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Deaton et al.

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(54) **OLED DEVICES WITH DINUCLEAR COPPER COMPOUNDS**

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(21) Appl. No.: **11/274,468**

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(51) **Int. Cl.**
H01L 51/50 (2006.01)

(52) **U.S. Cl.** **428/690**; 428/917; 313/504; 313/506

(58) **Field of Classification Search** 428/690, 428/917; 313/504, 506; 257/E51.041, E51.044
See application file for complete search history.

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N. Mankad et al., "Structural Snapshots of a Flexible Cu_2P_2 Core that Accommodates the Oxidation States Cu^ICu^I, $Cu^{1.5}Cu^{1.5}$, and $Cu^{II}Cu^{II}$", J. Am. Chem. Soc. 2005, 127, pp. 16032-16033.

S. B. Harkins, et al., "A Highly Emissive Cu_2N_2 Diamond Core Complex Supported by a $[PNP]^-$ Ligand", J. Am. Chem., Soc., 2005, 127, pp. 2030-2031.

* cited by examiner

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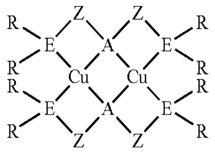
(74) *Attorney, Agent, or Firm*—Arthur E. Kluegel

(57) **ABSTRACT**

An OLED device comprises an anode, a cathode and therebetween a light emitting layer containing a compound represented by Formula I below:

Formula I

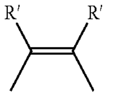


wherein:

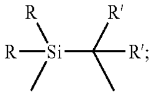
each A is independently selected from N and P;

each E is independently selected from N, P, and As;

each Z is a radical independently selected from



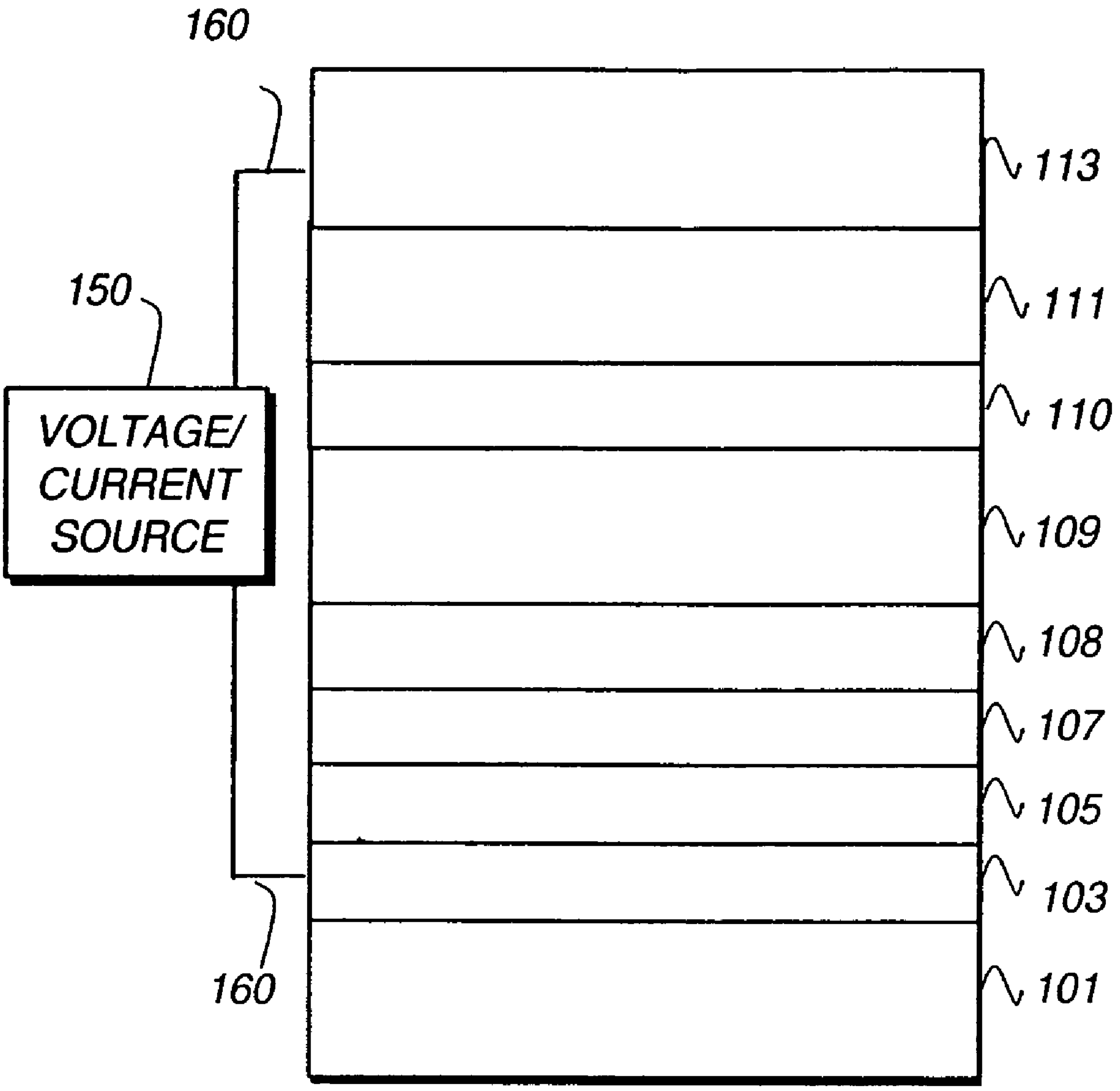
and



each R is an independently selected substituent; and

each R' is independently selected from H and a substituent; provided that two substituent groups can join to form a ring.

21 Claims, 1 Drawing Sheet


160
150
VOLTAGE/ CURRENT SOURCE
113
111
110
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107
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103
101
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OLED DEVICES WITH DINUCLEAR COPPER COMPOUNDS

FIELD OF INVENTION

This invention relates to organic electroluminescent (EL) devices employing certain copper based light emitting compounds.

BACKGROUND OF THE INVENTION

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, Vol. 30, pp. 322-334, 1969; and Dresner U.S. Pat. No. 3,710,167, issued Jan. 9, 1973. The organic layers in these devices, usually composed of a polycyclic aromatic hydrocarbon, were very thick (much greater than 1 μm). Consequently, operating voltages were very high, often >100V.

More recent organic EL devices include an organic EL element consisting of extremely thin layers (e.g. <1.0 μm) between the anode and the cathode. Herein, the term "organic EL element" encompasses the layers between the anode and cathode electrodes. Reducing the thickness lowered the resistance of the organic layer and has enabled devices that operate 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, therefore, it is referred to as the hole-transporting layer, and the other organic layer is specifically chosen to transport electrons, referred to as the electron-transporting layer. Recombination of the injected holes and electrons within the organic EL element results in efficient electroluminescence.

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 Tang et al [*J. Applied Physics*, Vol. 65, Pages 3610-3616, 1989]. The light-emitting layer commonly consists of a host material doped with a guest material. 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 transport/injection layer (ETL). These structures have resulted in improved device efficiency.

Many emitting materials that have been described as useful in an OLED device emit light from their excited singlet state by fluorescence. The excited singlet state is created when excitons formed in an OLED device transfer their energy to the excited state of the dopant. However, it is generally believed that only 25% of the excitons created in an EL device are singlet excitons. The remaining excitons are triplet, which cannot readily transfer their energy to the singlet excited state of a dopant. This results in a large loss in efficiency since 75% of the excitons are not used in the light emission process.

Triplet excitons can transfer their energy to a dopant if it has a triplet excited state that is low enough in energy. If the triplet state of the dopant is emissive it can produce light by phosphorescence. In many cases singlet excitons can also transfer their energy to lowest singlet excited state of the same dopant. The singlet excited state can often relax, by an intersystem crossing process, to the emissive triplet excited state. Thus, it is possible, by the proper choice of host and dopant, to collect energy from both the singlet and triplet excitons created in an OLED device and to produce a very efficient phosphorescent emission.

Typical phosphorescent dopants are orthometallated Ir or Pt complexes, such as fac-tris(2-phenyl-pyridinato-N^C-)Iridium(III) ($Ir(ppy)_3$) that emits green light (K. A. King, P. J. Spellane, and R. J. Watts, *J. Am. Chem. Soc.,* 107, 1431 (1985), M. G. Colombo, T. C. Brunold, T. Reidener, H. U. Güdel, M. Fortsch, and H.-B. Bürgi, *Inorg. Chem.,* 33, 545 (1994)). Organic electroluminescent devices having high efficiency have been demonstrated with $Ir(ppy)_3$ as the phosphorescent material and 4,4'-N,N'-dicarbazole-biphenyl (CBP) as the host (M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.,* 75, 4 (1999), T. Tsutsui, M.-J. Yang, M. Yahiro, K. Nakamura, T. Watanabe, T. Tsuji, Y. Fukuda, T. Wakimoto, S. Miyaguchi, *Jpn. J. Appl. Phys.,* 38, L1502 (1999)).

An amido-bridged bimetallic copper system, $\{(PNP)Cu^1\}_2$, derived from a chelating bis(phosphine)amide ligand ([PNP]-=bis(2-(diisobutylphosphino)phenyl)amide) was reported by Seth B. Harkins and Jonas C. Peters, J. Am. Chem. Soc., 127, 2030-2031 (2005) to emit strongly in solution and in the solid state when irradiated by visible light. Electrochemical analysis of $\{(PNP)Cu^1\}_2$ in CH_2Cl_2 (Fc^+/Fc, 0.3 M $[^nBu_4N][PF_6]$, 250 mV/s, Fc=ferrocene) revealed two reversible waves, one centered at −550 mV and the other at 300 mV. A value of −3.2 V (vs Fc^+/Fc) was estimated for the excited-state reduction potential of $\{(PNP)Cu^1\}_2$, suggesting that it is possible that $\{(PNP)Cu^1\}_2$ will prove to be a potent photoreductant/photosensitizer, and given the presence of two reversible redox couples within this bimetallic copper system, there may be an opportunity to drive multielectron reaction processes.

