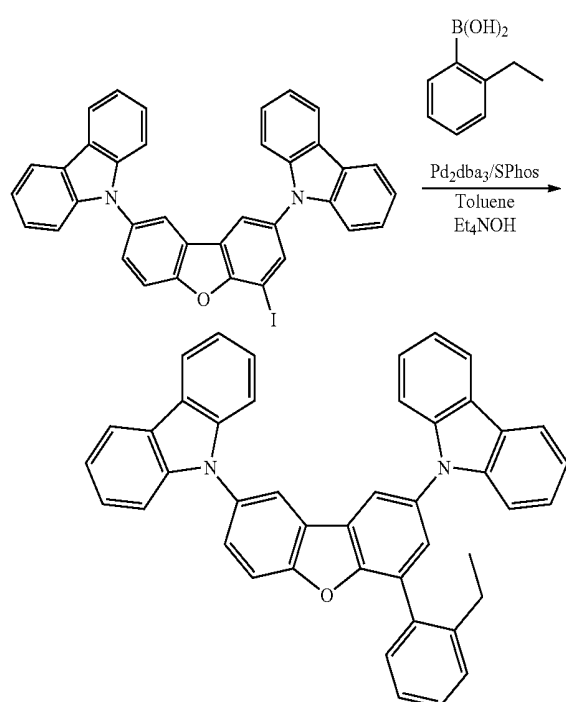
[0143] Crude (2,8-di(9H-carbazol-9-yl)4-iododibenzo[b, d]furan) (25 g, 40 mmol), 2-tolylboronic acid (5.4 g, 40 mmol) and SPhos (3.2 mg, 8 mmol) were dissolved in toluene (250 mL). The solution was purged with nitrogen for 1 h. At the same time a solution of tetraethylammonium hydroxide (20 wt % in water, 88 mL) was also purged with nitrogen for 1 h. The base was added to the toluene solution along with tri(dibenzylidene)dipalladium 3.6 g, 4 mmol) and the mixture was stirred at 110° C. overnight. After cooling the reaction mixture was filtered into a separating funnel. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organics were washed with water (1 L) and brine (1 L), dried with sodium sulfate, filtered and concentrated. The solid was purified by column chromatography on silica using ethyl acetate in hexanes followed by repeated reverse phase columns using acetonitrile and THF to give the product as a white solid at 99.66% purity by HPLC. The material could be purified further by sublimation.

Example 5

[0144]



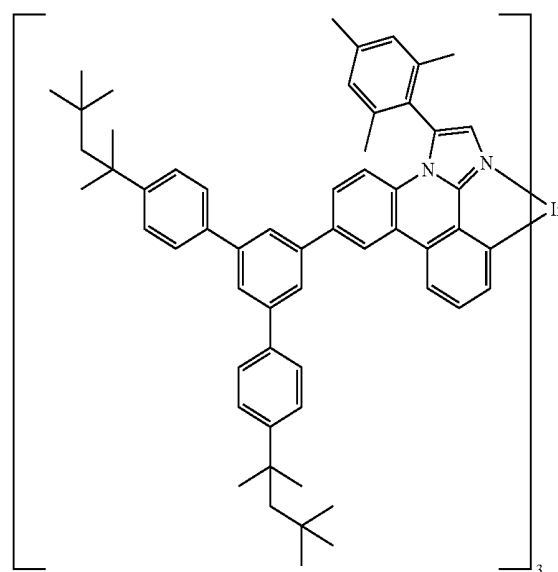
[0145] Compound Example 5 was prepared according to the following reaction scheme:



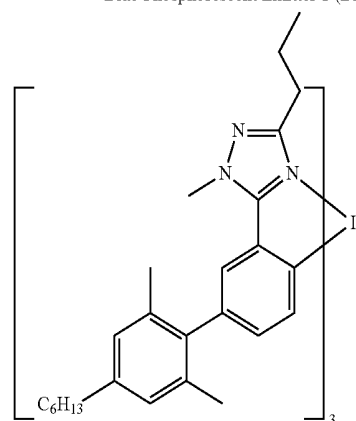
[0146] Crude (2,8-di(9H-carbazol-9-yl)4-iododibenzo[b, d]furan) (22 g, 35 mmol), 2-ethylphenylboronic acid (5.2 g, 35 mmol) and SPhos (2.8 g, 7 mmol) were dissolved in toluene (250 mL). The solution was purged with nitrogen for 1 h. At the same time a solution of tetraethylammonium hydroxide (20 wt % in water, 77 mL) was also purged with nitrogen for 1 h. The base was added to the toluene solution along with tri(dibenzylidene)dipalladium 3.2 g, 3.5 mmol) and the mixture was stirred at 110° C. overnight. After cooling the reaction mixture was filtered into a separating funnel. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organics were washed with water (1 L) and brine (1 L), dried with sodium sulfate, filtered and concentrated. The solid was purified by column chromatography on silica using ethyl acetate in hexanes followed by repeated reverse phase columns using acetonitrile and THF and recrystallized from toluene to give the product as a white solid at 99.70% purity by HPLC. The material could be purified further by sublimation.

