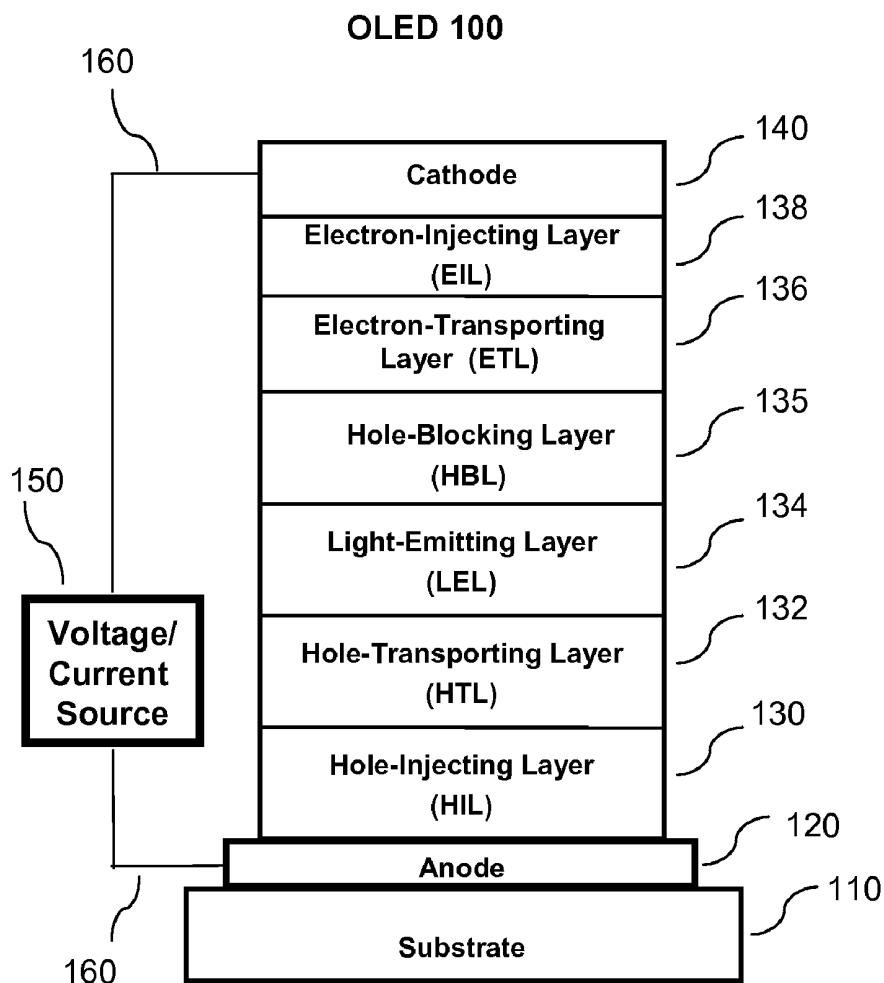




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Begley et al.(10) **Pub. No.: US 2010/0207513 A1**(43) **Pub. Date: Aug. 19, 2010**(54) **OLED WITH
FLUORANTHENE-MACROCYCLIC
MATERIALS**(76) Inventors: **William J. Begley**, Webster, NY
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WASHINGTON, DC 20006 (US)(21) Appl. No.: **12/370,696**(22) Filed: **Feb. 13, 2009****Publication Classification**(51) **Int. Cl.**
H01L 51/54 (2006.01)(52) **U.S. Cl.** **313/504**(57) **ABSTRACT**

The invention provides an OLED device including a cathode, an anode, and having therebetween a light-emitting layer, further including, between the cathode and the light emitting layer, a first layer containing a fluoranthene-macrocyclic compound. The fluoranthene-macrocyclic compound includes a fluoranthene nucleus having the 7,10-positions connected by a linking group. The fluoranthene nucleus can be further substituted, provided substituents in the 8- and 9-positions cannot combine to form a five-membered ring group. The OLED device includes at least one layer, between the light-emitting layer and the cathode, containing an alkali metal material. Desirably, the OLED device includes an organic alkali metal compound present in the first layer or in a second layer located between the cathode and the first layer. The OLED device can include an anthracene derivative that is present in the first layer, in addition to the fluoranthene-macrocyclic compound. Devices of the invention provide improvement in features such as efficiency and drive voltage.



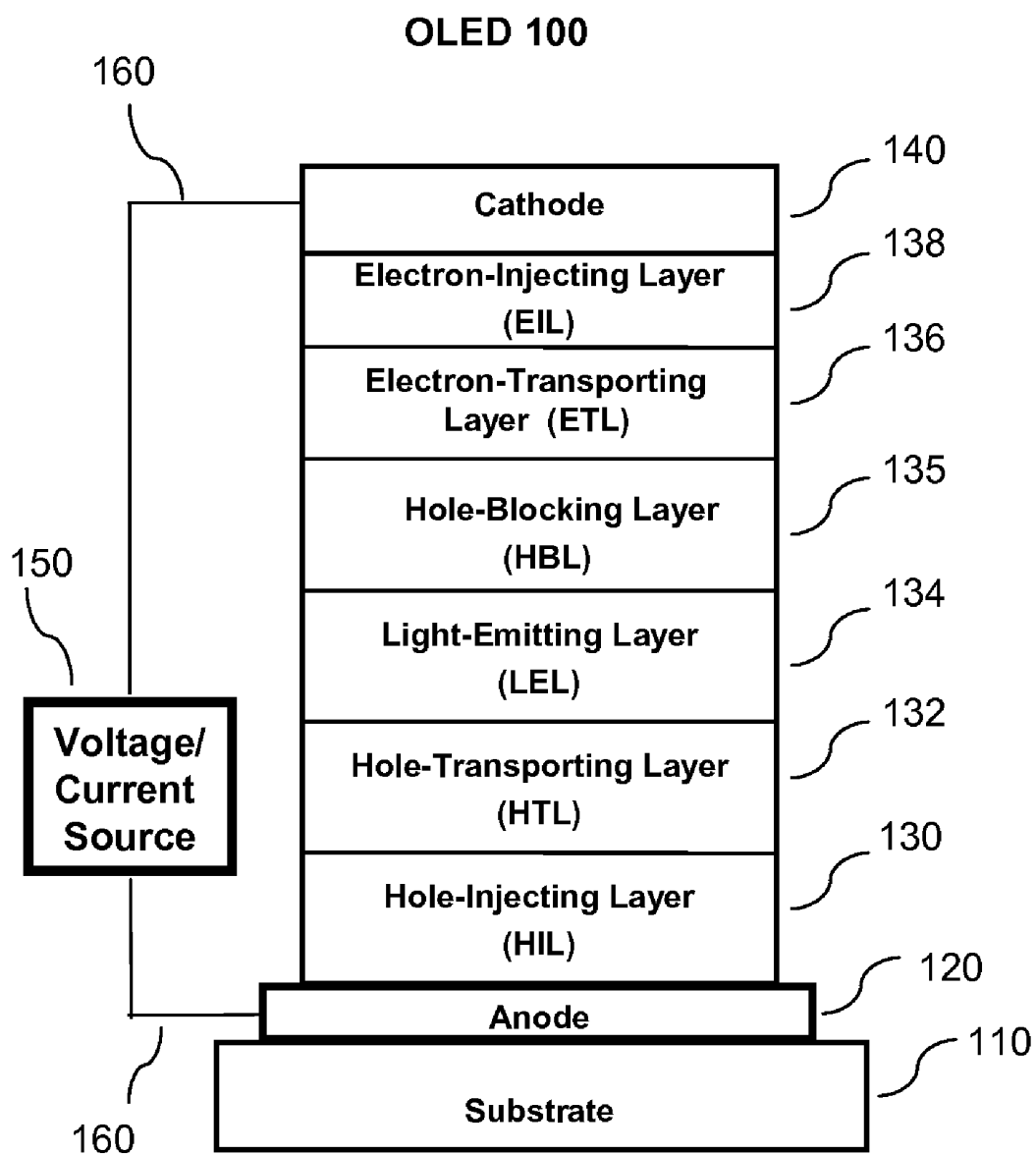


FIG 1

OLED WITH FLUORANTHENE-MACROCYCLIC MATERIALS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] Reference is made to commonly assigned U.S. patent application Ser. No. 11/924,629 filed Oct. 26, 2007 entitled OLED DEVICE WITH CERTAIN FLUORANTHENE LIGHT-EMITTING DOPANTS, by William J. Begley, et al and U.S. patent application Ser. No. 11/924,626 filed Oct. 26, 2007 entitled OLED DEVICE WITH CERTAIN FLUORANTHENE HOST, by William J. Begley, et al and U.S. patent application Ser. No. 11/924,631 filed Oct. 26, 2007 entitled OLED DEVICE WITH FLUORANTHENE ELECTRON TRANSPORT MATERIALS, by William J. Begley et al and U.S. patent applications Ser. No. 12/266,802, filed Nov. 7, 2008 entitled ELECTROLUMINESCENT DEVICE CONTAINING A FLOURANTHENE COMPOUND by William J. Begley, et al and U.S. patent application Ser. No. 12/269,066, filed Nov. 12, 2008 entitled OLED DEVICE WITH FLUORANTHENE ELECTRON INJECTION MATERIALS, by William J. Begley, et al, and U.S. patent application Ser. No. 12/330,547 filed Dec. 9, 2008 entitled OLED DEVICE WITH CYCLOBUTENE ELECTRON INJECTION MATERIALS by William J. Begley, et al, the disclosure of which are incorporated herein.

FIELD OF THE INVENTION

[0002] This invention relates to an organic light-emitting diode (OLED) electroluminescent (EL) device having a light-emitting layer and wherein an electron-transporting layer includes a specific type of fluoranthene-macrocyclic compound.

BACKGROUND OF THE INVENTION

[0003] While organic electroluminescent (EL) devices have been known for over two decades, their performance limitations have represented a barrier to many desirable applications. In simplest form, an organic EL device is comprised of an anode for hole injection, a cathode for electron injection, and an organic medium sandwiched between these electrodes to support charge recombination that yields emission of light. These devices are also commonly referred to as organic light-emitting diodes, or OLEDs. Representative of earlier organic EL devices are Gurnee et al. U.S. Pat. No. 3,172,862 issued Mar. 9, 1965; Gurnee U.S. Pat. No. 3,173,050 issued Mar. 9, 1965; Dresner, "Double Injection Electroluminescence in Anthracene", RCA Review, 30, 322, (1969); and Dresner U.S. Pat. No. 3,710,167, issued Jan. 9, 1973. The organic layers in these devices, usually composed of a polycyclic aromatic hydrocarbon, were very thick (much greater than 1 μm). Consequently, operating voltages were very high, often greater than 100V.

[0004] More recent organic EL devices include an organic EL element consisting of extremely thin layers (e.g. <1.0 μm) between the anode and the cathode. Herein, the term "organic EL element" encompasses the layers between the anode and cathode. Reducing the thickness lowered the resistance of the organic layers and has enabled devices that operate at much lower voltage. In a basic two-layer EL device structure, described first in U.S. Pat. No. 4,356,429, one organic layer of the EL element adjacent to the anode is specifically chosen to

transport holes, and therefore is referred to as the hole-transporting layer, and the other organic layer is specifically chosen to transport electrons and is referred to as the electron-transporting layer. Recombination of the injected holes and electrons within the organic EL element results in efficient electroluminescence.

[0005] There have also been proposed three-layer organic EL devices that contain an organic light-emitting layer (LEL) between the hole-transporting layer and electron-transporting layer, such as that disclosed by C. Tang et al. (*J. Applied Physics*, Vol. 65, 3610 (1989)). The light-emitting layer commonly contains a host material doped with a guest material, otherwise known as a dopant. Still further, there has been proposed in U.S. Pat. No. 4,769,292 a four-layer EL element comprising a hole-injecting layer (HIL), a hole-transporting layer (HTL), a light-emitting layer (LEL) and an electron-transporting/injecting layer (ETL). These structures have resulted in improved device efficiency.

[0006] EL devices in recent years have expanded to include not only single color emitting devices, such as red, green and blue, but also white-devices, devices that emit white light. Efficient white light producing OLED devices are highly desirable in the industry and are considered as a low cost alternative for several applications such as paper-thin light sources, backlights in LCD displays, automotive dome lights, and office lighting. White light producing OLED devices should be bright, efficient, and generally have Commission International d'Eclairage (CIE) chromaticity coordinates of about (0.33, 0.33). In any event, in accordance with this disclosure, white light is that light which is perceived by a user as having a white color.

[0007] Since the early inventions, further improvements in device materials have resulted in improved performance in attributes such as color, stability, luminance efficiency and manufacturability, e.g., as disclosed in U.S. Pat. Nos. 5,061,569; 5,409,783; 5,554,450; 5,593,788; 5,683,823; 5,908,581; 5,928,802; 6,020,078, and 6,208,077, amongst others.

[0008] Notwithstanding all of these developments, there are continuing needs for organic EL device components, such as electron-transporting materials and electron-injecting materials, which will provide even lower device drive voltages and hence lower power consumption, while maintaining high luminance efficiencies and long lifetimes combined with high color purity.

[0009] Examples of electron-injecting layers include those described in U.S. Pat. Nos. 5,608,287; 5,776,622; 5,776,623; 6,137,223, and 6,140,763. An electron-injecting layer generally contains a material having a work function less than 4.0 eV. The definition of work function can be found in *CRC Handbook of Chemistry and Physics*, 70th Edition, 1989-1990, CRC Press Inc., page F-132 and a list of the work functions for various metals can be found on pages E-93 and E-94. Typical examples of such metals include Li, Na, K, Be, Mg, Ca, Sr, Ba, Y, La, Sm, Gd, Yb. A thin-film containing low work-function alkali metals or alkaline earth metals, such as Li, Cs, Ca, Mg can be employed for electron-injection. In addition, an organic material doped with these low work-function metals can also be used effectively as the electron-injecting layer. Examples are Li- or Cs-doped Alq.

[0010] U.S. Pat. No. 6,509,109 and U.S. Patent Application Publication 20030044643 describe an organic electroluminescent device wherein the electron injection region contains a nitrogen-free aromatic compound as a host material and a reducing dopant, such as an alkali metal compound. U.S. Pat.

No. 6,396,209 describes an electron injection layer of an electron-transporting organic compound and an organic metal complex compound containing at least one alkali metal ion, alkaline earth metal ion or rare earth metal ion. Additional examples of organic lithium compounds in an electron-injection layer of an EL device include U.S. Patent Application Publications 20060286405; 20020086180; 20040207318; U.S. Pat. Nos. 6,396,209; 6,468,676, JP 2000053957, and WO 9963023

[0011] A useful class of electron-transporting materials is that derived from metal chelated oxinoid compounds including chelates of oxine itself, also commonly referred to as 8-quinolinol or 8-hydroxyquinoline. Tris(8-quinolinolato) aluminum (III), also known as Alq or Alq₃, and other metal and non-metal oxine chelates are well known in the art as electron-transporting materials. Tang et al., in U.S. Pat. No. 4,769,292 and VanSlyke et al., in U.S. Pat. No. 4,539,507 lower the drive voltage of the EL devices by teaching the use of Alq as an electron transport material in the luminescent layer or luminescent zone. Baldo et al., in U.S. Pat. No. 6,097,147 and Hung et al., in U.S. Pat. No. 6,172,459 teach the use of an organic electron-transporting layer adjacent to the cathode so that when electrons are injected from the cathode into the electron-transporting layer, the electrons traverse both the electron-transporting layer and the light-emitting layer.

[0012] The use of substituted fluoranthenes in an electron-transporting layer is also known, examples include devices described in U.S. Patent Application Publications 20080007160; 20070252516; 20060257684; 20060097227, and JP 200409144.

[0013] JP 2003123978 describes an organic electroluminescent element that includes a 7,14-alkanoacenaphtho[1,2-k]fluoranthene derivative and in particular the use of this type of material in a light-emitting layer is disclosed.

[0014] Notwithstanding all these developments, there remains a need to develop novel compounds that improve efficiency and reduce drive voltage of OLED devices, as well as to provide embodiments with other improved features.

SUMMARY OF THE INVENTION

[0015] The invention provides an OLED device including a cathode, an anode, and having therebetween a light-emitting layer, further including, between the cathode and the light emitting layer, a first layer containing a fluoranthene-macrocylic compound. The fluoranthene-macrocylic compound includes a fluoranthene nucleus having the 7,10-positions connected by a linking group. The fluoranthene nucleus can be further substituted, provided substituents in the 8- and 9-positions cannot combine to form a five-membered ring group. The OLED device includes at least one layer, between the light-emitting layer and the cathode, containing an alkali metal material.

[0016] In a second embodiment, the OLED device includes an alkali metal or an organic alkali metal compound present in the first layer or in a second layer located between the cathode and the first layer.

[0017] In a third embodiment, the OLED device includes an anthracene derivative which is present in the first layer, in addition to the fluoranthene-macrocylic compound.

[0018] Devices of the invention provide improvement in features such as efficiency and drive voltage.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. 1 shows a schematic cross-sectional view of one embodiment of the OLED device of the present invention. It will be understood that FIG. 1 is not to scale since the individual layers are too thin and the thickness differences of various layers are too great to permit depiction to scale.

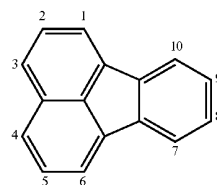
DETAILED DESCRIPTION OF THE INVENTION

[0020] The invention is generally as described above. An OLED device of the invention is a multilayer electroluminescent device comprising a cathode, an anode, light-emitting layer(s) (LEL), electron-transporting layer(s) (ETL) and electron-injecting layer(s) (EIL) and optionally additional layers such as hole-injecting layer(s), hole-transporting layer(s), exciton-blocking layer(s), spacer layer(s), connecting layer(s) and hole-blocking layer(s).

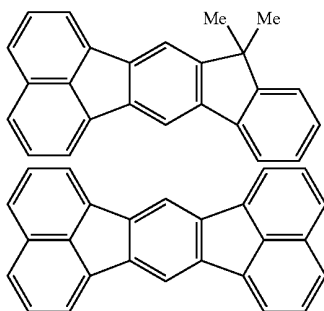
[0021] A first layer, between the light-emitting layer and the cathode, includes a fluoranthene-macrocylic compound. The fluoranthene-macrocylic compound facilitates the transport of electrons from the cathode to the light-emitting layer. Desirably, the first layer is an electron-transporting layer. The thickness of electron-transporting layer is often in the range of 2 nm to 750 nm, frequently 5 nm to 50 nm, and typically from 10 nm to 40 nm. The electron-transporting layer can be subdivided further into two or more sub-layers, for example, it can be divided into a first (ETL1) and a second (ETL2) transporting layer and it can be further divided.

[0022] In one embodiment, a fluoranthene-macrocylic compound is present in at least one electron-transporting layer that is a non-luminescent layer; that is, it should provide less than 25% of the total device emission. Ideally, it should have substantially no light emission.

[0023] The fluoranthene-macrocylic compound includes a fluoranthene nucleus that contains 4 annulated rings; the nucleus numbering sequence is illustrated below.



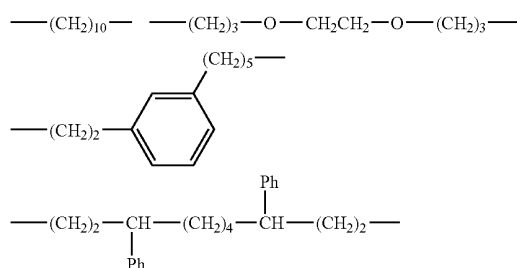
[0024] The fluoranthene-macrocylic compound can contain additional rings annulated to the fluoranthene nucleus, provided that it does not contain a five-membered ring annulated to the 8,9-position. Annulated rings, also commonly referred to as fused rings, are those rings that share a common ring bond between any two carbon atoms of the fluoranthene nucleus. Illustrative examples of compounds containing a fluoranthene nucleus with a five-membered ring annulated to the 8,9-position, and that are excluded from the present invention are shown below. In one embodiment, the fluoranthene-macrocylic compound does not contain any aromatic rings annulated to the fluoranthene nucleus.



[0025] The 7,10-positions of the fluoranthene nucleus are connected by a linking group, wherein the linking group is a divalent species that bonds to both the 7-position and the 10-position. The linking group contains carbon atoms and can contain heteroatoms such as N, O, and S.

[0026] Linking the 7,10-positions forms a ring and the linking group must be of sufficient length so that excess ring strain is not present or the compound will be unstable. Thus, in order to avoid ring strain, it is desirable to form a large ring, referred to herein as a macrocyclic ring. Preferably, the linking group is chosen so that the macrocyclic ring formed is a 10-membered ring or larger, more suitably a 12-membered ring or larger, and desirably a 14-membered ring or larger.

[0027] In the present application, the length of the linking group is defined as the lowest number of consecutive atoms, not including substituents on the atoms that create a chain connecting positions 7 and 10 of the fluoranthene nucleus. Desirably, the length of the linking group is 6 atoms or more, suitably 8 atoms or more, and more desirably 10 atoms or more. If the linking group is too long, one can obtain compounds that do not have desirable physical properties, such as suitable sublimation temperatures. Desirably, the linking group has a length of 30 atoms or less and suitably 25 atoms or less or even 20 atoms or less. By way of example, each of the linking groups listed below have a length of 10 atoms.



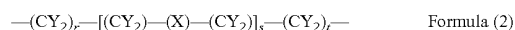
[0028] An example of a useful divalent linking group is represented by Formula (1).



[0029] In Formula (1), the dash marks represent bonds connecting the fragment of Formula (1) to the 7- and 10-positions of the fluoranthene nucleus. Each Y can be the same or different and each Y represents hydrogen or a substituent such as, for example, an alkyl group having 1-24 carbon atoms or an aryl group having 6-24 carbon atoms. Adjacent Y groups

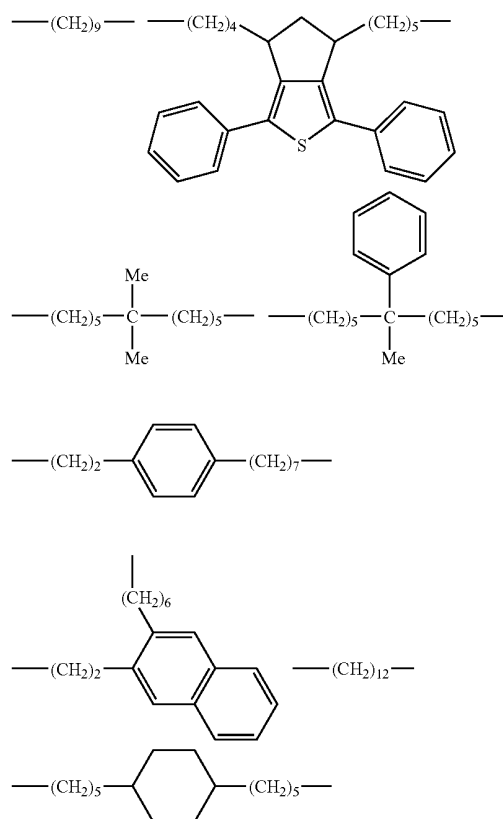
can combine to form a ring group, for example, a five- or six-membered ring group and wherein the ring group can be aromatic, for example, a benzene ring group, or nonaromatic, for example, a cyclohexane ring group, and the ring group can contain heteroatoms. In one embodiment, each Y represents hydrogen. In Formula (1), n is an integer having a value of 6-30. In another suitable embodiment, n has a value of 8-25, and desirably n has a value of 10-20.