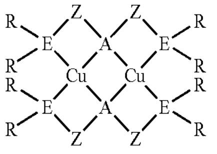
In selecting materials for use in an OLED device, in particular as a phosphorescent emitter, it is not sufficient that the material is emissive when irradiated by visible light. The excited state must be formed by applying an electric potential to an OLED, and further, the excited state must emit light from the OLED device rather than simply reacting chemically with the surrounding materials comprising the device structure.

Iridium or platinum organometallic compounds have been the predominant triplet dopants proposed for use in OLED devices. It would be desirable to have alternatives to iridium or platinum organometallic compounds for use as triplet dopants. New compounds need to be discovered in order to improve the properties of OLED devices such as efficiency and color. In addition, iridium and platinum are particularly expensive metals.

SUMMARY OF THE INVENTION

The invention provides an OLED device comprising an anode, a cathode and therebetween a light emitting layer containing a compound represented by Formula I below:

Formula I

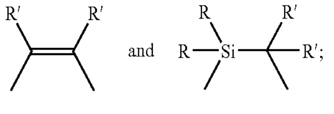


wherein:

each A is independently selected from N and P;

each E is independently selected from N, P, and As;

each Z is a radical independently selected from



each R is an independently selected substituent; and

each R' is independently selected from H and a substituent;

provided that two substituent groups can join to form a ring.

The device of the invention exhibits light emissions having desirable efficiency and color.

BRIEF DESCRIPTION OF THE DRAWINGS

The FIGURE shows a schematic cross-section of a typical OLED device in which this invention may be used.

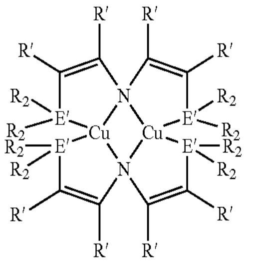
DETAILED DESCRIPTION OF THE INVENTION

The invention is generally described above.

Suitably A in Formula I represents nitrogen. In one embodiment E represents phosphorus or arsenic; and R is independently selected from alkyl, aryl, and cyano substituents

In one embodiment the emitting layer contains a dinuclear copper compound represented by Formula II below:

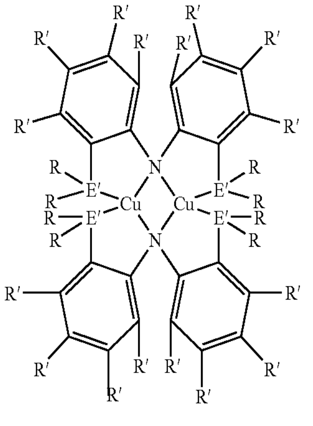
Formula II



wherein each E' is independently selected from P and As; each R' is independently selected from H and a substituent; each R_2 is independently selected from alkyl, aryl, heteroaryl and cyano substituents; and provided two substituent groups can join to form a ring. In some embodiments the E' represents P. In another embodiment R_2 is independently selected from alkyl, aryl, and cyano substituents

In another embodiment the emitting layer contains a dinuclear copper compound represented by Formula III below:

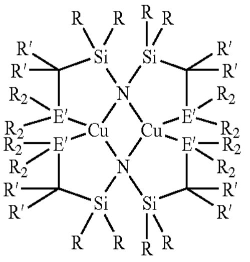
Formula III



wherein each E' is independently selected from P and As; each R is an independently selected substituent; each R' is independently selected from H or a substituent; and provided two substituent groups on adjacent atoms can join to form a ring. A typical substituent represented by R is an alkyl, aryl, and CN substituent. In some cases R substituents on adjacent atoms join to form an aromatic ring. In some embodiments E' represents P. Representative examples of the R substituent are isobutyl and phenyl.

In another embodiment the emitting layer contains a dinuclear copper compound represented by Formula IV below:

Formula IV



wherein each E' is independently selected from P and As; each R is an independently selected substituent; each R' is independently selected from H and a substituent; each R_2 is independently selected from alkyl, aryl, heteroaryl and cyano substituents; and provided two substituent groups on adjacent atoms can join to form a ring. In some embodiments E' represents P. In another embodiment R_2 is independently selected from alkyl, aryl, and cyano substituents

The choice of host material in the light emitting layer is important for the optimal operation of the electroluminescent device. A worthwhile host material is one from a class of compounds that contain a carbazole substituent, representative examples are CBP, 9,9'-(1,3-phenylene)bis-9H-carbazole (mCP), 9,9'-(2,2'-dimethyl[1,1'-biphenyl]-4,4'-diyl)bis-9H-carbazole (CDBP), and 4-(9H-carbazol-9-yl)-N,N-bis[4-(9H-carbazol-9-yl)phenyl]-benzenamine (TCTA).

The concentration of the light emitting compound in the light emitting layer is typically 1% to 25%, and often between 1% at 15% and usually 6% or less. The concentration can be changed to provide optimum device performance.

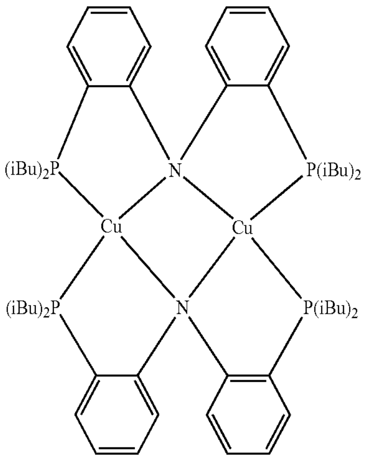
In one embodiment at least one exciton blocking layer is adjacent to the light emitting layer on the anode side, comprising a material having a triplet energy that exceed that of the phosphorescent emitter and is greater than 2.5 eV. In a preferred embodiment, the material of the exciton blocking layer should have a LUMO energy level greater by 0.2 eV or more than that of the host material in the light emitting layer. A suitable material in the exciton blocking layer is a triarylamine. A suitable host material of the light emitting layer is a carbazole. In non-limiting examples, if the host material is selected from carbazole-containing molecules according to formulae PHF-10 or PHF-11, then the exciton blocking layer would suitably be selected from the triarylamines. Suitable triarylamines are described by formulae EBF-1 or EBF-2.

Desirable triaryl amines are selected from 1,1-Bis(4-(N,N-di-p-tolylamino)phenyl)cyclohexane (TAPC) and 2,2'-dimethyl-N,N,N',N'-tetrakis(4-methylphenyl)-1,1'-biphenyl-4,4'-diamine. Desirable host materials are selected from 9,9'-(2,2'-dimethyl[1,1'-biphenyl]-4,4'-diyl)bis-9H-carbazole; 9,9'-(1,3-phenylene)bis-9H-carbazole; and 4-(9H-carbazol-9-yl)-N,N-bis[4-(9H-carbazol-9-yl)phenyl]-benzenamine.

A material that satisfies the requirements for the exciton blocking layer in one embodiment of the present invention is TAPC. The triplet energy is approximately equal to that of the structurally related compound, triphenylamine, namely 3.0 eV (S. L. Murov, I. Carmichael, and G. L. Hug, Handbook of Photochemistry, 2nd ed. (Marcel Dekker, New York, 1993)). The triplet energy of a green phosphorescent material is typically about 2.5 eV, and the triplet energy of a blue phosphorescent material can be about 2.8 eV. Thus, TAPC meets the requirement that the triplet energy of the exciton blocking layer exceeds 2.5 eV provided that it is used with a green phosphorescent material or a blue phosphorescent material whose triplet energy is below 3.0 eV. The requirement is also met if the triplet energy of the phosphorescent material is yet lower, as is usually the case if the characteristic phosphorescence is yellow, orange, or red.

Useful compounds of this invention include:

Inv-1



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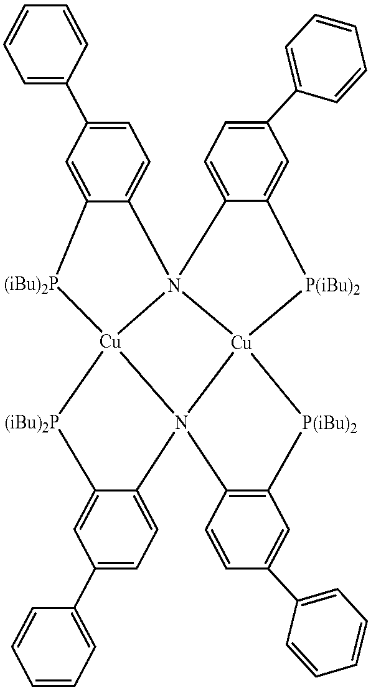
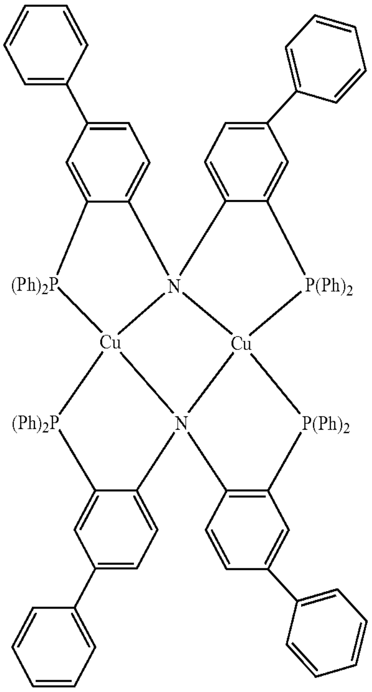
Inv-2



