

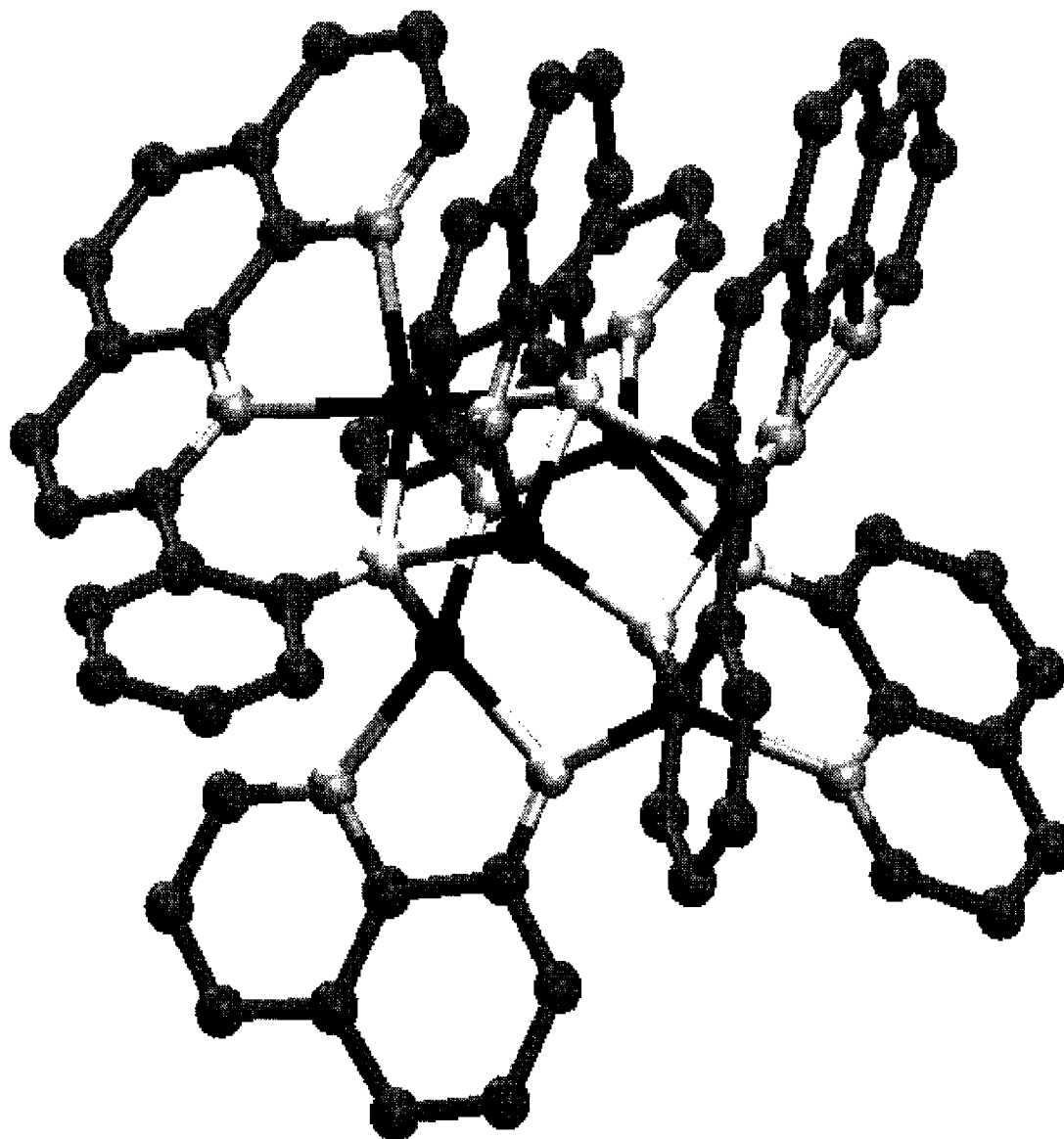


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(19) **United States**(12) **Patent Application Publication**
Begley et al.(10) **Pub. No.: US 2009/0142618 A1**(43) **Pub. Date: Jun. 4, 2009**(54) **OLED DEVICE EMPLOYING ALKALI
METAL CLUSTER COMPOUNDS****Publication Classification**(76) Inventors: **William J. Begley**, Webster, NY
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(US)(51) **Int. Cl.**
C09K 11/00 (2006.01)
C07D 221/02 (2006.01)(52) **U.S. Cl. 428/690; 546/94; 546/48; 546/71**(57) **ABSTRACT**

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The invention provides an OLED device containing certain alkali metal cluster compounds with mixed ligands, such compounds, and methods of making them. In particular, the cluster compound is a neutrally charged mixed cluster compound comprising first and second subunits with the first subunit comprising an alkali metal salt of a nitrogen containing a heterocyclic ligand bearing a anionic hydroxy group and the second subunit consisting of an organic alkali metal salt different than the first subunit.

(21) Appl. No.: **11/947,000**(22) Filed: **Nov. 29, 2007**

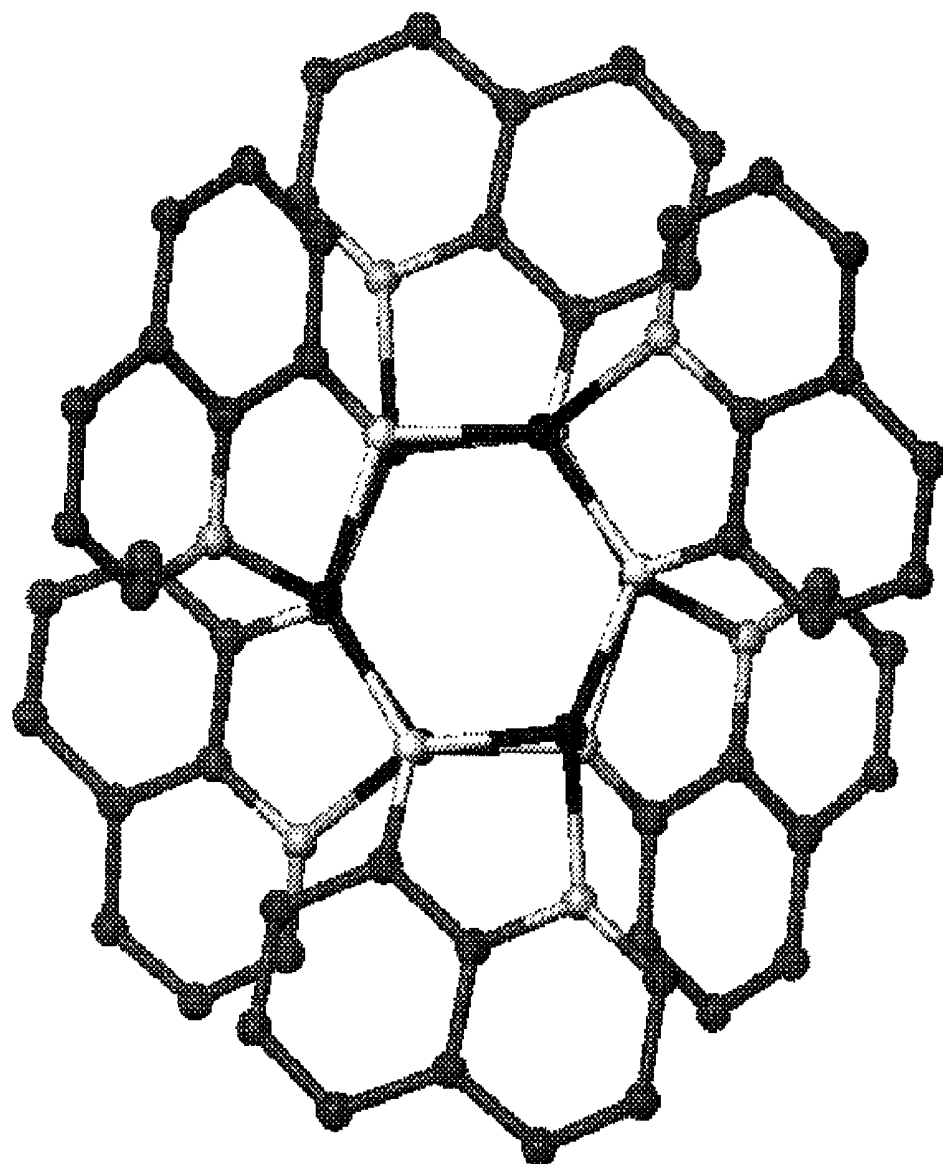


FIG. 1 (Comparative)

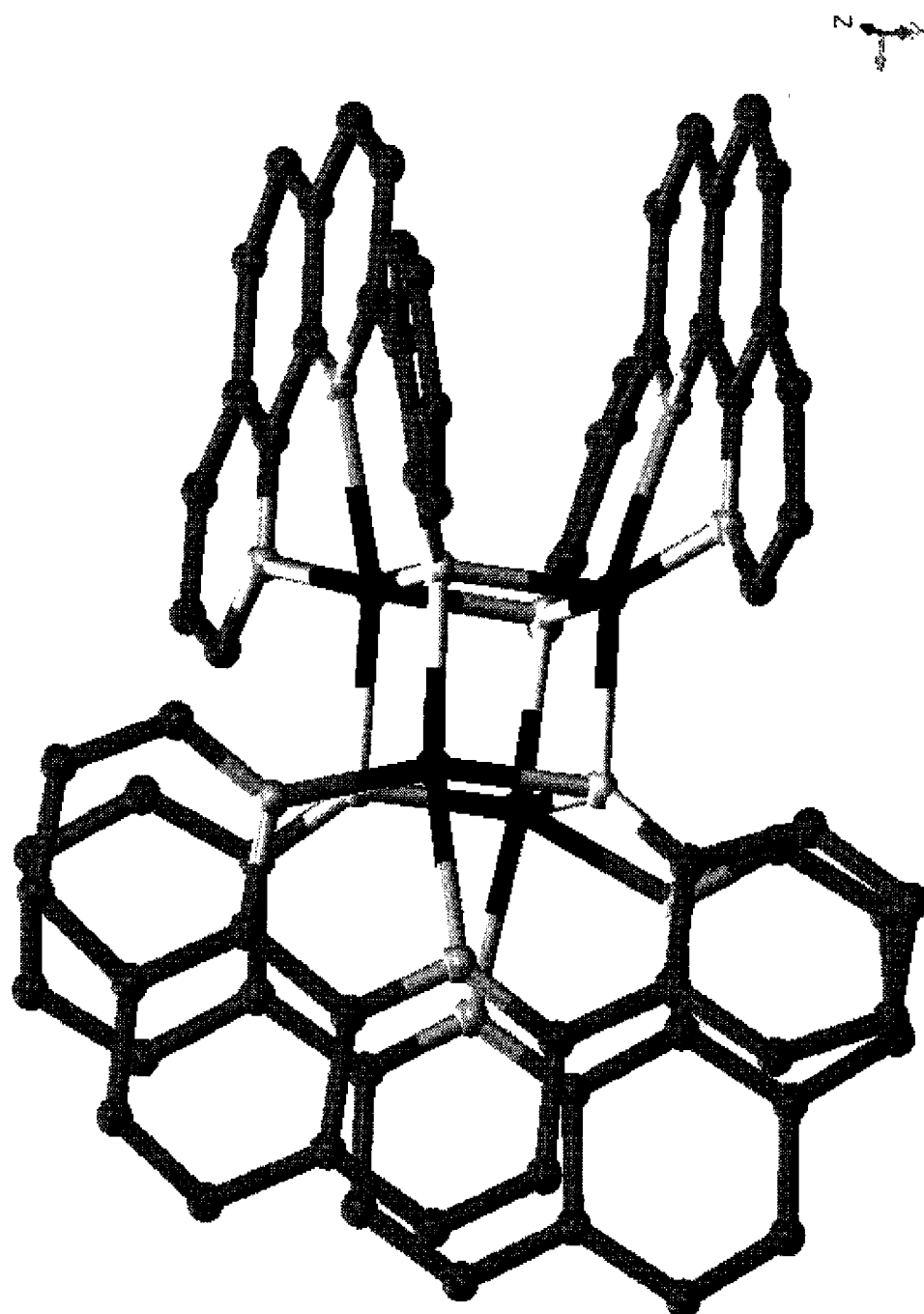


FIG. 2 (Comparative)