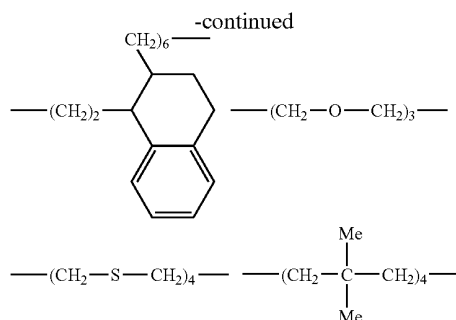
[0030] Another example of a useful linking group is represented by Formula (2).



[0031] In Formula (2), the first and last dash marks represent bonds connecting the fragment of Formula (2) to the 7- and 10-positions of the fluoranthene nucleus. Each X can be the same or different, and each independently represents CY_2 , N, O, or S. In Formula (2), each Y independently represents hydrogen or a substituent, provided adjacent Y groups can combine to form a ring group. Examples of Y groups include alkyl groups having 1-24 carbon atoms and aryl groups having 6-24 carbon atoms. In Formula (2), r is 0 to 10, t is 0 to 10, and s is 1 to 10, provided that r, t, and s are chosen so that the linking group represented by Formula (2) has a length of between 6 and 30 atoms, suitably between 8 and 25 atoms, and desirably between 10 and 20 atoms.

[0032] Illustrative, non-limiting, examples of specific useful linking groups are shown below.

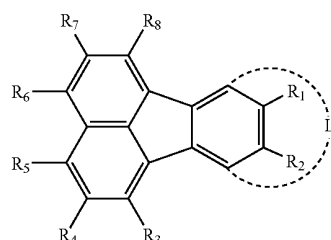




[0033] In one desirable embodiment, the fluoranthene-macrocycle compound, which includes the fluoranthene nucleus and its substituents, contains less than a total of ten fused aromatic rings, or less than eight fused aromatic rings, or even less than six fused aromatic rings. The fluoranthene-macrocycle compounds of the invention can contain more than one fluoranthene nucleus that is, two or more fluoranthene groups can be linked through a single bond or annulated together. However, in one embodiment, the fluoranthene-macrocycle compound contains one, and only one, fluoranthene nucleus.

[0034] The fluoranthene-macrocycle compounds used in the invention do not include multiple fluoranthene groups covalently attached to a polymeric backbone or compounds where the fluoranthene nucleus is directly part of a polymeric chain. The fluoranthene-macrocycle compounds of the invention are small molecules with molecular weights typically below 1500, preferably below 1000 daltons.

[0035] In one desirable embodiment, the fluoranthene-macrocycle compound is represented by Formula (I).



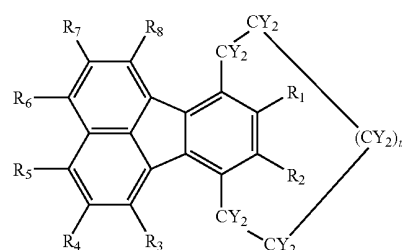
Formula (I)

[0036] In Formula (I), R_1 through R_8 each independently represent hydrogen or individually chosen substituents and wherein adjacent substituents can combine to form a ring group, provided R_1 and R_2 cannot combine to form a five-membered ring group. Suitable substituents include, for example, alkyl groups having 1-24 carbon atoms such as methyl groups and t-butyl groups, and aryl groups having 6-24 carbon atoms such as, for example, phenyl and naphthyl groups. In one embodiment, adjacent R_1 through R_8 substituents can combine to form a fused benzene ring group, which can be further substituted. In a further embodiment, the fluoranthene-macrocycle compound contains no aromatic rings fused to the fluoranthene nucleus.

[0037] In Formula (I), L represents the atoms necessary to form a linking group. Desirably, L has a length of 6-30 atoms, suitably 8-25 atoms, and more desirably, 10-20 atoms. The

length of L is defined as the lowest number of consecutive atoms of the linking group that create a chain connecting positions 7 and 10 of the fluoranthene nucleus, but not including substituents on the atoms of the chain. The linking group can contain carbon, hydrogen, and heteroatoms such as N, O, and S. The linking group can also contain ring groups. In one desirable embodiment, L is represented by Formula (1) or Formula (2), which have also been described previously.

[0038] In another desirable embodiment, the fluoranthene-macrocycle compound is represented by Formula (II).



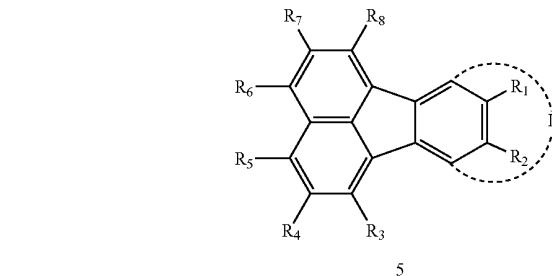
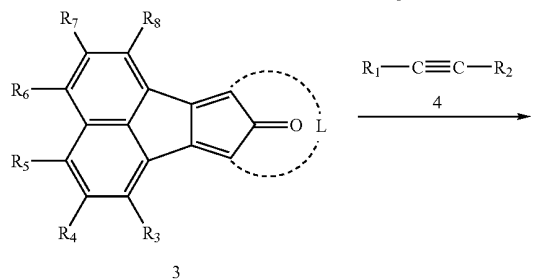
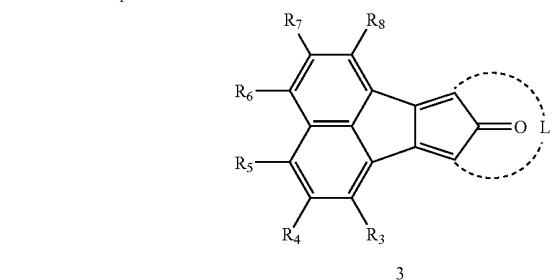
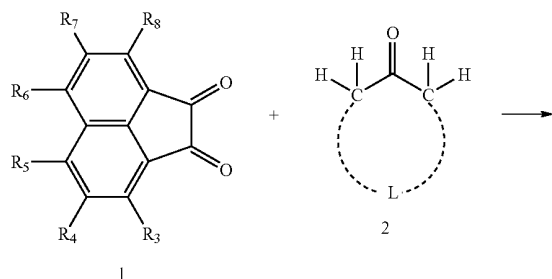
Formula (II)

[0039] In Formula (II), R_1 through R_8 each independently represent hydrogen or individually chosen substituents. Adjacent substituents can combine to form a ring group, provided R_1 and R_2 cannot combine to form a five-membered ring group. However, in one embodiment, adjacent R_1 - R_8 substituents cannot combine to form a ring group of any type. Thus, in one suitable embodiment, the fluoranthene-macrocycle compound of Formula (II) contains no aromatic rings annulated to the fluoranthene nucleus. In a further embodiment, at least one of R_1 and R_2 represents an alkyl group having 1-24 carbon atoms or an aryl group having 6-24 carbon atoms.

[0040] In Formula (II), each Y can be the same or different and each independently represents hydrogen or a substituent, provided adjacent Y groups can combine to form a ring group. In one embodiment, each Y independently represents hydrogen, an alkyl group having 1-24 carbon atoms, or an aryl group having 6-24 carbon atoms, provided adjacent Y groups can combine to form a ring group. In Formula (II), m is 4 or greater, but less than 30, and suitably m is 6 or greater, but less than 25, and desirably m is 8 or greater, but less than 20.

[0041] In a still further embodiment, the fluoranthene-macrocycle compounds of the invention contain no heteroatoms, either as a substituent or contained within a substituent.

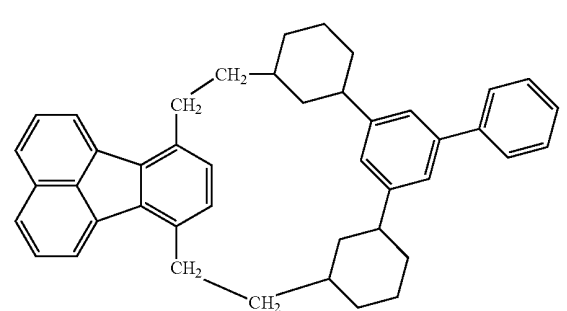
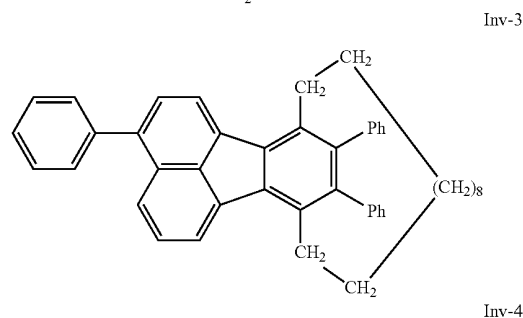
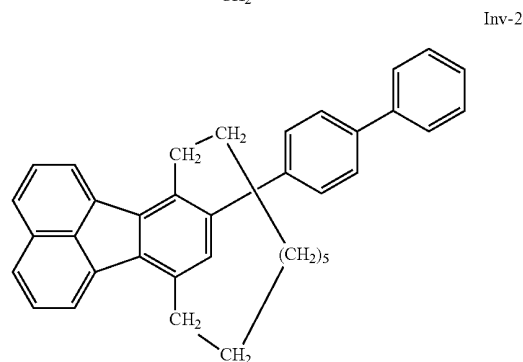
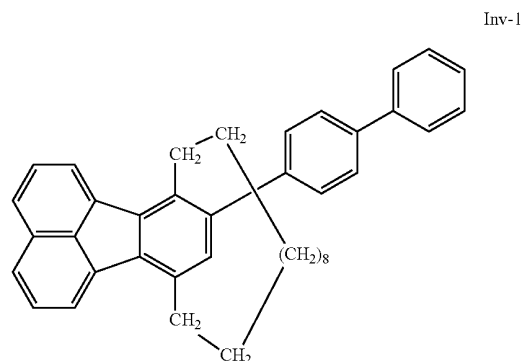
[0042] Suitable fluoranthene-macrocycle compounds can be prepared utilizing modifications of known synthetic methods, for example, by methods similar to those described by Marappan Velusamy et al., *Dalton Trans.*, 3025-3034 (2007) or P. Bergmann et al., *Chemische Berichte*, 828-35 (1967). An example of one general synthetic route is shown below (Scheme A). Compound 1 is reacted with ketone 2 in the presence of base, such as potassium hydroxide, to yield 3. Treatment of 3 with the acetylene 4 at high temperatures in a high-boiling solvent such as o-dichlorobenzene or diphenyl ether forms the fluoranthene-macrocycle compound 5.



[0043] It should be understood that in the synthesis of organic molecules, particular synthetic pathways can give rise to molecules, either exclusively or as mixtures of molecules, which have the same molecular formulae but differ only in having a particular substituent located at a different site somewhere in the molecule. In other words, the molecules or the molecules in the mixtures can differ from each other by the arrangement of their substituents or more generally, the arrangement of some of their atoms in space. When this occurs, the materials are referred to as isomers. A broader definition of an isomer can be found in *Grant and Hack's Chemical Dictionary*, Fifth Edition, McGraw-Hill Book Company, page 313. The synthetic pathway outlined in Scheme A is an example of a pathway that can give rise to isomers by virtue of how the acetylene molecule, 4, reacts spatially with compound 3, when compound 3 is unsymmetrical. It should be realized that the current invention includes not only examples of molecules represented by generic Formulae (I) and (II) and their specific molecular examples, but also includes all the isomers associated with these structures.

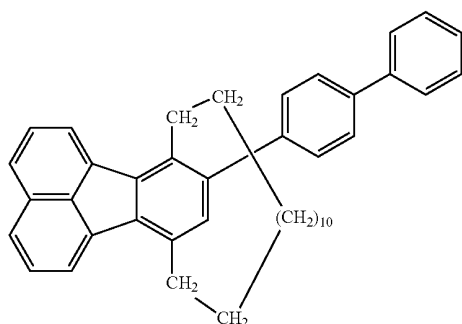
In addition, examples of compounds of the invention and their isomers are not limited to those derived from symmetrical or unsymmetrical compounds of general structure 3, but can also include other frameworks and methods of preparation that are useful in producing compounds of Formulae (I) and (II). In some embodiments, it is desirable to use a fluoranthene-macrocyclic compound that consists of a mixture of isomers.

[0044] Illustrative, non-limiting, examples of useful fluoranthene-macrocyclic compounds are shown below.



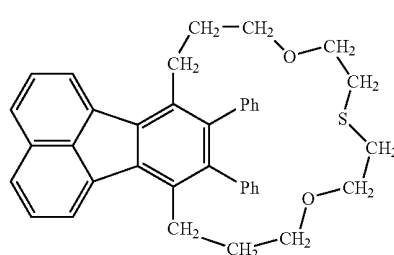
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Inv-5

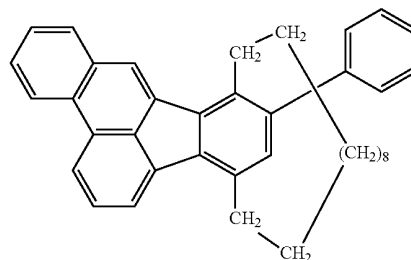


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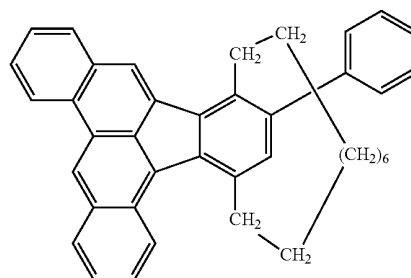
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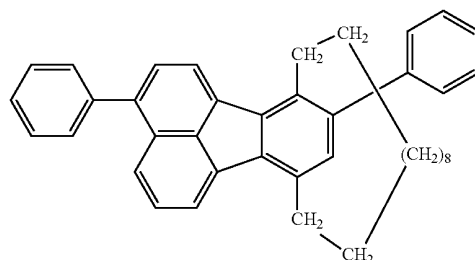
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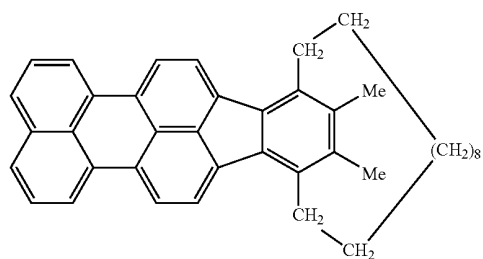
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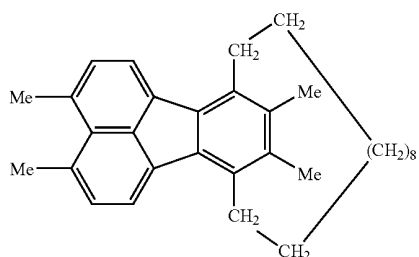
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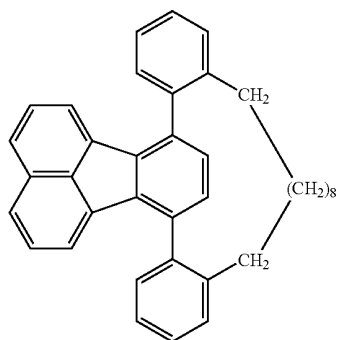
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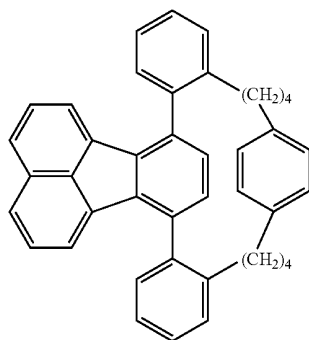
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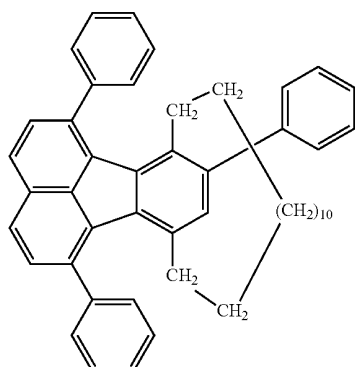


Inv-8



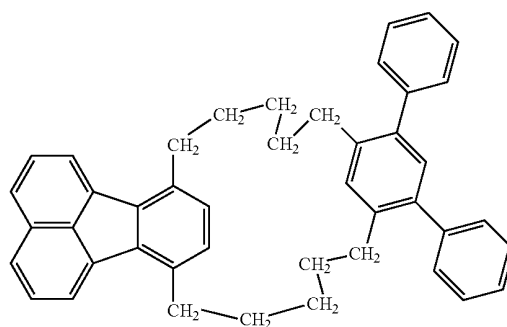
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Inv-14

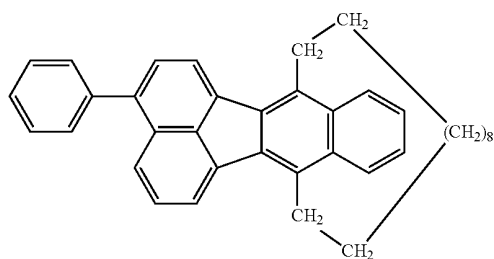


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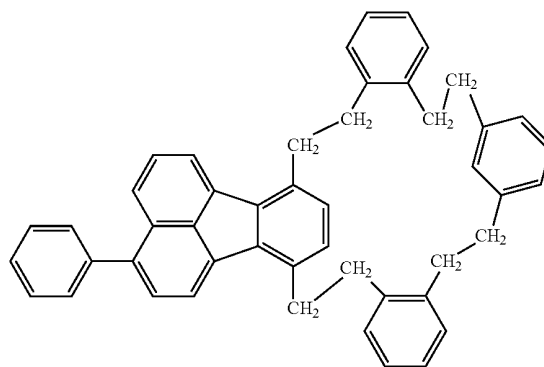
Inv-18



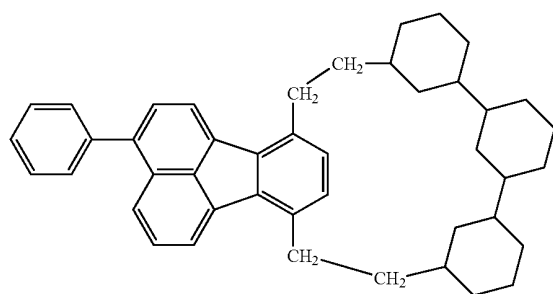
Inv-15



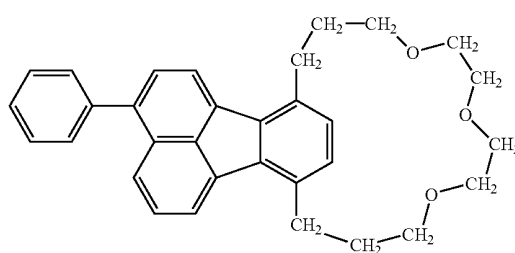
Inv-19



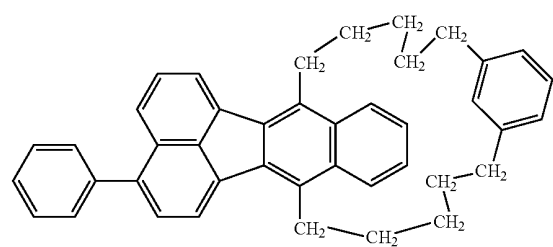
Inv-16



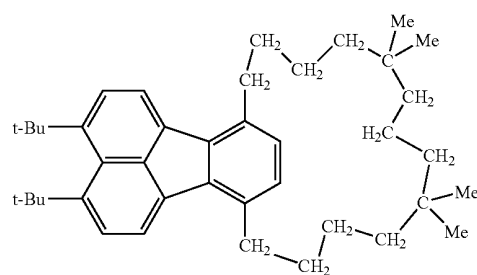
Inv-20

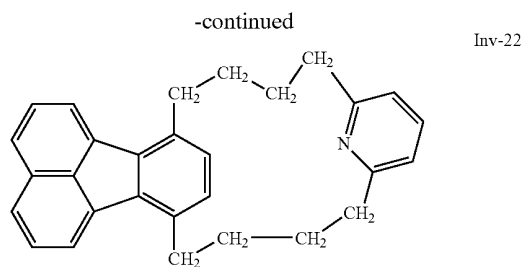


Inv-17



Inv-21





[0045] The OLED device includes at least one layer, between the light-emitting layer and the cathode, containing an alkali metal material. In the present application, an alkali metal material is defined as an alkali metal, an organic alkali metal compound, or an inorganic alkali metal compound.

[0046] Desirably, there is additionally present a second layer, located between the cathode and the first layer and preferably contiguous to the first layer, that contains an alkali metal or an organic alkali metal compound. This layer is typically referred to as an electron-injection layer (EIL). Such layers are commonly located in direct contact with the cathode and assist in the efficient transfer of electrons towards the light emitting layer. A common layer order is LEL|ETL|EIL|cathode. The ETL and EIL can be split into multiple sublayers. There can be intermediate layers between any of these 3 interfaces; for example, a thin layer of an inorganic alkali metal compound between the cathode and the EIL. Examples of useful inorganic alkali metal compounds include LiF and CsF. The alkali metal or the organic alkali metal compound can also be present in the ETL as well as the EIL.

[0047] The EIL can be composed only of a single alkali metal or organic alkali metal compound or can be a mixture of two or more alkali metals or organic alkali metal compounds. In addition to the alkali metal or organic alkali metal compound, the EIL can also contain one or more additional materials; for example, it can contain a polycyclic aromatic hydrocarbon having 12-50 carbon atoms. The % volume ratio of alkali metal to additional material can be anywhere from 0.1% to 10%, typically 0.5% to 8%, suitably 0.5% to 5%. The % volume ratio of organic alkali metal compound to additional material can be anywhere from 0.1% to 99%, typically 0.5% to 95%, more suitably 10% to 90% and most desirably, 30 to 70%. The first layer can include additional materials. The thickness of the EIL can be typically 0.1 nm to 20 nm, frequently 0.4 nm to 10 nm, and often from 1 nm to 8 nm.

[0048] Examples of useful alkali metals include Li, Na, K, Rb, and Cs metals, with Li metal being preferred.

[0049] The organic alkali metal compound is an organometallic compound in which an organic ligand is bonded to an alkali metal ion. Alkali metals belong to Group 1 of the periodic table. Of these, lithium is highly preferred.

[0050] Useful organic alkali metal compounds include organic lithium compounds according to Formula (III):



Formula (III)

wherein:

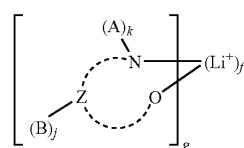
[0051] Q is an anionic organic ligand; and

[0052] f and g are independently selected integers selected to provide a neutral charge on the complex.

[0053] The anionic organic ligand Q is most suitably monoanionic and contains at least one ionizable site consisting of oxygen, nitrogen, or carbon. In the case of enolates or

other tautomeric systems containing oxygen, it will be considered and drawn with the lithium bonded to the oxygen although the lithium can in fact be bonded elsewhere to form a chelate. It is also desirable that the ligand contains at least one nitrogen atom that can form a coordinate or dative bond with the lithium ion. The integers f and g can be greater than 1 reflecting a known propensity for some organic lithium compounds to form cluster complexes.

[0054] Useful organic alkali metal compounds also include organic lithium compounds according to Formula (IV):



Formula (IV)

wherein:

[0055] Z and the dashed arc represent two to four atoms and the bonds necessary to complete a 5- to 7-membered ring with the lithium cation;

[0056] each A represents hydrogen or a substituent and each B represents hydrogen or an independently selected substituent on the Z atoms, provided that two or more substituents can combine to form a fused ring or a fused ring system; and

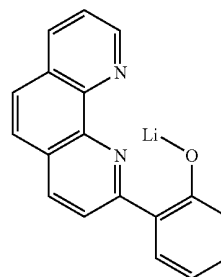
[0057] j is 0-3 and k is 1 or 2; and

[0058] f and g are independently selected integers selected to provide a neutral charge on the complex.