Inv-3



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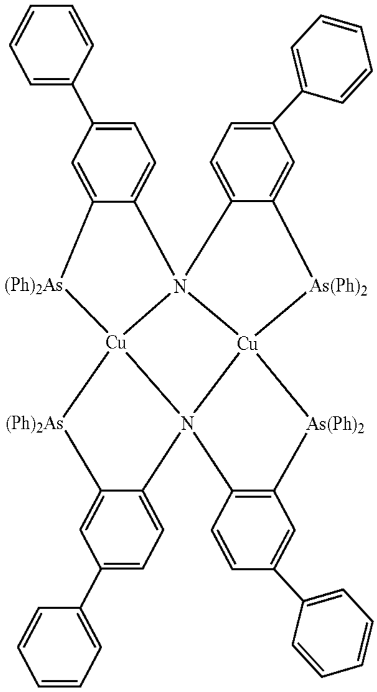
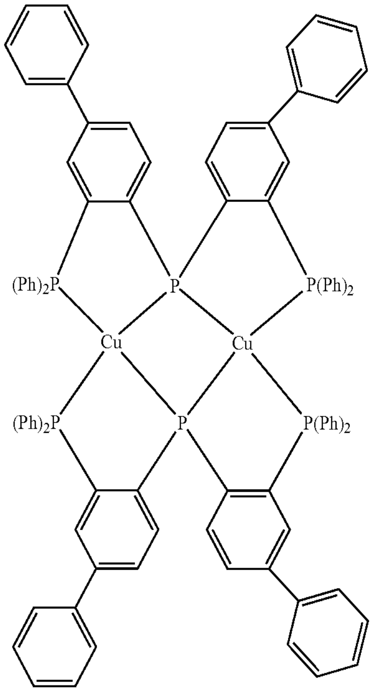
Inv-4



Inv-5



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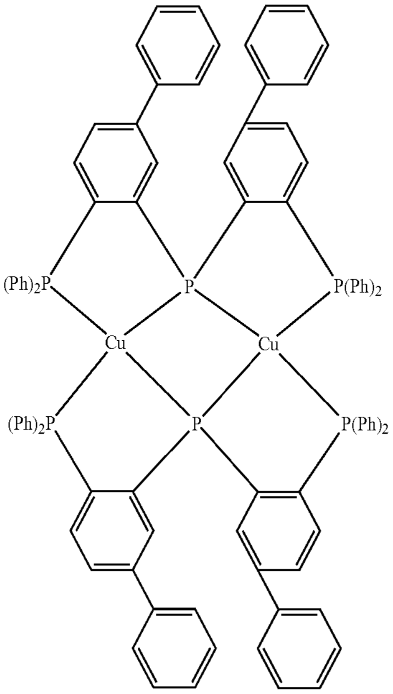
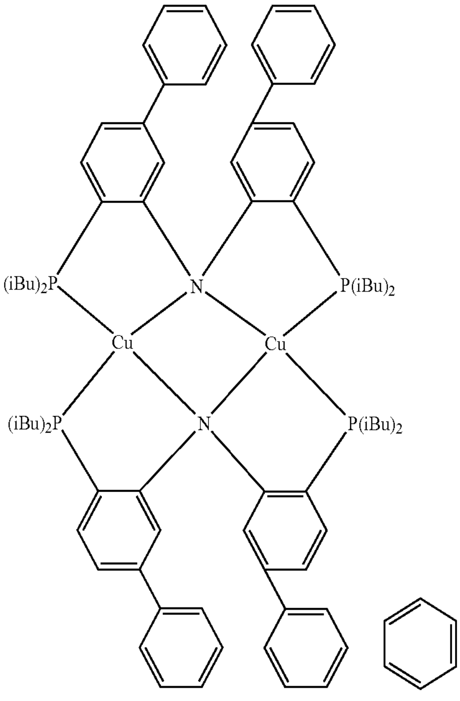
Inv-6



Inv-7



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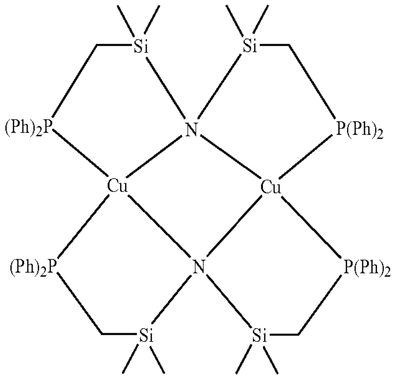
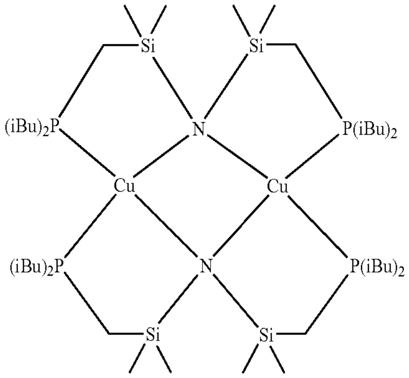
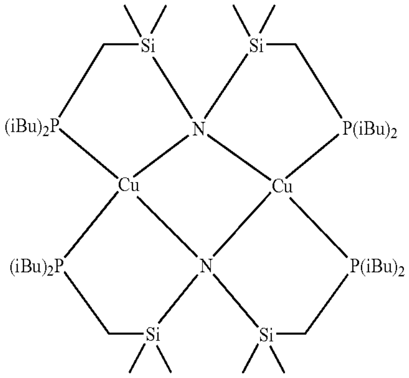
Inv-8



Inv-9



Inv-9



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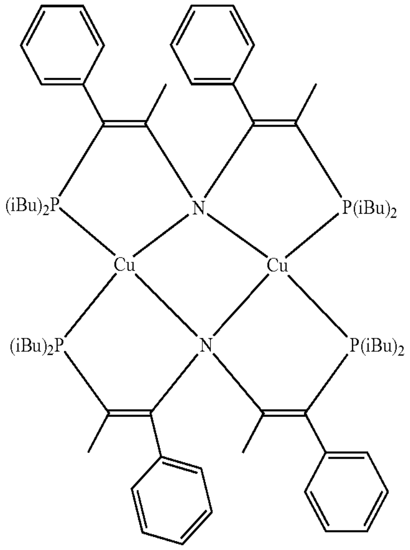
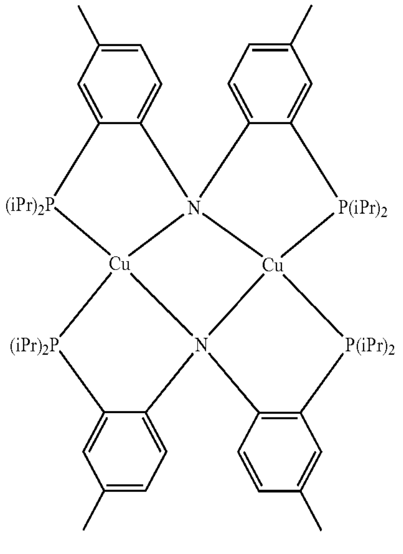
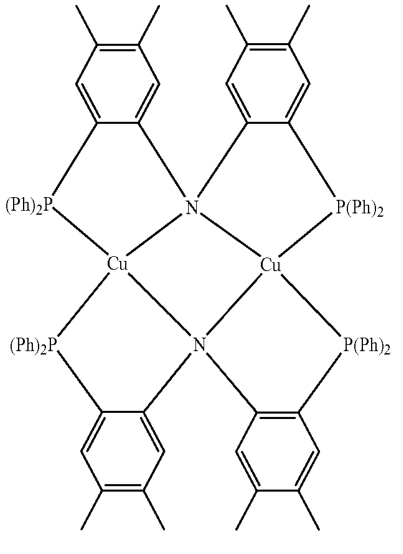
Inv-10



Inv-11



Inv-12



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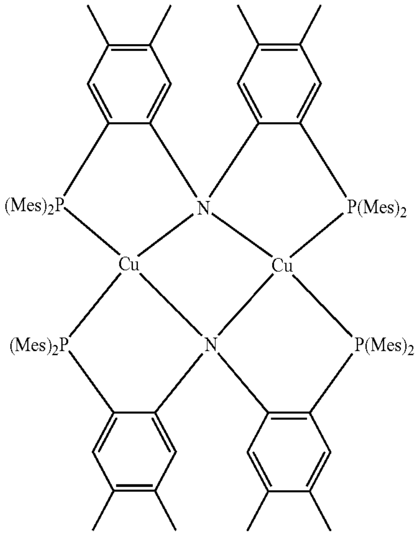
Inv-13



These dinuclear copper compounds may be synthesized by a procedure shown in Harkins, S. B.; Peters, J. C. *J. Am. Chem. Soc.* 2005, 127, 2030-2031.

Unless otherwise specifically stated, use of the term “substituted” or “substituent” means any group or atom other than hydrogen. Additionally, when the term “group” is used, it means that when a substituent group contains a substitutable hydrogen, it is also intended to encompass not only the substituent’s unsubstituted form, but also its form further substituted with any substituent group or groups as herein mentioned, so long as the substituent does not destroy properties necessary for device utility. Suitably, a substituent group 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-naphthyloxy, and 4-tolyloxy; carbonamido, such as acetamido, benzamido, butyramido, tetradecanamido, alpha-(2,4-di-t-pentyl-phenoxy)acetamido, alpha-(2,4-di-t-pentylphenoxy)butyramido, alpha-(3-pentadecylphenoxy)-hexanamido, alpha-(4-hydroxy-3-t-butylphenoxy)-tetradecanamido, 2-oxo-pyrrolidin-1-yl, 2-oxo-5-tetradecylpyrrolin-1-yl, N-methyltetradecanamido, N-succinimido, N-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2,5-dioxo-1-imidazolyl, and N-acetyl-N-dodecylamino, ethoxycarbonylamino, phenoxycarbonylamino, 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-dioctadecylureido, N,N-dioctyl-N'-ethylureido, N-phenylureido, N,N-diphenylureido, N-phenyl-N-p-tolylureido, N-(m-hexadecylphenyl) ureido, N,N-(2,5-di-t-pentylphenyl)-N'-ethylureido, and t-butylcarbonamido; sulfonamido, such as methylsulfonamido, benzenesulfonamido, p-tolylsulfonamido, p-dodecylbenzenesulfonamido, N-methyltetradecylsulfonamido, N,N-dipropyl-sulfamoylamino, and hexadecylsulfonamido; sulfamoyl, such as N-methylsulfamoyl, N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-hexadecylsulfamoyl, N,N-dimethylsulfamoyl, N-[3-(dodecyloxy)propyl]sulfamoyl, N-[4-(2,4-di-t-pentylphenoxy)butyl]sulfamoyl, N-methyl-N-tetradecylsulfamoyl, and N-dodecylsulfamoyl; carbamoyl, such as N-methylcarbamoyl, N,N-dibutylcarbamoyl, N-octadecylcarbamoyl, N-[4-(2,4-di-t-pentylphenoxy)butyl]carbamoyl, N-methyl-N-tetradecylcarbamoyl, and N,N-dioctylcarbamoyl; acyl, such as acetyl, (2,4-di-t-amylphenoxy)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, benzoyloxy, octadecanoyloxy, p-dodecylamidobenzoyloxy, 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 or phosphorous, such as pyridyl, thienyl, furyl, azolyl, thiazolyl, oxazolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyrolidinonyl, quinolinyl, isoquinolinyl, 2-furyl, 2-thienyl, 2-benzimidazolyloxy or 2-benzothiazolyl; quaternary ammonium, such as triethylammonium; quaternary phosphonium, such as triphenylphosphonium; and silyloxy, such as trimethylsilyloxy.