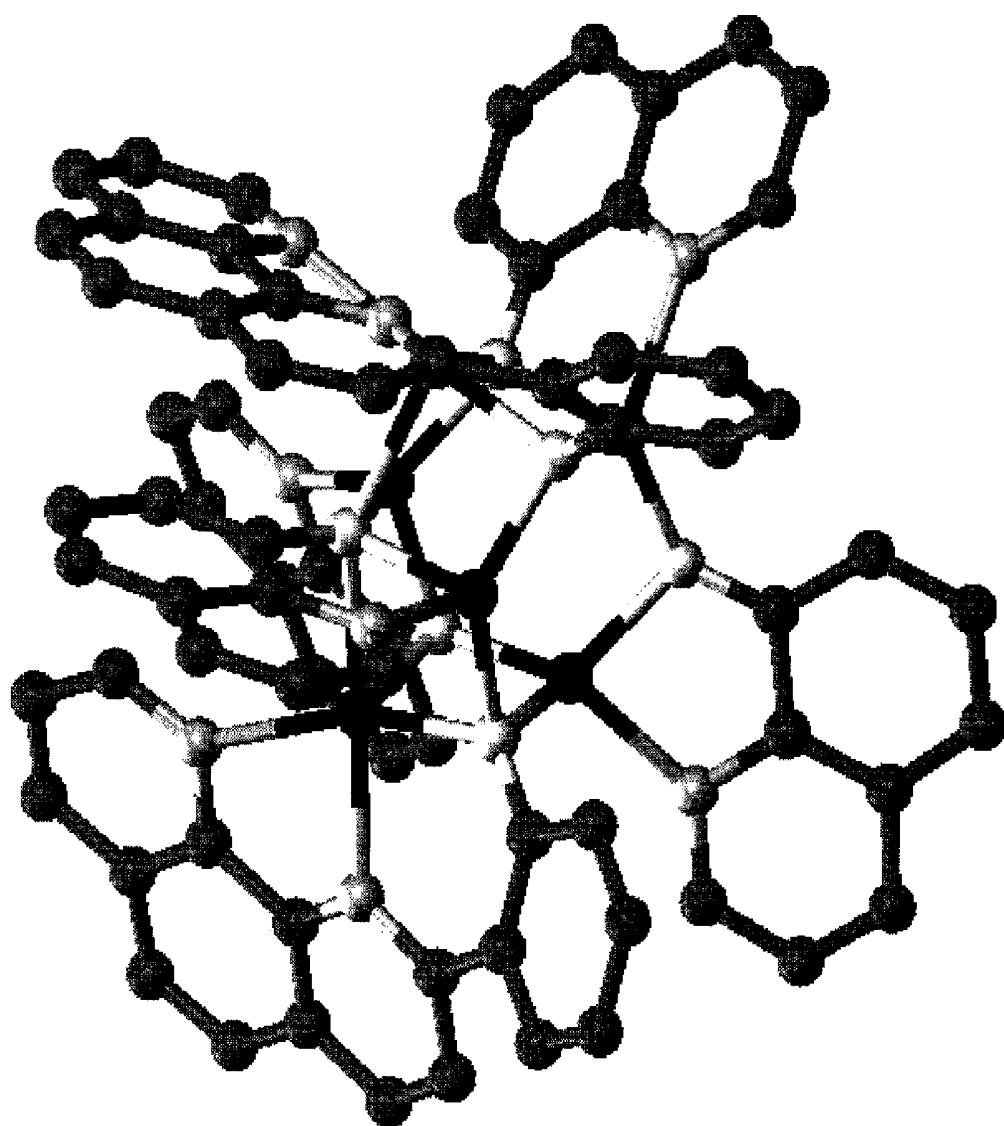


FIG. 3

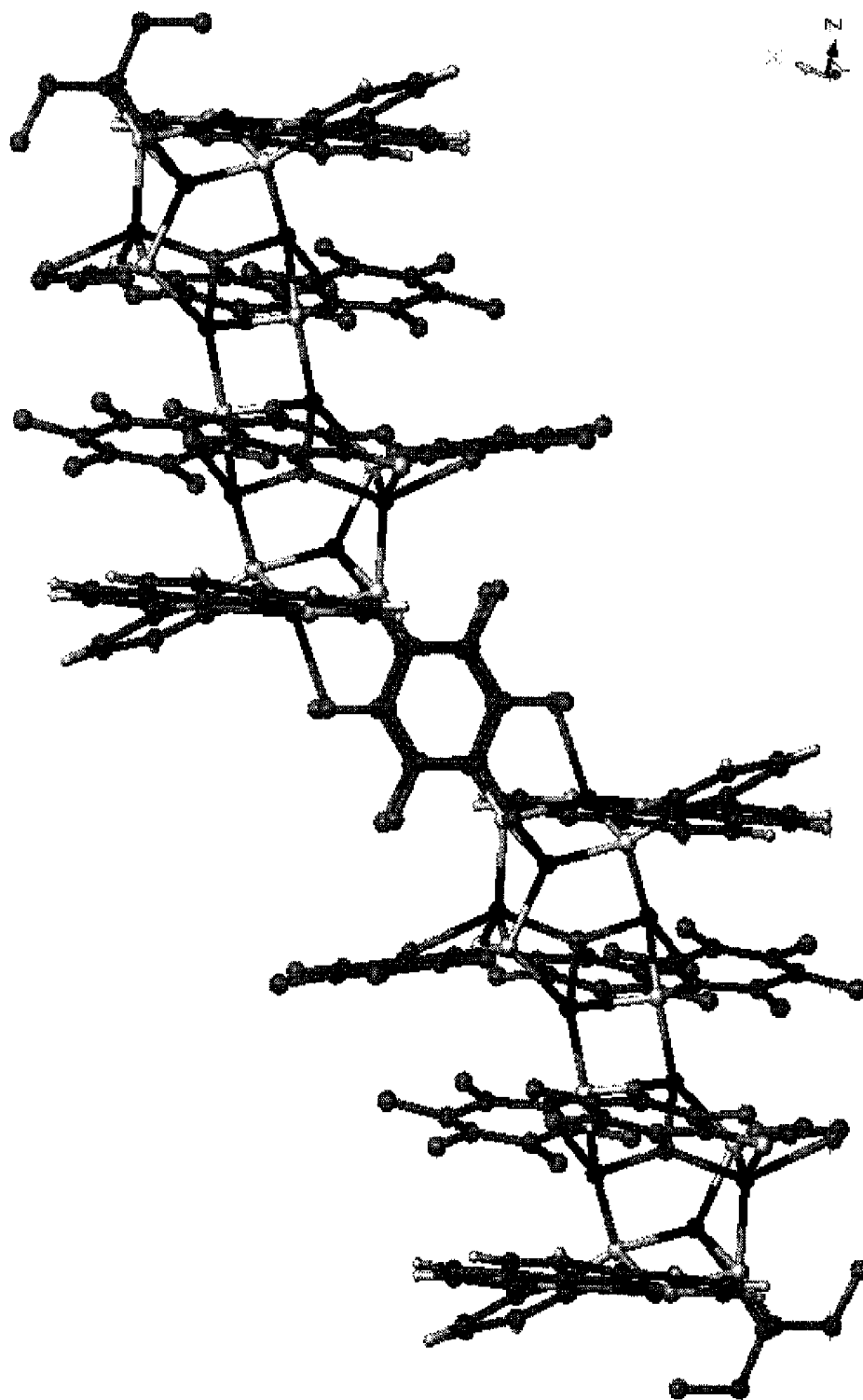


FIG. 4

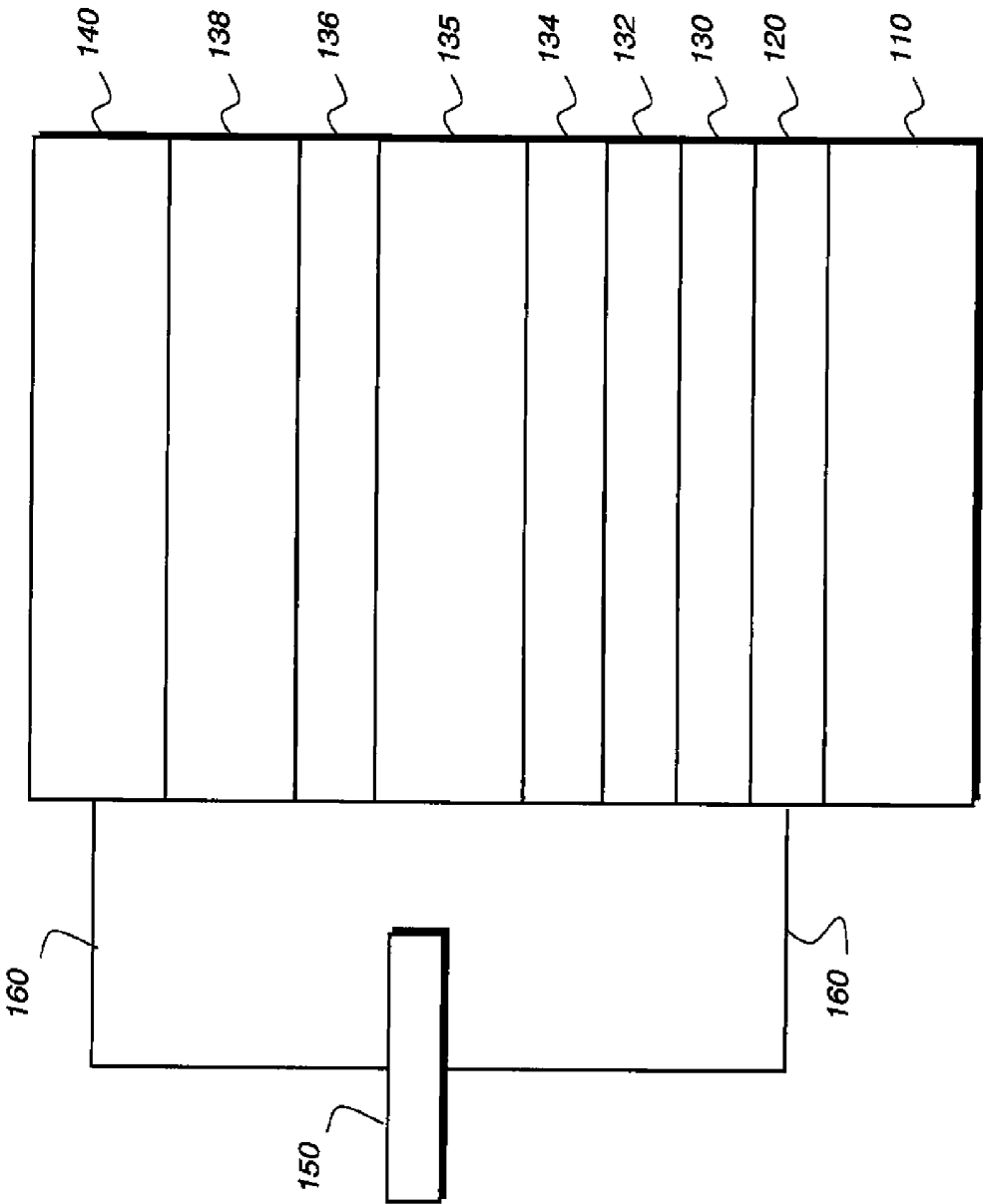


FIG. 5

OLED DEVICE EMPLOYING ALKALI METAL CLUSTER COMPOUNDS

FIELD OF THE INVENTION

[0001] This invention relates to new and novel alkali metal cluster compounds with mixed ligands and their use in an organic light-emitting diode (OLED) electroluminescent (EL) device.

BACKGROUND OF THE INVENTION

[0002] It is well known that alkali metal salts such as lithium and sodium of aromatic phenols can form discrete cluster compounds in which multiple alkali metal atoms are coordinated by multiple ligands in an organized fashion. For example, see "Lithium Chemistry: A Theoretical and Experimental Overview", A-M. Sapse and P. Von Rague Schleyer, Eds., J. Wiley & Sons, NY, 1995, Chapters 7-9 and Kissling et al, J. Org. Chem, 66(26), 9006 (2001).

[0003] Such cluster compounds are stable, neutral in overall charge and can form spontaneously and reproducibly from mixtures. The number of alkali metal atoms and ligands present in the cluster compound can vary depending on the nature of the ligand. In the case of lithium, examples of cluster compounds with 2, 3, 4 and 6 lithium atoms are known. For examples, see Fenton et al, JCS, Chem Comm, (23), 1303 (1972); Hao et al, Fagang Xuebao, 25(4), 419-424 (2004); Baker et al, Organometallics, 13(11), 4170-2 (1994) and Prakash et al, J Indian Chem Soc, 62(6), 424-5 (1985).

[0004] Metal salts of 2-(2-hydroxyphenyl)pyridine derivatives are well known in the art and their use in electroluminescent devices have been described. For example, see CN1245822, CN1544574 and US2005/0019605A1. However, it has not been reported whether these materials form cluster compounds.

[0005] The cluster compound of lithium sodium di-(8-hydroxyquinolate) has been described as useful in electroluminescent devices in CN1900213.

[0006] Banerjee et al, JCS, Inorg, Phys and Theor. (17), 2536-43 (1969) describes the isolation of a charged species of lithium 8-hydroxyquinolate complexed with an additional molecule of 8-hydroxyquinoline. A crystal structure was not reported.

[0007] Lithium 8-hydroxyquinolate (LiQ) is a well known compound that has been used in electroluminescent devices. As disclosed in M. Rajeswaran et al, Polyhedron, 26(14), 3653-3660 (2007) and W. Begley et al, Acta Crystallographica, Section E: Structure Reports Online (2006) E62(6), m1200-m1202, LiQ is a discrete cluster compound and is sometimes correctly referred to as $[Li_3Q_3]_2$ or Li_6Q_6 , which is a dimer of a trimer. It is likely that the material described as LiQ and used in electroluminescent devices is in fact the cluster form of the compound and not the monomer.

[0008] LiQ has been reported to be useful in emitting layers of electroluminescent devices; for example, see US20060003089A1; US2005016412A1; WO2003080758A2; EP1458834A1; Zhao et al, Guangxue Xuebao, 20(2), 288 (2000) and Zhu et al, Bandaoti Guardian, 22(4), 279-281 (2001). LiQ has been reported as useful in electron-injecting layers; for example, see Liu et al, Synthetic Metals, 128(2), 211-214 (2002); Wu et al, Fagang Xuebao, 24(5), 473-476 (2003); Zheng et al, Thin Solid Films, 478(1-2), 252-255 (2005) and Schmitz et al, Chemistry of Materials, 12(10), 3012-3019 (2000). The use of LiQ and other organic

lithium salts in electron-transporting layers has also been reported in US20060286405, US20020086180, US20040207318, U.S. Pat. No. 6,396,209, JP2000053957, WO9963023 and U.S. Pat. No. 6,468,676.

[0009] Various uses of organic alkali metal salts in OLED devices have also been disclosed in US20060286402, US20070092753, US20070207347, US20070092754, US20070092756 and US20070092755.

[0010] All of the above references disclose only organic alkali metal salts with only one kind of ligand present.

[0011] Banerjee et al, J Indian Chem Soc, 50(10), 691-3 (1973) describes a compound formed between lithium 8-hydroxyquinolate and a 1,10-phenanthroline ligand which is not an anion. The crystal structure was not reported. Prakash et al, J Indian Chem. Soc., 62(6), 424-5 (1985) describes charged complexes of LiQ and picolinic or quinaldinic acid. The crystal structure was not reported. It is generally recognized that when materials such as these are sublimed, they sublime separately as their individual component parts.

[0012] 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 μ m). Consequently, operating voltages were very high, often greater than 100V.

[0013] More recent organic EL devices include an organic EL element consisting of extremely thin layers (e.g. <1.0 μ m) 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.

[0014] 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 consists of 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.

[0015] 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.

[0016] 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. No. 5,061,569, U.S. Pat. No. 5,409,783, U.S. Pat. No. 5,554,450, U.S. Pat. No. 5,593,788, U.S. Pat. No. 5,683,823, U.S. Pat. No. 5,908,581, U.S. Pat. No. 5,928,802, U.S. Pat. No. 6,020,078, and U.S. Pat. No. 6,208,077, amongst others.

[0017] Notwithstanding all of these developments, there are continuing needs for organic EL device components, such as light-emitting materials, electron transporting materials and electron injecting materials, that will provide even lower device drive voltages and hence lower power consumption, while maintaining high luminance efficiencies and long lifetimes.

SUMMARY OF THE INVENTION

[0018] The invention provides An OLED device comprising a cathode, an anode, and having therebetween a layer containing a neutrally charged mixed cluster compound comprising first and second subunits with the first subunit comprising an alkali metal salt of a nitrogen containing heterocyclic ligand bearing an anionic hydroxy group and the second subunit comprises an organic alkali metal salt different than the first subunit, wherein the alkali metal cations of both subunits are the same. The invention also provides such compounds and a method of making them.

[0019] OLED devices containing the cluster compounds of the invention provide improved efficiency and reduced drive voltage and provide embodiments with other improved features such as operational stability.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] FIG. 1 shows an X-ray crystal structure of a comparative lithium 8-hydroxyquinolate cluster.

[0021] FIG. 2 shows an X-ray crystal structure of a comparative lithium 2-(1,10-phenanthrolin-2-yl)-phenolate cluster.

[0022] FIG. 3 shows an X-ray crystal structure of the mixed cluster compound of the invention formed of lithium 8-hydroxyquinolate and lithium 2-(1,10-phenanthrolin-2-yl)-phenolate.

[0023] FIG. 4 shows an X-ray crystal structure of the mixed cluster compound of the invention formed of lithium 2-(1,10-phenanthrolin-2-yl)-phenolate and lithium pentafluorophenolate.

[0024] In FIGS. 1-4, black represents lithium atoms, white represents oxygen atoms, light grey represents nitrogen atoms and dark grey represents carbon atoms. For the sake of clarity, hydrogen atoms are omitted.

[0025] FIG. 5 shows a schematic cross-sectional view of one embodiment of the OLED device of the present invention. It will be understood that FIG. 5 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

[0026] In the following discussions, the term 'subunit' refers to an individual molecule whose structure represents the smallest indivisible component part of the cluster compound. The term 'moiety' refers to a grouping of the subunit molecules that are held together through some type of coordinate or dative bonding. In some instances, a moiety may be a single subunit. The terms 'subunit' and 'moiety' are both used in the current invention to describe parts or sections of the cluster compound and may or may not exist as individual species. The term 'alkali metal salt' refers to a neutral ionic species composed of an alkali metal cation and an anion. In the specific case where the anion is a hydroxy anion which is part of a nitrogen containing heterocycle, the corresponding alkali metal salt can also be referred to as a complex since the nitrogen of the heterocycle is coordinated to the alkali metal cation.

[0027] The invention is generally as described above. The cluster compounds of the invention are discrete complexes composed of multiple individual moieties, which can be composed of single or multiple subunits. They have a definite and organized crystal structure in which the various moieties and their subunits coordinate to each other via dative or other types of coordinate bonds. They can be formed reproducibly and are not simple admixtures of individual compounds. They can be recrystallized or sublimed without losing their integrity and without variations between the relative amounts of subunits present in the cluster.

[0028] Overall, the cluster compounds of the invention are neutral in charge, being comprised of at least 2 different subunits, each of which are neutral in overall charge. One subunit is an alkali metal salt of a nitrogen containing heterocyclic ligand bearing an anionic hydroxy group. The second subunit is an organic alkali metal salt that is different from the first subunit.

[0029] These subunits can coordinate with other subunits to form a more complex moiety such as a dimer or trimer. The individual moieties can further coordinate with each other to form the mixed cluster compound. For example, two individual subunits can coordinate together to form a dimeric moiety, and two dimeric moieties can coordinate together to form a discrete cluster compound having a total of four alkali metal salts. Alternatively, three individual subunits can coordinate together to form a trimeric moiety and two of these moieties can then coordinate together to form a discrete cluster compound having a total of six alkali metal salts. Other combinations of subunits and moieties are possible, although these are the most common.

[0030] In the nitrogen containing heterocyclic ligand bearing the anionic hydroxy group of the first subunit, the hydroxy group can either be directly attached to the nitrogen containing heterocycle or it can be attached indirectly to the heterocycle as part of a substituent. As an example of the latter, the hydroxy group may be attached to a phenyl substituent on the heterocycle. In either case, the hydroxyl group must be capable of ionization and forming a neutrally charged alkali metal salt. Heterocyclic ligands that do not contain an ioniz-

able group and only form a charged complex with an alkali metal cation are not part of this invention.

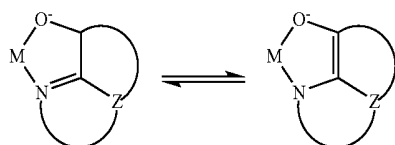
[0031] The alkali metal is selected from any of the group Ia alkali metals of the Periodic Table. Of these, lithium and sodium are preferred with lithium being most preferred. In the current invention, only one kind of alkali metal cation is present in the cluster compound.

[0032] One of the subunits that make up the individual moieties present in the mixed cluster compound are neutral alkali metal salts of a nitrogen containing heterocyclic ligand bearing at least one ionized hydroxy group. Preferably, the nitrogen of the heterocycle is spatially arranged relative to the hydroxy group so that an alkali metal cation can be coordinated both by the nitrogen(s) of the heterocycle and the hydroxy anion in a five or 5-, 6-, 7- or 8-membered ring arrangement. Suitably, the nitrogen is part of the heterocyclic ring system and not external to it, the nitrogen containing heterocycle is aromatic and the group containing the hydroxy anion is aromatic such that the pKa of the hydroxy group is less than 14, and preferably less than 12.

[0033] Some non-limiting examples of suitable nitrogen containing heterocycles are quinolines, isoquinolines, phenanthrolines, pyrroles, pyrazoles, imidazoles, benzimidazoles, triazoles, benzotriazoles, tetrazoles, indoles, isoindoles, pyridines, pyrazines, pyrimidines, indolizines, purines and quinoxalines. The nitrogen containing heterocycle may also contain other heteroatoms such as sulfur or oxygen. Non-limiting examples of these would be isothiazoles, phenothiazines, isoxazoles, thiazoles, benzothiazoles, oxazoles and benzooxazoles. Quinolines, phenanthrolines and pyridines are preferred.