[0059] Of compounds of Formula (IV), it is most desirable that the A and B substituents together form an additional ring system. This additional ring system can further contain additional heteroatoms to form a multidentate ligand with coordinate or dative bonding to the lithium. Desirable heteroatoms are nitrogen or oxygen.

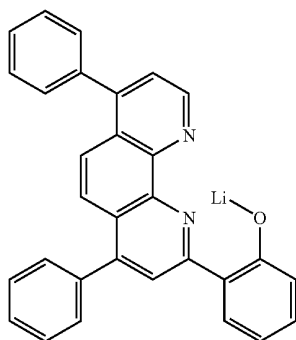
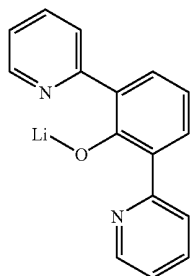
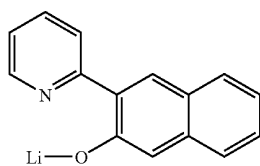
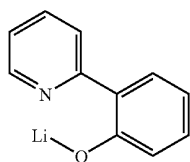
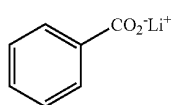
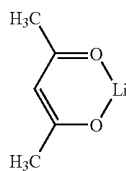
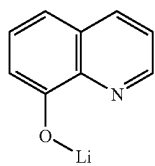
[0060] In Formula (IV), it is preferred that the oxygen shown is part of a hydroxyl, carboxy or keto group. Examples of suitable nitrogen ligands are 8-hydroxyquinoline, 2-hydroxymethylpyridine, pipecolinic acid or 2-pyridinecarboxylic acid.

[0061] Specific illustrative examples of useful organic alkali metal compounds are listed below.



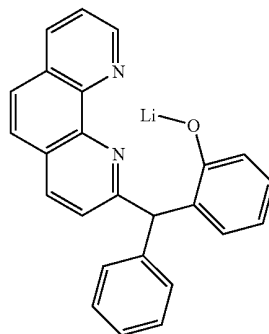
AM-1

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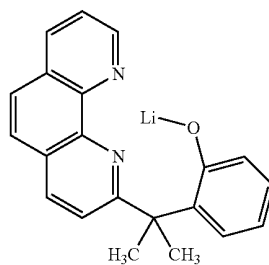


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AM-2

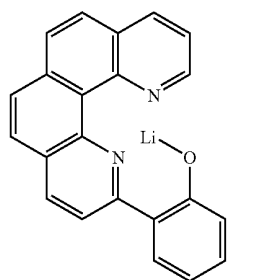


AM-3



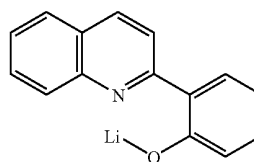
AM-4

AM-5

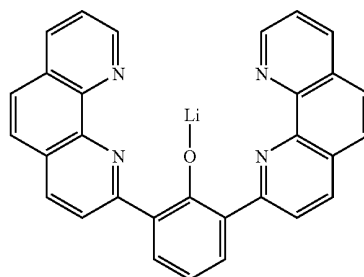


AM-7

AM-8



AM-9



AM-10

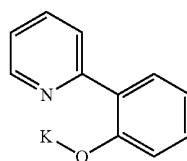
AM-11

AM-12

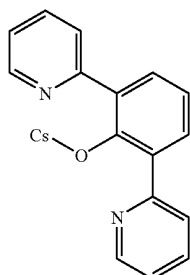
AM-13

AM-14

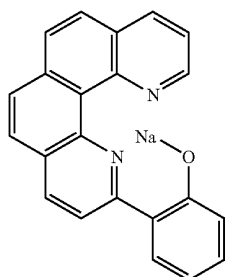
AM-15



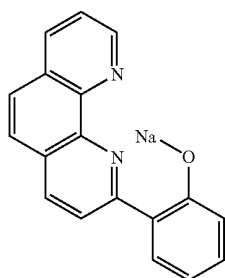
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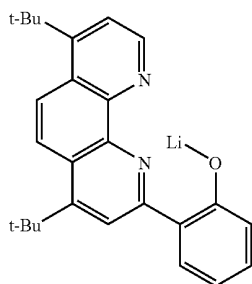
AM-16



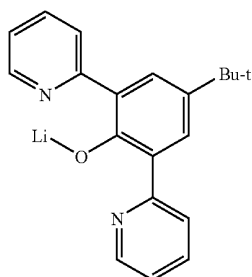
AM-17



AM-18



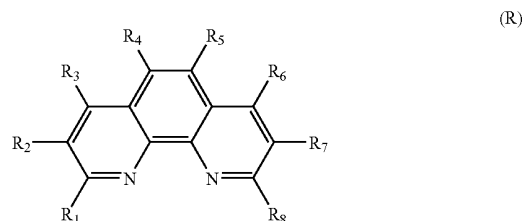
AM-19



AM-20

[0062] A useful second layer (EIL) includes an organic alkali metal compound that is formed in situ, that is, formed by mixing an alkali metal and an organic ligand during the formation of the layer. For example, a useful EIL contains

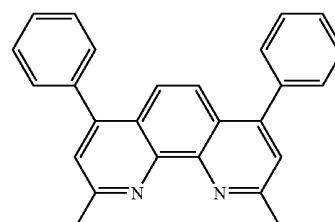
both an organic ligand such as a phenanthroline derivative, and an alkali metal such as Li metal. Suitable alkali metals include Li, Na, K, Rb, and Cs, with lithium metal being the most preferred. Suitable substituted phenanthroline derivatives include those represented by Formula (R).



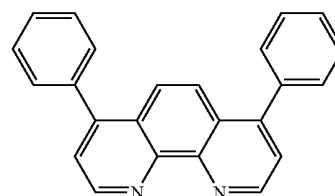
(R)

[0063] In Formula (R), R_1 - R_8 are independently hydrogen, alkyl group, aryl or substituted aryl group, and at least one of R_1 - R_8 is aryl group or substituted aryl group.

[0064] Specific examples of the phenanthrolines useful in the EIL are 2,9-dimethyl-4,7-diphenyl-phenanthroline (BCP) (see Formula (R-1)) and 4,7-diphenyl-1,10-phenanthroline (Bphen) (see Formula (R-2)).



R-1



R-2

[0065] In another embodiment, the fluoranthene-macrocylic compound is present in the ETL and the EIL is subdivided into two or more sublayers, for example, an EIL1 (adjacent to the ETL) and an EIL2 (adjacent to the cathode). A phenanthroline compound is present in the EIL1 and an organic alkali metal compound or an inorganic alkali metal compound is present in the EIL2. Examples of useful inorganic alkali metal compounds include LiF and CsF.

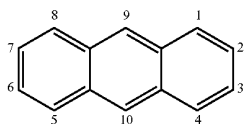
[0066] FIG. 1 shows one embodiment of the invention in which electron-transporting (ETL, 136) and electron-injecting layers (EIL, 138) are present. An optional hole-blocking layer (HBL, 135) is shown between the light-emitting layer and the electron-transporting layer. The figure also shows an optional hole-injecting layer (HIL, 130). In another embodiment, there is no hole-blocking layer (HBL, 135) located between the ETL and the LEL. In yet other embodiments, the electron-injecting layer can be subdivided into two or more sublayers (not shown).

[0067] In one illustrative example, the OLED device 100 has no hole-blocking layer and only one hole-injecting, electron-injecting and electron-transporting layer. The fluoranthene-macrocylic compound is present in the ETL (136) and an organic alkali metal compound, for example AM-1, is present in the EIL (138).

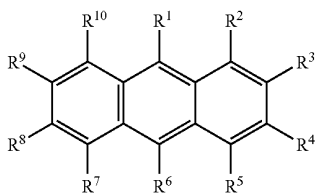
[0068] The fluoranthene-macrocylic compound can comprise 100% of the first layer or there can be other components in the layer, in which case the fluoranthene-macrocylic compound can be present at a level of substantially less than 100% of the layer, for instance it can be present at 90% by volume, 80%, 70%, or 50% by volume, or even less. Desirably, when other components are present in the layer they also have good electron-transporting properties.

[0069] As described previously, the alkali metal or the organic alkali metal compound can also be present in the ETL as well as the EIL. For example, a particularly useful combination includes an ETL containing both a fluoranthene-macrocylic compound and organic lithium compound AM-2, and wherein this layer is adjacent to an EIL also containing AM-2.

[0070] In a further desirable embodiment, the first layer includes, in addition to the fluoranthene-macrocylic compound, an anthracene derivative. The anthracene derivative includes an anthracene nucleus having in the 9- and 10-positions independently selected aryl groups having 6-24 carbon atoms, and the anthracene nucleus can be further substituted. The numbering system for the anthracene nucleus is shown below.



[0071] Useful anthracene derivatives include those represented according to Formula (V).

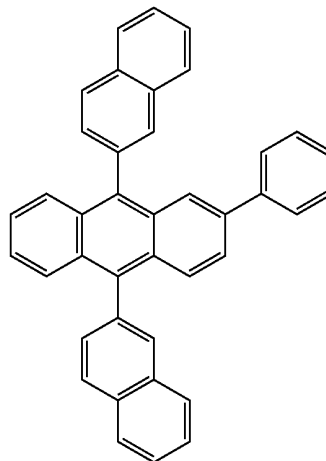


Formula (V)

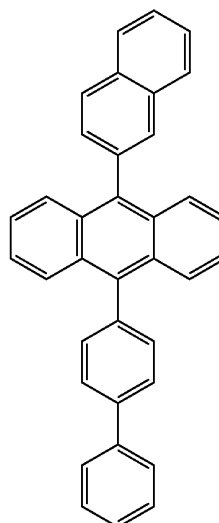
[0072] In Formula (V), R^1 and R^6 each independently represent an aryl group having 6-24 carbon atoms such as a phenyl group or a naphthyl group. R^2 - R^5 and R^7 - R^{10} are each independently chosen from hydrogen, alkyl groups having from 1-24 carbon atoms or aromatic groups having from 6-24 carbon atoms.

[0073] In one suitable embodiment R^1 and R^6 each represent an independently selected phenyl group, biphenyl group, or naphthyl group. R^3 represents hydrogen or a phenyl or naphthyl group. R^2 , R^4 , R^5 , R^7 - R^{10} represent hydrogen.

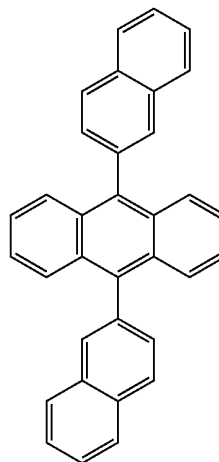
[0074] Illustrative examples of useful anthracenes are listed below.



P-1

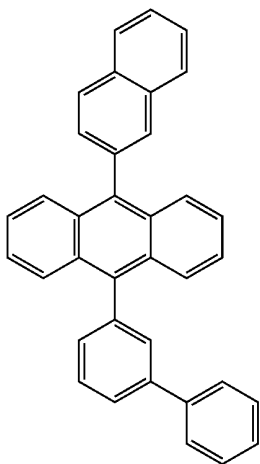
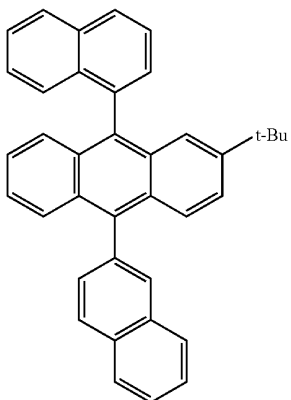
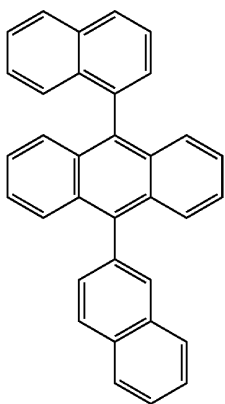


P-2

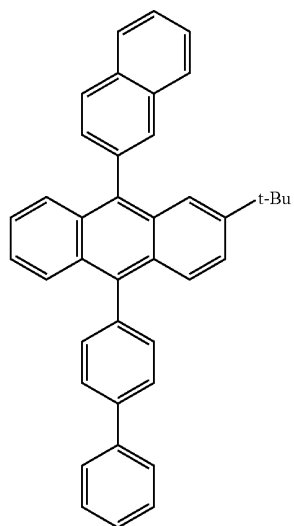
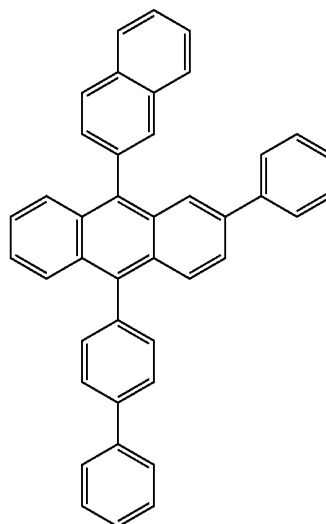


P-3

-continued



-continued



P-4

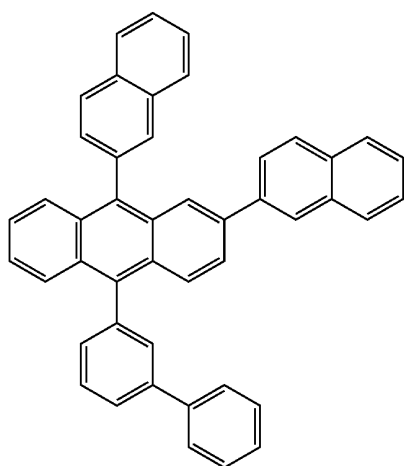
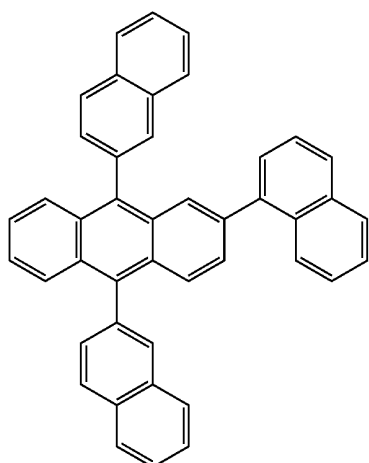
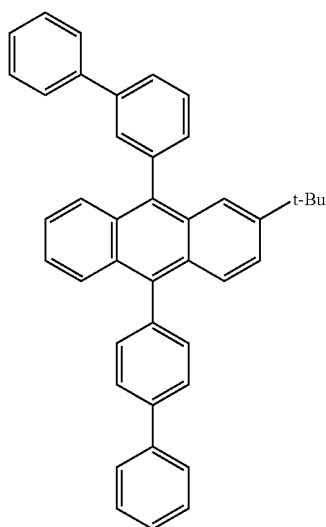
P-7

P-5

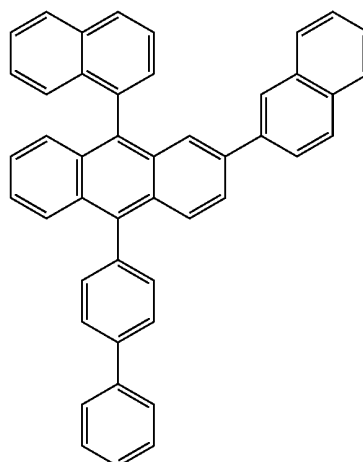
P-8

P-6

-continued



-continued



P-9

P-12

P-10

P-11

[0075] Examples of preferred combinations of the invention are those wherein the fluorene-macroscopic compound is selected from Inv-1, Inv-2, Inv-3, Inv-4, and Inv-5 or mixtures thereof, the alkali metal is Li metal, the organic alkali metal compound is selected from AM-1, AM-2 and AM-3 or mixtures thereof; and the anthracene derivative (when present) is selected from P-1, P-2, P-3, and P-4 or mixtures thereof.

[0076] In one suitable embodiment the EL device emits white light, which can be achieved by including complementary emitters, a white emitter, or filters. This invention can be used in so-called stacked device architecture, for example, as taught in U.S. Pat. Nos. 5,703,436 and 6,337,492. Embodiments of the current invention can be used in stacked devices that comprise solely fluorescent elements to produce white light. The device can also include combinations of fluorescent emitting materials and phosphorescent emitting materials (sometimes referred to as hybrid OLED devices). To produce a white emitting device, ideally the hybrid fluorescent/phosphorescent device would comprise a blue fluorescent emitter and proper proportions of a green and red phosphorescent emitter, or other color combinations suitable to make white emission. However, hybrid devices having non-white emission can also be useful by themselves. Hybrid fluorescent/phosphorescent elements having non-white emission can also be combined with additional phosphorescent elements in series in a stacked OLED. For example, white emission can be produced by one or more hybrid blue fluorescent/red phosphorescent elements stacked in series with a green phosphorescent element using p/n junction connectors as disclosed in Tang et al. U.S. Pat. No. 6,936,961B2.

[0077] In one desirable embodiment the EL device is part of a display device. In another suitable embodiment the EL device is part of an area lighting device.

[0078] The EL device of the invention is useful in any device where stable light emission is desired such as a lamp or a component in a static or motion imaging device, such as a television, cell phone, DVD player, or computer monitor.

[0079] As used herein and throughout this application, the term carbocyclic and heterocyclic rings or groups are generally as defined by the *Grant & Hack's Chemical Dictionary*, Fifth Edition, McGraw-Hill Book Company. A carbocyclic

ring is any aromatic or non-aromatic ring system containing only carbon atoms and a heterocyclic ring is any aromatic or non-aromatic ring system containing both carbon and non-carbon atoms such as nitrogen (N), oxygen (O), sulfur (S), phosphorous (P), silicon (Si), gallium (Ga), boron (B), beryllium (Be), indium (In), aluminum (Al), and other elements found in the periodic table useful in forming ring systems. For the purpose of this invention, also included in the definition of a heterocyclic ring are those rings that include coordinate bonds. The definition of a coordinate or dative bond can be found in *Grant & Hackh's Chemical Dictionary*, pages 91 and 153. In essence, a coordinate bond is formed when electron rich atoms such as O or N, donate a pair of electrons to electron deficient atoms or ions such as aluminum, boron or alkali metal ions such as Li^+ , Na^+ , K^+ and Cs^+ . One such example is found in tris(8-quinolinolato)aluminum(III), also referred to as Alq, wherein the nitrogen on the quinoline moiety donates its lone pair of electrons to the aluminum atom thus forming the heterocycle and hence providing Alq with a total of 3 fused rings. The definition of a ligand, including a multidentate ligand, can be found in *Grant & Hackh's Chemical Dictionary*, pages 337 and 176, respectively.

[0080] Unless otherwise specifically stated, use of the term “substituted” or “substituent” means any group or atom other than hydrogen. Additionally, when the term “group” is used, it means that when a substituent group contains a substitutable hydrogen, it is also intended to encompass not only the substituent’s unsubstituted form, but also its form further substituted with any substituent group or groups as herein mentioned, so long as the substituent does not destroy properties necessary for device utility. Suitably, a substituent group can be halogen or can be bonded to the remainder of the molecule by an atom of carbon, silicon, oxygen, nitrogen, phosphorous, sulfur, selenium, or boron. The substituent can be, for example, halogen, such as chloro, bromo or fluoro; nitro; hydroxyl; cyano; carboxyl; or groups which can be further substituted, such as alkyl, including straight or branched chain or cyclic alkyl, such as methyl, trifluoromethyl, ethyl, t-butyl, 3-(2,4-di-t-pentylphenoxy) propyl, and tetradecyl; alkenyl, such as ethylene, 2-butene; alkoxy, such as methoxy, ethoxy, propoxy, butoxy, 2-methoxyethoxy, sec-butoxy, hexyloxy, 2-ethylhexyloxy, tetradecyloxy, 2-(2,4-di-t-pentylphenoxy)ethoxy, and 2-dodecyloxyethoxy; aryl such as phenyl, 4-t-butylphenyl, 2,4,6-trimethylphenyl, naphthyl; aryloxy, such as phenoxy, 2-methylphenoxy, alpha- or beta-naphthyloxy, and 4-tolyloxy; carbonamido, such as acetamido, benzamido, butyramido, tetradecanamido, alpha-(2,4-di-t-pentyl-phenoxy)acetamido, alpha-(2,4-di-t-pentylphenoxy)butyramido, alpha-(3-pentadecylphenoxy)-hexanamido, alpha-(4-hydroxy-3-t-butylphenoxy)-tetradecanamido, 2-oxo-pyrrolidin-1-yl, 2-oxo-5-tetradecylpyrrolin-1-yl, N-methyltetradecanamido, N-succinimido, N-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2,5-dioxo-1-imidazolyl, and N-acetyl-N-dodecylamino, ethoxycarbonylamino, phenoxycarbonylamino, benzyloxy-carbonylamino, hexadecyloxy-carbonylamino, 2,4-di-t-butylphenoxy-carbonylamino, phenylcarbonylamino, 2,5-(di-t-pentylphenyl)carbonylamino, p-dodecyl-phenylcarbonylamino, p-tolylcarbonylamino, N-methylureido, N,N-dimethylureido, N-methyl-N-dodecylureido, N-hexadecylureido, N,N-di-octadecylureido, N,N-di-octyl-N'-ethylureido, N-phenylureido, N,N-diphenylureido, N-phenyl-N-p-tolylureido, N-(m-hexadecylphenyl)

ureido, N,N-(2,5-di-t-pentylphenyl)-N'-ethylureido, and t-butylcarbonamido; sulfonamido, such as methylsulfonamido, benzenesulfonamido, p-tolylsulfonamido, p-dodecylbenzenesulfonamido, N-methyltetradecylsulfonamido, N,N-dipropyl-sulfamoylamino, and hexadecylsulfonamido; sulfamoyl, such as N-methylsulfamoyl, N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-hexadecylsulfamoyl, N,N-dimethylsulfamoyl, N-[3-(dodecyloxy)propyl]sulfamoyl, N-[4-(2,4-di-t-pentylphenoxy)butyl]sulfamoyl, N-methyl-N-tetradecylsulfamoyl, and N-dodecylsulfamoyl; carbamoyl, such as N-methylcarbamoyl, N,N-dibutylcarbamoyl, N-octadecylcarbamoyl, N-[4-(2,4-di-t-pentylphenoxy)butyl]carbamoyl, N-methyl-N-tetradecylcarbamoyl, and N,N-di-octylcarbamoyl; acyl, such as acetyl, (2,4-di-t-amyloxy)acetyl, phenoxycarbonyl, p-dodecyloxyphenoxycarbonyl methoxycarbonyl, butoxycarbonyl, tetradecyloxy-carbonyl, ethoxycarbonyl, benzyloxy-carbonyl, 3-pentadecyloxy-carbonyl, and dodecyloxy-carbonyl; sulfonyl, such as methoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl, 2-ethylhexyloxysulfonyl, phenoxysulfonyl, 2,4-di-t-pentylphenoxy-sulfonyl, methylsulfonyl, octylsulfonyl, 2-ethylhexylsulfonyl, dodecylsulfonyl, hexadecylsulfonyl, phenylsulfonyl, 4-nonylphenylsulfonyl, and p-tolylsulfonyl; sulfonyloxy, such as dodecylsulfonyloxy, and hexadecylsulfonyloxy; sulfinyl, such as methylsulfinyl, octylsulfinyl, 2-ethylhexylsulfinyl, dodecylsulfinyl, hexadecylsulfinyl, phenylsulfinyl, 4-nonylphenylsulfinyl, and p-tolylsulfinyl; thio, such as ethylthio, octylthio, benzylthio, tetradecylthio, 2-(2,4-di-t-pentylphenoxy)ethylthio, phenylthio, 2-butoxy-5-t-octylphenylthio, and p-tolylthio; acyloxy, such as acetyloxy, benzoyloxy, octadecanoyloxy, p-dodecylamidobenzoyloxy, N-phenylcarbamoyloxy, N-ethylcarbamoyloxy, and cyclohexylcarbamoyloxy; amine, such as phenylanilino, 2-chloroanilino, diethylamine, dodecylamine; imino, such as 1 (N-phenylimido)ethyl, N-succinimido or 3-benzylhydantoinyl; phosphate, such as dimethylphosphate and ethylbutylphosphate; phosphite, such as diethyl and dihexylphosphite; a heterocyclic group, a heterocyclic oxy group or a heterocyclic thio group, each of which can be substituted and which contain a 3 to 7 membered heterocyclic ring composed of carbon atoms and at least one hetero atom selected from the group consisting of oxygen, nitrogen, sulfur, phosphorous, or boron, such as 2-furyl, 2-thienyl, 2-benzimidazolyl or 2-benzothiazolyl; quaternary ammonium, such as triethylammonium; quaternary phosphonium, such as triphenylphosphonium; and silyloxy, such as trimethylsilyloxy.