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.

For the purpose of this invention, also included in the definition of a heterocyclic ring are those rings that include coordinate or dative bonds. The definition of a coordinate bond can be found in *Grant & Hackh's Chemical Dictionary*, page 91. 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 such as Al or B.

It is well within the skill of the art to determine whether a particular group is electron donating or electron accepting. The most common measure of electron donating and accepting properties is in terms of Hammett σ values. Hydrogen has a Hammett σ value of zero, while electron donating groups have negative Hammett σ values and electron accepting groups have positive Hammett σ values. Lange's handbook of Chemistry, 12th Ed., McGraw Hill, 1979, Table 3-12, pp. 3-134 to 3-138, here incorporated by reference, lists Hammett σ values for a large number of commonly encountered groups. Hammett σ values are assigned based on phenyl ring substitution, but they provide a practical guide for qualitatively selecting electron donating and accepting groups.

Suitable electron donating groups may be selected from —R', —OR', and —NR'(R") where R' is a hydrocarbon containing up to 6 carbon atoms and R" is hydrogen or R'. Specific examples of electron donating groups include methyl, ethyl, phenyl, methoxy, ethoxy, phenoxy, $—N(CH_3)_2$, $—N(CH_2CH_3)_2$, $—NHCH_3$, $—N(C_6H_5)_2$, $—N(CH_3)(C_6H_5)$, and $—NHC_6H_5$.

Suitable electron accepting groups may be selected from the group consisting of cyano, α-haloalkyl, α-haloalkoxy, amido, sulfonyl, carbonyl, carbonyloxy and oxycarbonyl substituents containing up to 10 carbon atoms. Specific examples include —CN, —F, $—CF_3$, $—OCF_3$, $—CONHC_6H_5$, $—SO_2C_6H_5$, $—COC_6H_5$, $—CO_2C_6H_5$, and $—OCOC_6H_5$.

Unless otherwise specified, the term "percentage" or "percent" and the symbol "%" of a material indicates the volume percent of the material in the layer in which it is present.

General Device Architecture

The present invention can be employed in many OLED device configurations using small molecule materials, oligomeric materials, polymeric materials, or combinations thereof. These include very simple structures comprising a single anode and cathode to more complex devices, such as passive matrix displays comprised of 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 can be successfully practiced. The essential requirements of an OLED are an anode, a cathode, and an organic light-emitting layer located between the anode and cathode. Additional layers may be employed as more fully described hereafter.

A typical structure, especially useful for of a small molecule device, is shown in the schematic cross-section of the FIGURE and is comprised of a substrate **101**, an anode **103**, a hole-injecting layer **105**, a hole-transporting layer **107**, a light-emitting layer **109**, a hole- or exciton-blocking layer **110**, an electron-transporting layer **111**, and a cathode **113**. Typically, an exciton-blocking layer **108** on the anode side of the light-emitting layer and/or a hole-blocking layer **110** on the cathode side of the light emitting layer are included as well. These layers are 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. The organic layers between the anode and cathode are conveniently referred to as the organic EL element. Also, the total combined thickness of the organic layers is desirably less than 500 nm.

The anode and cathode of the OLED are connected to a voltage/current source **150** through electrical conductors **160**. The OLED is operated by applying a potential between the anode and cathode such that the anode is at a more positive potential than the cathode. Holes are injected into the organic EL element from the anode and electrons are injected into the organic EL element at the cathode. Enhanced device stability can sometimes be achieved when the OLED is operated in an AC mode where, for some time period in the 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.

Substrate

The OLED device of this invention is typically provided over a supporting substrate **101** where either the cathode or anode can be in contact with the substrate. 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 pixilated areas, be comprised of largely transparent materials. The electrode in contact with the substrate is conveniently referred to as the bottom electrode. Conventionally, the bottom electrode is the anode, but this invention is not limited to that configuration. The substrate can either be light transmissive or opaque, depending on the intended direction of light emission. The light transmissive property is desirable for viewing the EL emission through the substrate. Transparent glass or plastic is commonly employed in such cases. For applications where the EL emission is viewed through the top electrode, the transmissive characteristic of the bottom support 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, silicon, ceramics, and circuit board materials. It is necessary to provide in these device configurations a light-transparent top electrode.

Anode

When the desired electroluminescent light emission (EL) is viewed through the anode, the anode **103** 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. For applications where EL emission is viewed only through the cathode, 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 shorts or enhance reflectivity.

Hole-Injecting Layer (HIL)

A hole-injecting layer **105** may be provided between the anode and the hole-transporting layer. The hole-injecting material can serve to improve the film formation property of subsequent organic layers and to facilitate injection of holes into the hole-transporting layer. Suitable materials for use in the hole-injecting layer include, but are not limited to, porphyrinic compounds as described in U.S. Pat. No. 4,720,432, plasma-deposited fluorocarbon polymers as described in U.S. Pat. No. 6,127,004, U.S. Pat. No. 6,208,075 and U.S. Pat. No. 6,208,077, some aromatic amines, for example, MTDATA (4,4',4"-tris[(3-methylphenyl)phenylamino]triphenylamine), and inorganic oxides including vanadium oxide (VOx), molybdenum oxide (MoOx), and nickel oxide (NiOx). Alternative hole-injecting materials reportedly useful in organic EL devices are described in EP 0 891 121 A1 and EP 1 029 909 A1.

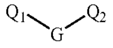
The thickness of a hole injection layer containing a plasma-deposited fluorocarbon polymer can be in the range of 0.2 nm to 15 nm and suitably in the range of 0.3 to 1.5 nm.

Hole-Transporting Layer (HTL)

It is usually advantageous to have a hole transporting layer **107** deposited between the anode and the emissive layer. A hole transporting material deposited in said hole transporting layer between the anode and the light emitting layer may be the same or different from a hole transporting compound used as a co-host or in exciton blocking layer according to the invention. The hole transporting layer may optionally include a hole injection layer. The hole transporting layer may include more than one hole transporting compound, deposited as a blend or divided into separate layers.

The hole-transporting layer contains at least one hole-transporting compound 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 can be an arylamine, such as a monoarylamine, diarylamine, triarylamine, or a polymeric arylamine. Exemplary monomeric triarylamines are illustrated by Klupfel et al. U.S. Pat. No. 3,180,730. Other suitable triarylamines substituted with one or more vinyl radicals and/or comprising at least one active hydrogen containing group are disclosed by Brantley et al U.S. Pat. Nos. 3,567,450 and 3,658,520.

A more preferred class of aromatic tertiary amines is those which include at least two aromatic tertiary amine moieties as described in U.S. Pat. No. 4,720,432 and U.S. Pat. No. 5,061,569. Such compounds include those represented by structural formula (HT1):

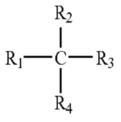


(HT1)

wherein

Q_1 and Q_2 are independently selected aromatic tertiary amine moieties, and G is a linking group such as an arylene, cycloalkylene, or alkylene group of a carbon to carbon bond. 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. A useful class of triarylamines satisfying structural formula (HT1) and containing two triarylamine moieties is represented by structural formula (HT2):

(HT2)



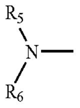
$$R_1-\overset{\overset{\large R_2}{|}}{\underset{\underset{\large R_4}{|}}{C}}-R_3$$

wherein

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

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 (HT3):

(HT3)



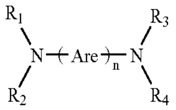
$$\begin{matrix} R_5 & & \\ & N- & \\ R_6 & & \end{matrix}$$

wherein

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.

Another class of aromatic tertiary amines is the tetraaryldiamines. Desirable tetraaryldiamines include two diarylamino groups, such as indicated by formula (HT3), linked through an arylene group. Useful tetraaryldiamines include those represented by formula (HT4):

(HT4)



$$\begin{matrix} R_1 & & & & R_3 \\ & N & (Are)_n & N & \\ R_2 & & & & R_4 \end{matrix}$$

wherein

each Are is an independently selected arylene group, such as a phenylene or anthracene moiety,

n is an integer of from 1 to 4, and

R_1, R_2, R_3, and R_4 are independently selected aryl groups.

In a typical embodiment, at least one of R_1, R_2, R_3, and R_4 is a polycyclic fused ring structure, e.g., a naphthalene.

The various alkyl, alkylene, aryl, and arylene moieties of the foregoing structural formulae (HT1), (HT2), (HT3), (HT4) can each in turn be substituted. Typical substituents include alkyl groups, alkoxy groups, aryl groups, aryloxy groups, and halide 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, such as cyclopentyl, cyclohexyl, and cycloheptyl ring structures. The aryl and arylene moieties are usually phenyl and phenylene moieties.