[0034] The following are preferred structures for the alkali metal salt of a nitrogen containing heterocyclic ligand bearing an anionic hydroxy group and are suitable for use as a first subunit. The same structures are also suitable as a second subunit. Both the first and second subunits can belong to the same formula as long as the individual subunits are not identical.

[0035] The structure of one preferred subunit is according to formula (I):



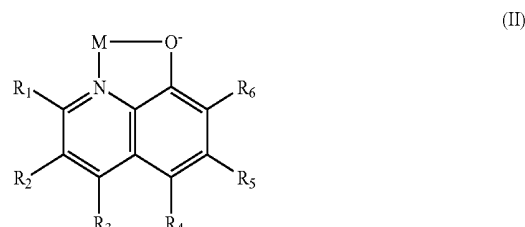
(I)

wherein:

[0036] M represents an alkali metal cation; and

[0037] Z independently in each occurrence represents the atoms completing a nucleus having at least two fused aromatic rings. The fused aromatic rings represented by Z can be composed solely of carbon or may have additional heteroatoms as part of the ring system.

[0038] A more preferred structure of formula (I) is according to formula (II):



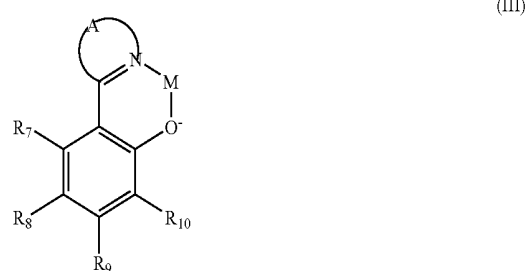
wherein:

[0039] M represents an alkali metal cation; and

[0040] R₁-R₆ individually represents a hydrogen, alkyl, alkenyl, alkynyl, alkyloxy, alkylthio, amino, aryl, aryloxy, arylthio, cyano or heterocyclic group with the proviso that any two adjacent R groups may be joined together to form an annulated saturated or aromatic ring system.

[0041] The most preferred structure of formula (II) is where M is a lithium cation and R₁-R₆ are all hydrogen.

[0042] The structure of another subunit is according to formula (III):



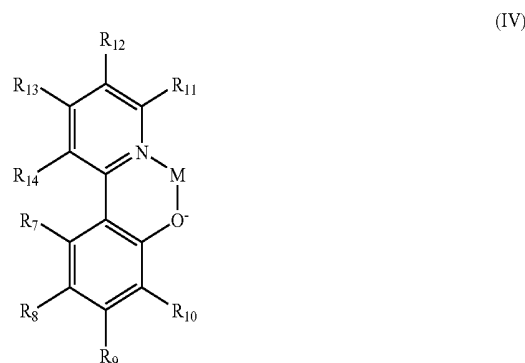
wherein:

[0043] M represents an alkali metal cation; and

[0044] R₇-R₁₀ individually represents a hydrogen, alkyl, alkenyl, alkynyl, alkyloxy, alkylthio, amino, aryl, aryloxy, arylthio, cyano or heterocyclic group with the proviso that any two adjacent R groups or R₇ and A may be joined together to form an annulated saturated or aromatic ring system; and A represent the atoms necessary to complete a 5, 6, 7 or 8 member ring system.

[0045] The most preferred subunits of formula (III) are where M is a lithium cation, A represents a 5 or 6 member ring and R₇-R₁₀ are all hydrogen.

[0046] Preferred structures for subunits of formula (III) are those of formula (IV):



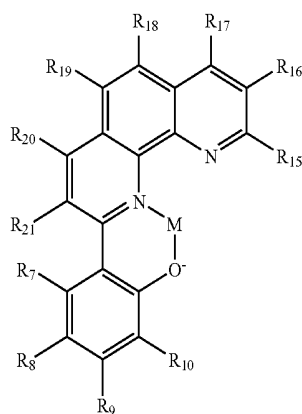
wherein:

[0047] M represents an alkali metal cation; and

[0048] R_7 - R_{14} individually represents a hydrogen, alkyl, alkenyl, alkynyl, alkyloxy, alkylthio, amino, aryl, aryloxy, arylthio, cyano or heterocyclic group with the proviso that any two adjacent R groups or specifically, R_7 and R_{14} may be joined together to form an annulated saturated or aromatic ring system.

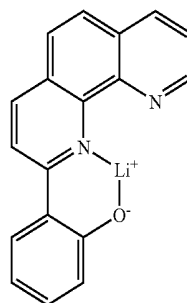
[0049] The most preferred subunit of formula (IV) is where M is a lithium cation and R_7 - R_{14} are all hydrogen.

[0050] More preferred subunits of formula (III) and (IV) are those according to formula (V):

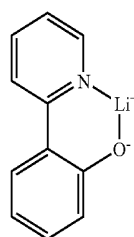


(V)

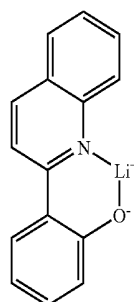
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L-2



L-3



L-4

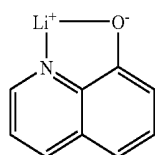
wherein:

[0051] M represents an alkali metal cation; and

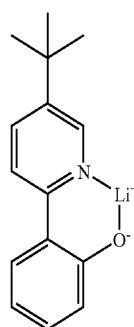
[0052] R_7 - R_{10} and R_{15} - R_{21} individually represents a hydrogen, alkyl, alkenyl, alkynyl, alkyloxy, alkylthio, amino, aryl, aryloxy, arylthio, cyano or heterocycle group with the proviso that any two adjacent R groups or specifically, R_7 and R_{21} may be joined together to form an annulated saturated or aromatic ring system.

[0053] The most preferred subunit of formula (V) is wherein M is a lithium cation and R_7 - R_{10} and R_{15} - R_{21} are all hydrogen.

[0054] Examples of suitable alkali metal salts of nitrogen containing heterocycles bearing hydroxy groups useful as first or second subunits in the cluster compounds of the invention are, but not limited to:



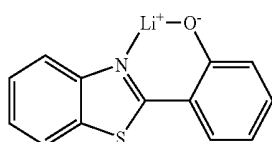
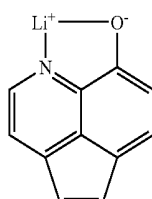
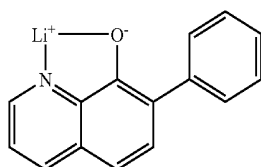
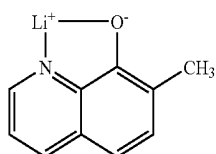
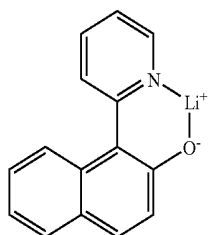
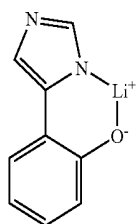
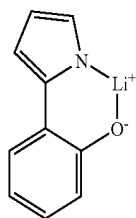
L-1



L-5

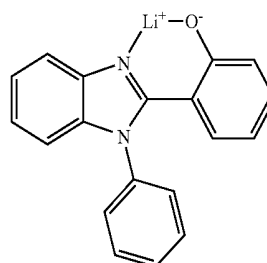
L-6

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L-14



L-7

L-8

L-9

L-10

L-11

L-12

L-13

[0055] In the mixed cluster compounds of the invention, there are at least two different subunits present overall. However, in the crystals of the cluster compounds, the subunits may form individual moieties such as dimers or trimers that are homogeneous (that is, contain only one kind of subunit) or heterogeneous (that is, may contain two or more different subunits). The cluster compound may then be composed of two or more homogeneous moieties so long as each moiety contains different subunits or alternatively, be composed of two or more heterogeneous moieties, each of which contain different subunits.

[0056] The second subunit present in the mixed cluster compound of the invention is an organic alkali metal salt. It cannot be the same material as the first subunit. Preferred organic alkali metal salts have a formula according to formula (VI):



where M is an alkali metal cation, X is an anionic atom including oxygen, nitrogen or sulfur and R is an organic radical containing carbon. In Formula (VI), X is preferably oxygen and R is preferably an aromatic hydrocarbon or heterocycle.

[0057] For example, the second subunit can be an aromatic species without nitrogen but with acidic hydroxyl groups. Phenols and naphthols are particularly suitable. Most preferred are phenols and naphthols where the hydroxy group of either has a pKa of 12 or less. The second subunit can also be another alkali metal salt of a nitrogen containing heterocyclic ligand bearing an anionic hydroxy group according to formulae (I)-(V) so long as it has a different structure than the first subunit.

[0058] FIG. 1. shows an X-ray crystal structure of lithium 8-hydroxyquinolate. It is a homogeneous cluster compound composed of a dimer of a trimeric moiety of 3 subunits with each subunit a single lithium 8-hydroxyquinolate molecule (L-1). Thus, lithium 8-hydroxyquinolate, typically written as LiQ, is more correctly described in terms of its structure as the hexameric cluster compound, Li_6Q_6 , composed of a dimer of the trimeric moiety, Li_3Q_3 . This is the crystal structure that typically forms via sublimation. Li_6Q_6 is not a cluster compound of the invention since it only contains one type of subunit.

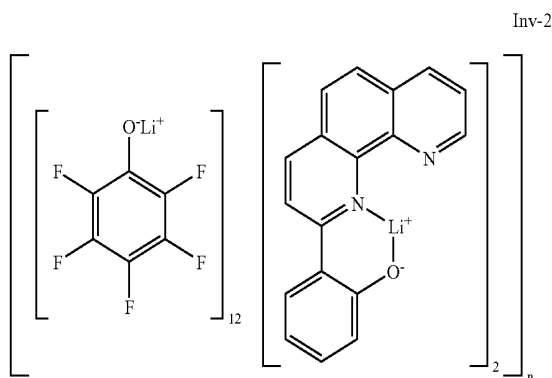
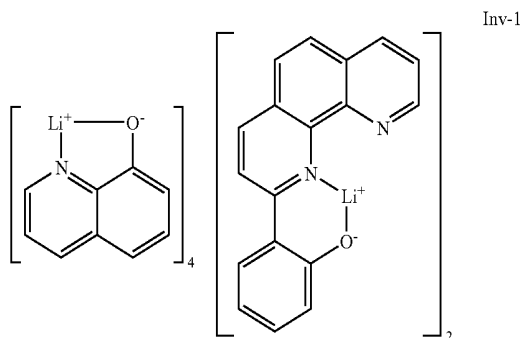
[0059] FIG. 2 shows an X-ray crystal structure of lithium 2-(1,10-phenanthroline-2-yl)-phenolate. It is a homogeneous cluster compound composed of a dimer of a dimeric moiety composed of two L-2 subunits. Thus, lithium 2-(1,10-phenanthroline-2-yl)-phenolate can be described as a tetrameric cluster compound $Li_4(L-2)_4$. This is the crystal struc-

ture that typically forms via sublimation. $\text{Li}_4(\text{L-2})_4$ is not a cluster compound of the invention since it only contains one type of subunit.

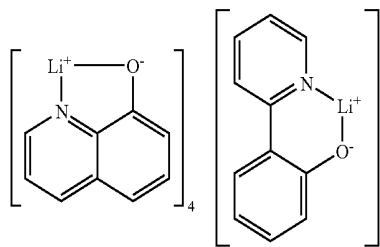
[0060] FIG. 3 shows an X-ray crystal structure of the mixed cluster compound (Inv-1) formed from lithium 8-hydroxyquinolate and lithium 2-(1,10-phenanthrolin-2-yl)-phenolate. It is a heterogeneous cluster composed of a dimer of a mixed trimeric moiety containing 2 molecules of L-1 and one molecule of L-2. Thus, Inv-1 can be described as a hexameric mixed cluster compound $\text{Li}_6(\text{L-1})_4(\text{L-2})_2$. This is the crystal structure that typically forms via sublimation. $\text{Li}_6(\text{L-1})_4(\text{L-2})_2$ is inventive since it contains two different types of subunit.

[0061] FIG. 4 shows an X-ray crystal structure of the mixed cluster compound (Inv-2) formed from lithium 2-(1,10-phenanthrolin-2-yl)-phenolate (L-2) and lithium pentafluorophenolate (LiPFP). It is a heterogeneous cluster compound with a linear or chain repeating form. One unit of the repeating linear chain consists of a moiety of 5 subunits of LiPFP, 1 subunit of L-2, a moiety consisting of 2 subunits of LiPFP, 1 subunit of L-2 and a moiety of 5 subunits of LiPFP. Thus, Inv-2 can be described as a linear polymeric mixed cluster compound $[\text{Li}_{14}(\text{PFP})_{12}(\text{L-2})_2]_n$. This is the crystal structure that forms via sublimation without change. This material is inventive since it contains two different types of subunit.

[0062] Some examples of inventive cluster compounds are as follows:



-continued



[0063] An OLED device including the mixed cluster compound 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).

[0064] The mixed cluster compound of the invention can be located anywhere between the anode and electrode. It is preferred that the mixed cluster compound be located in a LEL or in a layer between the LEL and the cathode and most preferably, located in an ETL or EIL.

[0065] When the mixed cluster compound is present in the LEL, it may be the only material present in which case, it serves as a light emitting material. More commonly, it is present as a host or co-host ranging from 0.5% to 50% by volume of all organic materials in that layer. Any known host or dopant can be present and suitable materials for these purposes will be discussed in later sections.

[0066] When the mixed cluster compound is present in an ETL, it can be the only material present or it may be mixed with any other material known to be effective in an ETL layer. Specific preferred classes of materials that can be used with the mixed cluster compound in the ETL are anthracenes, rubrene derivatives, metal oxinoids such as Alq or phenanthrolines such as Bphen. Suitable examples of these classes will be discussed in later sections. It is preferred that the ETL be in direct contact with the LEL and on the same side of the LEL as the cathode.

[0067] When the mixed cluster compound is present in an EIL, it can be the only material present or it may be mixed with any other material known to be effective in an EIL layer. Specific preferred classes of materials that can be used with the mixed cluster compound in the EIL are polyaromatic hydrocarbons such as anthracene or rubrene derivatives. The % volume ratio of mixed cluster compound to additional material can be anywhere from 1% to 99%, more suitably 10% to 90% and most desirably, 30 to 70%. The thickness of the EIL can be 0.1 nm to 20 nm in thickness, but preferably 0.4 nm to 10 nm, and more preferable from 1 nm to 8 nm.

[0068] The mixed cluster compound can be used in more than one layer at a time and more than one mixed cluster compound can be used together. It is also possible to use the mixed cluster compound together with homogeneous cluster compounds such as Li_6Q_6 .

[0069] As demonstrated in the experimental section, the mixed cluster compounds can be prepared by reaction of the individual subunits in solvent. Any solvent that is capable of forming the materials of the current invention can be useful. It is preferred that the solvents completely dissolve the reac-

tants, but solvents that only partially dissolve the reactants are also useful. Indeed solvents in which the reactants are insoluble at ambient temperatures are also useful, because in such cases the solubility of the starting materials can increase as the temperature is increased. Even solvents in which the reactants are insoluble may be employed, as it is possible that dissolution of some reactants is not necessary for reaction to occur, as some chemical reactions are known to occur in the solid state. In any case, there are some solvents that are more suited for the reaction than others because of solvent properties such as polarity, boiling points and melting points. The polarity of the reactants should be a factor when considering solvent choice. The solvent should be non-reactive; that is, does not chemically react with either subunit or the mixed cluster compound.

[0070] Solvents selected from the following classes are useful in the current invention: aromatic and non-aromatic hydrocarbons, halogenated aromatic and non-aromatic hydrocarbons such as chlorinated hydrocarbons, nitro-hydrocarbons, carbohydrates, cyclic and non-cyclic ketones, cyclic and non-cyclic alcohols, cyclic and non-cyclic esters, cyclic and non-cyclic ethers, phenols, primary amines, secondary amines, tertiary amines, nitrites, nitro-solvents, cyclic and non-cyclic amides, lactones, lactams and the derivatives of these classes. Indeed any material, liquid or solid, can be used as a solvent in the current invention with the proviso that the boiling points or the melting points are sufficiently low that decomposition of the reactants and products does not occur. Particularly useful solvents are selected from chlorobenzene, ortho-dichlorobenzene, para-dichlorobenzene, hexachlorobenzene, tetrachloroethylene, amyl alcohol, butyl alcohol, cyclohexanone, cyclohexanol, ethylbenzene, toluene, xylenes, diphenylketone, diphenylether, methyl isobutylketone, cresols, phenols, pentachlorophenol, nitrobenzene, nitropropane, pyridines, dimethylformamide, and N-methylpyrrolidone. The most preferred solvents are those that have a boiling point of at least 100° C.

[0071] The mixed cluster compounds can also be directly prepared by taking a physical mixture of the individual subunits and heating the solid mixture at high temperature. The temperature required is usually greater than 150 deg C. If a sublimation unit is used for heating at low pressure, the mixed cluster compound can then be easily harvested directly from the cooled surfaces of the sublimation unit. In the case of sublimation, it is unknown whether the mixed cluster compound is formed in the solid state upon heating, upon deposition of the crystals or in the gaseous state during sublimation; however, any of these possibilities are considered a solid state reaction for the purposes of this invention.

[0072] FIG. 5 shows one embodiment of the invention in which electron-transporting and electron-injecting layers are present. The mixed cluster compound of the invention can be located in the electron-transporting layer (ETL, 136). In another embodiment, it is located in the electron-injecting layer (EIL, 138). 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, there may be more than one hole-injecting, electron-injecting and electron-transporting layers.