[0081] If desired, the substituents can themselves be further substituted one or more times with the described substituent groups. The particular substituents used can be selected by those skilled in the art to attain desirable properties for a specific application and can include, for example, electron-withdrawing groups, electron-donating groups, and steric groups. When a molecule can have two or more substituents, the substituents can be joined together to form a ring such as a fused ring unless otherwise provided. Generally, the above groups and substituents thereof can include those having up to 48 carbon atoms, typically 1 to 36 carbon atoms and usually less than 24 carbon atoms, but greater numbers are possible depending on the particular substituents selected.

[0082] The following is the description of the layer structure, material selection, and fabrication process for OLED devices.

General OLED Device Architecture

[0083] The present invention can be employed in many OLED configurations using small molecule materials, oligo-

meric materials, polymeric materials, or combinations thereof. These include from very simple structures having a single anode and cathode to more complex devices, such as passive matrix displays having orthogonal arrays of anodes and cathodes to form pixels, and active-matrix displays where each pixel is controlled independently, for example, with thin film transistors (TFTs). There are numerous configurations of the organic layers wherein the present invention is successfully practiced. For this invention, essential requirements are a cathode, an anode, a LEL, an ETL and a HIL.

[0084] As previously discussed, one embodiment according to the present invention and especially useful for a small molecule device is shown in FIG. 1. OLED **100** contains a substrate **110**, an anode **120**, a hole-injecting layer **130**, a hole-transporting layer **132**, a light-emitting layer **134**, a hole-blocking layer **135**, an electron-transporting layer **136**, an electron-injecting layer **138** and a cathode **140**. In some other embodiments, there are optional spacer layers on either side of the LEL. These spacer layers do not typically contain light emissive materials. All of these layer types will be described in detail below. Note that the substrate can alternatively be located adjacent to the cathode, or the substrate can actually constitute the anode or cathode. Also, the total combined thickness of the organic layers is preferably less than 500 nm.

[0085] The anode and cathode of the OLED are connected to a voltage/current source **150**, through electrical conductors **160**. Applying a potential between the anode and cathode such that the anode is at a more positive potential than the cathode operates the OLED. Holes are injected into the organic EL element from the anode. Enhanced device stability can sometimes be achieved when the OLED is operated in an AC mode where, for some time period in cycle, the potential bias is reversed and no current flows. An example of an AC driven OLED is described in U.S. Pat. No. 5,552,678.

Anode

[0086] When the desired EL emission is viewed through the anode, anode **120** should be transparent or substantially transparent to the emission of interest. Common transparent anode materials used in this invention are indium-tin oxide (ITO), indium-zinc oxide (IZO) and tin oxide, but other metal oxides can work including, but not limited to, aluminum- or indium-doped zinc oxide, magnesium-indium oxide, and nickel-tungsten oxide. In addition to these oxides, metal nitrides, such as gallium nitride, and metal selenides, such as zinc selenide, and metal sulfides, such as zinc sulfide, can be used as the anode **120**. For applications where EL emission is viewed only through the cathode **140**, the transmissive characteristics of the anode **120** are immaterial and any conductive material can be used, transparent, opaque or reflective. Example conductors for this application include, but are not limited to, gold, iridium, molybdenum, palladium, and platinum. Typical anode materials, transmissive or otherwise, have a work function of 4.1 eV or greater. Desired anode materials are commonly deposited by any suitable techniques such as evaporation, sputtering, chemical vapor deposition, or electrochemical techniques. Anodes can be patterned using well-known photolithographic processes. Optionally, anodes can be polished prior to application of other layers to reduce surface roughness so as to reduce short circuits or enhance reflectivity.

Hole Injection Layer

[0087] Although it is not always necessary, it is often useful to provide an HIL in the OLEDs. HIL **130** in the OLEDs can

serve to facilitate hole injection from the anode into the HTL, thereby reducing the drive voltage of the OLEDs. Suitable materials for use in HIL **130** include, but are not limited to, porphyrinic compounds as described in U.S. Pat. No. 4,720,432 and some aromatic amines, for example, 4,4',4''-tris[(3-ethylphenyl)phenylamino]triphenylamine (m-TDATA). Alternative hole-injecting materials reportedly useful in OLEDs are described in EP 0 891 121 A1 and EP 1 029 909 A1. Aromatic tertiary amines discussed below can also be useful as hole-injecting materials. Other useful hole-injecting materials such as dipyrazino[2,3-f:2',3'-h]quinoxalinehexacarbonitrile are described in U.S. Patent Application Publication 2004/0113547 A1 and U.S. Pat. No. 6,720,573. In addition, a p-type doped organic layer is also useful for the HIL as described in U.S. Pat. No. 6,423,429. The term "p-type doped organic layer" means that this layer has semiconducting properties after doping, and the electrical current through this layer is substantially carried by the holes. The conductivity is provided by the formation of a charge-transfer complex as a result of hole transfer from the dopant to the host material.

[0088] The thickness of the HIL **130** is in the range of from 0.1 nm to 200 nm, preferably, in the range of from 0.5 nm to 150 nm.

Hole Transport Layer

[0089] The HTL **132** contains at least one hole-transporting material such as an aromatic tertiary amine, where the latter is understood to be a compound containing at least one trivalent nitrogen atom that is bonded only to carbon atoms, at least one of which is a member of an aromatic ring. In one form the aromatic tertiary amine is an arylamine, such as a monoarylamine, diarylamine, triarylamine, or a polymeric arylamine. Exemplary monomeric triarylamine are illustrated by Klupfel et al. U.S. Pat. No. 3,180,730. Other suitable triarylamine substituted with one or more vinyl radicals or at least one active hydrogen-containing group are disclosed by Brantley, et al. in U.S. Pat. Nos. 3,567,450 and 3,658,520.

[0090] A more preferred class of aromatic tertiary amines are those which include at least two aromatic tertiary amine moieties as described in U.S. Pat. Nos. 4,720,432 and 5,061,569. Such compounds include those represented by structural Formula (A)



wherein:

[0091] Q₁ and Q₂ are independently selected aromatic tertiary amine moieties; and

[0092] G is a linking group such as an arylene, cycloalkylene, or alkylene group of a carbon to carbon bond.

[0093] In one embodiment, at least one of Q₁ or Q₂ contains a polycyclic fused ring structure, e.g., a naphthalene. When G is an aryl group, it is conveniently a phenylene, biphenylene, or naphthalene moiety.

[0094] A useful class of triarylamine satisfying structural Formula A and containing two triarylamine moieties is represented by structural Formula (B)



wherein:

[0095] R_1 and R_2 each independently represents a hydrogen atom, an aryl group, or an alkyl group or R_1 and R_2 together represent the atoms completing a cycloalkyl group; and

[0096] R_3 and R_4 each independently represents an aryl group, which is in turn substituted with a diaryl substituted amino group, as indicated by structural Formula (C)



wherein:

[0097] R_5 and R_6 are independently selected aryl groups. In one embodiment, at least one of R_5 or R_6 contains a polycyclic fused ring structure, e.g., a naphthalene.

[0098] Another class of aromatic tertiary amines are the tetraaryldiamines. Desirable tetraaryldiamines include two diarylamino groups, such as indicated by Formula (C), linked through an arylene group. Useful tetraaryldiamines include those represented by Formula (D)



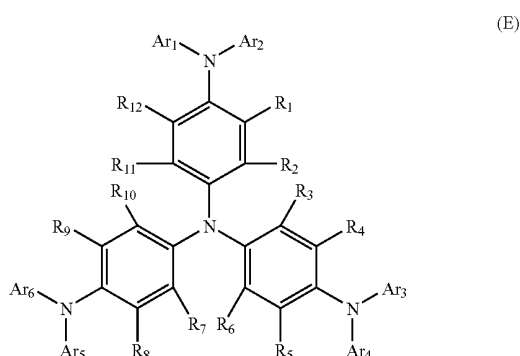
wherein:

[0099] each ARE is an independently selected arylene group, such as a phenylene or anthracene moiety;

[0100] n is an integer of from 1 to 4; and

[0101] Ar , R_7 , R_8 , and R_9 are independently selected aryl groups. In a typical embodiment, at least one of Ar , R_7 , R_8 , and R_9 is a polycyclic fused ring structure, e.g., a naphthalene.

[0102] Another class of the hole-transporting material comprises a material of Formula (E):



[0103] In Formula (E), Ar_1 - Ar_6 independently represent aromatic groups, for example, phenyl groups or tolyl groups;

[0104] R_1 - R_{12} independently represent hydrogen or independently selected substituent, for example an alkyl group containing from 1 to 4 carbon atoms, an aryl group, a substituted aryl group.

[0105] The various alkyl, alkylene, aryl, and arylene moieties of the foregoing structural Formulae (A), (B), (C), (D), and (E) can each in turn be substituted. Typical substituents include alkyl groups, alkoxy groups, aryl groups, aryloxy groups, and halogen such as fluoride, chloride, and bromide. The various alkyl and alkylene moieties typically contain from about 1 to 6 carbon atoms. The cycloalkyl moieties can contain from 3 to about 10 carbon atoms, but typically contain five, six, or seven ring carbon atoms, e.g. cyclopentyl, cyclohexyl, and cycloheptyl ring structures. The aryl and arylene moieties are typically phenyl and phenylene moieties.

[0106] The HTL is formed of a single or a mixture of aromatic tertiary amine compounds. Specifically, one can employ a triarylamine, such as a triarylamine satisfying the Formula (B), in combination with a tetraaryldiamine, such as indicated by Formula (D). When a triarylamine is employed in combination with a tetraaryldiamine, the latter is positioned as a layer interposed between the triarylamine and the electron injecting and transporting layer. Aromatic tertiary amines are useful as hole-injecting materials also. Illustrative of useful aromatic tertiary amines are the following:

[0107] 1,1-bis(4-di-p-tolylaminophenyl)cyclohexane;

[0108] 1,1-bis(4-di-p-tolylaminophenyl)-4-phenylcyclohexane;

[0109] 1,5-bis[N-(1-naphthyl)-N-phenylamino]naphthalene;

[0110] 2,6-bis(di-p-tolylamino)naphthalene;

[0111] 2,6-bis[di-(1-naphthyl)amino]naphthalene;

[0112] 2,6-bis[N-(1-naphthyl)-N-(2-naphthyl)amino]naphthalene;

[0113] 2,6-bis[N,N-di(2-naphthyl)amine]fluorene;

[0114] 4-(di-p-tolylamino)-4'-[4(di-p-tolylamino)-styryl]stilbene;

[0115] 4,4'-bis(diphenylamino)quadruphenyl;

[0116] 4,4'-bis[N-(1-anthryl)-N-phenylamino]-p-terphenyl;

[0117] 4,4'-bis[N-(1-coroneryl)-N-phenylamino]biphenyl;

[0118] 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB);

[0119] 4,4'-bis[N-(1-naphthyl)-N-(2-naphthyl)amino]biphenyl (TNB);

[0120] 4,4''-bis[N-(1-naphthyl)-N-phenylamino]p-terphenyl;

[0121] 4,4'-bis[N-(2-naphthacetyl)-N-phenylamino]biphenyl;

[0122] 4,4'-bis[N-(2-naphthyl)-N-phenylamino]biphenyl;

[0123] 4,4'-bis[N-(2-perylenyl)-N-phenylamino]biphenyl;

[0124] 4,4'-bis[N-(2-phenanthryl)-N-phenylamino]biphenyl;

[0125] 4,4'-bis[N-(2-pyrenyl)-N-phenylamino]biphenyl;

[0126] 4,4'-bis[N-(3-acenaphthenyl)-N-phenylamino]biphenyl;

[0127] 4,4'-bis[N-(3-methylphenyl)-N-phenylamino]biphenyl (TPD);

[0128] 4,4'-bis[N-(8-fluoranthryl)-N-phenylamino]biphenyl;

[0129] 4,4'-bis[N-(9-anthryl)-N-phenylamino]biphenyl;

[0130] 4,4'-bis {N-phenyl-N-[4-(1-naphthyl)-phenyl]amino}biphenyl;

[0131] 4,4'-bis[N-phenyl-N-(2-pyrenyl)amino]biphenyl;

[0132] 4,4',4''-tris[(3-methylphenyl)phenylamino]triphenylamine (m-TDATA);

- [0133] Bis(4-dimethylamino-2-methylphenyl)-phenyl-methane;
 [0134] N-phenylcarbazole;
 [0135] N,N'-bis[4-([1,1'-biphenyl]-4-ylphenylamino)phenyl]-N,N'-di-1-naphthalenyl-[1,1'-biphenyl]-4,4'-diamine;
 [0136] N,N'-bis[4-(di-1-naphthalenylamino)phenyl]-N,N'-di-1-naphthalenyl-[1,1'-biphenyl]-4,4'-diamine;
 [0137] N,N'-bis[4-[(3-methylphenyl)phenylamino]phenyl]-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine;
 [0138] N,N-bis [4-(diphenylamino)phenyl]-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine;
 [0139] N,N'-di-1-naphthalenyl-N,N'-bis[4-(1-naphthalenylphenylamino)phenyl]-[1,1'-biphenyl]-4,4'-diamine;
 [0140] N,N'-di-1-naphthalenyl-N,N'-bis[4-(2-naphthalenylphenylamino)phenyl]-[1,1'-biphenyl]-4,4'-diamine;
 [0141] N,N,N-tri(p-tolyl)amine;
 [0142] N,N,N',N'-tetra-p-tolyl-4,4'-diaminobiphenyl;
 [0143] N,N,N',N'-tetraphenyl-4,4'-diaminobiphenyl;
 [0144] N,N,N',N'-tetra-1-naphthyl-4,4'-diaminobiphenyl;
 [0145] N,N,N',N'-tetra-2-naphthyl-4,4'-diaminobiphenyl; and
 [0146] N,N,N',N'-tetra(2-naphthyl)-4,4''-diamino-p-terphenyl.
 [0147] Another class of useful hole-transporting materials includes polycyclic aromatic compounds as described in EP 1 009 041. Tertiary aromatic amines with more than two amine groups can be used including oligomeric materials. In addition, polymeric hole-transporting materials are used such as poly(N-vinylcarbazole) (PVK), polythiophenes, polypyrrole, polyaniline, and copolymers such as poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) also called PEDOT/PSS.
 [0148] The thickness of the HTL 132 is in the range of from 5 nm to 200 nm, preferably, in the range of from 10 nm to 150 nm.

Exciton Blocking Layer (EBL)

[0149] An optional exciton- or electron-blocking layer can be present between the HTL and the LEL (not shown in FIG. 1). Some suitable examples of such blocking layers are described in U.S. Patent Application Publication 20060134460 A1.

Light Emitting Layer

[0150] As more fully described in U.S. Pat. Nos. 4,769,292 and 5,935,721, the light-emitting layer(s) (LEL) 134 of the organic EL element shown in FIG. 1 comprises a luminescent, fluorescent or phosphorescent material where electroluminescence is produced as a result of electron-hole pair recombination in this region. The light-emitting layer can be comprised of a single material, but more commonly contains non-electroluminescent compounds (generally referred to as the host) doped with an electroluminescent guest compound (generally referred to as the dopant) or compounds where light emission comes primarily from the electroluminescent compound and can be of any color. Electroluminescent compounds can be coated as 0.01 to 50% into the non-electroluminescent component material, but typically coated as 0.01 to 30% and more typically coated as 0.01 to 15% into the non-electroluminescent component. The thickness of the LEL can be any suitable thickness. It can be in the range of from 0.1 nm to 100 nm.

[0151] An important relationship for choosing a dye as an electroluminescent component is a comparison of the band-gap potential which is defined as the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital of the molecule. For efficient energy transfer from the non-electroluminescent compound to the electroluminescent compound molecule, a necessary condition is that the band gap of the electroluminescent compound is smaller than that of the non-electroluminescent compound or compounds. Thus, the selection of an appropriate host material is based on its electronic characteristics relative to the electronic characteristics of the electroluminescent compound, which itself is chosen for the nature and efficiency of the light emitted. As described below, fluorescent and phosphorescent dopants typically have different electronic characteristics so that the most appropriate hosts for each can be different. However in some cases, the same host material can be useful for either type of dopant.

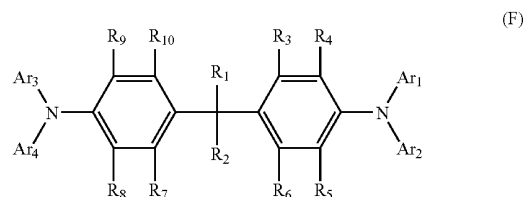
[0152] Non-electroluminescent compounds and emitting molecules known to be of use include, but are not limited to, those disclosed in U.S. Pat. Nos. 5,141,671; 5,150,006; 5,151,629; 5,405,709; 5,484,922; 5,593,788; 5,645,948; 5,683,823; 5,755,999; 5,928,802; 5,935,720; 5,935,721, and 6,020,078.

a) Phosphorescent Light Emitting Layers

[0153] Suitable hosts for phosphorescent LELs should be selected so that transfer of a triplet exciton can occur efficiently from the host to the phosphorescent dopant(s) but cannot occur efficiently from the phosphorescent dopant(s) to the host. Therefore, it is highly desirable that the triplet energy of the host be higher than the triplet energies of phosphorescent dopant. Generally speaking, a large triplet energy implies a large optical band gap. However, the band gap of the host should not be chosen so large as to cause an unacceptable barrier to injection of holes into the fluorescent blue LEL and an unacceptable increase in the drive voltage of the OLED. The host in a phosphorescent LEL can include any of the aforementioned hole-transporting material used for the HTL 132, as long as it has a triplet energy higher than that of the phosphorescent dopant in the layer. The host used in a phosphorescent LEL can be the same as or different from the hole-transporting material used in the HTL 132. In some cases, the host in the phosphorescent LEL can also suitably include an electron-transporting material (it will be discussed thereafter), as long as it has a triplet energy higher than that of the phosphorescent dopant.

[0154] In addition to the aforementioned hole-transporting materials in the HTL 132, there are several other classes of hole-transporting materials suitable for use as the host in a phosphorescent LEL.

[0155] One desirable host comprises a hole-transporting material of Formula (F):



[0156] In Formula (F), R_1 and R_2 represent substituents, provided that R_1 and R_2 can join to form a ring. For example, R_1 and R_2 can be methyl groups or join to form a cyclohexyl ring;

[0157] Ar_1 - Ar_4 represent independently selected aromatic groups, for example phenyl groups or tolyl groups;

[0158] R_3 - R_{10} independently represent hydrogen, alkyl, substituted alkyl, aryl, substituted aryl group.

[0159] Examples of suitable materials include, but are not limited to:

[0160] 1,1-Bis(4-(N,N-di-p-tolylamino)phenyl)cyclohexane (TAPC);

[0161] 1,1-Bis(4-(N,N-di-p-tolylamino)phenyl)cyclopentane;

[0162] 4,4'-(9H-fluoren-9-ylidene)bis[N,N-bis(4-methylphenyl)-benzenamine];

[0163] 1,1-Bis(4-(N,N-di-p-tolylamino)phenyl)-4-phenylcyclohexane;

[0164] 1,1-Bis(4-(N,N-di-p-tolylamino)phenyl)-4-methylcyclohexane;

[0165] 1,1-Bis(4-(N,N-di-p-tolylamino)phenyl)-3-phenylpropane;

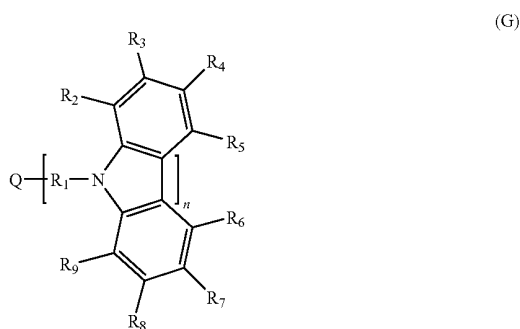
[0166] Bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methane;

[0167] Bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)ethane;

[0168] 4-(4-Diethylaminophenyl)triphenylmethane;

[0169] 4,4'-Bis(4-diethylaminophenyl)diphenylmethane.

[0170] A useful class of triarylamines suitable for use as the host includes carbazole derivatives such as those represented by Formula (G):



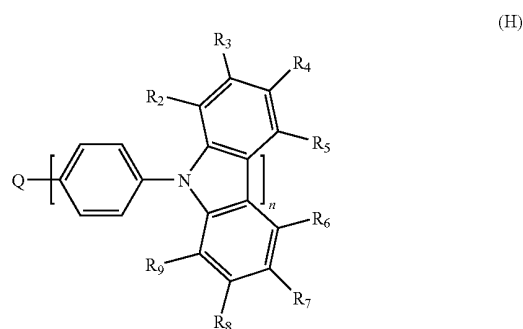
[0171] In Formula (G), Q independently represents nitrogen, carbon, an aryl group, or substituted aryl group, preferably a phenyl group;

[0172] R_1 is preferably an aryl or substituted aryl group, and more preferably a phenyl group, substituted phenyl, biphenyl, substituted biphenyl group;

[0173] R_2 through R_7 are independently hydrogen, alkyl, phenyl or substituted phenyl group, aryl amine, carbazole, or substituted carbazole;

[0174] and n is selected from 1 to 4.

[0175] Another useful class of carbazoles satisfying structural Formula (G) is represented by Formula (H):



wherein:

[0176] n is an integer from 1 to 4;

[0177] Q is nitrogen, carbon, an aryl, or substituted aryl;

[0178] R_2 through R_7 are independently hydrogen, an alkyl group, phenyl or substituted phenyl, an aryl amine, a carbazole and substituted carbazole.

[0179] Illustrative of useful substituted carbazoles are the following:

[0180] 4-(9H-carbazol-9-yl)-N,N-bis[4-(9H-carbazol-9-yl)phenyl]-benzenamine (TCTA);

[0181] 4-(3-phenyl-9H-carbazol-9-yl)-N,N-bis[4(3-phenyl-9H-carbazol-9-yl)phenyl]-benzenamine;

[0182] 9,9'-[5'-[4-(9H-carbazol-9-yl)phenyl]][1,1':3',1''-terphenyl]-4,4''-diyl]bis-9H-carbazole.