The hole transporting layer can be formed of a single tertiary amine compound or a mixture of such compounds. Specifically, one may employ a triarylamine, such as a triarylamine satisfying the formula (HT2), in combination with a tetraaryldiamine, such as indicated by formula (HT4). Illustrative of useful aromatic tertiary amines are the following:

1,1-Bis(4-di-p-tolylaminophenyl)cyclohexane (TAPC);
1,1-Bis(4-di-p-tolylaminophenyl)-4-phenylcyclohexane;
N,N,N',N'-tetraphenyl-4,4'''-diamino-1,1':4',1'':4'',1'''-quaterphenyl;
Bis(4-dimethylamino-2-methylphenyl)phenylmethane;
1,4-bis[2-[4-[N,N-di(p-tolyl)amino]phenyl]vinyl]benzene (BDTAPVB);
N,N,N',N'-Tetra-p-tolyl-4,4'-diaminobiphenyl;
N,N,N',N'-Tetraphenyl-4,4'-diaminobiphenyl;
N,N,N',N'-tetra-1-naphthyl-4,4'-diaminobiphenyl;
N,N,N',N'-tetra-2-naphthyl-4,4'-diaminobiphenyl;
N-Phenylcarbazole;
4,4'-Bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB);
4,4'-Bis[N-(3-methylphenyl)-N-phenylamino]biphenyl (TPD);
4,4'-Bis[N-(1-naphthyl)-N-(2-naphthyl)amino]biphenyl (TNB);
4,4'-Bis[N-(1-naphthyl)-N-phenylamino]p-terphenyl;
4,4'-Bis[N-(2-naphthyl)-N-phenylamino]biphenyl;
4,4'-Bis[N-(3-acenaphthenyl)-N-phenylamino]biphenyl;
1,5-Bis[N-(1-naphthyl)-N-phenylamino]naphthalene;
4,4'-Bis[N-(9-anthryl)-N-phenylamino]biphenyl;
4,4'-Bis[N-(1-anthryl)-N-phenylamino]-p-terphenyl;
4,4'-Bis[N-(2-phenanthryl)-N-phenylamino]biphenyl;
4,4'-Bis[N-(8-fluoranthenyl)-N-phenylamino]biphenyl;
4,4'-Bis[N-(2-pyrenyl)-N-phenylamino]biphenyl;
4,4'-Bis[N-(2-naphthacenyl)-N-phenylamino]biphenyl;
4,4'-Bis[N-(2-perylenyl)-N-phenylamino]biphenyl;
4,4'-Bis[N-(1-coronenyl)-N-phenylamino]biphenyl;
2,6-Bis(di-p-tolylamino)naphthalene;
2,6-Bis[di-(1-naphthyl)amino]naphthalene;
2,6-Bis[N-(1-naphthyl)-N-(2-naphthyl)amino]naphthalene;
N,N,N',N'-Tetra(2-naphthyl)-4,4''-diamino-p-terphenyl;
4,4'-Bis {N-phenyl-N-[4-(1-naphthyl)-phenyl]amino}biphenyl;
2,6-Bis[N,N-di(2-naphthyl)amino]fluorine;
4,4',4''-tris[(3-methylphenyl)phenylamino]triphenylamine(MTDATA);
N,N-bis[2,5-dimethyl-4-[(3-methylphenyl)phenylamino]phenyl]-2,5-dimethyl-N'-(3-methylphenyl)-N'-phenyl-1,4-benzenediamine;
4-(9H-carbazol-9-yl)-N,N-bis[4-(9H-carbazol-9-yl)phenyl]-benzenamine (TCTA);
4-(3-phenyl-9H-carbazol-9-yl)-N,N-bis[4(3-phenyl-9H-carbazol-9-yl)phenyl]-benzenamine;
9,9'-(2,2'-dimethyl[1,1'-biphenyl]-4,4'-diyl)bis-9H-carbazole (CDBP);
9,9'-[1,1'-biphenyl]-4,4'-diylbis-9H-carbazole (CBP);
9,9'-(1,3-phenylene)bis-9H-carbazole (mCP);
9-[4-(9H-carbazol-9-yl)phenyl]-N,N-diphenyl-9H-carbazol-3-amine;
9,9'-(1,4-phenylene)bis[N,N-diphenyl-9H-carbazol-3-amine;
9-[4-(9H-carbazol-9-yl)phenyl]-N,N,N',N'-tetraphenyl-9H-carbazole-3,6-diamine.

Another class of useful hole-transporting materials includes polycyclic aromatic compounds as described in EP 1 009 041. Some hole-injecting materials described in EP 0 891 121 A1 and EP 1 029 909 A1, can also make useful hole-transporting materials. In addition, polymeric hole-transporting materials can be used including poly(N-vinylcarbazole) (PVK), polythiophenes, polypyrrole, polyaniline, and copolymers including poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) also called PEDOT/PSS.

Blocking Layer

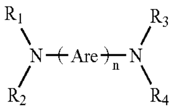
An OLED device according to the invention may include at least one exciton blocking layer **108** placed adjacent the light emitting layer **109** on the anode side, to help confine triplet excitons to the light emitting layer. For the exciton blocking layer to be capable of confining triplet excitons, the material or materials of this layer should have triplet energies that exceed that of the phosphorescent emitter. If the triplet energy level of any material in the layer adjacent the light emitting layer is lower than that of the phosphorescent emitter, often that material will quench excited states in the light emitting layer, decreasing device luminous efficiency. In a preferred embodiment, the exciton blocking layer also helps to confine electron-hole recombination events to the light emitting layer by blocking the escape of electrons from the light emitting layer into the exciton blocking layer. In order for the exciton blocking layer to have this electron blocking property, the material of this layer should have a lowest unoccupied molecular orbital (LUMO) energy level that is greater than that of the host material in the light emitting layer by at least 0.2 eV. In an embodiment wherein the host comprises a mixture of host materials, the LUMO energy level of the exciton block should be greater by at least 0.2 eV than that of the host material having the lowest LUMO energy level in order to have the preferred electron blocking property.

The relative energy levels of the highest occupied molecular orbital (HOMO) and the LUMO of materials may be estimated by several methods known in the art. When comparing energy levels of two materials, it is important to use estimated energy levels obtained by the same method for each. Two methods for estimating the HOMO energy level include measuring the ionization potential of the material by ultraviolet photoelectron spectroscopy and measuring the oxidation potential by an electrochemical technique such as cyclic voltammetry. The LUMO energy level may then be estimated by adding the optical band gap energy to the previously determined HOMO energy level. The optical band gap is estimated to be the energy difference between the LUMO and the HOMO. The relative LUMO energy levels of materials may also be estimated from reduction potentials of the materials measured in solution by an electrochemical technique such as cyclic voltammetry.

We have found that luminous yield and power efficiency in the OLED device employing a phosphorescent emitter in the light emitting layer can be improved significantly if the selected exciton blocking material or materials have a triplet energy greater or equal to 2.5 eV, especially for the case of green or blue-emitting phosphorescent emitters.

The exciton blocking layer is often between 1 and 500 nm thick and suitably between 10 and 300 nm thick. Thicknesses in this range are relatively easy to control in manufacturing. In addition to having high triplet energy, the exciton blocking layer **108** must be capable of transporting holes to the light emitting layer **109**. Exciton blocking layer **108** can be used alone or with a hole-transporting layer **107**. The exciton blocking layer may include more than one compound, deposited as a blend or divided into separate layers. In an embodiment wherein a hole transporting compound is used as a host or co-host, a hole transporting material deposited in the exciton blocking layer between the anode and the light emitting layer may be the same or different from the hole transporting compound used as a host or co-host. The exciton blocking material can comprise compounds containing one or more triarylamine groups, provided that their triplet energy exceeds that of the phosphorescent material. In a preferred embodiment the triplet energy is greater or equal to 2.5 eV. To meet the triplet energy requirement for the preferred embodiment of 2.5 eV or greater, said compounds should not contain aromatic hydrocarbon fused rings (e.g., a naphthalene group).

The substituted triarylamines that function as the exciton blocking material in the present invention may be selected from compounds having the chemical formula (EBF-1):



(EBF-1)

In formula (EBF-1), Are is independently selected from alkyl, substituted alkyl, aryl, or substituted aryl group;

R_1—R_4 are independently selected aryl groups;

n is an integer of from 1 to 4.

In a preferred embodiment, Are and R_1—R_4 do not include aromatic hydrocarbon fused rings.

Example materials useful in the exciton blocking layer **108** include, but are not limited to:

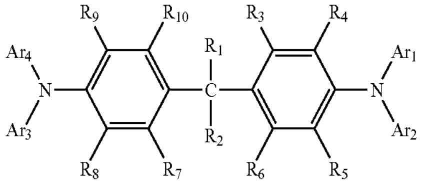
2,2'-dimethyl-N,N,N',N'-tetrakis(4-methylphenyl)-1,1'-biphenyl-4,4'-diamine.

4,4',4"-tris[(3-methylphenyl)phenylamino]triphenylamine (MTDATA);

4,4',4"-tris(N,N-diphenyl-amino)triphenylamine (TDATA);

N,N-bis[2,5-dimethyl-4-[(3-methylphenyl)phenylamino]phenyl]-2,5-dimethyl-N'-(3-methylphenyl)-N'-phenyl-1,4-benzenediamine.

In one desirable embodiment the material in the exciton blocking layer is selected from formula (EBF-2):



(EBF-2)

In formula (EBF-2), 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. Ar_1—Ar_4 represent independently selected aromatic groups, for example phenyl groups or tolyl groups. R_3—R_{10} independently represent hydrogen, alkyl, substituted alkyl, aryl, substituted aryl group. In one desirable embodiment, R_1—R_2, Ar_1—Ar_4 and R_3—R_{10} do not contain fused aromatic rings.

Some non-limiting examples of such materials are:

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

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

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

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

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

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

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

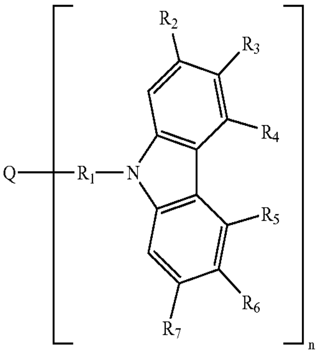
Bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)ethane;

4-(4-Diethylaminophenyl)triphenylmethane;

4,4'-Bis(4-diethylaminophenyl)diphenylmethane.