[0073] In one suitable embodiment the EL device includes a means for emitting white light, which may include compli-

mentary emitters, a white emitter, or a filtering means. The device may 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 may also be useful by themselves. Hybrid fluorescent/phosphorescent elements having non-white emission may also be combined with additional phosphorescent elements in series in a stacked OLED. For example, white emission may 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. This invention may be used in so-called stacked device architecture, for example, as taught in U.S. Pat. No. 5,703,436 and U.S. Pat. No. 6,337,492.

[0074] 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.

[0075] 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.

[0076] As used herein and throughout this application, the term carbocyclic and heterocyclic rings or groups are generally as defined by the *Grant & Hackh'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 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.

[0077] 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 substituents 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 may be halogen or may be bonded to the remainder of the molecule by an atom of carbon, silicon, oxygen, nitrogen, phosphorous,

sulfur, selenium, or boron. The substituent may be, for example, halogen, such as chloro, bromo or fluoro; nitro; hydroxyl; cyano; carboxyl; or groups which may 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-naphthyl, and 4-tolyl, 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-tetradecylpyrrolidin-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, benzyloxycarbonylamino, hexadecyloxycarbonylamino, 2,4-di-t-butylphenoxycarbonylamino, phenylcarbonylamino, 2,5-(di-t-pentylphenyl)carbonylamino, p-dodecylphenylcarbonylamino, 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-propylsulfamoyl, 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-di-butylcarbamoyl, 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-amyphenoxy)acetyl, phenoxycarbonyl, p-dodecyloxyphenoxycarbonyl methoxycarbonyl, butoxycarbonyl, tetradecyloxycarbonyl, ethoxycarbonyl, benzyloxycarbonyl, 3-pentadecyloxycarbonyl, and dodecyloxycarbonyl; sulfonyl, such as methoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl, 2-ethylhexyloxysulfonyl, phenoxysulfonyl, 2,4-di-t-pentylphenoxysulfonyl, 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, benzyloxy, octadecanoyloxy, p-dodecylamidobenzyloxy, N-phenylcarbamoyloxy, N-ethylcarbamoyloxy, and cyclohexylcarbonyloxy, 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 may 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.

[0078] If desired, the substituents may themselves be further substituted one or more times with the described substituent groups. The particular substituents used may 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 may have two or more substituents, the substituents may be joined together to form a ring such as a fused ring unless otherwise provided. Generally, the above groups and substituents thereof may 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.

[0079] The following is the description of the layer structure, material selection, and fabrication process for OLED devices.

General OLED Device Architecture

[0080] The present invention can be employed in many OLED configurations using small molecule materials, oligomeric 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.

[0081] One embodiment according to the present invention and especially is 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 may alternatively be located adjacent to the cathode, or the substrate may actually constitute the anode or cathode. Also, the total combined thickness of the organic layers is preferably less than 500 nm.

[0082] 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

[0083] 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 means such as evaporation, sputtering, chemical vapor deposition, or electrochemical means. Anodes can be patterned using well-known photolithographic processes. Optionally, anodes may be polished prior to application of other layers to reduce surface roughness so as to minimize short circuits or enhance reflectivity.

Hole Injection Layer

[0084] 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 dipyrzino[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.

[0085] 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

[0086] 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.

[0087] 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:

[0088] Q_1 and Q_2 are independently selected aromatic tertiary amine moieties; and

[0089] G is a linking group such as an arylene, cycloalkylene, or alkylene group of a carbon to carbon bond.

[0090] In one embodiment, at least one of Q_1 or Q_2 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.

[0091] A useful class of triarylamine satisfying structural Formula A and containing two triarylamine moieties is represented by structural Formula (B)



wherein:

[0092] 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

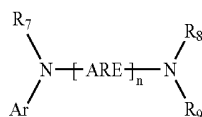
[0093] R_3 and R_4 each independently represents an aryl group, which is in turn substituted with a diaryl substituted amino group, as indicated by structural Formula (C)



wherein:

[0094] 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.

[0095] 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)



(D)

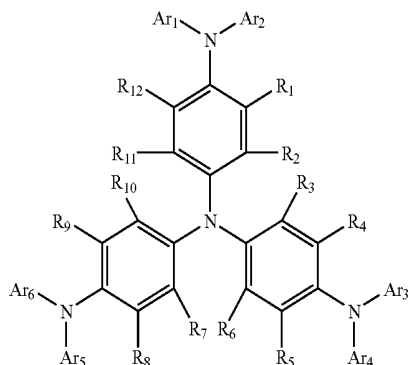
wherein:

[0096] each ARE is an independently selected arylene group, such as a phenylene or anthracene moiety,

[0097] n is an integer of from 1 to 4; and

[0098] Ar, R₇, R₈, and R₉ are independently selected aryl groups. In a typical embodiment, at least one of Ar, R₇, R₈, and R₉ is a polycyclic fused ring structure, e.g., a naphthalene.

[0099] Another class of the hole-transporting material comprises a material of formula (E):



(E)

[0100] In formula (E), Ar₁-Ar₆ independently represent aromatic groups, for example, phenyl groups or tolyl groups;

[0101] R₁-R₁₂ 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.

[0102] 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.

[0103] 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:

[0104] 1,1-bis(4-di-p-tolylaminophenyl)cyclohexane;

[0105] 1,1-bis(4-di-p-tolylaminophenyl)-4-phenylcyclohexane;

[0106] 1,5-bis[N-(1-naphthyl)-N-phenylamino]naphthalene;

[0107] 2,6-bis(di-p-tolylamino)naphthalene;

[0108] 2,6-bis[di-(1-naphthyl)amino]naphthalene;

[0109] 2,6-bis[N-(1-naphthyl)-N-(2-naphthyl)amino]naphthalene;

[0110] 2,6-bis[N,N-di(2-naphthyl)amine]fluorene;

[0111] 4-(di-p-tolylamino)-4'-[4(di-p-tolylamino)-styryl]stilbene;

[0112] 4,4'-bis(diphenylamino)quadruphenyl;

[0113] 4,4''-bis[N-(1-anthryl)-N-phenylamino]-p-terphenyl;

[0114] 4,4'-bis[N-(1-coroneryl)-N-phenylamino]biphenyl;

[0115] 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB);

[0116] 4,4'-bis[N-(1-naphthyl)-N-(2-naphthyl)amino]biphenyl (TNB);

[0117] 4,4''-bis[N-(1-naphthyl)-N-phenylamino]p-terphenyl;

[0118] 4,4'-bis[N-(2-naphthacetyl)-N-phenylamino]biphenyl;

[0119] 4,4'-bis[N-(2-naphthyl)-N-phenylamino]biphenyl;

[0120] 4,4'-bis[N-(2-perylenyl)-N-phenylamino]biphenyl;

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

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

[0123] 4,4'-bis[N-(3-acenaphthenyl)-N-phenylamino]biphenyl;

[0124] 4,4'-bis[N-(3-methylphenyl)-N-phenylamino]biphenyl (TPD);

[0125] 4,4'-bis[N-(8-fluoranthryl)-N-phenylamino]biphenyl;

[0126] 4,4'-bis[N-(9-anthryl)-N-phenylamino]biphenyl;

[0127] 4,4'-bis[N-phenyl-N-[4-(1-naphthyl)-phenyl]amino]biphenyl;

[0128] 4,4'-bis[N-phenyl-N-(2-pyrenyl)amino]biphenyl;

[0129] 4,4',4''-tris[(3-methylphenyl)phenylamino]triphenylamine (m-TDATA);

[0130] Bis(4-dimethylamino-2-methylphenyl)-phenylmethane;

[0131] N-phenylcarbazole;

[0132] N,N'-bis[4-([1,1'-biphenyl]-4-ylphenylamino)phenyl]-N,N'-di-1-naphthalenyl-[1,1'-biphenyl]-4,4'-diamine;

[0133] N,N'-bis[4-(di-1-naphthalenylamino)phenyl]-N,N'-di-1-naphthalenyl-[1,1'-biphenyl]-4,4'-diamine;

[0134] N,N'-bis[4-[(3-methylphenyl)phenylamino]phenyl]-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine;

[0135] N,N'-bis[4-(diphenylamino)phenyl]-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine;

[0136] N,N'-di-1-naphthalenyl-N,N'-bis[4-(1-naphthalenylphenylamino)phenyl]-[1,1'-biphenyl]-4,4'-diamine;

[0137] N,N'-di-1-naphthalenyl-N,N'-bis[4-(2-naphthalenylphenylaminophenyl)-[1,1'-biphenyl]-4,4'-diamine;

[0138] N,N,N'-tri(p-tolyl)amine;

[0139] N,N,N',N'-tetra-p-tolyl-4,4'-diaminobiphenyl;

[0140] N,N,N',N'-tetraphenyl-4,4'-diaminobiphenyl;

[0141] N,N,N',N'-tetra-1-naphthyl-4,4'-diaminobiphenyl;

[0142] N,N,N',N'-tetra-2-naphthyl-4,4'-diaminobiphenyl; and

[0143] N,N,N',N'-tetra(2-naphthyl)-4,4''-diamino-p-terphenyl.

[0144] 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.

[0145] 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)

[0146] An optional exciton- or electron-blocking layer may 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. App 20060134460 A1.

Light Emitting Layer

[0147] 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 consists of 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.

[0148] An important relationship for choosing a dye as a 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 may be different. However in some cases, the same host material can be useful for either type of dopant.

[0149] Non-electroluminescent compounds and emitting molecules known to be of use include, but are not limited to, those disclosed in U.S. Pat. No. 4,768,292, U.S. Pat. No. 5,141,671, U.S. Pat. No. 5,150,006, U.S. Pat. No. 5,151,629, U.S. Pat. No. 5,405,709, U.S. Pat. No. 5,484,922, U.S. Pat. No. 5,593,788, U.S. Pat. No. 5,645,948, U.S. Pat. No. 5,683,

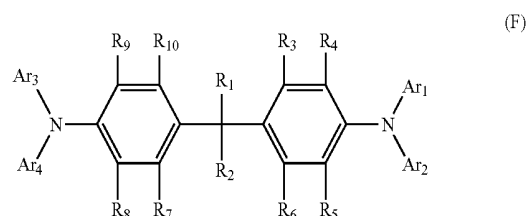
823, U.S. Pat. No. 5,755,999, U.S. Pat. No. 5,928,802, U.S. Pat. No. 5,935,720, U.S. Pat. No. 5,935,721, and U.S. Pat. No. 6,020,078.

a) Phosphorescent Light Emitting Layers

[0150] 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 may 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 may 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.

[0151] 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.

[0152] One desirable host comprises a hole-transporting material of formula (F):



[0153] 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;

[0154] Ar_1 - Ar_4 represent independently selected aromatic groups, for example phenyl groups or tolyl groups;

[0155] R_3 - R_{10} independently represent hydrogen, alkyl, substituted alkyl, aryl, substituted aryl group.

[0156] Examples of suitable materials include, but are not limited to:

[0157] 1,1-Bis(4-(N,N-di-p-tolylamino)phenyl)cyclohexane (TAPC);

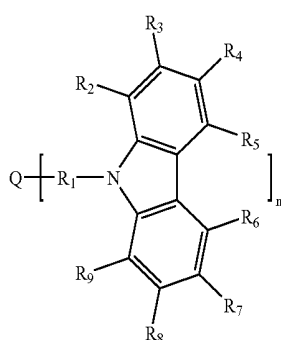
[0158] 1,1-Bis(4-(N,N-di-p-tolylamino)phenyl)cyclopentane;

[0159] 4,4'-(9H-fluoren-9-ylidene)bis[N,N-bis(4-methylphenyl)-benzenamine];

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

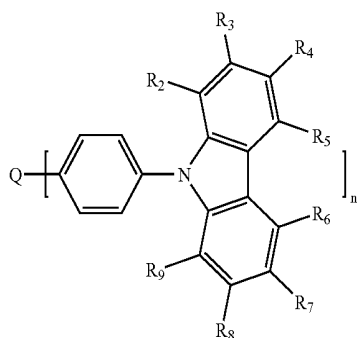
[0161] 1,1-Bis(4-(N,N-di-p-tolylamino)phenyl)-4-methylcyclohexane;

- [0162] 1,1-Bis(4-(N,N-di-p-tolylamino)phenyl)-3-phenylpropane;
 [0163] Bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methane;
 [0164] Bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)ethane;
 [0165] 4-(4-Diethylaminophenyl)triphenylmethane;
 [0166] 4,4'-Bis(4-diethylaminophenyl)diphenylmethane.
 [0167] A useful class of triaryl amines suitable for use as the host includes carbazole derivatives such as those represented by formula (G):



(G)

- [0168] In formula (G), Q independently represents nitrogen, carbon, an aryl group, or substituted aryl group, preferably a phenyl group;
 [0169] R₁ is preferably an aryl or substituted aryl group, and more preferably a phenyl group, substituted phenyl, biphenyl, substituted biphenyl group;
 [0170] R₂ Through R₇ are independently hydrogen, alkyl, phenyl or substituted phenyl group, aryl amine, carbazole, or substituted carbazole;
 [0171] and n is selected from 1 to 4.
 [0172] Another useful class of carbazoles satisfying structural formula (G) is represented by formula (H):



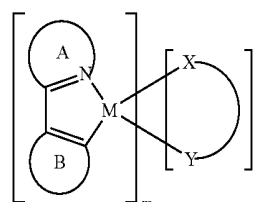
(H)

wherein:

- [0173] n is an integer from 1 to 4;
 [0174] Q is nitrogen, carbon, an aryl, or substituted aryl;
 [0175] R₂ through R₇ are independently hydrogen, an alkyl group, phenyl or substituted phenyl, an aryl amine, a carbazole and substituted carbazole.

[0176] Illustrative of useful substituted carbazoles are the following:

- [0177] 4-(9H-carbazol-9-yl)-N,N-bis[4-(9H-carbazol-9-yl)phenyl]-benzenamine (TCTA);
 [0178] 4-(3-phenyl-9H-carbazol-9-yl)-N,N-bis[4(3-phenyl-9H-carbazol-9-yl)phenyl]-benzenamine;
 [0179] 9,9'-[5'-(4-(9H-carbazol-9-yl)phenyl)][1,1':3',1''-terphenyl]-4,4''-diyl]bis-9H-carbazole.
 [0180] 9,9'-(2,2'-dimethyl[1,1'-biphenyl]-4,4'-diyl)bis-9H-carbazole (CDBP);
 [0181] 9,9'-[1,1'-biphenyl]-4,4'-diylbis-9H-carbazole (CBP);
 [0182] 9,9'-(1,3-phenylene)bis-9H-carbazole (mCP);
 [0183] 9,9'-(1,4-phenylene)bis-9H-carbazole;
 [0184] 9,9',9''-(1,3,5-benzenetriyl)tris-9H-carbazole;
 [0185] 9,9'-(1,4-phenylene)bis[N,N,N',N'-tetraphenyl-9H-carbazole-3,6-diamine];
 [0186] 9-[4-(9H-carbazol-9-yl)phenyl]-N,N-diphenyl-9H-carbazol-3-amine;
 [0187] 9,9'-(1,4-phenylene)bis[N,N-diphenyl-9H-carbazol-3-amine];
 [0188] 9-[4-(9H-carbazol-9-yl)phenyl]-N,N,N',N'-tetraphenyl-9H-carbazole-3,6-diamine.
 [0189] The above classes of hosts suitable for phosphorescent LELs may also be used as hosts in fluorescent LELs as well.
 [0190] Suitable phosphorescent dopants for use in a phosphorescent LEL can be selected from the phosphorescent materials described by formula (J) below:

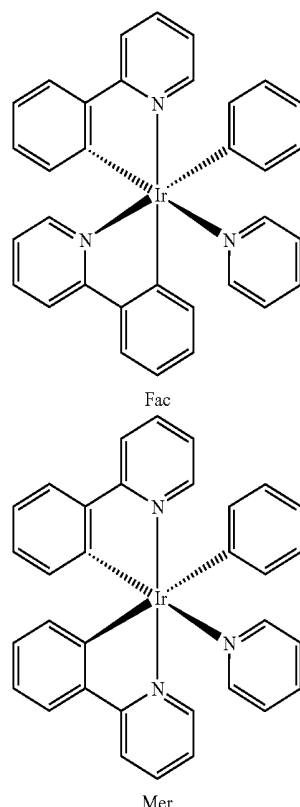


(J)

wherein:

- [0191] A is a substituted or unsubstituted heterocyclic ring containing at least one nitrogen atom;
 [0192] B is a substituted or unsubstituted aromatic or heteroaromatic ring, or ring containing a vinyl carbon bonded to M;
 [0193] X—Y is an anionic bidentate ligand;
 [0194] m is an integer from 1 to 3 and
 [0195] n is an integer from 0 to 2 such that m+n=3 for M=Rh or Ir; or
 [0196] m is an integer from 1 to 2 and n is an integer from 0 to 1 such that m+n=2 for M=Pt or Pd.
 [0197] Compounds according to formula (J) may be referred to as C_nN_m- (or CⁿN^m-) 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) may 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.

[0198] 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 stereodiagrams as facial (fac-) or meridional (mer-) isomers.



[0199] 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'-dimethylindolato-N,C^{2'})Ir(III), tris(1-phenyl-1H-indazolato-N,C^{2'})Ir(III).

[0200] 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.