[0183] 9,9'-(2,2'-dimethyl[1,1'-biphenyl]-4,4'-diyl)bis-9H-carbazole (CDBP);

[0184] 9,9'-[1,1'-biphenyl]-4,4'-diylbis-9H-carbazole (CBP);

[0185] 9,9'-(1,3-phenylene)bis-9H-carbazole (mCP);

[0186] 9,9'-(1,4-phenylene)bis-9H-carbazole;

[0187] 9,9',9''-(1,3,5-benzenetriyl)tris-9H-carbazole;

[0188] 9,9'-(1,4-phenylene)bis[N,N,N',N'-tetraphenyl-9H-carbazole-3,6-diamine];

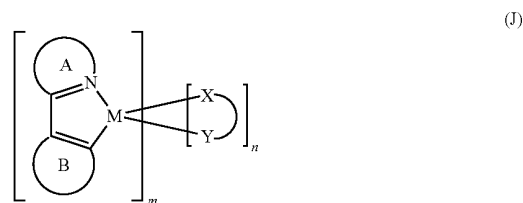
[0189] 9-[4-(9H-carbazol-9-yl)phenyl]-N,N-diphenyl-9H-carbazol-3-amine;

[0190] 9,9'-(1,4-phenylene)bis[N,N-diphenyl-9H-carbazol-3-amine];

[0191] 9-[4-(9H-carbazol-9-yl)phenyl]-N,N,N',N'-tetraphenyl-9H-carbazole-3,6-diamine.

[0192] The above classes of hosts suitable for phosphorescent LELs can also be used as hosts in fluorescent LELs as well.

[0193] Suitable phosphorescent dopants for use in a phosphorescent LEL can be selected from the phosphorescent materials described by Formula (J) below:



wherein:

[0194] A is a substituted or unsubstituted heterocyclic ring containing at least one nitrogen atom;

[0195] B is a substituted or unsubstituted aromatic or heteroaromatic ring, or ring containing a vinyl carbon bonded to M;

[0196] X—Y is an anionic bidentate ligand;

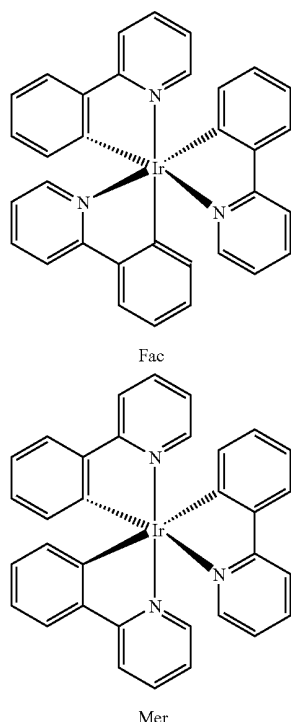
[0197] m is an integer from 1 to 3 and

[0198] n is an integer from 0 to 2 such that $m+n=3$ for $M=\text{Rh}$ or Ir ; or

[0199] m is an integer from 1 to 2 and n is an integer from 0 to 1 such that $m+n=2$ for $M=\text{Pt}$ or Pd .

[0200] Compounds according to Formula (J) can be referred to as C,N- (or C²N-) cyclometallated complexes to indicate that the central metal atom is contained in a cyclic unit formed by bonding the metal atom to carbon and nitrogen atoms of one or more ligands. Examples of heterocyclic ring A in Formula (J) include substituted or unsubstituted pyridine, quinoline, isoquinoline, pyrimidine, indole, indazole, thiazole, and oxazole rings. Examples of ring B in Formula (J) include substituted or unsubstituted phenyl, naphthyl, thienyl, benzothienyl, furanyl rings. Ring B in Formula (J) can also be a N-containing ring such as pyridine, with the proviso that the N-containing ring bonds to M through a C atom as shown in Formula (J) and not the N atom.

[0201] An example of a tris-C,N-cyclometallated complex according to Formula (J) with $m=3$ and $n=0$ is tris(2-phenylpyridinato-N,C^{2'})-Iridium(III), shown below in stereoisomers as facial (fac-) or meridional (mer-) isomers.



[0202] Generally, facial isomers are preferred since they are often found to have higher phosphorescent quantum yields than the meridional isomers. Additional examples of tris-C,N-cyclometallated phosphorescent materials according to Formula (J) are tris(2-(4'-methylphenyl)pyridinato-N,

C^{2'})Iridium(III), tris(3-phenylisoquinolinato-N,C^{2'})Iridium(III), tris(2-phenylquinolinato-N,C^{2'})Iridium(III), tris(1-phenylisoquinolinato-N,C^{2'})Iridium(III), tris(1-(4'-methylphenyl)isoquinolinato-N,C^{2'})Iridium(III), tris(2-(4',6'-difluorophenyl)-pyridinato-N,C^{2'})Iridium(III), tris(2-((5'-phenyl)-phenyl)pyridinato-N,C^{2'})Iridium(III), tris(2-(2'-benzothienyl)pyridinato-N,C^{3'})Iridium(III), tris(2-phenyl-3,3'-dimethyl)indolato-N,C^{2'})Ir(III), tris(1-phenyl-1H-indazolato-N,C^{2'})Ir(III).

[0203] Of these, tris(1-phenylisoquinoline) iridium (III) (also referred to as Ir(piq)₃) and tris(2-phenylpyridine) iridium (also referred to as Ir(ppy)₃) are particularly suitable for this invention.

[0204] Tris-C,N-cyclometallated phosphorescent materials also include compounds according to Formula (J) wherein the monoanionic bidentate ligand X-Y is another C,N-cyclometallating ligand. Examples include bis(1-phenylisoquinolinato-N,C^{2'})(2-phenylpyridinato-N,C^{2'})Iridium(III) and bis(2-phenylpyridinato-N,C^{2'})(1-phenylisoquinolinato-N,C^{2'})Iridium(III). Synthesis of such tris-C,N-cyclometallated complexes containing two different C,N-cyclometallating ligands can be conveniently synthesized by the following steps. First, a bis-C,N-cyclometallated diridium dihalide complex (or analogous dirhodium complex) is made according to the method of Nonoyama (*Bull. Chem. Soc. Jpn.*, 47, 767 (1974)). Secondly, a zinc complex of the second, dissimilar C,N-cyclometallating ligand is prepared by reaction of a zinc halide with a lithium complex or Grignard reagent of the cyclometallating ligand. Third, the thus formed zinc complex of the second C,N-cyclometallating ligand is reacted with the previously obtained bis-C,N-cyclometallated diridium dihalide complex to form a tris-C,N-cyclometallated complex containing the two different C,N-cyclometallating ligands. Desirably, the thus obtained tris-C,N-cyclometallated complex containing the two different C,N-cyclometallating ligands can be converted to an isomer wherein the C atoms bonded to the metal (e.g. Ir) are all mutually cis by heating in a suitable solvent such as dimethyl sulfoxide.

[0205] Suitable phosphorescent materials according to Formula (J) can in addition to the C,N-cyclometallating ligand(s) also contain monoanionic bidentate ligand(s) X-Y that are not C,N-cyclometallating. Common examples are beta-diketones such as acetylacetonate, and Schiff bases such as picolinate. Examples of such mixed ligand complexes according to Formula (J) include bis(2-phenylpyridinato-N,C^{2'})Iridium(III)(acetylacetonate), bis(2-(2'-benzothienyl)pyridinato-N,C^{3'})Iridium(III)(acetylacetonate), and bis(2-(4',6'-difluorophenyl)-pyridinato-N,C^{2'})Iridium(III)(picolinate).

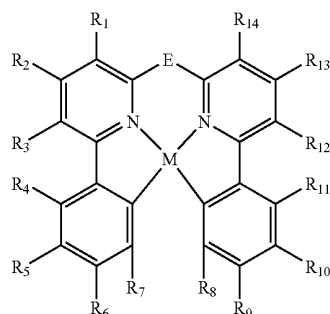
[0206] Other important phosphorescent materials according to Formula (J) include C,N-cyclometallated Pt(II) complexes such as cis-bis(2-phenylpyridinato-N,C^{2'})platinum(II), cis-bis(2-(2'-thienyl)pyridinato-N,C^{3'}) platinum(II), cis-bis(2-(2'-thienyl)quinolinato-N,C^{5'}) platinum(II), or (2-(4',6'-difluorophenyl)pyridinato-N,C^{2'}) platinum(II) (acetylacetonate).

[0207] The emission wavelengths (color) of C,N-cyclometallated phosphorescent materials according to Formula (J) are governed principally by the lowest energy optical transition of the complex and hence by the choice of the C,N-cyclometallating ligand. For example, 2-phenylpyridinato-N,C^{2'} complexes are typically green emissive while 1-phenylisoquinolinolato-N,C^{2'} complexes are typically red emissive. In the case of complexes having more than one C,N-cyclometallating ligand, the emission will be that of the ligand having

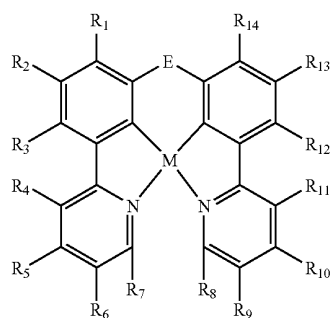
the property of longest wavelength emission. Emission wavelengths can be further shifted by the effects of substituent groups on the C,N-cyclometallating ligands. For example, substitution of electron donating groups at appropriate positions on the N-containing ring A or electron accepting groups on the C-containing ring B tend to blue-shift the emission relative to the unsubstituted C,N-cyclometallated ligand complex. Selecting a monodentate anionic ligand X,Y in Formula (J) having more electron accepting properties also tends to blue-shift the emission of a C,N-cyclometallated ligand complex. Examples of complexes having both monoanionic bidentate ligands possessing electron accepting properties and electron accepting substituent groups on the C-containing ring B include bis(2-(4',6'-difluorophenyl)-pyridinato-N,C^{2'})iridium(III)(picolinate) and bis(2-(4',6'-difluorophenyl)-pyridinato-N,C^{2'})iridium(III)(tetrakis(1-pyrazolyl)borate).

[0208] The central metal atom in phosphorescent materials according to Formula (J) can be Rh or Ir ($m+n=3$) and Pd or Pt ($m+n=2$). Preferred metal atoms are Ir and Pt since they tend to give higher phosphorescent quantum efficiencies according to the stronger spin-orbit coupling interactions generally obtained with elements in the third transition series.

[0209] In addition to bidentate C,N-cyclometallating complexes represented by Formula (J), many suitable phosphorescent materials contain multidentate C,N-cyclometallating ligands. Phosphorescent materials having tridentate ligands suitable for use in the present invention are disclosed in U.S. Pat. No. 6,824,895B1. Phosphorescent materials having tetradentate ligands suitable for use in the present invention are described by the following Formulae:



(K)



(L)

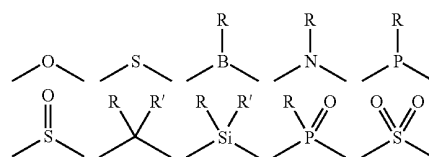
wherein:

[0210] M is Pt or Pd;

[0211] R¹-R⁷ represent hydrogen or independently selected substituents, provided that R¹ and R², R² and R³, R³ and R⁴, R⁴ and R⁵, R⁵ and R⁶, as well as R⁶ and R⁷ can join to form a ring group;

[0212] R⁸-R¹⁴ represent hydrogen or independently selected substituents, provided that R⁸ and R⁹, R⁹ and R¹⁰, R¹⁰ and R¹¹, R¹¹ and R¹², R¹² and R¹³, as well as R¹³ and R¹⁴, can join to form a ring group;

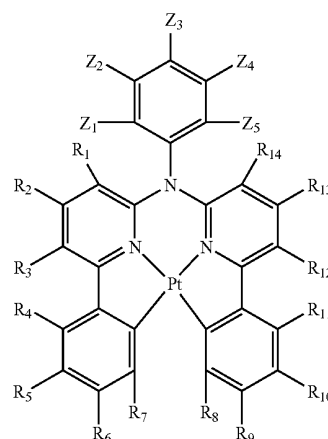
[0213] E represents a bridging group selected from the following:



wherein:

[0214] R and R' represent hydrogen or independently selected substituents; provided R and R' can combine to form a ring group.

[0215] One desirable tetradentate C,N-cyclometallated phosphorescent material suitable for use in as the phosphorescent dopant is represented by the following Formula:



(M)

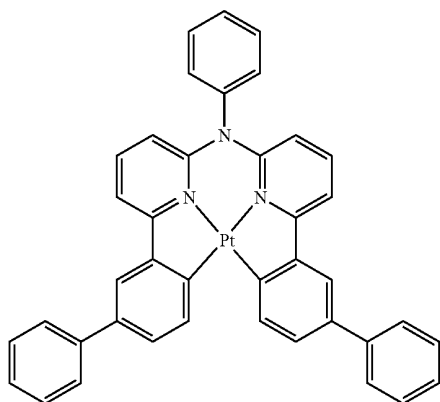
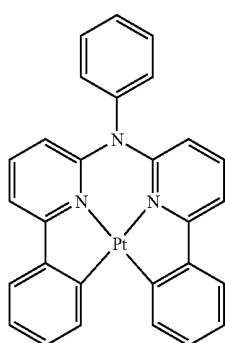
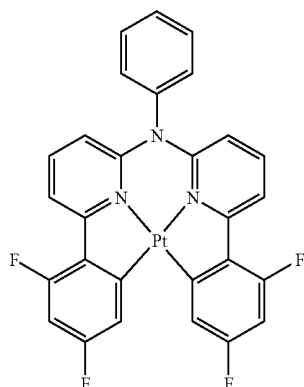
wherein:

[0216] R¹-R⁷ represent hydrogen or independently selected substituents, provided that R¹ and R², R² and R³, R³ and R⁴, R⁴ and R⁵, R⁵ and R⁶, as well as R⁶ and R⁷ can combine to form a ring group;

[0217] R⁸-R¹⁴ represent hydrogen or independently selected substituents, provided that R⁸ and R⁹, R⁹ and R¹⁰, R¹⁰ and R¹¹, R¹¹ and R¹², R¹² and R¹³, as well as R¹³ and R¹⁴ can combine to form a ring group;

[0218] Z¹-Z⁵ represent hydrogen or independently selected substituents, provided that Z¹ and Z², Z² and Z³, Z³ and Z⁴, as well as Z⁴ and Z⁵ can combine to form a ring group.

[0219] Specific examples of phosphorescent materials having tetradentate C,N-cyclometallating ligands suitable for use in the present invention include compounds (M-1), (M-2) and (M-3) represented below.



[0220] Phosphorescent materials having tetradentate C,N-cyclometallating ligands can be synthesized by reacting the tetradentate C,N-cyclometallating ligand with a salt of the desired metal, such as K_2PtCl_4 , in a proper organic solvent such as glacial acetic acid to form the phosphorescent material having tetradentate C,N-cyclometallating ligands. A tetraalkylammonium salt such as tetrabutylammonium chloride can be used as a phase transfer catalyst to accelerate the reaction.

[0221] Other phosphorescent materials that do not involve C,N-cyclometallating ligands are known. Phosphorescent complexes of Pt(II), Ir(I), and Rh(I) with malonitriledithiolate have been reported (Johnson et al., *J. Am. Chem. Soc.*, 105,1795 (1983)). Re(I) tricarbonyl diimine complexes are also known to be highly phosphorescent (Wrighton and

Morse, *J. Am. Chem. Soc.*, 96, 998 (1974); Stufkens, *Comments Inorg. Chem.*, 13, 359 (1992); Yam, *Chem. Commun.*, 789 (2001)). Os(II) complexes containing a combination of ligands including cyano ligands and bipyridyl or phenanthroline ligands have also been demonstrated in a polymer OLED (Ma et al., *Synthetic Metals*, 94, 245 (1998)).

[0222] Porphyrin complexes such as 2,3,7,8,12,13,17,18-octaethyl-21H, 23H-porphine platinum(II) are also useful phosphorescent dopant.

[0223] Still other examples of useful phosphorescent materials include coordination complexes of the trivalent lanthanides such as Tb^{3+} and Eu^{3+} (Kido et al., *Chem. Lett.*, 657 (1990); *J. Alloys and Compounds*, 192, 30 (1993); *Jpn. J. Appl. Phys.*, 35, L394 (1996) and *Appl. Phys. Lett.*, 65, 2124 (1994)).

[0224] The phosphorescent dopant in a phosphorescent LEL is typically present in an amount of from 1 to 20 % by volume of the LEL, and conveniently from 2 to 8 % by volume of the LEL. In some embodiments, the phosphorescent dopant(s) can be attached to one or more host materials. The host materials can further be polymers. The phosphorescent dopant in the first phosphorescent light-emitting layer is selected from green and red phosphorescent materials.

[0225] The thickness of a phosphorescent LEL is greater than 0.5 nm, preferably, in the range of from 1.0 nm to 40 nm.

b) Fluorescent Light Emitting Layers

[0226] Although the term "fluorescent" is commonly used to describe any light-emitting material, in this case it refers to a material that emits light from a singlet excited state. Fluorescent materials can be used in the same layer as the phosphorescent material, in adjacent layers, in adjacent pixels, or any combination. Care must be taken not to select materials that will adversely affect the performance of the phosphorescent materials of this invention. One skilled in the art will understand that concentrations and triplet energies of materials in the same layer as the phosphorescent material or in an adjacent layer must be appropriately set so as to prevent unwanted quenching of the phosphorescence.

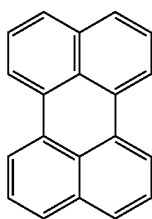
[0227] Typically, a fluorescent LEL includes at least one host and at least one fluorescent dopant. The host can be a hole-transporting material or any of the suitable hosts for phosphorescent dopants as defined above or can be an electron-transporting material as defined below.

[0228] The dopant is typically chosen from highly fluorescent dyes, e.g., transition metal complexes as described in WO 98/55561 A1; WO 00/18851 A1; WO 00/57676 A1, and WO 00/70655.

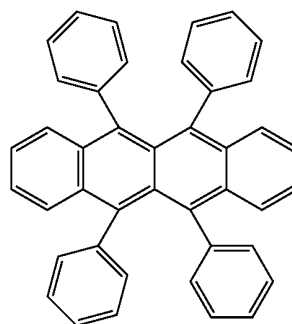
[0229] Useful fluorescent dopants include, but are not limited to, derivatives of anthracene, tetracene, xanthene, perylene, phenylene, dicyanomethylenepyran compounds, thiopyran compounds, polymethine compounds, pyrylium and thiapyrylium compounds, arylpyrene compounds, arylenevinylene compounds, perfluoranthene derivatives, indenoperylene derivatives, bis(aziryl)amine boron compounds, bis(aziryl)methane boron compounds, distyrylbenzene derivatives, distyrylbiphenyl derivatives, distyrylamine derivatives and carbostyryl compounds.

[0230] Some fluorescent emitting materials include, but are not limited to, derivatives of anthracene, tetracene, xanthene, perylene, rubrene, coumarin, rhodamine, and quinacridone, dicyanomethylenepyran compounds, thiopyran compounds, polymethine compounds, pyrylium and thiapyrylium compounds, fluorene derivatives, perfluoranthene derivatives, indenoperylene derivatives, bis(aziryl)amine boron compounds, bis(aziryl)methane compounds (as described in U.S. Pat. No. 5,121,029) and carbostyryl compounds. Illustrative examples of useful materials include, but are not limited to, the following:

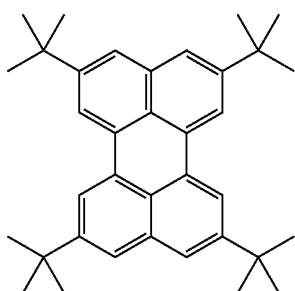
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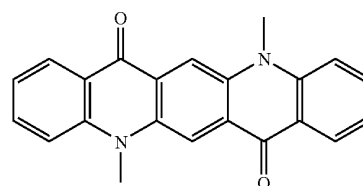
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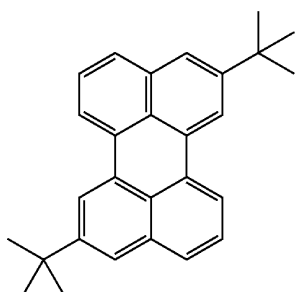
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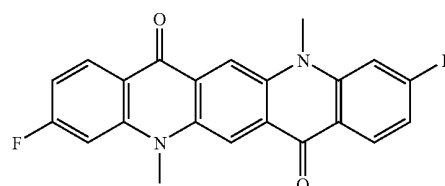
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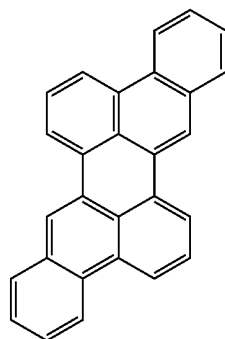
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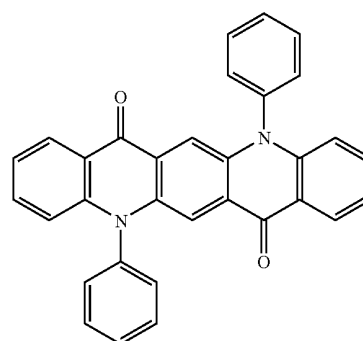
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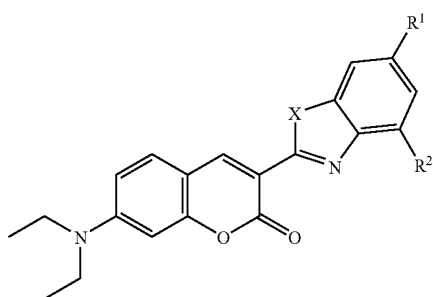
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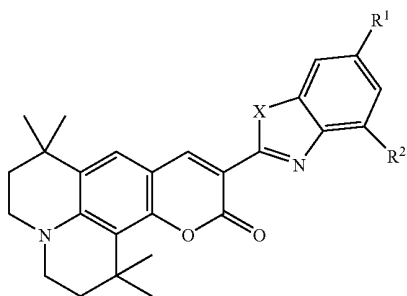
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FD-8

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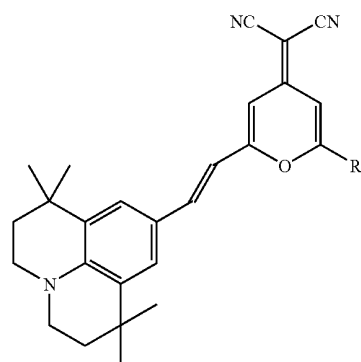


	X	R1	R2
FD-9	O	H	H
FD-10	O	H	Methyl
FD-11	O	Methyl	H
FD-12	O	Methyl	Methyl
FD-13	O	H	t-butyl
FD-14	O	t-butyl	H
FD-15	O	t-butyl	t-butyl
FD-16	S	H	H
FD-17	S	H	Methyl
FD-18	S	Methyl	H
FD-19	S	Methyl	Methyl
FD-20	S	H	t-butyl
FD-21	S	t-butyl	H
FD-22	S	t-butyl	t-butyl

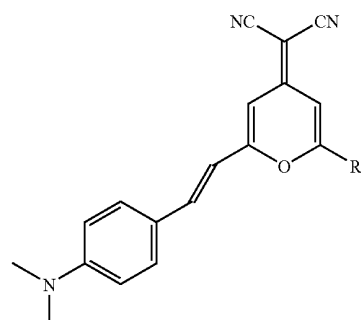


	X	R1	R2
FD-13	O	H	H
FD-24	O	H	Methyl
FD-25	O	Methyl	H
FD-26	O	Methyl	Methyl
FD-27	O	H	t-butyl
FD-28	O	t-butyl	H
FD-29	O	t-butyl	t-butyl
FD-30	S	H	H
FD-31	S	H	Methyl
FD-32	S	Methyl	H
FD-33	S	Methyl	Methyl
FD-34	S	H	t-butyl
FD-35	S	t-butyl	H
FD-36	S	t-butyl	t-butyl