In one suitable embodiment the exciton blocking material comprises a material of formula (EBF-3):

(EBF-3)



wherein n is an integer from 1 to 4;

Q is N, C, aryl, or substituted aryl group;

R_1 is phenyl, substituted phenyl, biphenyl, substituted biphenyl, aryl or substituted aryl;

R_2 through R_7 are independently hydrogen, alkyl, phenyl or substituted phenyl, aryl amine, carbazole, or substituted carbazole; provided that R_2—R_7 do not contain aromatic hydrocarbon fused rings.

Some non-limiting examples of such materials are:

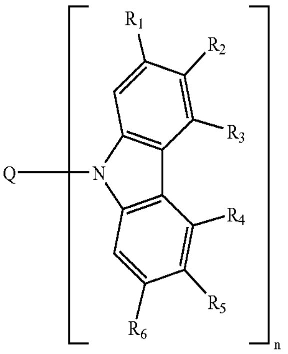
4-(9H-carbazol-9-yl)-N,N-bis[4-(9H-carbazol-9-yl)phenyl]-benzenamine (TCTA);

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

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

In one suitable embodiment the exciton blocking material comprises a material of formula (EBF-4):

(EBF-4)



wherein n is an integer from 1 to 4;

Q is phenyl, substituted phenyl, biphenyl, substituted biphenyl, aryl, or substituted aryl group;

R_1 through R_6 are independently hydrogen, alkyl, phenyl or substituted phenyl, aryl amine, carbazole, or substituted carbazole;

provided that R_1—R_6 do not contain aromatic hydrocarbon fused rings.

Non-limiting examples of suitable materials are:

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

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

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

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

9,9',9"-(1,3,5-benzenetriyl)tris-9H-carbazole;

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

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

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

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

9-phenyl-9H-carbazol.

Metal complexes may also serve as exciton blocking layers as long as they have the desired triplet energies and hole transport and electron blocking properties. An example of this is, fac-tris(1-phenylpyrazolato-N,C$^{2'}$)iridium(III) (Ir(ppz)$_3$), as described in US 20030175553.

Light-Emitting Layer (LEL)

Suitably, the light-emitting layer of the OLED device comprises a host material and one or more guest materials for emitting light. At least one of the guest materials is suitably a fluorescent or phosphorescent material. The light-emitting guest material(s) is usually present in an amount less than the amount of host materials and is typically present in an amount of up to 15 wt % of the host, more typically from 0.1-10 wt % of the host. For convenience, the light-emitting guest material may be referred to as a light emitting dopant. A phosphorescent guest material may be referred to herein as a phosphorescent material, or phosphorescent dopant. The phosphorescent material is preferably a low molecular weight compound, but it may also be an oligomer or a polymer. It may be provided as a discrete material dispersed in the host material, or it may be bonded in some way to the host material, for example, covalently bonded into a polymeric host.

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 to select materials that will not 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.

Host Materials for Phosphorescent Materials

Suitable host materials have a triplet energy (the difference in energy between the lowest triplet excited state and the singlet ground state of the host) that is greater than or equal to the triplet energy of the phosphorescent emitter. This energy level state is necessary so that triplet excitons are transferred to the phosphorescent emitter molecules and any triplet excitons formed directly on the phosphorescent emitter molecules remain until emission occurs. However, efficient emission from devices in which the host material has a lower triplet energy than the phosphorescent emitter is still possible in some cases as reported by C. Adachi, et al Appl. Phys. Lett., 79 2082-2084 (2001). Triplet energy is conveniently measured by any of several means, as discussed for instance in S. L. Murov, I. Carmichael, and G. L. Hug, *Handbook of Photochemistry,* 2nd ed. (Marcel Dekker, New York, 1993).

In the absence of experimental data the triplet energies may be estimated in the following manner. The triplet state energy for a molecule is defined as the difference between the ground state energy (E(gs)) of the molecule and the energy of the lowest triplet state (E(ts)) of the molecule, both given in eV. These energies can be calculated using the B3LYP method as implemented in the Gaussian98 (Gaussian, Inc., Pittsburgh, Pa.) computer program. The basis set for use with the B3LYP method is defined as follows: MIDI! for all atoms for which

MIDI! is defined, 6-31 G* for all atoms defined in 6-31 G* but not in MIDI!, and either the LACV3P or the LANL2DZ basis set and pseudopotential for atoms not defined in MIDI! or 6-31 G*, with LACV3P being the preferred method. For any remaining atoms, any published basis set and pseudopotential may be used. MIDI!, 6-31G* and LANL2DZ are used as implemented in the Gaussian98 computer code and LACV3P is used as implemented in the Jaguar 4.1 (Schrodinger, Inc., Portland Oreg.) computer code. The energy of each state is computed at the minimum-energy geometry for that state. The difference in energy between the two states is further modified by Equation 1 to give the triplet state energy (E(t)):

$$E(t)=0.84*(E(ts)-E(gs))+0.35 \tag{1}$$

For polymeric or oligomeric materials, it is sufficient to compute the triplet energy over a monomer or oligomer of sufficient size so that additional units do not substantially change the computed triplet energy of the material.

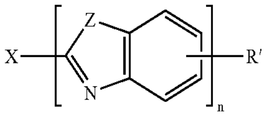
Desirable host materials are capable of forming a continuous film. The light-emitting layer may contain more than one host material in order to improve the device's film morphology, electrical properties, light emission efficiency, and lifetime. Suitable host materials are described in WO00/70655; WO01/39234; WO01/93642; WO02/074015; WO02/15645, and US20020117662.

Types of triplet host materials may be categorized according to their charge transport properties. The two major types are those that are predominantly electron-transporting and those that are predominantly hole-transporting. It should be noted that some host materials which may be categorized as transporting dominantly one type of charge, may transport both types of charges, especially in certain device structures, for example CBP which is described in C. Adachi, R. Kwong, and S. R. Forrest, Organic Electronics, 2, 37-43 (2001). Another type of host are those having a wide energy gap between the HOMO and LUMO such that they do not readily transport charges of either type and instead rely on charge injection directly into the phosphorescent dopant molecules.

A desirable electron transporting host may be any suitable electron transporting compound, such as benzazole, phenanthroline, 1,3,4-oxadiazole, triazole, triazine, or triarylborane, as long as it has a triplet energy that is higher than that of the phosphorescent emitter to be employed.

A preferred class of benzazoles is described by Jianmin Shi et al. in U.S. Pat. No. 5,645,948 and U.S. Pat. No. 5,766,779. Such compounds are represented by structural formula (PHF-1):

(PHF-1)



In formula (PHF-1), n is selected from 2 to 8;

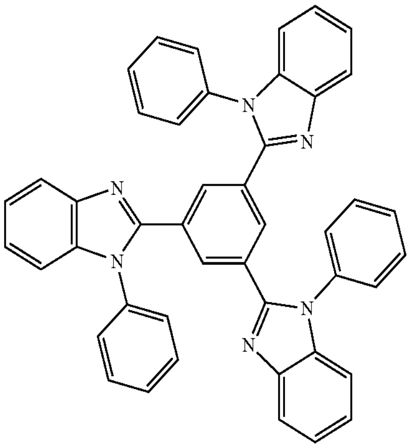
Z is independently O, NR or S;

R and R' 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, quinolinyl and other heterocyclic systems; or halo such as chloro, fluoro; or atoms necessary to complete a fused aromatic ring; and

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

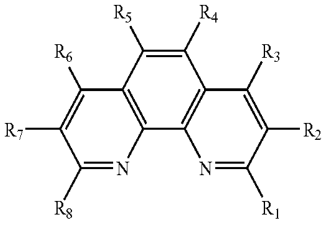
An example of a useful benzazole is 2,2',2"-(1,3,5-phenylene)tris[1-phenyl-1H-benzimidazole] (TPBI) represented by a formula (PHF-2) shown below:

(PHF-2)



Another class of the electron transporting materials suitable for use as a host includes various substituted phenanthrolines as represented by formula (PHF-3):

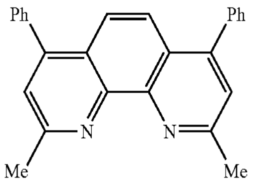
(PHF-3)



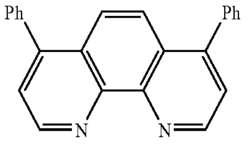
In formula (PHF-3), R_1—R_8 are independently hydrogen, alkyl group, aryl or substituted aryl group, and at least one of R_1—R_8 is aryl group or substituted aryl group.

Examples of suitable materials are 2,9-dimethyl-4,7-diphenyl-phenanthroline (BCP) (see formula (PH-1)) and 4,7-diphenyl-1,10-phenanthroline (Bphen) (see formula (PH-2)).

(PH-1)

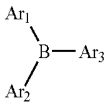


(PH-2)



A triarylboranes that functions as an electron transporting host may be selected from compounds having the chemical formula (PHF-4):

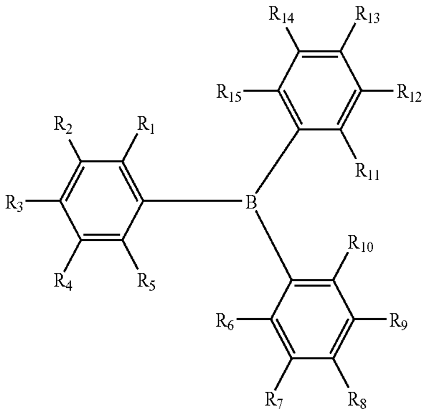
(PHF-4)



wherein

Ar_1 to Ar_3 are independently an aromatic hydrocarbocyclic group or an aromatic heterocyclic group which may have one or more substituent. It is preferable that compounds having the above structure are selected from formula (PHF-5):

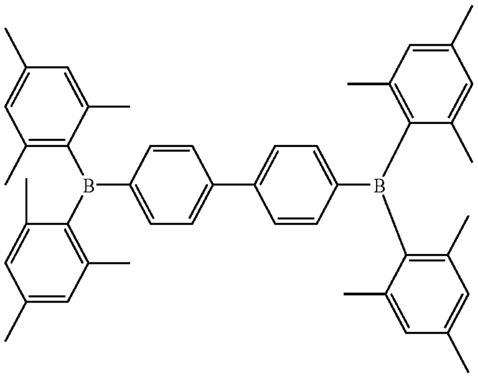
(PHF-5)



wherein R_1—R_{15} are independently hydrogen, fluoro, cyano, trifluoromethyl, sulfonyl, alkyl, aryl or substituted aryl group.