[0201] 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-phenylisoquinolinato-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 may be conveniently synthesized by the following steps. First, a bis-C,N-cyclometallated diiridium

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 diiridium dihalide complex to form a tris-C,N-cyclometallated complex containing the two different CN-cyclometallating ligands. Desirably, the thus obtained tris-C,N-cyclometallated complex containing the two different C,N-cyclometallating ligands may 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.

[0202] Suitable phosphorescent materials according to formula (J) may 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-diketonates 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).

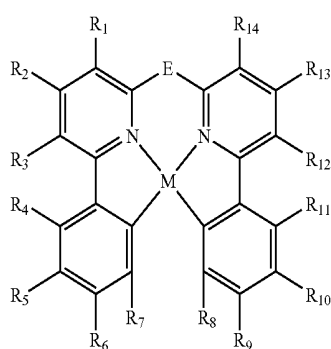
[0203] Other important phosphorescent materials according to formula (J) include C,N-cyclometallated Pt(II) complexes such as cis-bis(2-phenylpyridinato-N,C^{2'})platinum(II), cis-bis(2-(2'-thienyl)pyridinato-N,C^{3'}) platinum(II), cis-bis(2-(2'-thienyl)quinolinato-N,C^{5'}) platinum(II), or (2-(4',6'-difluorophenyl)pyridinato-N,C^{2'}) platinum(II) (acetylacetonate).

[0204] 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-phenyl-pyridinato-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 may 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)(tetakis(1-pyrazolyl)borate).

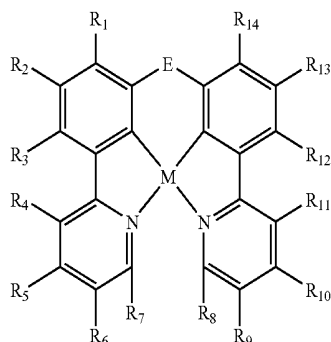
[0205] The central metal atom in phosphorescent materials according to formula (J) may be Rh or Ir ($m+n=3$) and Pd or Pt ($m+n=2$). Preferred metal atoms are Ir and Pt since they tend to give higher phosphorescent quantum efficiencies

according to the stronger spin-orbit coupling interactions generally obtained with elements in the third transition series.

[0206] 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. 6,824,895 B1 and references therein, incorporated in their entirety herein by reference. Phosphorescent materials having tetradentate ligands suitable for use in the present invention are described by the following formulae:



(K)



(L)

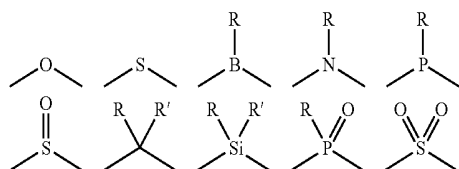
wherein:

[0207] M is Pt or Pd;

[0208] 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 may join to form a ring group;

[0209] 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, may join to form a ring group;

[0210] E represents a bridging group selected from the following:

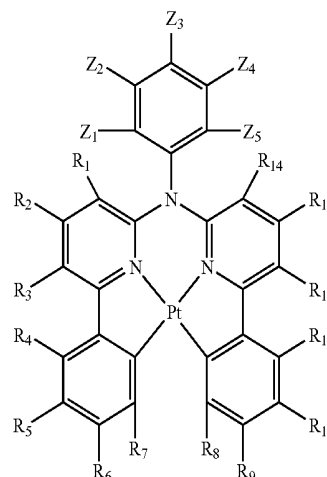


wherein:

[0211] R and R' represent hydrogen or independently selected substituents; provided R and R' may combine to form a ring group.

[0212] One desirable tetradentate C,N-cyclometallated phosphorescent material suitable for use in as the phosphorescent dopant is represented by the following formula:

(M)



wherein:

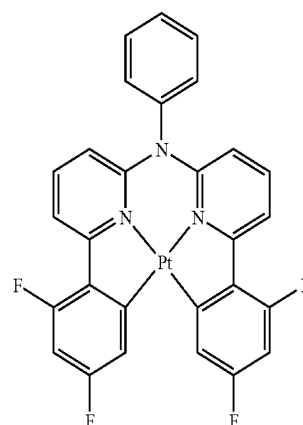
[0213] R¹-R⁷ represent hydrogen or independently selected substituents, provided that R¹ and R², R² and R³, R³ and R⁴, R⁴ and R⁵, R⁵ and R⁶, as well as R⁶ and R⁷ may combine to form a ring group;

[0214] 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 may combine to form a ring group;

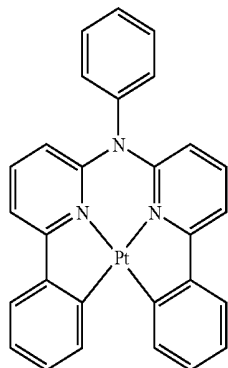
[0215] Z¹-Z⁵ represent hydrogen or independently selected substituents, provided that Z¹ and Z², Z² and Z³, Z³ and Z⁴, as well as Z⁴ and Z⁵ may combine to form a ring group.

[0216] 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.

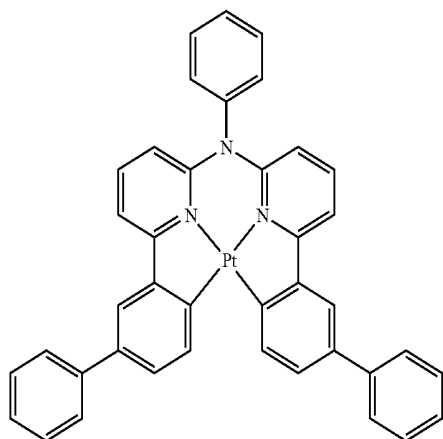
(M-1)



-continued



(M-2)



(M-3)

[0217] Phosphorescent materials having tetradentate C,N-cyclometallating ligands may 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.

[0218] Other phosphorescent materials that do not involve C,N-cyclometallating ligands are known. Phosphorescent complexes of Pt(II), Ir(I), and Rh(I) with maleonitriledithiolate 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)).

[0219] Porphyrin complexes such as 2,3,7,8,12,13,17,18-octaethyl-21H, 23H-porphine platinum(II) are also useful phosphorescent dopant.

[0220] 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)).

[0221] 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) may be attached to one or more host materials. The host materials may further be polymers. The phosphorescent dopant in the first phosphorescent light-emitting layer is selected from green and red phosphorescent materials.

[0222] 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

[0223] 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 may 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.

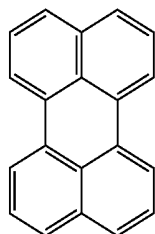
[0224] Typically, a fluorescent LEL includes at least one host and at least one fluorescent dopant. The host may be a hole-transporting material or any of the suitable hosts for phosphorescent dopants as defined above or may be an electron-transporting material as defined below.

[0225] 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.

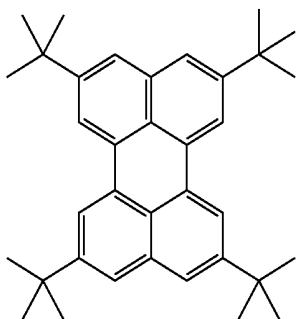
[0226] Useful fluorescent dopants include, but are not limited to, derivatives of anthracene, tetracene, xanthene, perylene, phenylene, dicyanomethylenepyrans compounds, thiopyran compounds, polymethine compounds, pyrylium and thiapyrylium compounds, arylpyrene compounds, arylenevinylene compounds, periflanthene derivatives, indenoperylene derivatives, bis(azanyl)amine boron compounds, bis(azanyl)methane boron compounds, distyrylbenzene derivatives, distyrylbiphenyl derivatives, distyrylamine derivatives and carbostyryl compounds.

[0227] Some fluorescent emitting materials include, but are not limited to, derivatives of anthracene, tetracene, xanthene, perylene, rubrene, coumarin, rhodamine, and quinacridone, dicyanomethylenepyrans compounds, thiopyran compounds, polymethine compounds, pyrylium and thiapyrylium compounds, fluorene derivatives, periflanthene derivatives, indenoperylene derivatives, bis(azanyl)amine boron compounds, bis(azanyl)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:

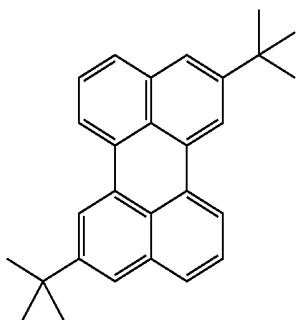
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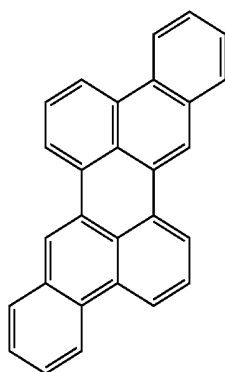
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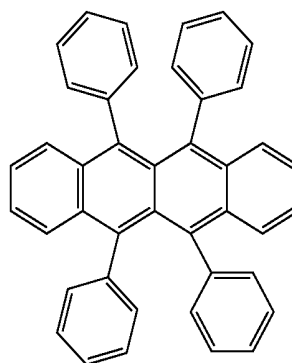
FD-2



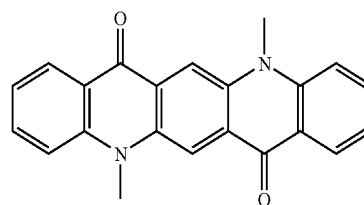
FD-3



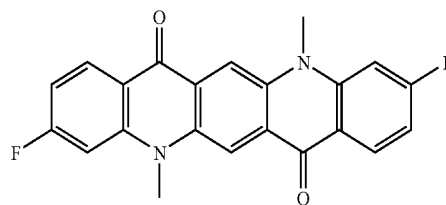
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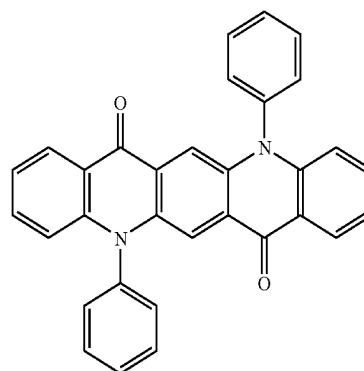
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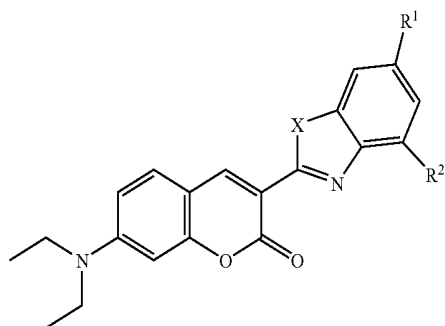
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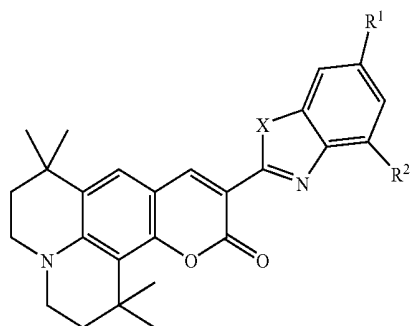
FD-7

FD-8

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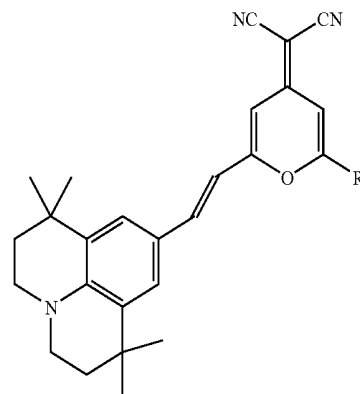


	X	R1	R2
FD-9	O	H	H
FD-10	O	H	Methyl
FD-11	O	Methyl	H
FD-12	O	Methyl	Methyl
FD-13	O	H	t-butyl
FD-14	O	t-butyl	H
FD-15	O	t-butyl	t-butyl
FD-16	S	H	H
FD-17	S	H	Methyl
FD-18	S	Methyl	H
FD-19	S	Methyl	Methyl
FD-20	S	H	t-butyl
FD-21	S	t-butyl	H
FD-22	S	t-butyl	t-butyl

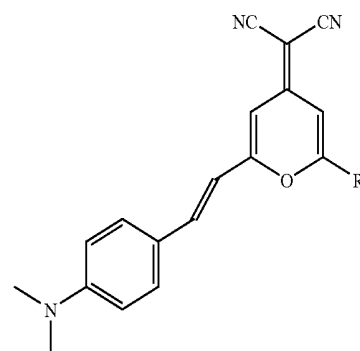


	X	R1	R2
FD-13	O	H	H
FD-24	O	H	Methyl
FD-25	O	Methyl	H
FD-26	O	Methyl	Methyl
FD-27	O	H	t-butyl
FD-28	O	t-butyl	H
FD-29	O	t-butyl	t-butyl
FD-30	S	H	H
FD-31	S	H	Methyl
FD-32	S	Methyl	H
FD-33	S	Methyl	Methyl
FD-34	S	H	t-butyl
FD-35	S	t-butyl	H
FD-36	S	t-butyl	t-butyl

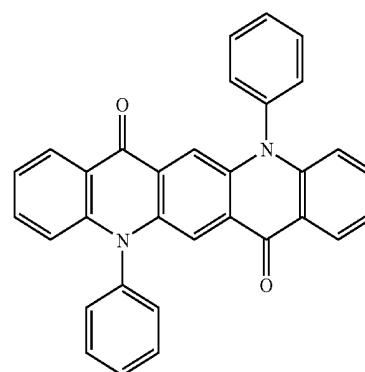
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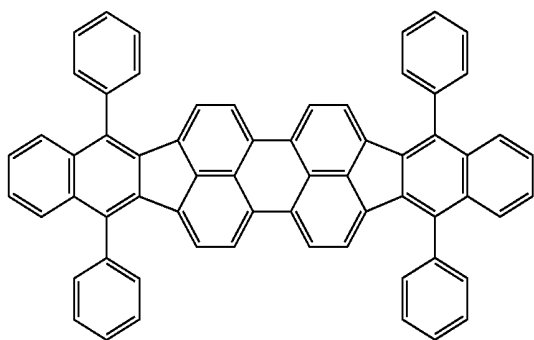
	R
FD-37	phenyl
FD-38	methyl
FD-39	t-butyl
FD-40	mesityl



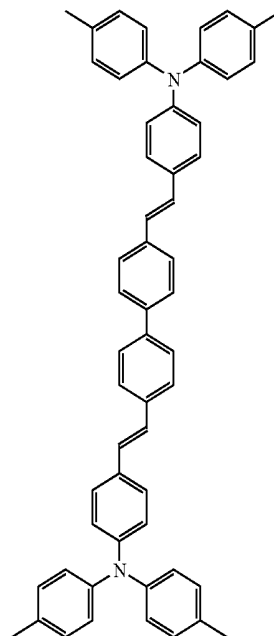
	R
FD-41	phenyl
FD-42	methyl
FD-43	t-butyl
FD-44	mesityl



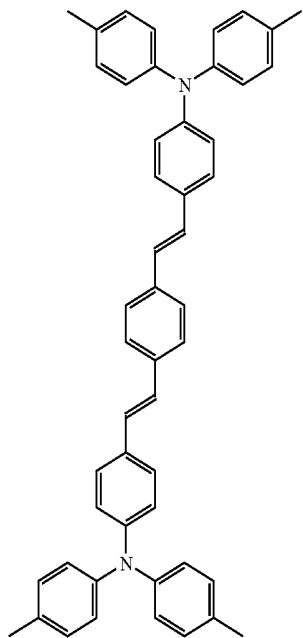
FD-45

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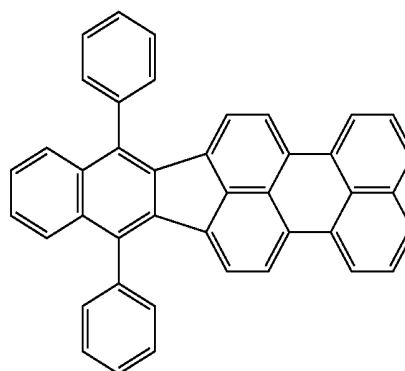
FD-46

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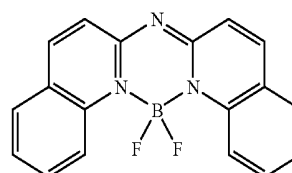
FD-48



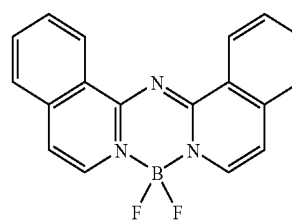
FD-47



FD-49

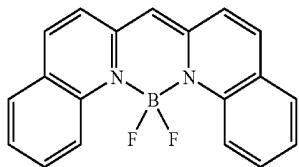


FD-50

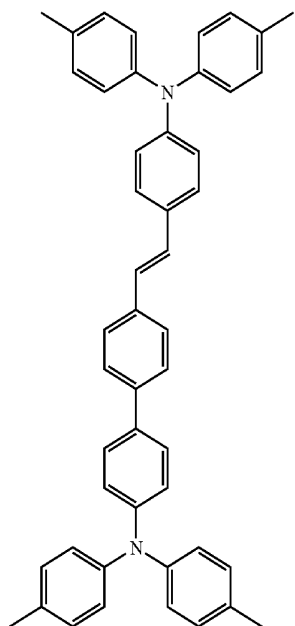


FD-51

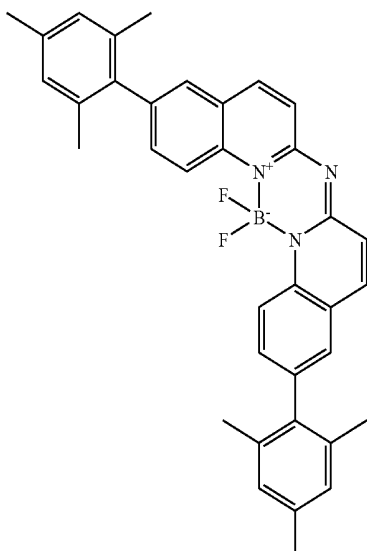
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FD-52

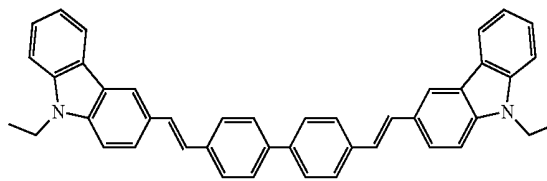


FD-53

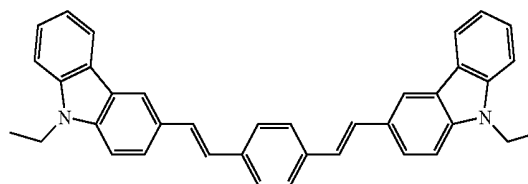


FD-54

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FD-55

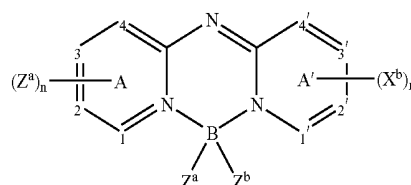


FD-56

[0228] Preferred fluorescent blue dopants may 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.