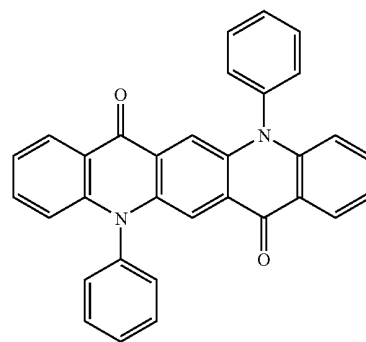
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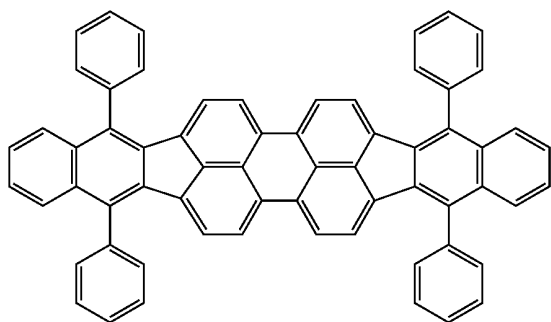
	R
FD-37	phenyl
FD-38	methyl
FD-39	t-butyl
FD-40	mesityl



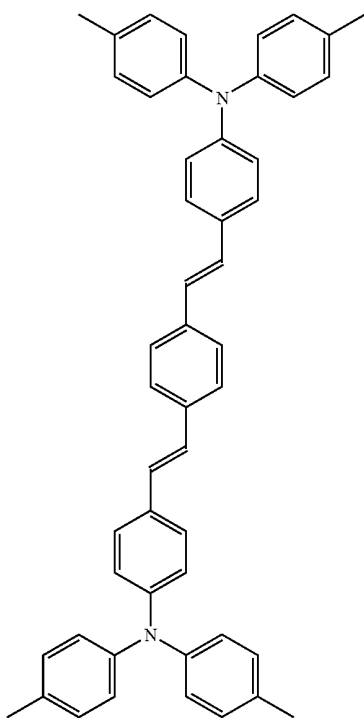
	R
FD-41	phenyl
FD-42	methyl
FD-43	t-butyl
FD-44	mesityl



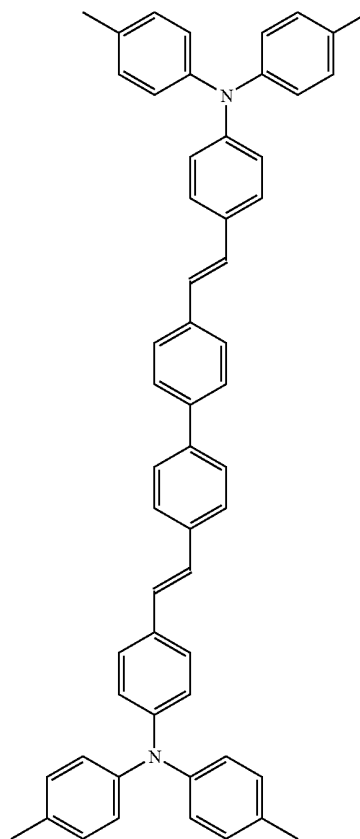
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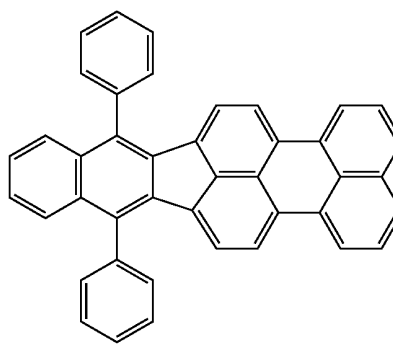
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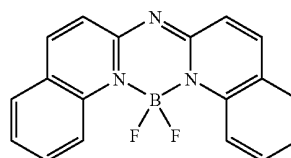
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FD-48

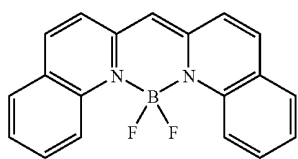
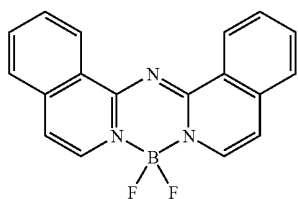


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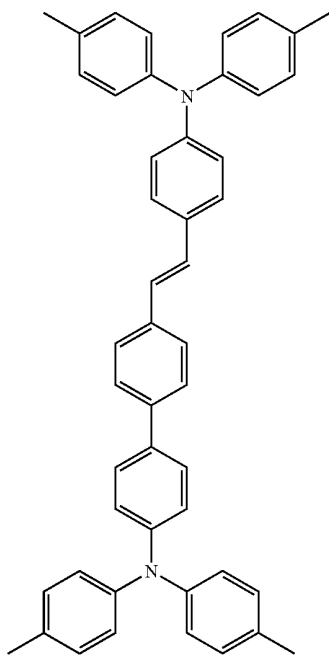


FD-50

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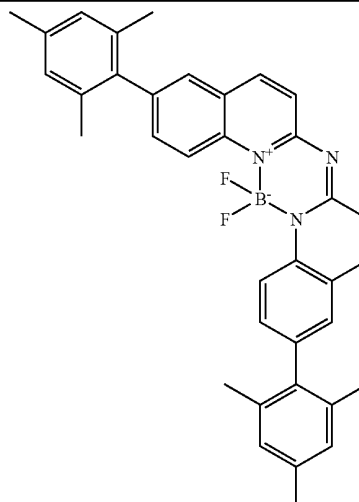


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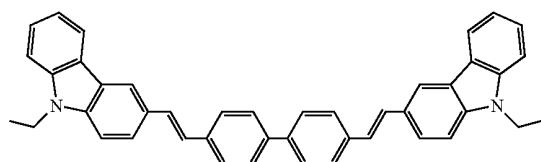


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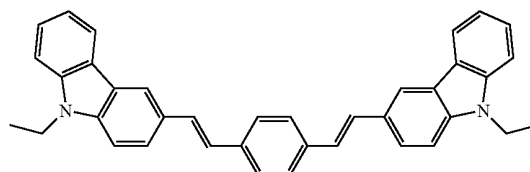
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FD-54



FD-55

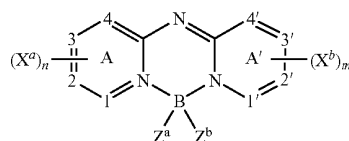


FD-56

[0231] Preferred fluorescent blue dopants can be found in Chen, Shi, and Tang, "Recent Developments in Molecular Organic Electroluminescent Materials," *Macromol. Symp.* 125, 1 (1997) and the references cited therein; Hung and Chen, "Recent Progress of Molecular Organic Electroluminescent Materials and Devices," *Mat. Sci. and Eng. R39*, 143 (2002) and the references cited therein.

[0232] A particularly preferred class of blue-emitting fluorescent dopants is represented by Formula (N), known as a bis(azirine)amine borane complex, and is described in U.S. Pat. No. 6,661,023.

Formula (N)



wherein:

[0233] A and A' represent independent azine ring systems corresponding to 6-membered aromatic ring systems containing at least one nitrogen;

[0234] each X^a and X^b is an independently selected substituent, two of which can join to form a fused ring to A or A';

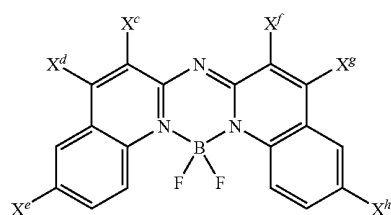
[0235] m and n are independently 0 to 4;

[0236] Z^a and Z^b are independently selected substituents; and

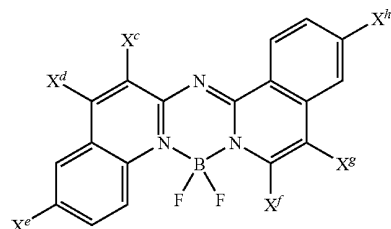
[0237] 1, 2, 3, 4, 1', 2', 3', and 4' are independently selected as either carbon or nitrogen atoms.

[0238] Desirably, the azine rings are either quinolinyl or isoquinolinyl rings such that 1, 2, 3, 4, 1', 2', 3', and 4' are all carbon; m and n are equal to or greater than 2; and X^a and X^b represent at least two carbon substituents which join to form an aromatic ring. Desirably, Z^a and Z^b are fluorine atoms.

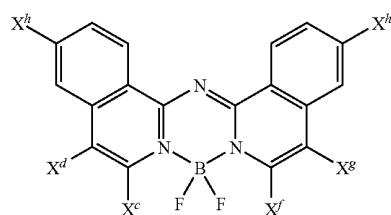
[0239] Preferred embodiments further include devices where the two fused ring systems are quinoline or isoquinoline systems; the aryl or heterocyclic substituent is a phenyl group; there are present at least two X^a groups and two X^b groups which join to form a 6-6 fused ring, the fused ring systems are fused at the 1-2, 3-4, 1'-2', or 3'-4' positions, respectively; one or both of the fused rings is substituted by a phenyl group; and where the dopant is depicted in Formulae (N-a), (N-b), or (N-c).



Formula (N-a)



Formula (N-b)



Formula (N-c)

wherein:

[0240] each X^c , X^d , X^e , X^f , X^g , and X^h is hydrogen or an independently selected substituent, one of which must be an aryl or heterocyclic group.

[0241] Desirably, the azine rings are either quinolinyl or isoquinolinyl rings such that 1, 2, 3, 4, 1', 2', 3', and 4' are all carbon; m and n are equal to or greater than 2; and X^a and X^b represent at least two carbon substituents which join to form

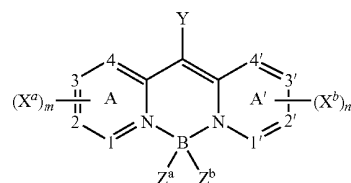
an aromatic ring, and one is an aryl or substituted aryl group. Desirably, Z^a and Z^b are fluorine atoms.

[0242] Of these, compound FD-54 is particularly useful.

[0243] Coumarins represent a useful class of green-emitting dopants as described by Tang et al. in U.S. Pat. Nos. 4,769,292 and 6,020,078. Green dopants or light-emitting materials can be coated as 0.01 to 50% by weight into the host material, but typically coated as 0.01 to 30 % and more typically coated as 0.01 to 15% by weight into the host material. Examples of useful green-emitting coumarins include C545T and C545TB. Quinacridones represent another useful class of green-emitting dopants. Useful quinacridones are described in U.S. Pat. No. 5,593,788, Japanese publication JP 09-13026A, and commonly assigned U.S. patent application Ser. No. 10/184,356 filed Jun. 27, 2002 by Lelia Cosimbescu, entitled "Device Containing Green Organic Light-Emitting Diode", now abandoned.

[0244] Examples of particularly useful green-emitting quinacridones are FD-7 and FD-8.

[0245] Formula (N-d) below represents another class of green-emitting dopants useful in the invention.



Formula (N-d)

wherein:

[0246] A and A' represent independent azine ring systems corresponding to 6-membered aromatic ring systems containing at least one nitrogen;

[0247] each X^a and X^b is an independently selected substituent, two of which can join to form a fused ring to A or A';

[0248] m and n are independently 0 to 4;

[0249] Y is H or a substituent;

[0250] Z^a and Z^b are independently selected substituents; and

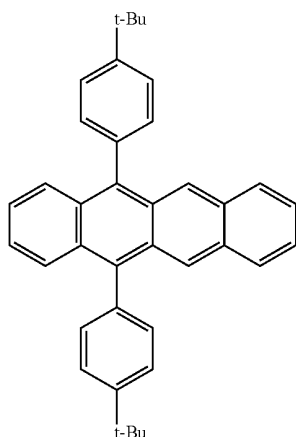
[0251] 1, 2, 3, 4, 1', 2', 3', and 4' are independently selected as either carbon or nitrogen atoms.

[0252] In the device, 1, 2, 3, 4, 1', 2', 3', and 4' are conveniently all carbon atoms. The device can desirably contain at least one or both of ring A or A' that contains substituents joined to form a fused ring. In one useful embodiment, there is present at least one X^a or X^b group selected from the group consisting of halide and alkyl, aryl, alkoxy, and aryloxy groups. In another embodiment, there is present a Z^a and Z^b group independently selected from the group consisting of fluorine and alkyl, aryl, alkoxy and aryloxy groups. A desirable embodiment is where Z^a and Z^b are F. Y is suitably hydrogen or a substituent such as an alkyl, aryl, or heterocyclic group.

[0253] The emission wavelength of these compounds can be adjusted to some extent by appropriate substitution around the central bis(azine)methene boron group to meet a color aim, namely green. Some examples of useful material are FD-50, FD-51 and FD-52.

[0254] Naphthalenes and derivatives thereof also represent a useful class of emitting dopants, which can also be used as stabilizers. These dopant materials can be coated as 0.01 to

50% by weight into the host material, but typically coated as 0.01 to 30% and more typically coated as 0.01 to 15% by weight into the host material. Naphthacene derivative YD-1 (t-BuDPN) below, is an example of a dopant material used as a stabilizer.

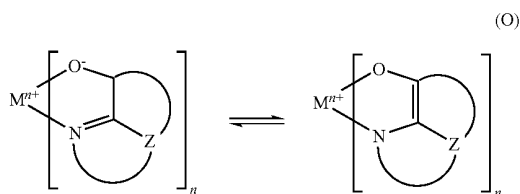


YD-1

[0255] Some examples of this class of materials are also suitable as host materials as well as dopants. For example, see U.S. Pat. No. 6,773,832 or U.S. Pat. No. 6,720,092. A specific example of this would be rubrene (FD-5).

[0256] Another class of useful dopants are perylene derivatives; for example see U.S. Pat. No. 6,689,493. A specific example is FD-46.

[0257] Metal complexes of 8-hydroxyquinoline and similar derivatives (Formula O) constitute one class of useful non-electroluminescent host compounds capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 500 nm, e.g., green, yellow, orange, and red.



(O)

wherein:

[0258] M represents a metal;

[0259] n is an integer of from 1 to 4; and

[0260] Z independently in each occurrence represents the atoms completing a nucleus having at least two fused aromatic rings.

[0261] From the foregoing it is apparent that the metal can be monovalent, divalent, trivalent, or tetravalent metal. The metal can, for example, be an alkali metal, such as lithium, sodium, or potassium; an alkaline earth metal, such as magnesium or calcium; an earth metal, such as aluminum or gallium, or a transition metal such as zinc or zirconium. Generally any monovalent, divalent, trivalent, or tetravalent metal known to be a useful chelating metal can be employed.

[0262] Z completes a heterocyclic nucleus containing at least two fused aromatic rings, at least one of which is an azole or azine ring. Additional rings, including both aliphatic and aromatic rings, can be fused with the two required rings, if required. To avoid adding molecular bulk without improving on function the number of ring atoms is usually maintained at 18 or less.

[0263] Illustrative of useful chelated oxinoid compounds are the following:

[0264] O-1: Aluminum trisoxine[alias, tris(8-quinolinolato)aluminum(III)]

[0265] O-2: Magnesium bisoxine[alias, bis(8-quinolinolato)magnesium(II)]

[0266] O-3: Bis[benzo{f}-8-quinolinolato]zinc (II)

[0267] O-4: Bis(2-methyl-8-quinolinolato)aluminum(III)-μ-oxo-bis(2-methyl-8-quinolinolato)aluminum(III)

[0268] O-5: Indium trisoxine[alias, tris(8-quinolinolato)indium]

[0269] O-6: Aluminum tris(5-methyloxine)[alias, tris(5-methyl-8-quinolinolato)aluminum(III)]

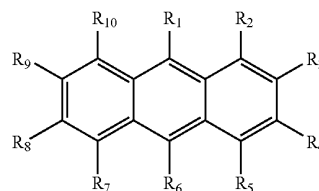
[0270] O-7: Lithium oxine[alias, (8-quinolinolato)lithium (I)]

[0271] O-8: Gallium oxine[alias, tris(8-quinolinolato)gallium(III)]

[0272] O-9: Zirconium oxine[alias, tetra(8-quinolinolato)zirconium(IV)]

[0273] O-10: Bis(2-methyl-8-quinolinolato)-4-phenylphenolatoaluminum (III)

[0274] Anthracene derivatives according to Formula (P) are also useful host materials in the LEL:



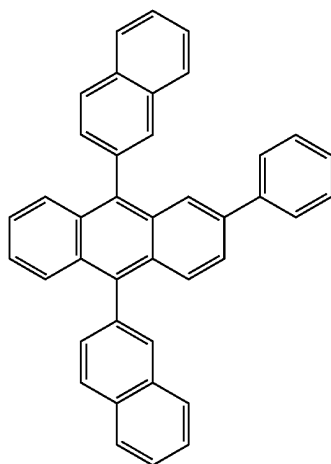
(P)

wherein:

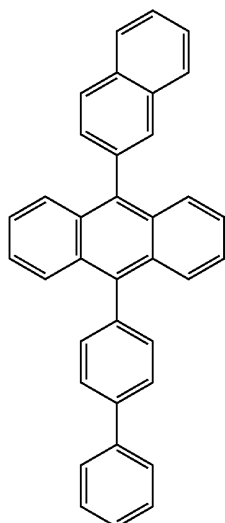
[0275] R₁-R₁₀ are independently chosen from hydrogen, alkyl groups from 1-24 carbon atoms or aromatic groups from 6-24 carbon atoms. Particularly preferred are compounds where R₁ and R₆ are phenyl, biphenyl or naphthyl, R₃ is phenyl, substituted phenyl or naphthyl and R₂, R₄, R₅, R₇-R₁₀ are all hydrogen. Such anthracene hosts are known to have excellent electron transporting properties.

[0276] Particularly desirable are derivatives of 9,10-di-(2-naphthyl)anthracene. Illustrative examples include 9,10-di-(2-naphthyl)anthracene (ADN) and 2-t-butyl-9,10-di-(2-naphthyl)anthracene (TBADN). Other anthracene derivatives can be useful as a non-electroluminescent materials in the LEL, such as diphenylanthracene and its derivatives, as described in U.S. Pat. No. 5,927,247. Styrylarylene derivatives as described in U.S. Pat. No. 5,121,029 and JP 08333569 are also useful non-electroluminescent materials. For example, 9,10-bis[4-(2,2-diphenylethenyl)phenyl]anthracene, 4,4'-Bis(2,2-diphenylethenyl)-1,1'-biphenyl (DPVBi) and phenylanthracene derivatives as described in EP 681,019 are useful non-electroluminescent materials.

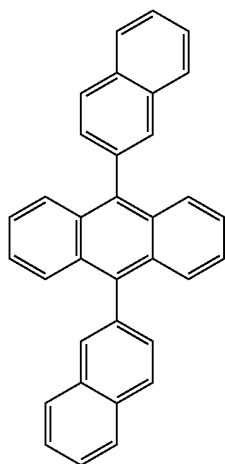
[0277] Some illustrative examples of suitable anthracenes are:



P-1



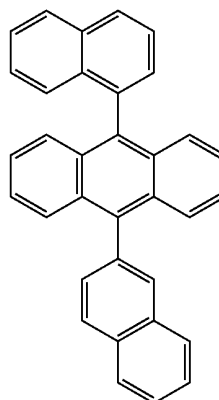
P-2



P-3

-continued

P-4



Spacer Layer

[0278] Spacer layers, when present, are located in direct contact to a LEL. They can be located on either the anode or cathode, or even both sides of the LEL. They typically do not contain any light-emissive dopants. One or more materials can be used and could be either a hole-transporting material as defined above or an electron-transporting material as defined below. If located next to a phosphorescent LEL, the material in the spacer layer should have higher triplet energy than that of the phosphorescent dopant in the LEL. Most desirably, the material in the spacer layer will be the same as used as the host in the adjacent LEL. Thus, any of the host materials described as also suitable for use in a spacer layer. The spacer layer should be thin; at least 0.1 nm, but preferably in the range of from 1.0 nm to 20 nm.

Hole-Blocking Layer (HBL)

[0279] When a LEL containing a phosphorescent emitter is present, it is desirable to locate a hole-blocking layer **135** between the electron-transporting layer **136** and the light-emitting layer **134** to help confine the excitons and recombination events to the LEL. In this case, there should be an energy barrier for hole migration from co-hosts into the hole-blocking layer, while electrons should pass readily from the hole-blocking layer into the light-emitting layer comprising co-host materials and a phosphorescent emitter. It is further desirable that the triplet energy of the hole-blocking material be greater than that of the phosphorescent material. Suitable hole-blocking materials are described in WO 00/70655A2, WO 01/41512 and WO 01/93642 A1. Two examples of useful hole-blocking materials are bathocuproine (BCP) and bis(2-methyl-8-quinolinolato)(4-phenylphenolato)aluminum(III) (BAIq). Metal complexes other than BAIq are also known to block holes and excitons as described in U.S. Patent Application Publication 20030068528. When a hole-blocking layer is used, its thickness can be between 2 and 100 nm and suitably between 5 and 10 nm.

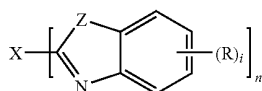
Electron Transporting Layer

[0280] As described previously, the electron-transporting layer **136** desirably contains the fluoranthene-macroscopic

compound or can be a mixture of the fluoranthene-macrocylic compound with other appropriate materials.

[0281] In some embodiments, additional electron-transporting materials can be suitable for use in the ETL or in additional electron-transporting layers. Included are, but not limited to, materials such as chelated oxinoid compounds, anthracene derivatives, pyridine-based materials, imidazoles, oxazoles, thiazoles and their derivatives, polybenzobisazoles, cyano-containing polymers and perfluorinated materials. Other electron-transporting materials include various butadiene derivatives as disclosed in U.S. Pat. No. 4,356,429 and various heterocyclic optical brighteners as described in U.S. Pat. No. 4,539,507.

[0282] A preferred class of benzazoles is described by Shi et al. in U.S. Pat. Nos. 5,645,948 and 5,766,779. Such compounds are represented by structural Formula (Q):



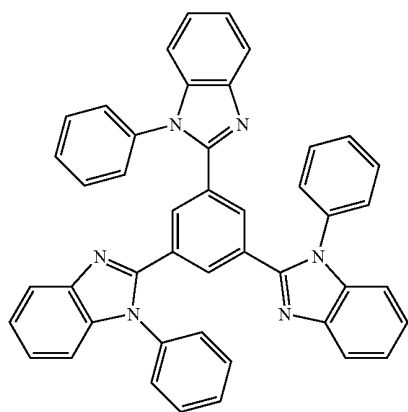
[0283] In Formula (Q), n is selected from 2 to 8 and i is selected from 1-5;

[0284] Z is independently O, NR or S;

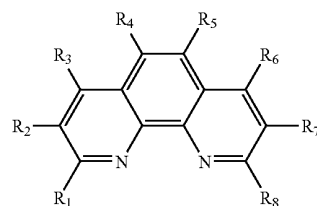
[0285] R is individually hydrogen; alkyl of from 1 to 24 carbon atoms, for example, propyl, t-butyl, heptyl, and the like; aryl or hetero-atom substituted aryl of from 5 to 20 carbon atoms, for example, phenyl and naphthyl, furyl, thienyl, pyridyl, quinolinyl and other heterocyclic systems; or halo such as chloro, fluoro; or atoms necessary to complete a fused aromatic ring; and

[0286] X is a linkage unit consisting of carbon, alkyl, aryl, substituted alkyl, or substituted aryl, which conjugately or unconjugately connects the multiple benzazoles together.

[0287] An example of a useful benzazole is 2,2',2''-(1,3,5-phenylene)tris[1-phenyl-1H-benzimidazole](TPBI) represented by a Formula (Q-1) shown below:

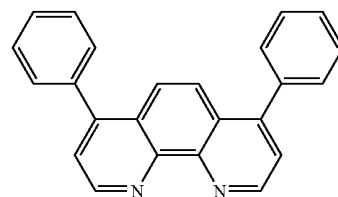
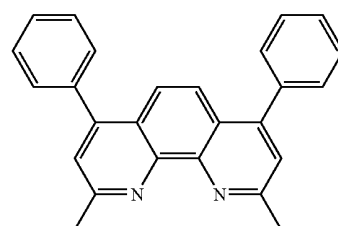


[0288] Another suitable class of the electron-transporting materials includes various substituted phenanthrolines as represented by Formula (R).