Specific representative embodiments of the triarylboranes include:

(PH-3)



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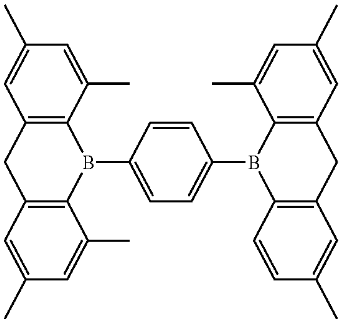
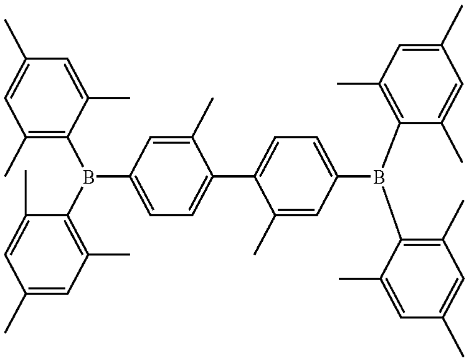
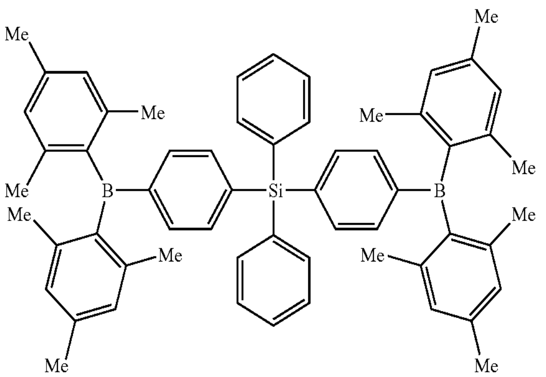
(PH-4)



(PH-5)

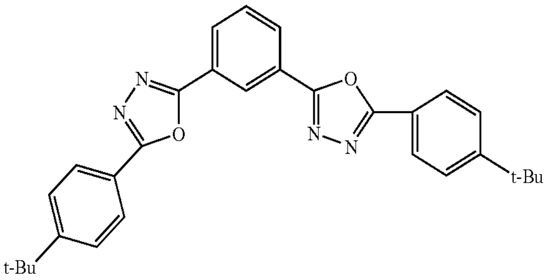


(PH-6)



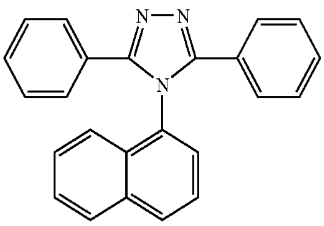
An electron transporting host may be selected from substituted 1,3,4-oxadiazoles. Illustrative of the useful substituted oxadiazoles are the following:

(PH-8)



An electron transporting host may be selected from substituted 1,2,4-triazoles. An example of a useful triazole is 3-phenyl-4-(1-naphtyl)-5-phenyl-1,2,4-triazole represented by formula (PHF-6):

(PHF-6)



The electron transporting host may be selected from substituted 1,3,5-triazines. Examples of suitable materials are:

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

2,4,6-tricarbazolo-1,3,5-triazine;

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

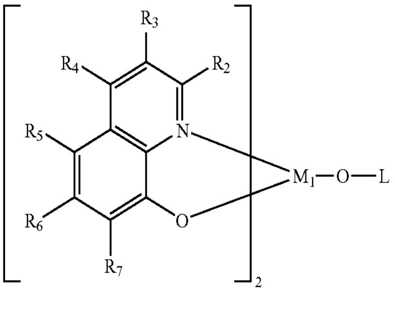
2,4,6-tris(N-phenyl-1-naphthylamino)-1,3,5-triazine;

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

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

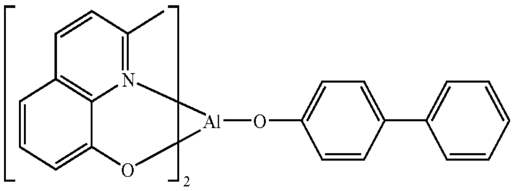
In one embodiment, a suitable host material is an aluminum or gallium complex. Particularly useful hosts materials are represented by Formula (PHF-7).

(PHF-7)

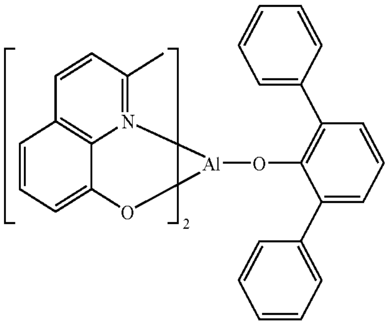


In Formula (PHF-7), M_1 represents Al or Ga. R_2—R_7 represent hydrogen or an independently selected substituent. Desirably, R_2 represents an electron-donating group, such as a methyl group. Suitably, R_3 and R_4 each independently represent hydrogen or an electron donating substituent. Preferably, 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. Illustrative examples of Formula (PHF-7) materials are listed below.

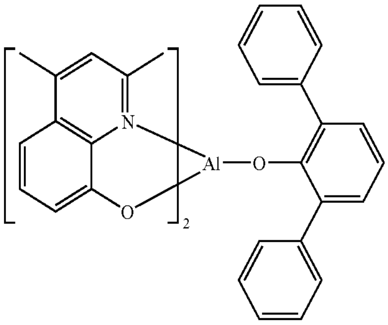
(PH-9)



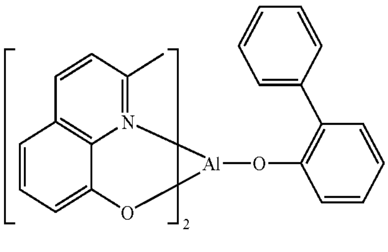
(PH-10)



(PH-11)



(PH-12)



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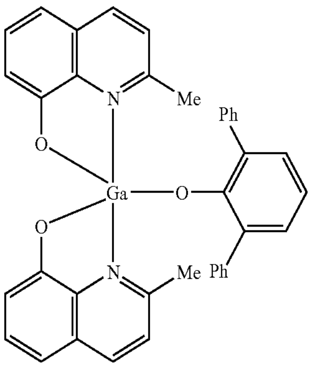
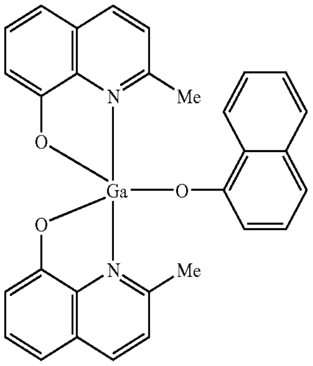
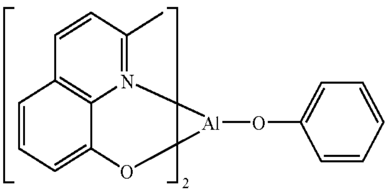
(PH-13)



(PH-14)



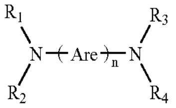
(PH-15)



A desirable hole transporting host may be any suitable hole transporting compound, such as a triarylamine or a carbazole, as long it has a triplet energy higher than that of the phosphorescent emitter to be employed. A suitable class of hole transporting compounds for use as a host are aromatic tertiary amines, by which it is understood to be compounds 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 can be an arylamine, such as a monoarylamine, diarylamine, triarylamine, or a polymeric arylamine. Exemplary monomeric triarylamines are illustrated by Klupfel et al. in U.S. Pat. No. 3,180,730. Other suitable triarylamines substituted with one or more vinyl radicals and/or comprising at least one active hydrogen containing group are disclosed by Brantley et al. in U.S. Pat. No. 3,567,450 and U.S. Pat. No. 3,658,520.

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. No. 4,720,432 and U.S. Pat. No. 5,061,569. Such as the tetraaryldiamines. Desirable tetraaryldiamines include two diarylamino groups, such as indicated by formula (PHF-8):

(PHF-8)



$$(R_1)(R_2)N\text{-}(\text{Are})_n\text{-}N(R_3)(R_4)$$

wherein each Are is an independently selected arylene group, such as a phenylene or anthracene moiety,

n is selected from 1 to 4, and

R_1—R_4 are independently selected aryl groups.

In a typical embodiment, at least one of R_1—R_4 is a polycyclic fused ring structure, e.g., a naphthalene. However, when the emission of the dopant is blue or green in color it is less preferred to have an aryl amine host material to have a polycyclic fused ring substituent.

Representative examples of the useful compounds include the following:

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

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

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

4,4'-Bis-diphenylamino-terphenyl;

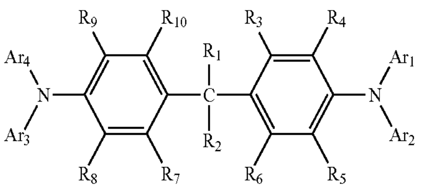
2,6,2',6'-tetramethyl-N,N,N',N'-tetraphenyl-benzidine.4,4',4"-tris[(3-methylphenyl)phenylamino]triphenylamine (MTDATA);

4,4',4"-tris(N,N-diphenyl-amino)triphenylamine (TDATA);

N,N-bis[2,5-dimethyl-4-[(3-methylphenyl)phenylamino]phenyl]-2,5-dimethyl-N'-(3-methylphenyl)-N'-phenyl-1,4-benzenediamine.

In one desirable embodiment the hole transporting host comprises a material of formula (PHF-9):

(PHF-9)



In formula (PHF-9), 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;

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

R_3—R_{10} independently represent hydrogen, alkyl, substituted alkyl, aryl, substituted aryl group.