[0147] Phosphorescent Composition

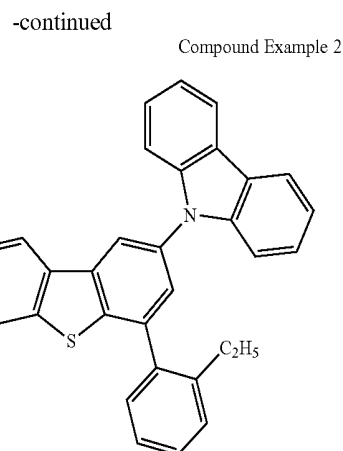
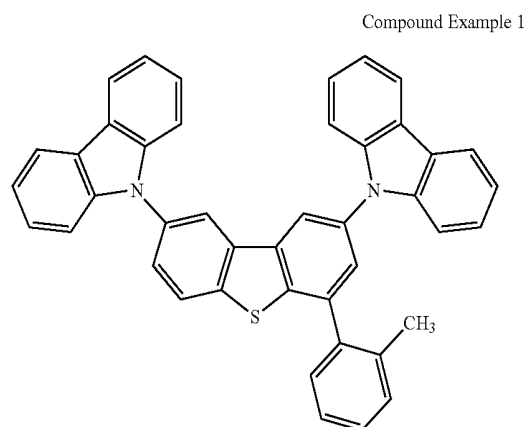
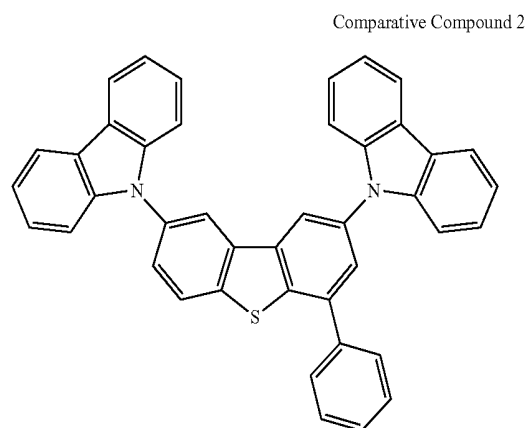
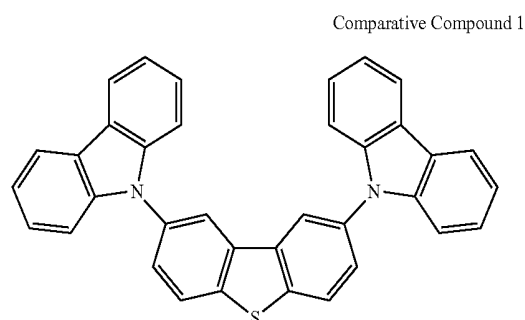
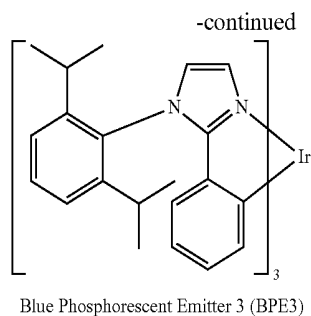
[0148] A film of a composition of Blue Phosphorescent Emitter 1 or 2 (5 wt %) and a host compound (95 wt %) selected from Comparative Compound 1 or 2 or Compound Example 1 or 2 was formed by dissolving the composition and spin-casting the film.



Blue Phosphorescent Emitter 1 (BPE1)



Blue Phosphorescent Emitter 2 (BPE2)



[0149] Photoluminescent quantum yields (PLQY) of films prepared by this method are set out in Table 1.