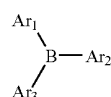


[0289] In Formula (R), R_1 - R_8 are independently hydrogen, alkyl group, aryl or substituted aryl group, and at least one of R_1 - R_8 is aryl group or substituted aryl group.

[0290] Specific examples of the phenanthrolines useful in the EIL are 2,9-dimethyl-4,7-diphenyl-phenanthroline (BCP) (see Formula (R-1)) and 4,7-diphenyl-1,10-phenanthroline (Bphen) (see Formula (R-2)).

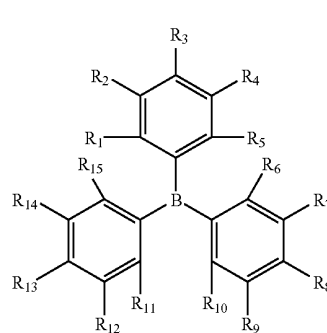


[0291] Suitable triarylboranes that function as an electron-transporting material can be selected from compounds having the chemical Formula (S):



wherein:

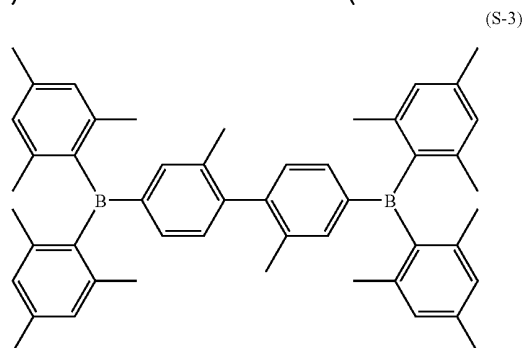
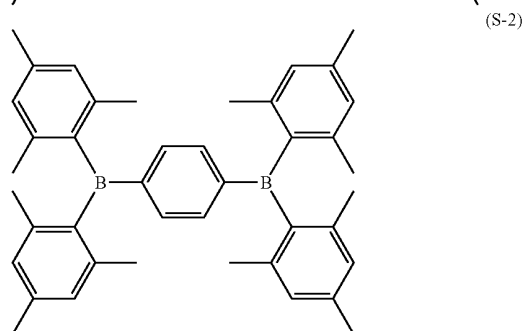
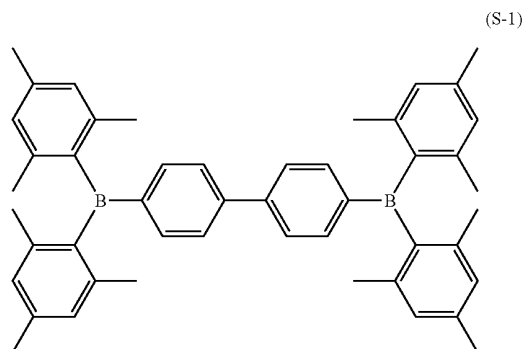
[0292] Ar_1 to Ar_3 are independently an aromatic hydrocarbocyclic group or an aromatic heterocyclic group which can have a substituent. It is preferable that compounds having the above structure are selected from Formula (S-1):



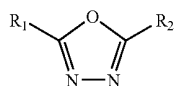
wherein:

[0293] R_1 - R_{15} are independently hydrogen, fluoro, cyano, trifluoromethyl, sulfonyl, alkyl, aryl or substituted aryl group.

[0294] Specific representative embodiments of the triarylboranes include:



[0295] The electron-transporting material can also be selected from substituted 1,3,4-oxadiazoles of Formula (T):

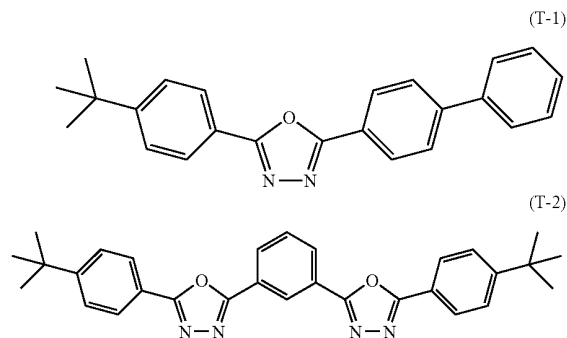


wherein:

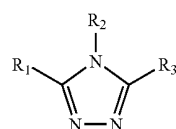
[0296] R_1 and R_2 are individually hydrogen; alkyl of from 1 to 24 carbon atoms, for example, propyl, t-butyl, heptyl, and the like; aryl or hetero-atom substituted aryl of from 5 to 20 carbon atoms, for example, phenyl and naphthyl, furyl, thie-

nyl, pyridyl, quinoliny and other heterocyclic systems; or halo such as chloro, fluoro; or atoms necessary to complete a fused aromatic ring.

[0297] Illustrative of the useful substituted oxadiazoles are the following:

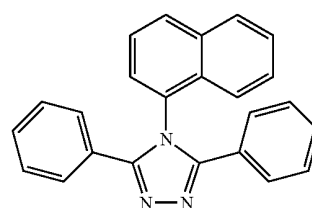


[0298] The electron-transporting material can also be selected from substituted 1,2,4-triazoles according to Formula (U):



wherein:

[0299] R_1 , R_2 and R_3 are independently hydrogen, alkyl group, aryl or substituted aryl group, and at least one of R_1 - R_3 is aryl group or substituted aryl group. An example of a useful triazole is 3-phenyl-4-(1-naphthyl)-5-phenyl-1,2,4-triazole represented by Formula (U-1):

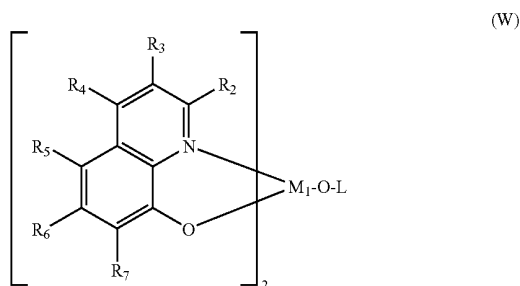


[0300] The electron-transporting material can also be selected from substituted 1,3,5-triazines. Examples of suitable materials are:

- [0301]** 2,4,6-tris(diphenylamino)-1,3,5-triazine;
- [0302]** 2,4,6-tricarbazo-1,3,5-triazine;
- [0303]** 2,4,6-tris(N-phenyl-2-naphthylamino)-1,3,5-triazine;
- [0304]** 2,4,6-tris(N-phenyl-1-naphthylamino)-1,3,5-triazine;
- [0305]** 4,4',6,6'-tetraphenyl-2,2'-bi-1,3,5-triazine;
- [0306]** 2,4,6-tris([1,1':3',1''-terphenyl]-5'-yl)-1,3,5-triazine.

[0307] In addition, any of the metal chelated oxinoid compounds including chelates of oxine itself (also commonly referred to as 8-quinolinol or 8-hydroxyquinoline) of Formula (O) useful as host materials in a LEL are also suitable for use in the ETL.

[0308] Some metal chelated oxinoid compounds having high triplet energy can be particularly useful as an electron-transporting materials. Particularly useful aluminum or gallium complex host materials with high triplet energy levels are represented by Formula (W).



[0309] In Formula (W), M_1 represents Al or Ga. R_2 - R_7 represent hydrogen or an independently selected substituent. Desirably, R_2 represents an electron-donating group. Suitably, R_3 and R_4 each independently represent hydrogen or an electron donating substituent. A preferred electron-donating group is alkyl such as methyl. Preferably, R_5 , R_6 , and R_7 each independently represent hydrogen or an electron-accepting group. Adjacent substituents, R_2 - R_7 , can combine to form a ring group. L is an aromatic moiety linked to the aluminum by oxygen, which can be substituted with substituent groups such that L has from 6 to 30 carbon atoms.

[0310] Illustrative of useful chelated oxinoid compounds for use in the ETL is Aluminum(III) bis(2-methyl-8-hydroxyquinoline)-4-phenylphenolate [alias, Balq].

[0311] The same anthracene derivatives according to Formula (P) useful as host materials in the LEL can also be used in the ETL.

[0312] The thickness of the ETL is typically in the range of from 5 nm to 200 nm, preferably, in the range of from 10 nm to 150 nm.

Electron Injection Layer

[0313] As described previously, in some embodiments an alkali metal or an organic alkali metal compound, for example, an organic lithium compound such as AM-1 or AM-2, is present in the EIL **138**. In further embodiments the EIL can be subdivided into two or more sublayers, for example, an EIL1 (adjacent to the ETL) and an EIL2 (adjacent to the cathode) wherein EIL1 and EIL2 can contain an alkali metal, an inorganic alkali metal compound, or an organic alkali metal compound or mixtures thereof. In a still further embodiment, the fluoranthene-macrocyclic compound is present in the ETL, a phenanthroline compound as represented by Formula (R), e.g., Bphen, is present in the EIL and an alkali metal is also present in the EIL. In yet another embodiment, the fluoranthene-macrocyclic compound is present in the ETL, a phenanthroline compound is present in

the EIL1 and an organic alkali metal compound such as AM-1 or an inorganic lithium compound such as LiF is present in the EIL2.

[0314] In some embodiments, additional electron-injecting materials can be suitable for use in the EIL or in additional electron-injecting layers. Included are, but not limited to, materials such as an n-type doped layer containing at least one electron-transporting material as a host and at least one n-type dopant. The dopant is capable of reducing the host by charge transfer. The term "n-type doped layer" means that this layer has semiconducting properties after doping, and the electrical current through this layer is substantially carried by the electrons.

[0315] The host in the EIL can be an electron-transporting material capable of supporting electron injection and electron transport. The electron-transporting material can be selected from the electron-transporting materials for use in the ETL region as defined above.

[0316] The n-type dopant in the n-type doped EIL can be selected from alkali metals, alkali metal compounds, alkaline earth metals, or alkaline earth metal compounds, or combinations thereof. The term "metal compounds" includes organometallic complexes, metal-organic salts, and inorganic salts, oxides and halides. Among the class of metal-containing n-type dopants, Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, La, Ce, Sm, Eu, Tb, Dy, or Yb, and their compounds, are particularly useful. The materials used as the n-type dopants in the n-type doped EIL also include organic reducing agents with strong electron-donating properties. By "strong electron-donating properties" it is meant that the organic dopant should be able to donate at least some electronic charge to the host to form a charge-transfer complex with the host. Nonlimiting examples of organic molecules include bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF), tetrathiafulvalene (TTF), and their derivatives. In the case of polymeric hosts, the dopant is any of the above or also a material molecularly dispersed or copolymerized with the host as a minor component. Preferably, the n-type dopant in the n-type doped EIL includes Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, or Yb, or combinations thereof. The n-type doped concentration is preferably in the range of 0.01-20% by volume of this layer.

[0317] The thickness of the EIL is typically less than 20 nm, often less than 10 nm, or even 5 nm or less.

Cathode

[0318] When light emission is viewed solely through the anode, the cathode **140** includes nearly any conductive material. Desirable materials have effective film-forming properties to ensure effective contact with the underlying organic layer, promote electron injection at low voltage, and have effective stability. Useful cathode materials often contain a low work function metal (<4.0 eV) or metal alloy. One preferred cathode material includes a Mg:Ag alloy as described in U.S. Pat. No. 4,885,221. Another suitable class of cathode materials includes bilayers including a thin inorganic EIL in contact with an organic layer (e.g., organic EIL or ETL), which is capped with a thicker layer of a conductive metal. Here, the inorganic EIL preferably includes a low work function metal or metal salt and, if so, the thicker capping layer does not need to have a low work function. One such cathode includes a thin layer of LiF followed by a thicker layer of Al as described in U.S. Pat. No. 5,677,572. Other useful cathode material sets include, but are not limited to, those disclosed in U.S. Pat. Nos. 5,059,861; 5,059,862, and 6,140,763.

[0319] When light emission is viewed through the cathode, cathode **140** should be transparent or nearly transparent. For such applications, metals should be thin or one should use transparent conductive oxides, or include these materials. Optically transparent cathodes have been described in more detail in U.S. Pat. Nos. 4,885,211; 5,247,190; 5,703,436; 5,608,287; 5,837,391; 5,677,572; 5,776,622; 5,776,623; 5,714,838; 5,969,474; 5,739,545; 5,981,306; 6,137,223; 6,140,763; 6,172,459; 6,278,236; 6,284,393, and EP 1 076 368. Cathode materials are typically deposited by thermal evaporation, electron beam evaporation, ion sputtering, or chemical vapor deposition. When needed, patterning is achieved through many well known methods including, but not limited to, through-mask deposition, integral shadow masking, for example as described in U.S. Pat. No. 5,276,380 and EP 0 732 868, laser ablation, and selective chemical vapor deposition.

[0320] The thickness of the EIL is often in the range of from 0.1 nm to 20 nm, and typically in the range of from 1 nm to 5 nm.

Substrate

[0321] OLED **100** is typically provided over a supporting substrate **110** where either the anode **120** or cathode **140** can be in contact with the substrate. The electrode in contact with the substrate is conveniently referred to as the bottom electrode. Conventionally, the bottom electrode is the anode **120**, but this invention is not limited to that configuration. The substrate can either be light transmissive or opaque, depending on the intended direction of light emission. The light transmissive property is desirable for viewing the EL emission through the substrate. Transparent glass or plastic is commonly employed in such cases. The substrate can be a complex structure comprising multiple layers of materials. This is typically the case for active matrix substrates wherein TFTs are provided below the OLED layers. It is still necessary that the substrate, at least in the emissive pixelated areas, be comprised of largely transparent materials such as glass or polymers. For applications where the EL emission is viewed through the top electrode, the transmissive characteristic of the bottom support is immaterial, and therefore the substrate can be light transmissive, light absorbing or light reflective. Substrates for use in this case include, but are not limited to, glass, plastic, semiconductor materials such as silicon, ceramics, and circuit board materials. Again, the substrate can be a complex structure comprising multiple layers of materials such as found in active matrix TFT designs. It is necessary to provide in these device configurations a light-transparent top electrode.

Deposition of Organic Layers

[0322] The organic materials mentioned above are suitably deposited through sublimation, but can be deposited from a solvent with an optional binder to improve film formation. If the material is a polymer, solvent deposition is usually preferred. The material to be deposited by sublimation can be vaporized from a sublimator "boat" often comprised of a tantalum material, e.g., as described in U.S. Pat. No. 6,237,529, or can be first coated onto a donor sheet and then sublimed in closer proximity to the substrate. Layers with a mixture of materials can utilize separate sublimator boats or the materials can be pre-mixed and coated from a single boat or donor sheet. Patterned deposition can be achieved using

shadow masks, integral shadow masks (U.S. Pat. No. 5,294,870), spatially-defined thermal dye transfer from a donor sheet (U.S. Pat. Nos. 5,851,709 and 6,066,357) and inkjet method (U.S. Pat. No. 6,066,357).

[0323] Organic materials useful in making OLEDs, for example organic hole-transporting materials, organic light-emitting materials doped with an organic electroluminescent components have relatively complex molecular structures with relatively weak molecular bonding forces, so that care must be taken to avoid decomposition of the organic material(s) during physical vapor deposition. The aforementioned organic materials are synthesized to a relatively high degree of purity, and are provided in the form of powders, flakes, or granules. Such powders or flakes have been used heretofore for placement into a physical vapor deposition source wherein heat is applied for forming a vapor by sublimation or vaporization of the organic material, the vapor condensing on a substrate to provide an organic layer thereon.

[0324] Several problems have been observed in using organic powders, flakes, or granules in physical vapor deposition. These powders, flakes, or granules are difficult to handle. These organic materials generally have a relatively low physical density and undesirably low thermal conductivity, particularly when placed in a physical vapor deposition source which is disposed in a chamber evacuated to a reduced pressure as low as 10^{-6} Torr. Consequently, powder particles, flakes, or granules are heated only by radiative heating from a heated source, and by conductive heating of particles or flakes directly in contact with heated surfaces of the source. Powder particles, flakes, or granules which are not in contact with heated surfaces of the source are not effectively heated by conductive heating due to a relatively low particle-to-particle contact area; this can lead to nonuniform heating of such organic materials in physical vapor deposition sources. Therefore, this can result in potentially nonuniform vapor-deposited organic layers formed on a substrate.

[0325] These organic powders can be consolidated into a solid pellet. These solid pellets consolidating into a solid pellet from a mixture of a sublimable organic material powder are easier to handle. Consolidation of organic powder into a solid pellet can be accomplished with relatively simple tools. A solid pellet formed from mixture comprising one or more non-luminescent organic non-electroluminescent component materials or luminescent electroluminescent component materials or mixture of non-electroluminescent component and electroluminescent component materials can be placed into a physical vapor deposition source for making organic layer. Such consolidated pellets can be used in a physical vapor deposition apparatus.

[0326] In one aspect, the present invention provides a method of making an organic layer from compacted pellets of organic materials on a substrate, which will form part of an OLED.

[0327] One preferred method for depositing the materials of the present invention is described in U.S. Patent Application Publication 20040255857 and U.S. patent application Ser. No. 10/945,941 where different source evaporators are used to evaporate each of the materials of the present invention. A second preferred method involves the use of flash evaporation where materials are metered along a material feed path in which the material feed path is temperature controlled. Such a preferred method is described in the following co-assigned U.S. Pat. Nos. 7,232,588; 7,238,389; 7,288,285; 7,288,286; 7,165,340; and U.S. patent application

Ser. No. 11/050,924. Using this second method, each material can be evaporated using different source evaporators or the solid materials can be mixed prior to evaporation using the same source evaporator.

Encapsulation

[0328] Most OLED devices are sensitive to moisture and oxygen so they are commonly sealed in an inert atmosphere such as nitrogen or argon, along with a desiccant such as alumina, bauxite, calcium sulfate, clays, silica gel, zeolites, alkaline metal oxides, alkaline earth metal oxides, sulfates, or metal halides and perchlorates. Methods for encapsulation and desiccation include, but are not limited to, those described in U.S. Pat. No. 6,226,890.

OLED Device Design Criteria

[0329] For full color display, the pixelation of LELs can be needed. This pixelated deposition of LELs is achieved using shadow masks, integral shadow masks, U.S. Pat. No. 5,294,870, spatially defined thermal dye transfer from a donor sheet, U.S. Pat. Nos. 5,688,551; 5,851,709, and 6,066,357, and inkjet method, U.S. Pat. No. 6,066,357.

[0330] OLEDs of this invention can employ various well-known optical effects in order to enhance their emissive properties if desired. This includes optimizing layer thicknesses to yield maximum light transmission, providing dielectric mirror structures, replacing reflective electrodes with light-absorbing electrodes, providing anti-glare or anti-reflection coatings over the display, providing a polarizing medium over the display, or providing colored, neutral density, or color-conversion filters over the display. Filters, polarizers, and anti-glare or anti-reflection coatings can be specifically provided over the OLED or as part of the OLED.

[0331] OLED devices of this invention can employ various well-known optical effects in order to enhance its properties if desired. This includes optimizing layer thicknesses to yield maximum light transmission, providing dielectric mirror structures, replacing reflective electrodes with light-absorbing electrodes, providing anti-glare or anti-reflection coatings over the display, providing a polarizing medium over the display, or providing colored, neutral density, or color-conversion filters over the display. Filters, polarizers, and anti-glare or anti-reflection coatings can be specifically provided over the cover or as part of the cover.

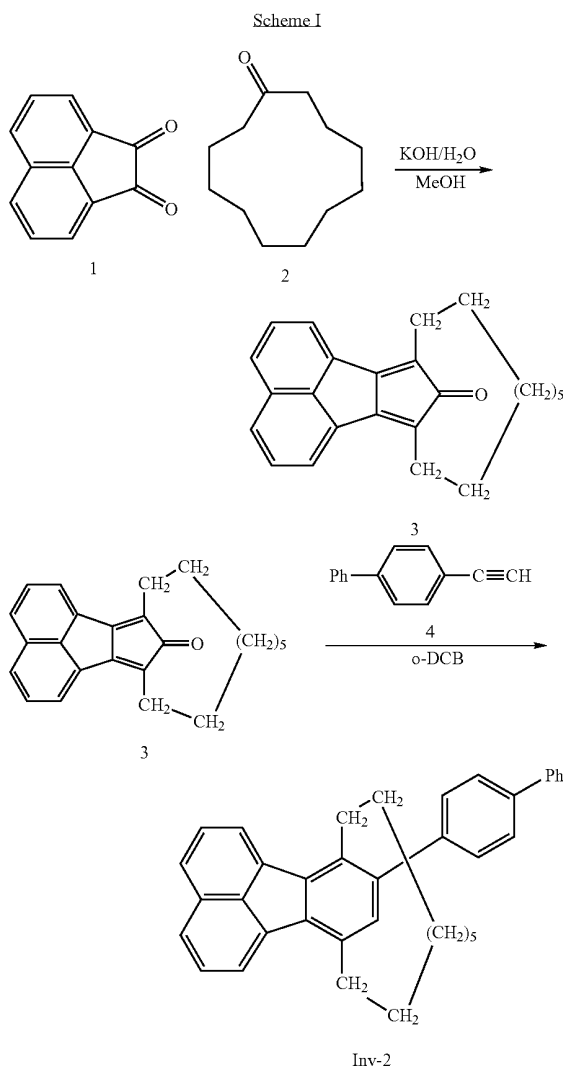
[0332] Embodiments of the invention can provide EL devices that have good luminance efficiency, good operational stability, and reduced drive voltages. Embodiments of the invention can also give reduced voltage rises over the lifetime of the devices and can be consistently produced with high reproducibility to provide good light efficiency. They can have lower power consumption requirements and, when used with a battery, provide longer battery lifetimes.

[0333] The invention and its advantages are further illustrated by the specific examples that follow. The term "percentage" or "percent" and the symbol "%" indicate the volume percent (or a thickness ratio as measured on a thin film thickness monitor) of a particular first or second compound of the total material in the layer of the invention and other components of the devices. If more than one second compound is present, the total volume of the second compounds can also be expressed as a percentage of the total material in the layer of the invention.

EXAMPLE 1

Synthesis of Inventive Compound Inv-2

[0334] Inv-2 was synthesized as outlined in Scheme 1 and described below.



Preparation on Compound 3.

[0335] Cyclododecanone (Cpd 2, 11 g, 60.3 mMole) in methanol (120 mL) was heated to 65° C. and 1,2-acenaphthylenedione (Cpd 1, 10 g, 54.9 mMole) was added. With good stirring, an aqueous solution of potassium hydroxide (20 mL of a 1 M solution, 20 mMole) was then added dropwise. At the end of the addition, the brown colored solution was heated at 65° C. for approximately 36 hours. The solution was then cooled and the precipitate filtered off, washed with methanol and air-dried to afford 8,9,10,11,12,13,14,15,16-nonahydro-7,17-methanocyclotridec[a]acenaphthylen-18-one, (Cpd 3, 6.4 g yield).

Preparation on Compound Inv-2.

[0336] Compound 3 (8,9,10,11,12,13,14,15,16-Nonahydro-7,17-methanocyclotridec[a]acenaphthylen-18-one, 5.4 g, 16.4 mMoles) and 4-ethynyl-1,1'-biphenyl (Cpd 4, 2.9 g, 16.3 mMoles) were heated in 1,2-dichlorobenzene (150 mL) at 200° C. for 12 hours. The solution was then cooled and the solvent removed under reduced pressure to leave approximately 50 mL of solvent. Methanol (50 mL) was added to induce crystallization. The resulting yellowish solid was filtered off, washed with methanol and air-dried to afford 6.4 g of Inv-2, melting point at 340° C. with shrinkage at 220° C. Inv-2 was sublimed at 180-210° C./ 3×10^{-1} Torr. Analysis of the ^1H NMR spectrum indicated that the desired product was obtained.