[0229] A particularly preferred class of blue-emitting fluorescent dopants is represented by Formula (N), known as a bis(azinylo)amine borane complex, and is described in U.S. Pat. No. 6,661,023.

Formula (N)



wherein:

[0230] A and A' represent independent azine ring systems corresponding to 6-membered aromatic ring systems containing at least one nitrogen;

[0231] each X^a and X^b is an independently selected substituent, two of which may join to form a fused ring to A or A';

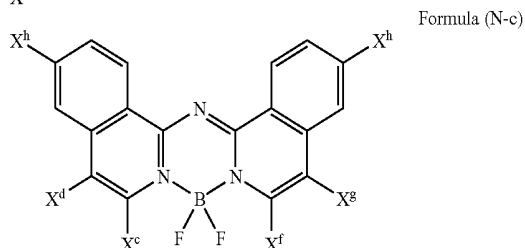
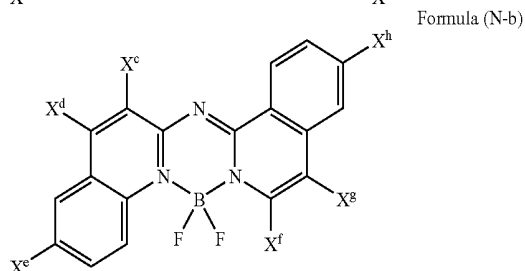
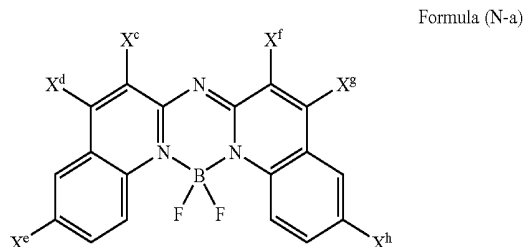
[0232] m and n are independently 0 to 4;

[0233] Z^a and Z^b are independently selected substituents; and

[0234] 1, 2, 3, 4, 1', 2', 3', and 4' are independently selected as either carbon or nitrogen atoms.

[0235] 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. 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).



wherein:

[0236] 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.

[0237] Desirably, the azine rings are either quinolynyl or isoquinolynyl 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.

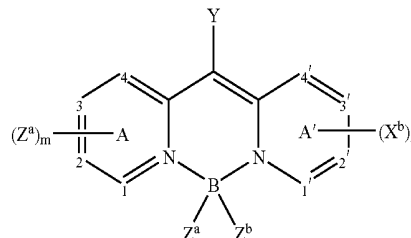
[0238] Of these, compound FD-54 is particularly useful.

[0239] 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, 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", the disclosure of which is incorporated herein.

[0240] Examples of particularly useful green-emitting quinacridones are FD-7 and FD-8.

[0241] Formula (N-d) below represents another class of green-emitting dopants useful in the invention.

Formula (N-d)



wherein:

[0242] A and A' represent independent azine ring systems corresponding to 6-membered aromatic ring systems containing at least one nitrogen;

[0243] each X^a and X^b is an independently selected substituent, two of which may join to form a fused ring to A or A';

[0244] m and n are independently 0 to 4;

[0245] Y is H or a substituent;

[0246] Z^a and Z^b are independently selected substituents; and

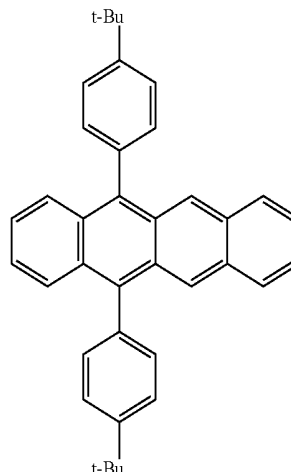
[0247] 1, 2, 3, 4, 1', 2', 3', and 4' are independently selected as either carbon or nitrogen atoms.

[0248] In the device, 1, 2, 3, 4, 1', 2', 3', and 4' are conveniently all carbon atoms. The device may 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.

[0249] The emission wavelength of these compounds may be adjusted to some extent by appropriate substitution around the central bis(azinyl)methene boron group to meet a color aim, namely green. Some examples of useful material are FD-50, FD-51 and FD-52.

[0250] 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. Naphthalene derivative YD-1 (t-BuDPN) below, is an example of a dopant material used as a stabilizer.

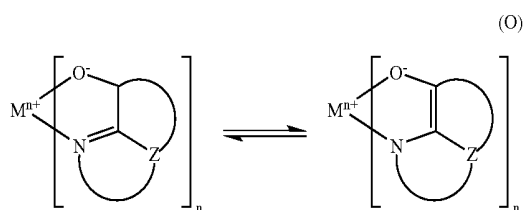
YD-1



[0251] 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).

[0252] Another class of useful dopants are perylene derivatives; for example see U.S. Pat. No. 6,689,493. A specific examples is FD-46.

[0253] 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.



wherein:

[0254] M represents a metal;

[0255] n is an integer of from 1 to 4; and

[0256] Z independently in each occurrence represents the atoms completing a nucleus having at least two fused aromatic rings.

[0257] 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.

[0258] 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.

[0259] Illustrative of useful chelated oxinoid compounds are the following:

[0260] O-1: Aluminum trisoxine [alias, tris(8-quinolinolato)aluminum(III)]

[0261] O-2: Magnesium bisoxine [alias, bis(8-quinolinolato)magnesium(II)]

[0262] O-3: Bis[benzo{f}-8-quinolinolato]zinc (II)

[0263] O-4: Bis(2-methyl-8-quinolinolato)aluminum(III)-μ-oxo-bis(2-methyl-8-quinolinolato)aluminum(III)

[0264] O-5: Indium trisoxine [alias, tris(8-quinolinolato)indium]

[0265] O-6: Aluminum tris(5-methyloxine) [alias, tris(5-methyl-8-quinolinolato)aluminum(III)]

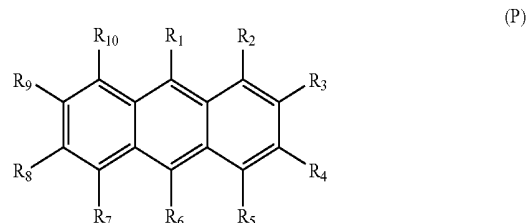
[0266] O-7: Lithium oxine [alias, (8-quinolinolato)lithium(I)]

[0267] O-8: Gallium oxine [alias, tris(8-quinolinolato)gallium(III)]

[0268] O-9: Zirconium oxine [alias, tetra(8-quinolinolato)zirconium(IV)]

[0269] O-10: Bis(2-methyl-8-quinolinato)-4-phenylphenolatoaluminum (III)

[0270] Anthracene derivatives according to formula (P) are also useful host materials in the LEL:

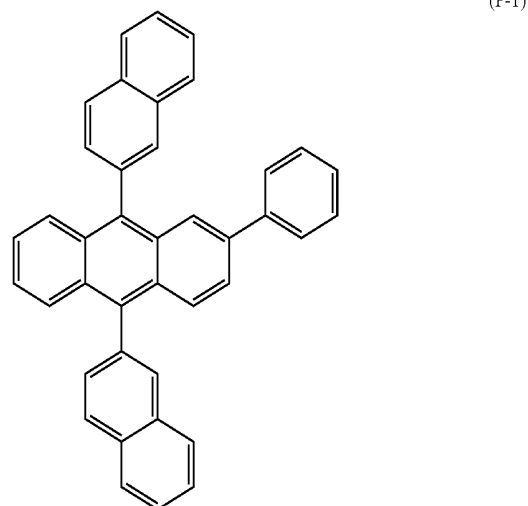


wherein:

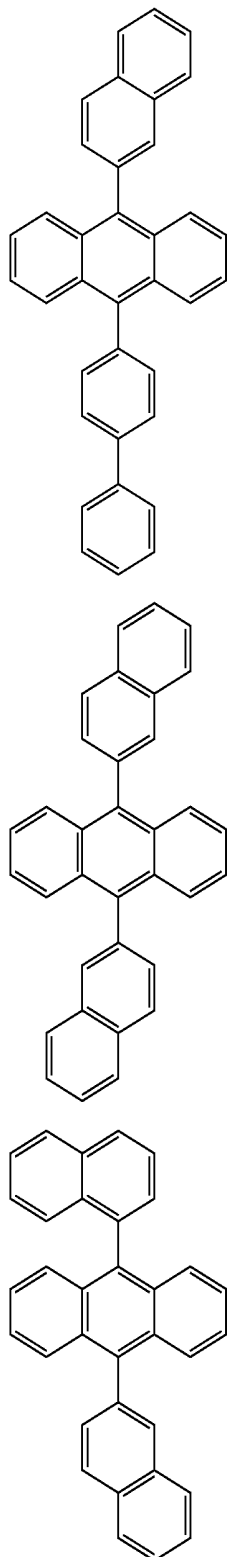
[0271] R₁-R₁₀ are independently chosen from hydrogen, alkyl groups from 1-24 carbon atoms or aromatic groups from 1-24 carbon atoms. Particularly preferred are compounds where R₁ and R₆ are phenyl, biphenyl or naphthyl, R₃ is phenyl, substituted phenyl or naphthyl and R₂, R₄, R₅, R₇-R₁₀ are all hydrogen. Such anthracene hosts are known to have excellent electron transporting properties.

[0272] 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 compound 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.

[0273] Some illustrative examples of suitable anthracenes are:



-continued



Spacer Layer

[0274] Spacer layers, when present, are located in direct contact to a LEL. They may 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 may 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)

[0275] 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) (BALq). Metal complexes other than BALq are also known to block holes and excitons as described in US 20030068528. When a hole-blocking layer is used, its thickness can be between 2 and 100 nm and suitably between 5 and 10 nm.

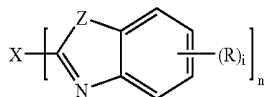
Electron Transporting Layer

[0276] The electron-transporting layer **136** may be composed only of the mixed cluster compound or may be a mixture of the cluster compound with other appropriate materials. The % volume ratio of mixed cluster compound to additional material can be anywhere from 1% to 99%, more suitably 10% to 90% and most desirably, 30 to 70%. The cluster compound or any additional materials used may be the same or different than used as a host in the LEL or the spacer layers. The ETL **136** may be optionally split into sublayers.

[0277] The anthracene class of electron-transporting materials are particularly desirable in combination with the compounds of the invention. These anthracene electron transporting derivatives are represented by Formula (P) as described above in connection with host materials for a LEL.

[0278] In addition to any of the electron-transporting materials previously described, any other materials known to be suitable for use in the ETL may be used. Included are, but are not limited to, chelated oxinoid compounds, fluoranthene 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.

[0279] 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):



(Q)

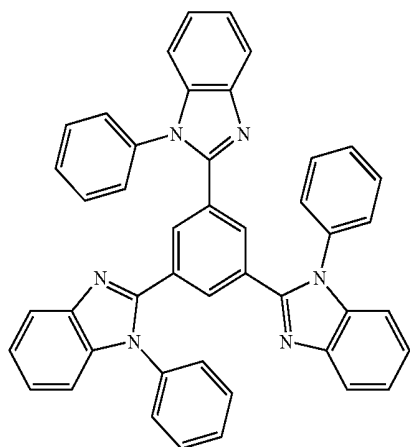
[0280] In formula (Q), n is selected from 2 to 8 and i is selected from 1-5;

[0281] Z is independently O, NR or S;

[0282] 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, quinoliny and other heterocyclic systems; or halo such as chloro, fluoro; or atoms necessary to complete a fused aromatic ring; and

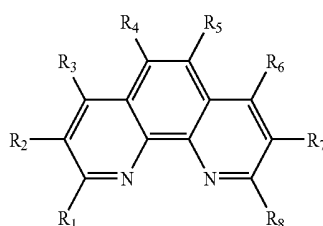
[0283] X is a linkage unit consisting of carbon, alkyl, aryl, substituted alkyl, or substituted aryl, which conjugately or unconjugately connects the multiple benzazoles together.

[0284] 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:



(Q-1)

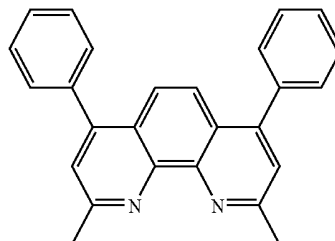
[0285] Another suitable class of the electron-transporting materials includes various substituted phenanthrolines as represented by formula (R):



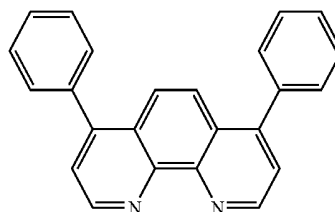
(R)

[0286] In formula (R), R₁-R₈ are independently hydrogen, alkyl group, aryl or substituted aryl group, and at least one of R₁-R₈ is aryl group or substituted aryl group.

[0287] 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)).

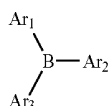


(R-1)



(R-2)

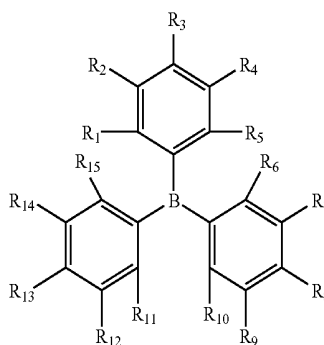
[0288] Suitable triarylboranes that function as an electron-transporting material may be selected from compounds having the chemical formula (S):



(S)

wherein:

[0289] Ar₁ to Ar₃ are independently an aromatic hydrocarbocyclic group or an aromatic heterocyclic group which may have a substituent. It is preferable that compounds having the above structure are selected from formula (S-1):

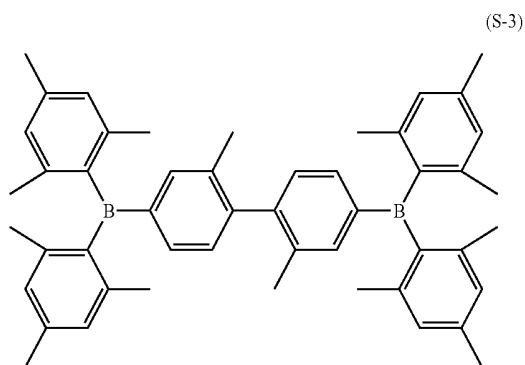
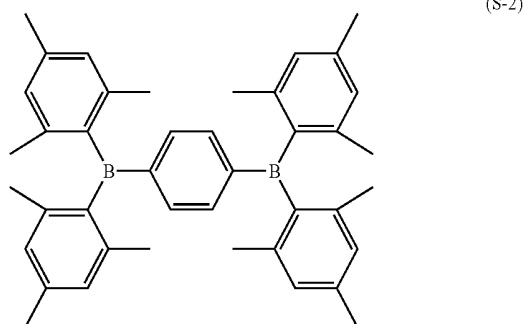
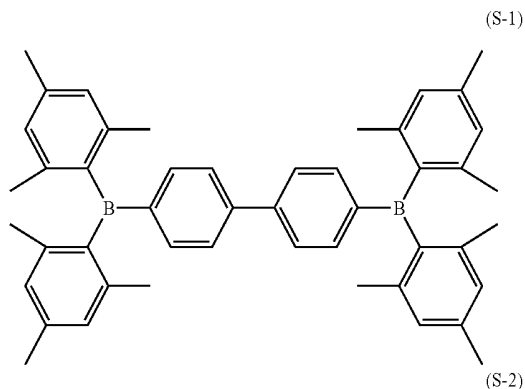


(S-1)

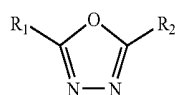
wherein:

[0290] R₁-R₁₅ are independently hydrogen, fluoro, cyano, trifluoromethyl, sulfonyl, alkyl, aryl or substituted aryl group.