[0150] Photoluminescent quantum yield (PLQY) was measured an integrating sphere, Hamamatsu, Model C9920-02. For each sample a film of the composition was formed by spin-coating a solution of the composition on a quartz substrate. The substrate carrying the film was placed in the integrating sphere. The sample was scanned with wavelengths 280 nm-350 nm approx and wavelength where the emission peak is the most intense is selected. A blank spectrum was measured at the chosen wavelength followed by measurement of the sample.

TABLE 1

Host	R ¹	Emitter	PLQY
Comparative Compound 1	n/a	BPE2	0.70
Comparative Compound 2	H	BPE2	0.42
Compound Example 1	Me	BPE2	0.70
Compound Example 2	Et	BPE2	0.71
Comparative Compound 1	n/a	BPE1	0.63
Comparative Compound 2	H	BPE1	0.43
Compound Example 1	Me	BPE1	0.60
Compound Example 2	Et	BPE1	0.64

[0151] PLQY values of compositions containing Comparative Compound 1 are similar to those containing Compound Examples 1 and 2.

[0152] PLQY values of Comparative Compound 2 are significantly lower than those of either Compound Example 1 or Compound Example 2.

[0153] LUMO values are given in Table 2.

TABLE 2

Compound	LUMO (eV)
Comparative Compound 1	-1.96
Comparative Compound 2	-2.17
Compound Example 1	-2.11
Compound Example 2	-2.08

TABLE 2-continued

Compound	LUMO (eV)
Compound Example 3	-2.07
Compound Example 4	-2.06
Compound Example 5	-2.07

Blue Device Examples

[0154] A blue organic light-emitting device having the following structure was prepared:

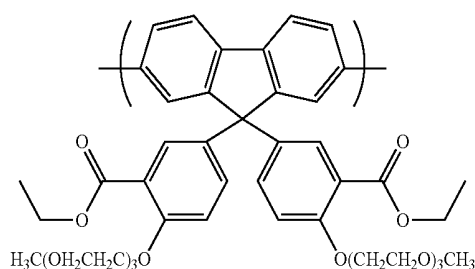
[0155] ITO/HIL/HTL/LEL/ETL/Cathode

[0156] 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, LEL is a light-emitting layer containing a compound of formula (I) and a blue phosphorescent material; and ETL is an electron-transporting layer.

[0157] A substrate carrying ITO was cleaned using UV/Ozone. A hole injection layer was formed to a thickness of about 35 nm by spin-coating a formulation of a hole-injection material. A hole transporting layer was formed to a thickness of about 22 nm by spin-coating a crosslinkable hole-transporting polymer and crosslinking the polymer by heating at 180° C. The light-emitting layer was formed by spin-coating a host material (75 wt %) and Blue Phosphorescent Emitter 3 (25 wt %). An electron-transporting layer was formed on the light-emitting layer. A cathode was formed on the electron-transporting layer of a first layer of sodium fluoride of about 2 nm thickness, a layer of silver of about 100 nm thickness and a layer of aluminium of about 100 nm thickness.

[0158] The hole-transporting layer was formed by spin-coating a polymer comprising repeat units of formula (VII-1) and phenylene repeat units substituted with crosslinkable groups.

[0159] The electron-transporting layer was formed by spin-coating a polymer comprising the cesium salt of electron-transporting unit 1 as described in WO 2012/133229 to a thickness of 10 nm.

**[0160]** Electron-Transporting Unit 1

[0161] With reference to Table 3, devices containing Compound Example 1 or Compound Example 2 require a lower drive voltage to reach a brightness of 1000 cd/m² and a lower drive voltage to reach a drive voltage of 10 mA/cm²:

TABLE 3

Device	Host	V at 1000 cd m ⁻² (V)	V at 10 mA cm ⁻² (V)
Comparative Device 1	Comparative Compound Example 1	3.93	4.7
Device Example 1	Compound Example 1	3.57	4.1
Device Example 2	Compound Example 2	3.57	4.1

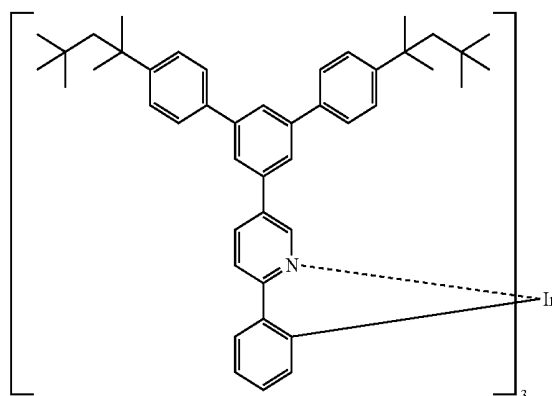
White Device Example 1

[0162] A white organic light-emitting device having the following structure was prepared:

[0163] ITO/HIL/LEL (R)/LEL (G, B)/ETL/Cathode

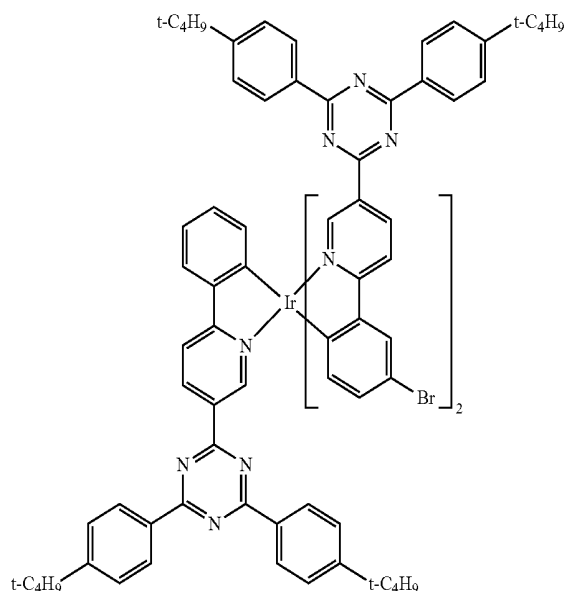
[0164] wherein ITO is an indium-tin oxide anode; HIL is a hole-injecting layer comprising a hole-injecting material, LEL (R) a hole-transporting, red light-emitting layer, LEL (G, B) is a light-emitting layer containing a compound of formula (I) and a host material, and ETL is an electron-transporting layer.

[0165] A substrate carrying ITO was cleaned using UV/Ozone. A hole injection layer was formed to a thickness of about 65 nm by spin-coating a formulation of a hole-injection material. A red light-emitting hole transporting layer was formed to a thickness of about 17 nm by spin-coating a crosslinkable red light-emitting hole-transporting polymer and crosslinking the polymer by heating at 180° C. The light-emitting layer was formed to a thickness of about 65 nm by spin-coating Compound Example 2 (74 wt %), and Blue Phosphorescent Emitter 3 (25 wt %) and Green Phosphorescent Emitter 1, illustrated below (1 wt %). An electron-transporting layer was formed on the light-emitting layer from a polymer as described in WO 2012/133229. A cathode was formed on the electron-transporting layer of a first layer of sodium fluoride of about 2 nm thickness, a layer of silver of about 100 nm thickness and a layer of aluminium of about 100 nm thickness.

**[0166]** Green Phosphorescent Emitter 1

[0167] The hole-transporting layer was formed by spin-coating a polymer comprising 1,4-phenylene repeat units substituted with crosslinkable groups; amine repeat units of

formula (VII-1); and a red phosphorescent emitting repeat unit formed from the following monomer:



[0168] Comparative White Device 1

[0169] A device was prepared as described for White Device Example 1 except that Comparative Compound 1 was used in place of Compound Example 2.

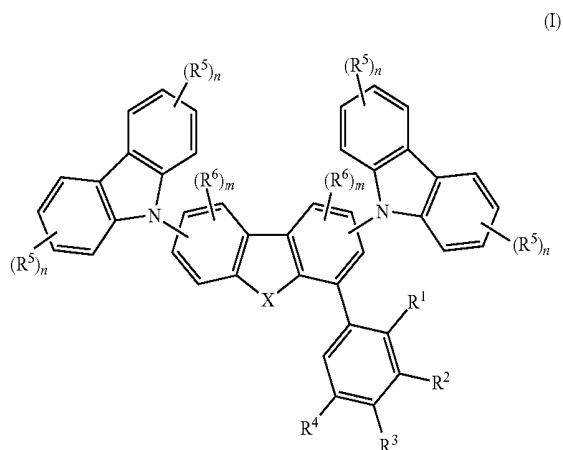
[0170] With reference to Table 4, White Device Example 1 has higher efficiency at a brightness of 1000 cd/m² and requires a lower drive voltage to reach this brightness or to reach a current density of 10 mA/cm².