EXAMPLE 2

Preparation of Blue-Light Emitting OLED Devices 2.1 Through 2.11

[0337] A series of OLED devices (2.1 through 2.6) were constructed in the following manner:

[0338] 1. A glass substrate coated with an 85 nm layer of indium-tin oxide (ITO), as the anode, was sequentially ultrasonicated in a commercial detergent, rinsed in deionized water and exposed to oxygen plasma for about 1 min.

[0339] 2. Over the ITO was deposited a 1 nm fluorocarbon (CF_x) hole-injecting layer (HIL) by plasma-assisted deposition of CHF_3 as described in U.S. Pat. No. 6,208,075.

[0340] 3. Next a layer of hole-transporting material 4,4'-Bis [N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) was deposited to a thickness of 95 nm.

[0341] 4. A 20 nm light-emitting layer (LEL) corresponding to a host material P-4 and 5.0% by volume of dopant FD-53 was then deposited.

[0342] 5. A 35.0 nm electron-transporting layer (ETL) containing a first electron-transporting material (ETM1) corre-

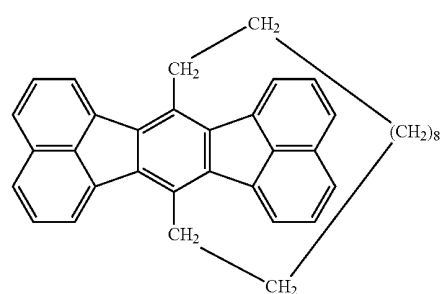
sponding to Inv-1, or a second-electron-transporting material (ETM2) corresponding to P-4, or mixtures of Inv-1 and P-4 as identified in Table 1, was deposited over the LEL.

[0343] 6. A 3.5 nm electron-injecting layer (EIL) corresponding to AM-1 was then deposited.

[0344] 7. And finally, a 100 nm layer of aluminum was deposited onto the EIL, to form the cathode.

[0345] The above sequence completes the deposition of the EL device. The device was then hermetically packaged in a dry glove box for protection against ambient environment.

[0346] Devices 2.7 through 2.11 were prepared in the same manner as Devices 2.1 through 2.6, except Inv-1, when present, was replaced with C-1 in the electron-transporting layer as identified in Table 1.



[0347] During their preparation each device was duplicated to give four identically fabricated devices for each example. The devices thus formed were tested for drive voltage and luminous efficiency at an operating current of 20 mA/cm². The results from the four duplicate devices were averaged and the results are reported in Table 1.

TABLE 1

Performance of Devices 2.1-2.11.							
Example (Type)	ETM1	ETM1 (%)	ETM2	ETM2 (%)	EIM	Drive Volt. (Volts)	Efficiency (cd/A)
2.1 (Inventive)	Inv-1	100	—	—	AM-1	5.4	8.1
2.2 (Inventive)	Inv-1	75	P-4	25	AM-1	5.5	8.0
2.3 (Inventive)	Inv-1	50	P-4	50	AM-1	5.5	7.8
2.4 (Inventive)	Inv-1	25	P-4	75	AM-1	5.6	7.6
2.5 (Inventive)	Inv-1	10	P-4	90	AM-1	5.7	7.5
2.6 (Comparative)	—	—	P-4	100	AM-1	5.6	7.3
2.7 (Comparative)	C-1	100	—	—	AM-1	5.9	5.0
2.8 (Comparative)	C-1	75	P-4	25	AM-1	5.7	6.2
2.9 (Comparative)	C-1	50	P-4	50	AM-1	7.1	7.0
2.10 (Comparative)	C-1	25	P-4	75	AM-1	6.5	7.3
2.11 (Comparative)	C-1	10	P-4	90	AM-1	7.1	7.2

[0348] From Table 1 it can be seen that devices including Inv-1 in the electron-transporting layer (devices 2.1-2.5), either alone or in combination with anthracene derivative P-4, afford higher luminance and similar or lower drive voltage relative to comparative device 2.6, which contains only P-4 in the ETL.

[0349] Comparative devices 2.7 through 2.11 were constructed in the same manner as inventive devices 2.1 through 2.5, except Inv-1 was replaced with fluoranthene derivative C-1. Compound C-1 falls outside the scope of the present invention and can be described as a fluoranthene nucleus with a 7,10-linking group, but having a five-membered ring group fused to the nucleus in the 8,9-positions. Compound C-1 and its use in an OLED device have been disclosed previously (JP 2003123978). One can see from Table 1 that, for each corresponding level, devices containing Inv-1 provide both lower drive voltage and higher luminance efficiency relative to those containing C-1. In addition, comparative devices 2.7-2.11 are disadvantaged relative to comparative device 2.6, which contains only anthracene derivative P-4 in the ETL; they afford higher drive voltage, but, only equal or lower luminance relative to device 2.6.

EXAMPLE 3

Preparation of Red-Light Emitting Devices 3.1 Through 3.6

[0350] A series of OLED devices (3.1 through 3.6) were constructed in the following manner:

[0351] 1. A glass substrate coated with an 85 nm layer of indium-tin oxide (ITO), as the anode, was sequentially ultrasonicated in a commercial detergent, rinsed in deionized water and exposed to oxygen plasma for about 1 min.

[0352] 2. Over the ITO was deposited a 1 nm fluorocarbon (CF_x) hole-injecting layer (HIL) by plasma-assisted deposition of CHF_3 as described in U.S. Pat. No. 6,208,075.

[0353] 3. Next a layer of hole-transporting material 4,4'-Bis [N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) was deposited to a thickness of 144.0 nm.

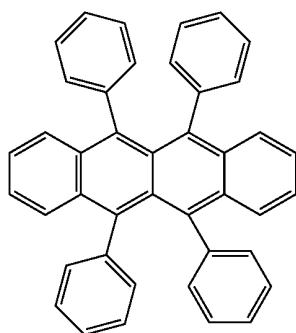
[0354] 4. A 40 nm light-emitting layer (LEL) containing a first host material (Host1) corresponding to rubrene (FD-5), or a mixture of FD-5 and a second host material (Host2) corresponding to Inv-1, as identified in Table 2, and 0.5% by volume of dopant FD-46 was then deposited.

[0355] 5. An electron-transporting layer (ETL) of Inv-1 at a thickness of 31.5 nm was vacuum-deposited over the LEL.

[0356] 6. An electron-injecting layer (EIL) corresponding to AM-1 was vacuum deposited onto the ETL at a thickness of 3.5 nm.

[0357] 7. And finally, a 100 nm layer of aluminum was deposited onto the EIL, to form the cathode.

[0358] The above sequence completes the deposition of the EL device. The device was then hermetically packaged in a dry glove box for protection against ambient environment.



FD-5

[0359] During their preparation each device was duplicated to give four identically fabricated devices for each example. The devices thus formed were tested for drive voltage and luminous efficiency at an operating current of 20 mA/cm². The results from the four duplicate devices were averaged and the results are reported in Table 2.

TABLE 2

Performance of Devices 3.1-3.6.							
Example (Type)	LEL Host1	Host1 Level (%)	LEL Host2	Host2 Level (%)	ETL	Drive Volt. (Volts)	Efficiency (cd/A)
3.1 (Inventive)	FD-5	99.5	—	—	Inv-1	4.3	3.7
3.2 (Inventive)	FD-5	79.5	Inv-1	20.0	Inv-1	4.3	4.6
3.3 (Inventive)	FD-5	74.5	Inv-1	25.0	Inv-1	4.3	4.7
3.4 (Inventive)	FD-5	69.5	Inv-1	30.0	Inv-1	4.4	5.0
3.5 (Inventive)	FD-5	64.5	Inv-1	35.0	Inv-1	4.2	5.1
3.6 (Inventive)	FD-5	59.5	Inv-1	40.0	Inv-1	4.3	5.3

[0360] It can be seen from Table 2 that if, in addition to using Inv-1 in the ETL, Inv-1 is also a co-host in the LEL (devices 3.2-3.6), one obtains devices having improved luminance efficiency and, except for device 3.4, the same or lower drive voltage relative to device 3.1, which does not contain Inv-1 in the LEL. All devices have the same overall thickness.

EXAMPLE 4

Preparation of Blue-Light Emitting OLED Devices 4.1 Through 4.6

[0361] A series of OLED devices (4.1 through 4.6) were constructed in the following manner:

[0362] 1. A glass substrate coated with an 85 nm layer of indium-tin oxide (ITO), as the anode, was sequentially ultrasonicated in a commercial detergent, rinsed in deionized water and exposed to oxygen plasma for about 1 min.

[0363] 2. Over the ITO was deposited a 1 nm fluorocarbon (CF_x) hole-injecting layer (HIL) by plasma-assisted deposition of CHF_3 as described in U.S. Pat. No. 6,208,075.

[0364] 3. Next a layer of hole-transporting material 4,4'-Bis [N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) was deposited to a thickness of 95 nm.

[0365] 4. A 20 nm light-emitting layer (LEL) corresponding to a host material P-4 and 5.0% by volume of dopant FD-53 was then deposited.

[0366] 5. An electron-transporting layer (ETL) containing a first electron-transporting material (ETM1) corresponding to Inv-2 at a level listed in Table 3 or a mixture of Inv-2 with a second electron-transporting material (ETM2) corresponding to AM-2 at a level also listed in Table 3 was deposited over the LEL.

[0367] 6. For devices 4.2-4.6, an electron-injecting layer (EIL) corresponding to AM-2 at a level listed in Table 3 was then deposited onto the ETL.

[0368] 7. And finally, a 100 nm layer of aluminum was deposited onto the EIL, to form the cathode. For device 4.1 this layer was deposited directly on the ETL.

[0369] The above sequence completes the deposition of the EL device. The device was then hermetically packaged in a dry glove box for protection against ambient environment.

[0370] During their preparation each device was duplicated to give four identically fabricated devices for each example. The devices thus formed were tested for drive voltage and luminous efficiency at an operating current of 20 mA/cm². The results from the four duplicate devices were averaged and the results are reported in Table 3.

[0374] 2. Over the ITO was deposited a 1 nm fluorocarbon (CF_x) hole-injecting layer (HIL) by plasma-assisted deposition of CHF₃ as described in U.S. Pat. No. 6,208,075.

[0375] 3. Next a layer of hole-transporting material 4,4'-Bis [N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) was deposited to a thickness of 95 nm.

[0376] 4. A 20 nm light-emitting layer (LEL) corresponding to host material P-4 and 1.5% by volume of dopant FD-54 was then deposited.

[0377] 5. A 35.0 nm electron-transporting layer (ETL) containing a first electron-transporting material (ETM1) corresponding to Inv-1, or a second-electron-transporting material

TABLE 3

Performance of Devices 4.1-4.6.							
Example (Type)	ETL Level (nm)	ETM1 Inv-2 (%)	ETM2 AM-2 (%)	EIL	EIL Level (nm)	Drive Volt. (Volts)	Efficiency (cd/A)
4.1 (Comparative)	35.0	100	0	None	None	16.3	0.09
4.2 (Inventive)	32.5	100	0	AM-2	2.5	6.4	7.9
4.3 (Inventive)	31.5	100	0	AM-2	3.5	7.9	7.2
4.4 (Inventive)	32.5	60	40	AM-2	2.5	6.4	7.8
4.5 (Inventive)	32.5	50	50	AM-2	2.5	7.0	7.6
4.6 (Inventive)	32.5	40	60	AM-2	2.5	7.0	7.3

[0371] All the devices fabricated and tested had the same overall thickness. As can be seen from Table 3, devices 4.2-4.6, which have an EIL containing AM-2 and an ETL containing either Inv-1, or Inv-1 in combination with AM-2, provided good luminance and relatively low drive voltage compared to device 4.1, which does not contain an alkali metal material.

EXAMPLE 3

Preparation of Blue-Light Emitting OLED Devices
5.1 Through 5.11

[0372] A series of OLED devices (5.1 through 5.5) were constructed in the following manner:

[0373] 1. A glass substrate coated with an 85 nm layer of indium-tin oxide (ITO), as the anode, was sequentially ultrasonicated in a commercial detergent, rinsed in deionized water and exposed to oxygen plasma for about 1 min.

(ETM2) corresponding to P-4, or mixtures of Inv-1 and P-4 as identified in Table 4, was deposited over the LEL.

[0378] 6. A 3.5 nm electron-injecting layer (EIL) corresponding to AM-1 was then deposited over the ETL.

[0379] 7. And finally, a 100 nm layer of aluminum was deposited onto the EIL, to form the cathode.

[0380] The above sequence completes the deposition of the EL device. The device was then hermetically packaged in a dry glove box for protection against ambient environment.

[0381] A second series of OLED devices (5.6-5.11) were constructed in the same manner as devices 5.1-5.5 (see Table 4), except Inv-1, when present, was replaced with Inv-2.

[0382] During their preparation each device was duplicated to give four identically fabricated devices for each example. The devices thus formed were tested for drive voltage and luminous efficiency at an operating current of 20 mA/cm². Results for the four duplicate devices were averaged and are reported in Table 4.

TABLE 4

Performance of Devices 5.1-5.11.							
Example (Type)	ETM1	ETM1 (%)	ETM2	ETM2 (%)	EIM	Drive Volt. (Volts)	Efficiency (cd/A)
5.1 (Inventive)	Inv-1	100	—	—	AM-1	4.9	6.5
5.2 (Inventive)	Inv-1	50	P-4	50	AM-1	4.8	6.4

TABLE 4-continued

Performance of Devices 5.1-5.11.							
Example (Type)	ETM1	ETM1 (%)	ETM2	ETM2 (%)	EIM	Drive Volt. (Volts)	Efficiency (cd/A)
5.3 (Inventive)	Inv-1	25	P-4	75	AM-1	4.8	6.5
5.4 (Inventive)	Inv-1	10	P-4	90	AM-1	4.8	6.2
5.5 (Comparative)	—	—	P-4	100	AM-1	4.8	6.0
5.6 (Inventive)	Inv-2	100	—	—	AM-1	5.5	4.2
5.7 (Inventive)	Inv-2	75	P-4	25	AM-1	5.5	4.7
5.8 (Inventive)	Inv-2	50	P-4	50	AM-1	5.5	4.4
5.9 (Inventive)	Inv-2	25	P-4	75	AM-1	5.7	4.1
5.10 (Inventive)	Inv-2	10	P-4	90	AM-1	5.8	4.6
5.11 (Comparative)	—	—	P-4	100	AM-1	4.9	5.8

[0383] All devices have the same overall thickness. Comparative devices 5.5 and 5.11 do not contain Inv-1 or Inv-2 and use anthracene derivative P-4 as the electron-transporting material. One can see from Table 4 that, by using an ETL containing Inv-1 or Inv-2, either alone or combined with P-4, one obtains, on average, devices affording both good luminance and drive voltage.

[0384] The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

PARTS LIST

- [0385]** 100 OLED
[0386] 110 Substrate
[0387] 120 Anode
[0388] 130 Hole-Injecting layer (HIL)
[0389] 132 Hole-Transporting layer (HTL)
[0390] 134 Light-Emitting layer (LEL)
[0391] 135 Hole-Blocking Layer (HBL)
[0392] 136 Electron-Transporting layer (ETL)
[0393] 138 Electron-Injecting layer (EIL)
[0394] 140 Cathode
[0395] 150 Voltage/Current Source
[0396] 160 Electrical Connectors

1. An OLED device comprising a cathode, an anode, and having therebetween a light-emitting layer and further comprising a first layer, between the light-emitting layer and the cathode, including a fluoranthene-macrocylic compound comprising a fluoranthene nucleus having the 7,10-positions connected by a linking group, and wherein said fluoranthene nucleus can be further substituted, provided substituents in the 8- and 9-positions cannot combine to form a five-membered ring group; and wherein the OLED device includes at least one layer, between the light-emitting layer and the cathode, comprising an alkali metal material.

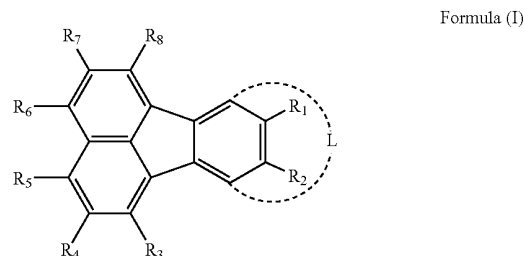
2. The OLED device of claim 1 wherein the linking group has a length of 8 atoms or more and less than 30 atoms.

3. The OLED device of claim 1 wherein the linking group has a length of 10 atoms or more and less than 20 atoms.

4. The OLED device of claim 1 wherein the fluoranthene-macrocylic compound contains one, and only one, fluoranthene nucleus.

5. The OLED device of claim 1 wherein there are no aromatic rings annulated to the fluoranthene nucleus.

6. The OLED device of claim 1 wherein the fluoranthene-macrocylic compound is represented by Formula (I),



wherein:

R₁-R₈ independently represent hydrogen or a substituent group, and wherein adjacent R₁-R₈ substituents can combine to form a ring group, provided R₁ and R₂ cannot combine to form a five-membered ring group; and

L represents the atoms necessary to complete a linking group.

7. The OLED device of claim 6 wherein L is represented by Formula (1),

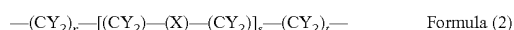


wherein:

each Y can be the same or different and each Y represents a hydrogen or a substituent, provided adjacent substituents can combine to form a ring group; and

n is 8-25.

8. The OLED device of claim 6 wherein L is represented by Formula (2),



wherein:

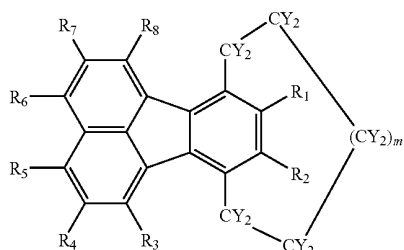
each Y can be the same or different and each Y represents a hydrogen or a substituent, provided adjacent substituents can combine to form a ring group; and

each X can be the same or different and each X represents CY_2 , N, O or S; and

r is 0 to 10, t is 0 to 10, and s is 1 to 10, provided that r, s, and t are chosen so that L has a length of at least 8 atoms, but less than 25 atoms.

9. The OLED device of claim 6 wherein each of R_1 - R_8 independently represents hydrogen, an alkyl group having 1-24 carbon atoms, or an aryl group having 6-24 carbon atoms, provided adjacent groups cannot combine to form an aromatic ring group fused to the fluoranthene nucleus.

10. The OLED device of claim 1 wherein the fluoranthene-macrocylic compound is represented by Formula (II),



Formula (II)

wherein:

each of R_1 - R_8 independently represents hydrogen, an alkyl group having 1-24 carbon atoms, or an aryl group having 6-24 carbon atoms, provided adjacent groups cannot combine to form an aromatic ring group fused to the fluoranthene nucleus;

each Y can be the same or different and each represents hydrogen, an alkyl group having 1-24 carbon atoms, or an aryl group having 6-24 carbon atoms, provided adjacent Y groups can combine to form a ring group; and

m is 4 or greater, but less than 30.

11. The OLED device of claim 10 wherein m is 6 or greater, but less than 25.

12. The OLED device of claim 1 wherein the alkali metal material comprises lithium metal or an organic lithium compound.

13. The OLED device of claim 1 wherein the first layer comprises an alkali metal or an organic alkali metal compound.

14. The OLED device of claim 1 wherein a second layer, located between the first layer and the cathode and contiguous to the first layer, comprises an alkali metal or an organic alkali metal compound.

15. The OLED device of claim 1 wherein the first layer comprises an alkali metal or an organic alkali metal compound, and a second layer, located between the first layer and the cathode and contiguous to the first layer, comprises an independently selected alkali metal or an independently selected organic alkali metal compound.

16. The OLED device of claim 1 wherein the alkali metal material comprises a compound represented by Formula (III),

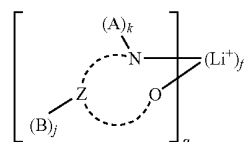


wherein:

Q is an anionic organic ligand; and

f and g are independently selected integers selected to provide a neutral charge on the complex.

17. The OLED device of claim 1 wherein the alkali metal material comprises a compound represented by Formula (IV),



Formula (IV)

wherein:

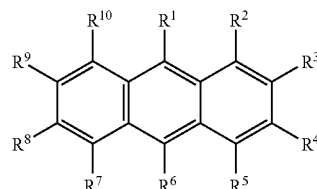
Z and the dashed arc represent two to four atoms and the bonds necessary to complete a 5- to 7-membered ring with the lithium cation;

each A represents hydrogen or a substituent and each B represents hydrogen or an independently selected substituent on the Z atoms, provided that two or more substituents can combine to form a fused ring or a fused ring system; and

j is 0-3 and k is 1 or 2; and

f and g are independently selected integers selected to provide a neutral charge on the complex.

18. The OLED device of claim 1 wherein the first layer comprises, in addition to the fluoranthene-macrocylic compound, an anthracene derivative according to Formula (V),



Formula (V)

wherein:

R^1 and R^6 each independently represent an aryl group having 6-24 carbon atoms;

R^2 - R^5 and R^7 - R^{10} are each independently chosen from hydrogen, alkyl groups having from 1-24 carbon atoms and aromatic groups having from 6-24 carbon atoms.

19. The OLED device of claim 1 wherein the fluoranthene-macrocylic compound is present in the first layer and in the light-emitting layer.

20. An OLED device comprising a cathode, an anode, and having therebetween a light-emitting layer and further comprising a first layer, between the light-emitting layer and the cathode, wherein the first layer is a non-luminescent electron-transporting layer, and wherein:

a) the first layer includes a fluoranthene-macrocycle compound comprising a fluoranthene nucleus having the 7,10-positions connected by a linking group, wherein the linking group has a length of at least 8 atoms, and

wherein the fluoranthene nucleus can be further substituted, provided substituents in the 8- and 9-positions cannot combine to form five-membered ring group; and
b) the first layer includes an alkali metal or an organic alkali metal compound; or a second layer, located between the first layer and the cathode and contiguous to the first

layer, includes an alkali metal or organic alkali metal compound, provided both the first and second layers can include an independently selected alkali metal or organic alkali metal compound.

* * * * *

专利名称(译)	OLED用荧蒹 - 大环材料		
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申请号	US12/370696	申请日	2009-02-13
[标]申请(专利权)人(译)	贝格利WILLIAM J ANDRIEVSKY娜塔莎		
申请(专利权)人(译)	贝格利WILLIAM J ANDRIEVSKY娜塔莎		
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发明人	BEGLEY, WILLIAM J. ANDRIEVSKY, NATASHA		
IPC分类号	H01L51/54		
CPC分类号	H01L51/0054 H01L51/0056 H01L51/0067 H01L51/0077 H01L51/008 C09K2211/1011 H01L51/0087 H01L51/5048 H01L51/5052 Y10S428/917 C09K11/06 H01L51/0085 H01L51/0084		
其他公开文献	US8216697		
外部链接	Espacenet USPTO		

摘要(译)

本发明提供一种OLED器件，其包括阴极，阳极，并且在它们之间具有发光层，在阴极和发光层之间还包括含有荧蒹 - 大环化合物的第一层。荧蒹 - 大环化合物包括荧蒹核，其具有通过连接基团连接的7,10位。荧蒹核可以进一步被取代，条件是8位和9位的取代基不能结合形成五元环基团。OLED器件包括在发光层和阴极之间的至少一个含有碱金属材料的层。理想地，OLED器件包括存在于第一层中或位于阴极和第一层之间的第二层中的有机碱金属化合物。除了荧蒹 - 大环化合物之外，OLED器件可以包括存在于第一层中的蒹衍生物。本发明的装置提供诸如效率和驱动电压之类的特征的改进。