[0291] Specific representative embodiments of the triarylboranes include:



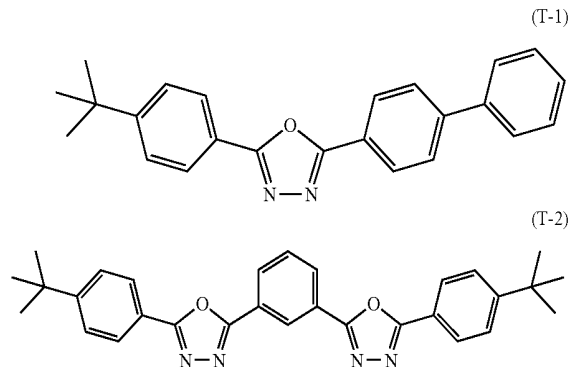
[0292] The electron-transporting material may also be selected from substituted 1,3,4-oxadiazoles of formula (T):



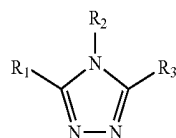
wherein:

[0293] 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, thienyl, pyridyl, quinolyl and other heterocyclic systems; or halo such as chloro, fluoro; or atoms necessary to complete a fused aromatic ring.

[0294] Illustrative of the useful substituted oxadiazoles are the following:

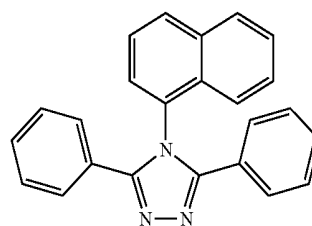


[0295] The electron-transporting material may also be selected from substituted 1,2,4-triazoles according to formula (U):



wherein:

[0296] 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):



[0297] The electron-transporting material may also be selected from substituted 1,3,5-triazines. Examples of suitable materials are:

[0298] 2,4,6-tris(diphenylamino)-1,3,5-triazine;

[0299] 2,4,6-tricarbazolo-1,3,5-triazine;

[0300] 2,4,6-tris(N-phenyl-2-naphthylamino)-1,3,5-triazine;

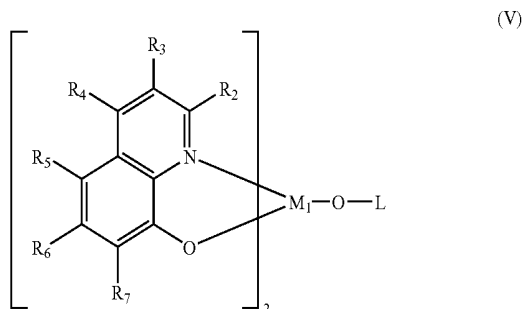
[0301] 2,4,6-tris(N-phenyl-1-naphthylamino)-1,3,5-triazine;

[0302] 4,4',6,6'-tetraphenyl-2,2'-bi-1,3,5-triazine;

[0303] 2,4,6-tris([1,1':3',1''-terphenyl]-5'-yl)-1,3,5-triazine.

[0304] 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.

[0305] 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 (V).



[0306] In Formula (V), 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 , may combine to form a ring group. L is an aromatic moiety linked to the aluminum by oxygen, which may be substituted with substituent groups such that L has from 6 to 30 carbon atoms.

[0307] Illustrative of useful chelated oxinoid compounds for use in the ETL is Aluminum(III) bis(2-methyl-8-hydroxyquinoline)4-phenylphenolate [alias, Balq].

[0308] The thickness of the ETL is in the range of from 5 nm to 200 nm, preferably, in the range of from 10 nm to 150 nm.

Electron Injection Layer

[0309] In some embodiments of the invention, the cluster compound is located in the EIL **138**. Other suitable materials can also be used in the EIL. For example, the EIL may be 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.

[0310] The host in the EIL may 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.

[0311] The n-type dopant in the n-type doped EIL may 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, Th, 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.

[0312] The thickness of the EIL is typically less than 20 nm, and preferably in the range of less than 5 nm. When an n-type doped EIL is employed, the thickness is typically less than 200 nm, and preferably in the range of less than 150 nm.

Cathode

[0313] 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 EL 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.

[0314] 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.

Substrate

[0315] 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, depend-

ing 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

[0316] 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. No. 5,851,709 and U.S. Pat. No. 6,066,357) and inkjet method (U.S. Pat. No. 6,066,357).

[0317] 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.

[0318] 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, result in potentially nonuniform vapor-deposited organic layers formed on a substrate.

[0319] 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.

[0320] 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.

[0321] One preferred method for depositing the materials of the present invention is described in US 2004/0255857 and U.S. 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 patent applications: U.S. Ser. No. 10/784,585; U.S. Ser. No. 10/805,980; U.S. Ser. No. 10/945,940; U.S. Ser. No. 10/945,941; U.S. Ser. No. 11/050,924; and U.S. Ser. No. 11/050,934. Using this second method, each material may be evaporated using different source evaporators or the solid materials may be mixed prior to evaporation using the same source evaporator.

Encapsulation

[0322] Most OLED devices are sensitive to moisture and/or 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

[0323] For fill 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.

[0324] 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 may be specifically provided over the OLED or as part of the OLED.

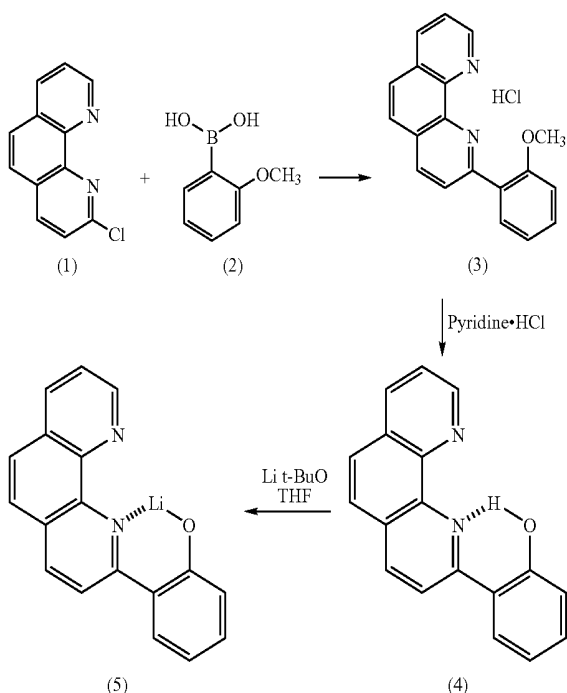
[0325] OLED devices of this invention can employ various well-known optical effects in order to enhance its properties if desired. This includes optimizing layer thicknesses to yield maximum light transmission, providing dielectric mirror structures, replacing reflective electrodes with light-absorbing 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 may be specifically provided over the cover or as part of the cover.

[0326] Embodiments of the invention may provide EL devices that have good luminance efficiency, good operational stability, and reduced drive voltages. They may have lower power consumption requirements and, when used with a battery, provide longer battery lifetimes.

EXPERIMENTAL EXAMPLES

[0327] Schematically the synthesis of lithium 2-(1,10-phenanthrolin-2-yl)-phenolate (5), the starting material needed for the preparation of Inv-1, is outlined in Scheme 1.

Scheme 1



2-Chloro-1,10-Phenanthroline, (1)

[0328] 2-Chloro-1,10-phenanthroline was prepared from 1,10-phenanthroline following the procedure of B. E. Halcrow, Wm. O. Kermack; Journal of the Chemical Society (1946), 155-7 and was isolated in satisfactory yield.

2-(2-Methoxyphenyl)-1,10-Phenanthroline Hydrochloride Chloride, (3)

[0329] 2-Chloro-1,10-phenanthroline (5.9 g, 27.5 mMole), 2-methoxyphenylboronic acid (2) (5 g, 33 mMole), tetrakis

(triphenylphosphine)palladium(0) (1 g, 0.825 mMole), 2M- Na_2CO_3 (33 mL, 66 mMole) and ethanol (8 mL) were suspended in toluene (70 mL) and heated to 100° C. with good stirring for 24 hours. At the end of this period the reaction was cooled, diluted with ethyl acetate (200 mL) and the aqueous layer run off. The organic layer was washed with water (3×100 mL) and intermittently with brine to break up any emulsion formed. The organic layer was filtered through a pad of celite, dried over MgSO_4 , filtered and concentrated to an oil. The oil was dissolved in CH_2Cl_2 (20 mL) and diethyl ether (150 mL) added. With good stirring, a 20% solution of concentrated HCl in ethanol (20 mL) was added. The yellow 2-(2-methoxyphenyl)-1,10-phenanthroline hydrochloride chloride was filtered off, washed with ether and air-dried. Yield 9.7 g.

2-(2-Hydroxyphenyl)-1,10-Phenanthroline, (4)

[0330] Concentrated HCl (17.6 mL) and pyridine (16 mL) were mixed together at room temperature. The resulting solution was heated on a sand bath while passing nitrogen over the surface of the solution and the distillate collected in a Dean-Stark trap. The internal temperature of the reaction was allowed to reach 215-220° C. over a 1 hour period. The solution was allowed to cool to 140° C. and 2-(2-methoxyphenyl)-1,10-phenanthroline hydrochloride chloride (6 g, 18.59 mMole) then added. With good stirring, the temperature of the resulting solution was allowed to rise back again to 215-220° C. and held at this temperature for 3 hours. The solution was then cooled to 100° C. and treated carefully with water (10 mL), then finally poured into an excess of water (70 mL) to precipitate a gummy solid. With good stirring, the pH of the solution was adjusted to 6-7 with solid Na_2CO_3 . The orange solid was filtered off, washed well with water and dried. Yield of the 2-(2-hydroxyphenyl)-1,10-phenanthroline was 4.6 g.

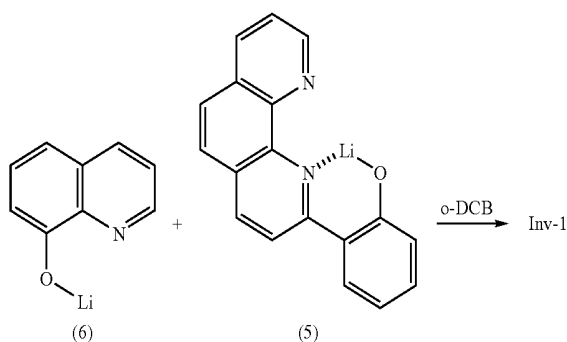
Lithium 2-(1,10-Phenanthrolin-2-yl)-Phenolate (5)

[0331] 2-(2-Hydroxyphenyl)-1,10-phenanthroline (4) (20 g, 73.45 mMole) was dissolved in tetrahydrofuran and with good stirring treated with lithium t-butoxide (5.65 g, 88.14 mMole). The precipitated product was stirred at room temperature in the reaction mixture for 1 hour to complete the reaction. The lithium 2-(1,10-phenanthrolin-2-yl)-phenolate was filtered off, washed well with diethyl ether and air-dried. Yield 21 g.

Example 1

(Route A):—Synthesis of Inventive Compound, Inv-1 in Solvent

[0332]



[0333] A mixture of lithium quinolate, (6) (3 g, 19.86 mMole), and lithium 2-(1,10-phenanthroline-2-yl)-phenolate, (5) (2.76 g, 9.92 mMole), in ortho-dichlorobenzene (50 mL) was gently refluxed for 45 minutes. The pale yellow solution was cooled and crystallization induced by scratching the wall of the flask. The crystals of Inv-1 were filtered off, washed well with ether and dried. Yield of product Inv-1, 4.0 g. Before use in device fabrication, Inv-1 was sublimed at 290° C./10⁻³ mm Hg.

Example 1

(Route B):—Alternative synthesis of Inventive Compound, Inv-1 via Direct Sublimation

[0334] Lithium quinolate, (5) (1.5 g, 9.93 mMole), and lithium 2-(1,10-phenanthroline-2-yl)-phenolate, (6) (1.4 g, 4.96 mMole) were ground to an intimate mixture in a mortar and pestle. This material mixture was then sublimed at 290° C./10⁻³ mm Hg to give 1.5 g of Inv-1.

Example 2

(Route B):—Synthesis of Inventive Compound, Inv-5 via Direct Sublimation

[0335] Lithium pentafluorophenolate (1g, 1.32 mMole), and lithium 2-((1,10-phenanthroline-2-yl)-phenolate, (6) (0.37 g, 0.66 mMole) were ground to an intimate mixture in a mortar and pestle. This material mixture was then sublimed at 235° C./10⁻³ mm Hg to give 0.2 g of Inv-5.

Example 3

Preparation of Devices 3.1 through 3.4

[0336] A series of EL devices (3.1 through 3.4) were constructed in the following manner:

[0337] 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.

[0338] 2. Over the ITO was deposited a 1 nm fluorocarbon (CFx) hole-injecting layer (HIL) by plasma-assisted deposition of CHF₃ as described in U.S. Pat. No. 6,208,075.

[0339] 3. Next a layer of hole-transporting material 4,4'-Bis [N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) was deposited to a thickness of 75 nm.

[0340] 4. A 20 nm light-emitting layer (LEL) corresponding to the host material P-1 and 1.5% by volume of FD-54 was then deposited.

[0341] 5. A 35 nm electron-transporting layer (ETL) of a 1:1 mixture of Li₆Q₆ and P-1 was vacuum-deposited over the LEL.

[0342] 6. An electron-injecting layer (EIL) of Li₆Q₆ or Inv-1 as shown in Table 1, was vacuum deposited onto the ETL.

[0343] 7. And finally, a 100 nm layer of aluminum was deposited onto the EIL, to form the cathode.

[0344] 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.

[0345] The devices thus formed were tested for luminous efficiency at an operating current of 20 mA/cm² and the results are reported in Table 1. T₇₀ is the time taken for the initial luminance to drop to 70% of the original value.

TABLE 1

Results from Devices 3.1-3.4				
Example (Type)	EIL (Thickness nm)	Drive Volt. (Volts)	Efficiency (cd/A)	T ₇₀ Fade @80 mA/cm ² (hours)
3.1 (Comparative)	Li ₆ Q ₆ (2)	4.6	6.5	38
3.2 (Comparative)	Li ₆ Q ₆ (3)	4.8	5.9	28
3.3 (Inventive)	Inv-1 (2)	4.3	6.8	82
3.4 (Inventive)	Inv-1 (3)	4.3	6.8	72

[0346] From Table 1 it can be seen that when the ETL is a 1:1 mixture of Li₆Q₆ and P-1, that at different EIL thicknesses, Inv-1 gives not only lower drive voltages but also higher luminance efficiency and better T₇₀ fade performances in comparison to the Li₆Q₆ comparisons.

Example 4

Preparation of Devices 4.1 through 4.4

[0347] A series of EL devices (4.1 through 4.4) were constructed in a similar manner to Example 3, except that Inv-1 was used in place of Li₆Q₆ for the ETL mixture of step 5. The results are reported in Table 2.

TABLE 2

Results from Devices 4.1-4.4				
Example (Type)	EIL (Thickness nm)	Drive Volt. (Volts)	Efficiency (cd/A)	T ₇₀ Fade @80 mA/cm ² (hours)
4.1 (Comparative)	Li ₆ Q ₆ (2 nm)	4.6	6.5	38
4.2 (Comparative)	Li ₆ Q ₆ (3 nm)	4.8	5.9	28
4.1 (Inventive)	Li ₆ Q ₆ (2 nm)	5.2	6.4	103
4.2 (Inventive)	Inv-1 (1 nm)	4.8	5.8	117
4.3 (Inventive)	Inv-1 (2 nm)	4.7	5.9	104
4.4 (Inventive)	Inv-1 (3 nm)	4.6	6.0	119

[0348] From Table 2 it can be seen that when the ETL is a 1:1 mixture of Inv-1 and P-1 and the EIL is either Li₆Q₆ or Inv-1, the compounds of the invention give similar drive voltage and luminance efficiency, but give much superior T₇₀ fade performances than the Li₆Q₆ comparisons of Examples 2.1 and 2.2.

Example 5

Preparation of Devices 5.1 through 5.4

[0349] A series of EL devices (5.1 through 5.4) were constructed in a similar manner to Example 3, except that Inv-1 was used for the ETL in Examples 5.1 through 5.3 and Li₆Q₆ was used for the comparison in Examples 5.4 through 5.6, of step 5. LiF (5 nm) was employed in the EIL in step 6. The results are reported in Table 3.

TABLE 3

Results from Devices 5.1-5.6			
Example (Type)	ETL (Thickness nm)	Drive Volt. (Volts)	Efficiency (cd/A)
5.1 (Comparative)	Li ₆ Q ₆ (10 nm)	6.6	0.25
5.2 (Comparative)	Li ₆ Q ₆ (20 nm)	7.7	0.76
5.3 (Comparative)	Li ₆ Q ₆ (30 nm)	8.6	1.3
5.4 (Inventive)	Inv-1 (10 nm)	5.1	2.05
5.5 (Inventive)	Inv-1 (20 nm)	5.7	2.47
5.6 (Inventive)	Inv-1 (30 nm)	6.4	2.79

[0350] From Table 3 it can be seen that when the EIL is LiF and the ETL is Inv-1, the compounds of the invention give lower drive voltage and higher luminance efficiency than the Li₆Q₆ comparisons, at various ETL thicknesses.