TABLE 4

Device	Voltage at 1000 cd/m ² (V)	Voltage at 10 mA/cm ² (V)	EQE at 1000 cd/m ² (%)	Efficiency at 1000 cd/m ² (Lm/W)
Comparative White Device 1	4.0	4.9	16.0	31.6
White Device Example 1	3.5	4.2	16.0	33.8

[0171] Although the present invention has been described in terms of specific exemplary embodiments, it will be appreciated that various modifications, alterations and/or combinations of features disclosed herein will be apparent to those skilled in the art without departing from the scope of the invention as set forth in the following claims.

1. A compound of formula (I)



wherein:

X is O, S, NR¹¹, CR¹¹₂ or SiR¹¹₂ wherein R¹¹ in each occurrence is independently a substituent;

R¹ is a substituent;

R², R³, and R⁴ are each independently H or a substituent;

R⁵ and R⁶ independently in each occurrence is a substituent;

m independently in each occurrence is 0, 1 or 2; and

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

2. A compound according to claim 1 wherein R¹ is a C₁₋₃₀ hydrocarbyl group.

3. A compound according to claim 1 wherein R¹ is selected from C₁₋₂₀ alkyl and phenyl which may be unsubstituted or substituted with one or more C₁₋₁₀ alkyl groups and biphenyl which may be unsubstituted or substituted with one or more C₁₋₁₀ alkyl groups.

4. A compound according to claim 1, wherein each m is 0.

5. A compound according to claim 1, wherein each n is 0.

6. A compound according to claim 1, wherein each of R², R³ and R⁴ is H.

7. A compound according to claim 1 wherein X is S or O.

8. A composition comprising a compound according to claim 1, and at least one light-emitting dopant.

9. A composition according to claim 8 wherein the dopant is a phosphorescent dopant.

10. A composition according to claim 8, wherein the light-emitting dopant is a blue light-emitting material.

11. A composition according to claim 8, wherein the composition is a white light-emitting composition.

12. A formulation comprising a compound according to claim 1, and at least one solvent.

13. An organic light-emitting device comprising an anode, a cathode and one or more organic layers between the anode and cathode including a light-emitting layer wherein at least one of the one or more organic layers comprises a compound according to claim 1.

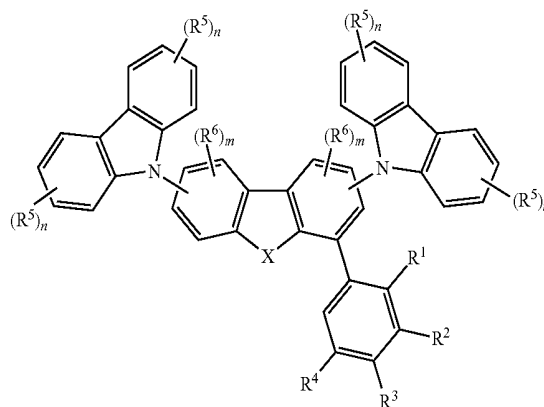
14. An organic light-emitting device comprising an anode, a cathode and one or more organic layers between the anode and cathode including a light-emitting layer wherein the organic light-emitting layer comprises a compound according to claim 1.

15. An organic light-emitting device comprising an anode, a cathode and one or more organic layers between the anode and cathode including a light-emitting layer wherein the organic light-emitting layer comprises a composition according to claim 8.

16. A method of forming an organic light-emitting device according to claim 13 comprising the step of forming the light-emitting layer over one of the anode and the cathode and forming the other of the anode and the cathode over the light-emitting layer.

17. A method according to claim 16 wherein the light-emitting layer is formed by depositing a formulation comprising a compound of formula (I)

(I)



wherein:

X is O, S, NR^{11} , CR^{11}_2 or SiR^{11}_2 wherein R^{11} in each occurrence is independently a substituent;

R^1 is a substituent;

R^2 , R^3 , and R^4 are each independently H or a substituent;

R^5 and R^6 independently in each occurrence is a substituent;

m independently in each occurrence is 0, 1 or 2; and

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

and at least one solvent,

and evaporating the at least one solvent.

* * * * *

专利名称(译)	化合物，组合物和有机发光器件		
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摘要(译)

式 (I) 化合物，其中：X是 O，S，NR¹¹，CR¹¹2 或 SiR¹¹2 其中 R¹¹ 在每次出现时独立地是取代基；R¹ 是取代基；R²，R³ 和 R⁴ 各自独立地为H或取代基；R⁵ 且R⁶ 在每次出现时独立地是取代基；m在每次出现时独立地为0,1或2;每次出现时，n和n独立地为0,1,2,3或4.该化合物可用作有机发光器件中磷光发光材料的主体。

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Priority Data

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