Example 6

Preparation of Devices 6.1 through 6.9

[0351] A series of EL devices (6.1 through 6.9) were constructed in the manner detailed below. Examples 6.1 through 6.3 are comparison devices that incorporate Li₆Q₆ for the EIL, while 6.4 through 6.6 are one set of inventive examples with Inv-1 as the EIL, and 6.7 through 6.9 are another set of inventive examples with Inv-2 as the EIL. For comparison, each set contains the same levels of EIL. The results are reported in Table 4.

[0352] 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.

[0353] 1. Over the ITO was deposited a 1 nm fluorocarbon (CFx) hole-injecting layer (HIL1) by plasma-assisted deposition of CHF₃ as described in U.S. Pat. No. 6,208,075.

[0354] 2. A hole-injecting layer (HIL2) of dipyrzazino[2,3-f:2',3'-h]quinoxalinehexacarbonitrile was deposited to a thickness of 10 nm.

[0355] 3. Next a layer of hole-transporting material 4,4'-Bis [N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) was deposited to a thickness of 85 nm.

[0356] 4. A 20 nm light-emitting layer (LEL) of 1.5% FD-54 in P-1 was then deposited.

[0357] 5. A 35 nm electron-transporting layer (ETL) of a (1:1) mixture of Li₆Q₆ and P-1 was vacuum-deposited over the LEL.

[0358] 6. A layer of electron-injecting material (EIL) was vacuum deposited onto the ETL as described in Table 4.

[0359] 7. And finally, a 100 nm layer of aluminum, to form a cathode layer.

[0360] 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.

[0361] The devices thus formed were tested for luminous efficiency at an operating current of 20 mA/cm² and the results are reported in Table 4.

TABLE 4

Results from Devices 6.1-6.9			
Example (type)	EIL (Thickness nm)	Drive Volt. (Volts)	Efficiency (cd/A)
6.1 (Comparative)	Li ₆ Q ₆ (2 nm)	5.2	6.6
6.2 (Comparative)	Li ₆ Q ₆ (3 nm)	6.3	5.2
6.3 (Comparative)	Li ₆ Q ₆ (4 nm)	8.3	3.7
6.4 (Inventive)	Inv-1 (2 nm)	5.1	6.5
6.5 (Inventive)	Inv-1 (3 nm)	5.0	6.8
6.6 (Inventive)	Inv-1 (4 nm)	4.7	6.9
6.7 (Inventive)	Inv-2 (2 nm)	5.1	6.1
6.8 (Inventive)	Inv-2 (3 nm)	4.8	6.6
6.9 (Inventive)	Inv-2 (4 nm)	4.9	6.7

[0362] From Table 4 it can be seen that on average, the devices incorporating the compounds of the invention in the EIL, Inv-1 and Inv-2, give superior performance, in terms of lower drive voltage and higher luminance, than the comparison devices with Li₆Q₆ as the EIL. Furthermore, at the higher EIL levels, the superiority of Inv-1 and Inv-2 is plainly evident.

[0363] 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. The patents and other publications referred to are incorporated herein in their entirety.

Parts List

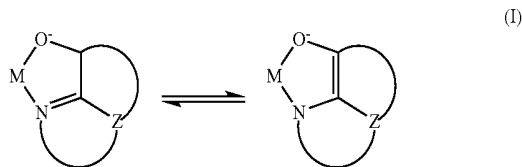
- [0364] 100 LED
- [0365] 110 Substrate
- [0366] 120 Anode
- [0367] 130 Hole-Injecting layer (HIL)
- [0368] 132 Hole-Transporting layer (HTL)
- [0369] 134 Light-Emitting layer (LEL)
- [0370] 135 Hole-Blocking Layer (HBL)
- [0371] 136 Electron-Transporting layer (ETL)
- [0372] 138 Electron-Injecting layer (EIL)
- [0373] 140 Cathode
- [0374] 150 Voltage/Current Source
- [0375] 160 Electrical Connectors

1. An OLED device comprising a cathode, an anode, and having therebetween a layer containing a neutrally charged mixed cluster compound comprising first and second subunits with the first subunit comprising an alkali metal salt of a nitrogen containing heterocyclic ligand bearing an anionic hydroxy group and the second subunit comprising an organic alkali metal salt different than the first subunit, wherein the alkali metal cations of both subunits are the same.

2. The OLED device of claim 1 further comprising a light-emitting layer located between the cathode and anode and wherein the layer containing the cluster compound is located between the light-emitting layer and the cathode.

3. The OLED device of claim 1 wherein the wherein the alkali metal cations are lithium.

4. The OLED device of claim 1 wherein the first subunit of the cluster compound is according to formula (I):

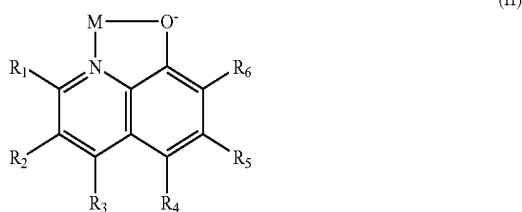


wherein:

M represents an alkali metal cation; and

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

5. The OLED device of claim 4 wherein the first subunit of the cluster compound is according to formula (II):

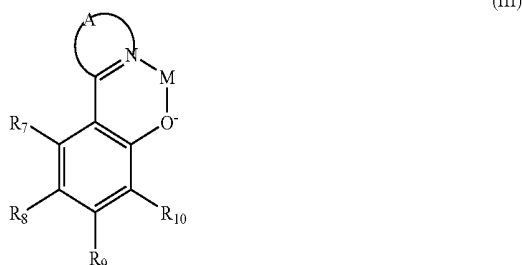


wherein:

M represents an alkali metal cation; and

R₁-R₆ individually represents a hydrogen, or an alkyl, alkenyl, alkynyl, alkoxy, alkylthio, amino, aryl, aryloxy, arylthio, cyano or heterocyclic group with the proviso that any two adjacent R groups may be joined together to form an annulated saturated or aromatic ring system.

6. The OLED device of claim 1 wherein the first subunit is according to formula (III):



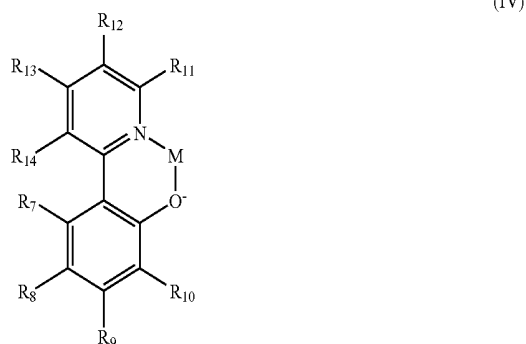
wherein:

M represents an alkali metal cation;

R₇-R₁₀ individually represents a hydrogen, alkyl, alkenyl, alkynyl, alkoxy, alkylthio, amino, aryl, aryloxy, arylthio, cyano or heterocyclic group with the proviso that any two adjacent R groups or specifically, R₇ and A may be joined together to form an annulated saturated or aromatic ring system; and

A represent the atoms necessary to complete a 5, 6, 7 or 8 member ring system.

7. The OLED device of claim 6 wherein first subunit is according to formula (IV):

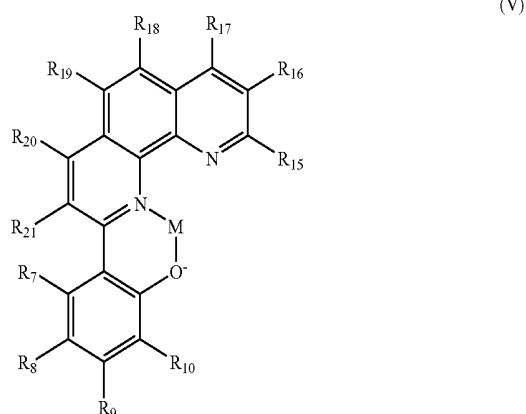


wherein:

M represents an alkali metal cation; and

R₇-R₁₄ individually represents a hydrogen, alkyl, alkenyl, alkynyl, alkoxy, alkylthio, amino, aryl, aryloxy, arylthio, cyano or heterocyclic group with the proviso that any two adjacent R groups or specifically, R₇ and R₁₄ may be joined together to form an annulated saturated or aromatic ring system.

8. The OLED device of claim 7 wherein the first subunit is according to formula (V):

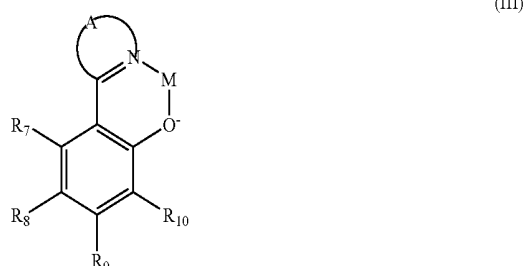


wherein:

M represents an alkali metal cation; and

R₇-R₁₀ and R₁₅-R₂₁ individually represents a hydrogen, alkyl, alkenyl, alkynyl, alkoxy, alkylthio, amino, aryl, aryloxy, arylthio, cyano or heterocyclic group with the proviso that any two adjacent R groups or specifically, R₇ and R₂₁ may be joined together to form an annulated saturated or aromatic ring system.

9. The OLED device of claim 4 wherein the second subunit is formula (III):



wherein:

M represents an alkali metal cation;

R₇-R₁₀ individually represents a hydrogen, alkyl, alkenyl, alkynyl, alkoxy, alkylthio, amino, aryl, aryloxy, arylthio, cyano or heterocyclic group with the proviso that any two adjacent R groups or specifically, R₇ and A may be joined together to form an annulated saturated or aromatic ring system; and

A represent the atoms necessary to complete a 5, 6, 7 or 8 member ring system.

10. The OLED device of claim 1 wherein the organic alkali metal salt of the second subunit is either:

(i) an alkali metal salt of a nitrogen containing heterocyclic ligand bearing an anionic hydroxy group different than the first subunit; or

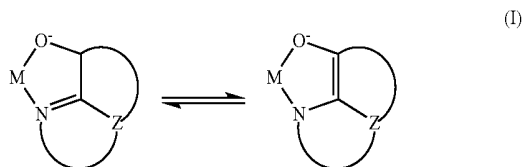
(ii) an alkali metal salt of a phenol or naphthol.

11. A neutrally charged mixed cluster compound comprising first and second subunits with the first subunit comprising an alkali metal salt of a nitrogen containing heterocyclic ligand bearing an anionic hydroxy group and the second subunit comprising an organic alkali metal salt different from the first subunit, wherein the alkali metal cations of both subunits are the same.

12. The cluster compound of claim 11 wherein the alkali metal cations are lithium.

13. The cluster compound of claim 11 wherein the organic alkali metal salt of the second subunit is an alkali metal salt of a nitrogen containing heterocyclic ligand bearing an anionic hydroxy group.

14. The cluster compound of claim 11 wherein the first subunit is according to formula (I):

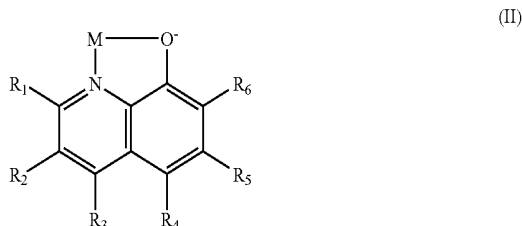


wherein:

M represents an alkali metal cation; and

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

15. The cluster compound of claim 14 wherein the first subunit is according to formula (II):



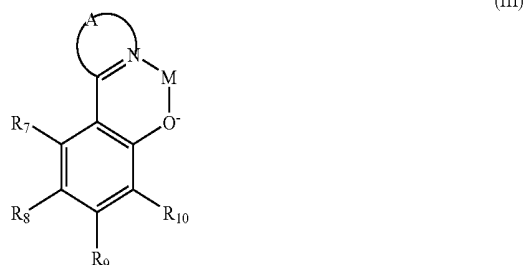
wherein:

M represents an alkali metal cation; and

R₁-R₆ individually represents a hydrogen, alkyl, alkenyl, alkynyl, alkoxy, alkylthio, amino, aryl, aryloxy, arylthio, cyano or heterocyclic group with the proviso

that any two adjacent R groups may be joined together to form an annulated saturated or aromatic ring system.

16. The cluster compound of claim 11 wherein the first subunit is according to formula (III):

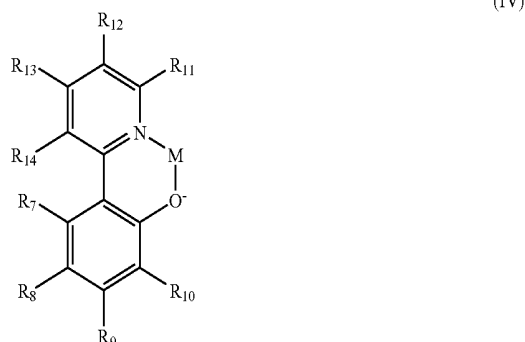


wherein:

M represents an alkali metal cation; and

R₇-R₁₀ individually represents a hydrogen, alkyl, alkenyl, alkynyl, alkoxy, alkylthio, amino, aryl, aryloxy, arylthio, cyano or heterocyclic group with the proviso that any two adjacent R groups or R₇ and A may be joined together to form an annulated saturated or aromatic ring system; and A represent the atoms necessary to complete a 5, 6, 7 or 8 member ring system.

17. The cluster compound of claim 16 wherein the first subunit is according to formula (IV):

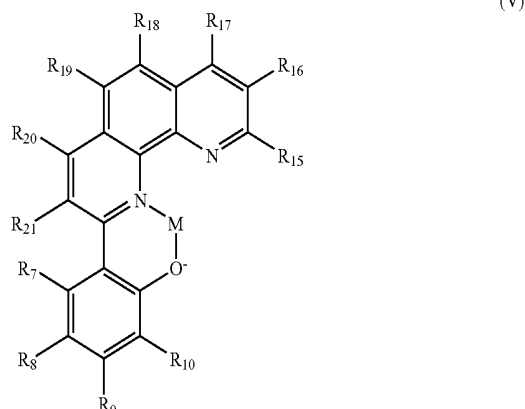


wherein:

M represents an alkali metal cation; and

R₇-R₁₄ individually represents a hydrogen, alkyl, alkenyl, alkynyl, alkoxy, alkylthio, amino, aryl, aryloxy, arylthio, cyano or heterocyclic group with the proviso that any two adjacent R groups or specifically, R₇ and R₁₄ may be joined together to form an annulated saturated or aromatic ring system.

18. The cluster compound of claim 17 wherein the first subunit is according to formula (V):

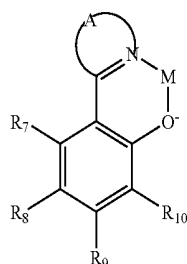


wherein:

M represents an alkali metal cation; and

R₇-R₁₀ and R₁₅-R₂₁ individually represents a hydrogen, alkyl, alkenyl, alkynyl, alkyloxy, alkylthio, amino, aryl, aryloxy, arylthio, cyano or heterocyclic group with the proviso that any two adjacent R groups or specifically, R₇ and R₂₁ may be joined together to form an annulated saturated or aromatic ring system.

19. The cluster compound of claim **14** wherein the second subunit is formula (III):



(III)

wherein:

M represents an alkali metal cation;

R₇-R₁₀ individually represents a hydrogen, alkyl, alkenyl, alkynyl, alkyloxy, alkylthio, amino, aryl, aryloxy, arylthio, cyano or heterocyclic group with the proviso that any two adjacent R groups or specifically, R₇ and A may be joined together to form an annulated saturated or aromatic ring system; and

A represent the atoms necessary to complete a 5, 6, 7 or 8 member ring system.

20. The cluster compound of claim **11** wherein the second subunit is an alkali metal salt of a phenol or naphthol.

21. A method of preparing the mixed cluster compound of claim **11** wherein compounds corresponding to the individual subunits are heated together in a non-reactive organic solvent with a boiling point of at least 100° C.

22. A method of preparing the mixed cluster compound of claim **11** wherein compounds corresponding to the individual subunits are heated together in the solid state.

23. The method of claim **22** wherein compounds corresponding to the individual subunits are heated together in the solid state and the mixed cluster compound is isolated via sublimation.

* * * * *

专利名称(译)	使用碱金属簇化合物的OLED器件		
公开(公告)号	US20090142618A1	公开(公告)日	2009-06-04
申请号	US11/947000	申请日	2007-11-29
[标]申请(专利权)人(译)	贝格利WILLIAM J RAJESWARAN MANJU hatwar tukaram K ANDRIEVSKY娜塔莎		
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IPC分类号	C09K11/00 C07D221/02		
CPC分类号	C09K11/06 H01L51/5092 H01L51/009 H01L51/0077 C07C39/44 C07D207/333 C07D213/30 C07D215/14 C07D215/30 C07D221/16 C07D233/64 C07D235/18 C07D277/66 C07D471/04 C09B1/00 C09B3/14 C09B19/02 C09B23/105 C09B23/148 C09B48/00 C09B57/00 C09B57/008 C09B57/02 C09B57/10		
其他公开文献	US8900722		
外部链接	Espacenet USPTO		

摘要(译)

本发明提供一种OLED装置，其包含具有混合配体的某些碱金属簇化合物，这些化合物及其制备方法。特别地，簇化合物是包含第一和第二亚基的中性电荷混合簇化合物，第一亚基包含含有带阴离子羟基的杂环配体的氮的碱金属盐，第二亚基含有有机碱金属盐。不同于第一个亚基。