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

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

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

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

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

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

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

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

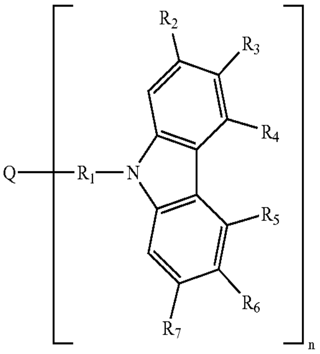
Bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)ethane;

4-(4-Diethylaminophenyl)triphenylmethane;

4,4'-Bis(4-diethylaminophenyl)diphenylmethane.

A useful class of compounds for use as the hole transporting host includes carbazole derivatives such as those represented by formula (PHF-0):

(PHF-10)



In formula (PHF-10), Q independently represents nitrogen, carbon, silicon, a substituted silicon group, an aryl group, or substituted aryl group, preferably a phenyl group;

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

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

and n is selected from 1 to 4.

Illustrative useful substituted carbazoles are the following:

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

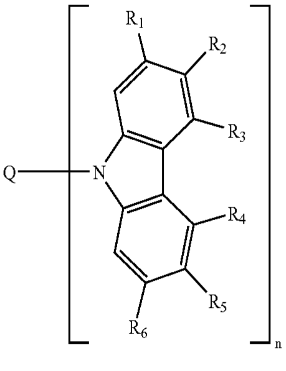
4-(3-phenyl-9H-carbazol-9-yl)-N,N-bis[4(3-phenyl-9H-carbazol-9-yl)phenyl]-benzenamine;

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

3,5-bis(9-carbazolyl)tetraphenylsilane (SimCP).

In one suitable embodiment the hole transporting host comprises a material of formula (PHF-11):

(PHF-11)



In formula (PHF-11), n is selected from 1 to 4;

Q independently represents phenyl group, substituted phenyl group, biphenyl, substituted biphenyl group, aryl, or substituted aryl group;

R_1 through R_6 are independently hydrogen, alkyl, phenyl or substituted phenyl, aryl amine, carbazole, or substituted carbazole.

Examples of suitable materials are the following:

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

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

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

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

9,9',9"-(1,3,5-benzenetriyl)tris-9H-carbazole;

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

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

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

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

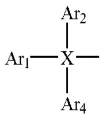
Host materials which are electron transporting or hole transporting with some electron transporting properties, such as carbazoles, are generally more desirable when used as a single host material. This is especially true for typical phosphorescent dopants that are hole-trapping or capable of accepting injected holes. Less preferable are host materials which are primarily hole transporting and have little electron transporting properties, such as triarlyamines. Injecting electrons into these latter hole transporting hosts may be difficult because of their relatively high LUMO energies.

Host materials may comprise a mixture of two or more host materials. Particularly useful is a mixture comprising at least one each of an electron-transporting and a hole-transporting co-host. The optimum concentration of the hole transporting co-host(s) may be determined by experimentation and may be within the range 10 to 60 weight % of the total of the hole- and electron transporting co-host materials in the light emitting layer, and is often found to be in the range 15 to 30 wt. %. It is further noted that electron-transporting molecules and hole-transporting molecules may be covalently joined together to form single host molecules having both electron-transporting and hole-transporting properties.

A wide energy gap host material may be any suitable compound having a large HOMO-LUMO gap such that the HOMO and LUMO of the phosphorescent emissive material are within the HOMO and LUMO for the host. In this case, the phosphorescent emissive material acts as the primary charge carrier for both electrons and holes, as well as the site for the trapping of excitons. Often the phosphorescent dopants for use with the wide energy gap hosts are selected to have electron-withdrawing substituents to facilitate electron injection. The "wide energy gap" host material functions as a non-charge carrying material in the system. Such a combination may lead to high operation voltage of the device, as the concentration of the charge-carrying dopant is typically below 10% in the emissive layer.

Thompson et al. disclosed in US 2004/0209115 and US 2004/0209116 a group of wide energy gap hosts having triplet energies suitable for blue phosphorescent OLEDs. Such compounds include those represented by structural formula (PHF-12):

(PHF-12)



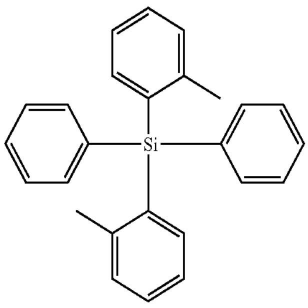
$$Ar_1-X(Ar_2)(Ar_4)-Ar_3$$

wherein:

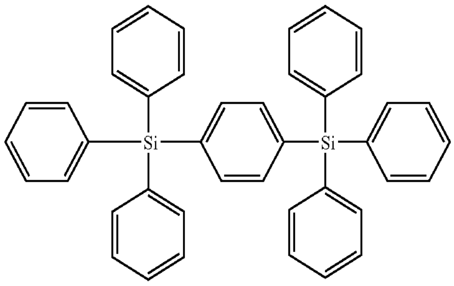
X is Si or Pb; Ar_1, Ar_2, Ar_3 and Ar_4 are each an aromatic group independently selected from phenyl and high triplet energy heterocyclic groups such as pyridine, pyrazole, thiophene, etc. It is believed that the HOMO-LUMO gaps in these materials is large due to the electronically isolated aromatic units, and the lack of any conjugating substituents.

Illustrative examples of this type of hosts include:

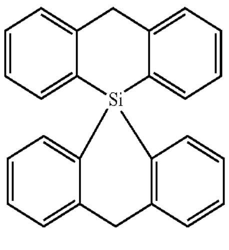
(PH-16)



(PH-17)



(PH-18)



Phosphorescent Materials

Phosphorescent materials may be used singly or in combination with other phosphorescent materials, either in the same or different layers. Some other phosphorescent materials are described in WO 00/57676, WO 00/70655, WO 01/41512, WO 02/15645, US 2003/0017361, WO 01/93642, WO 01/39234, U.S. Pat. No. 6,458,475, WO 02/071813, U.S. Pat. No. 6,573,651, US 2002/0197511, WO 02/074015, U.S. Pat. No. 6,451,455, US 2003/0072964, US 2003/0068528, U.S. Pat. No. 6,413,656, U.S. Pat. No. 6,515,298, U.S. Pat. No. 6,451,415, U.S. Pat. No. 6,097,147, US 2003/0124381, US 2003/0059646, US 2003/0054198, EP 1 239 526, EP 1 238 981, EP 1 244 155, US 2002/0100906, US 2003/0068526, US 2003/0068535, JP 2003073387, JP 2003073388, US 2003/0141809, US 2003/0040627, JP 2003059667, JP 2003073665, and US 2002/0121638.

In many known hosts and device architectures for phosphorescent OLEDs, the optimum concentration of the phosphorescent dopant for luminous efficiency is found to be about 1 to 20 vol % and often 6 to 8 vol % relative to the host material. However, in a preferred embodiment, wherein the host comprises at least one electron-transporting co-host and at least one hole-transporting co-host in the light-emitting layer, a phosphorescent material concentration from about 0.5% to about 6% often provides high luminous efficiencies.

The emission wavelengths of cyclometallated Ir(III) complexes of the type IrL_3 and IrL_2L', such as the green-emitting fac-tris(2-phenylpyridinato-N,$C^{2'}$)Iridium(III) and bis(2-phenylpyridinato-N,$C^{2'}$)Iridium(III)(acetylacetonate) may be shifted by substitution of electron donating or withdrawing groups at appropriate positions on the cyclometallating ligand L, or by choice of different heterocycles for the cyclometallating ligand L. The emission wavelengths may also be shifted by choice of the ancillary ligand L'. Examples of red emitters are the bis(2-(2'-benzothienyl)pyridinato-N,$C^{3'}$)Iridium(III)(acetylacetonate) and tris(2-phenylisoquinolinato-N,C)Iridium(III). A blue-emitting example is bis(2-(4,6-diflourophenyl)-pyridinato-N,$C^{2'}$)Iridium(III)(picolinate).

Red electrophosphorescence has been reported, using bis (2-(2'-benzo[4,5-a]thienyl)pyridinato-N, $C^{3'}$) iridium (acetylacetonate) $[Btp_2Ir(acac)]$ as the phosphorescent material (Adachi, C., Lamansky, S., Baldo, M. A., Kwong, R. C., Thompson, M. E., and Forrest, S. R., *App. Phys. Lett.,* 78, 1622-1624 (2001).

Other important phosphorescent materials include 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-diflourophenyl)pyridinato-N$C^{2'}$) platinum (II) acetylacetonate. Pt(II) porphyrin complexes such as 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum(II) are also useful phosphorescent materials.

Still other examples of useful phosphorescent materials include coordination complexes of the trivalent lanthanides such as Tb^{3+} and Eu^{3+} (J. Kido et al, *Appl. Phys. Lett.,* 65, 2124 (1994))

Blocking Layers

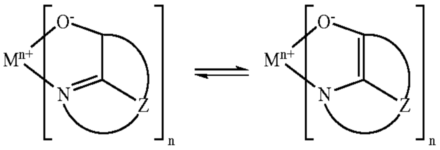
In addition to suitable hosts and transporting materials, an OLED device employing a phosphorescent material often requires at least one exciton or hole blocking layer to help confine the excitons or electron-hole recombination centers to the light emitting layer comprising the host and phosphorescent material. In one embodiment, a hole-blocking layer (EBL) **110** would be placed between the electron transporting layer and the light emitting layer. In this case, the ionization potential of the blocking layer should be such that there is an energy barrier for hole migration from the light emitting layer into the electron-transporting layer, while the electron affinity should be such that electrons pass readily from the electron transporting layer into the light emitting layer. It is further desired, but not absolutely required, that the triplet energy of the blocking material be greater than that of the phosphorescent material. Suitable hole blocking materials are described in WO 00/70655 and WO 01/93642. Two examples of useful 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.

Electron-Transporting Layer (ETL)

The electron transporting material deposited in said electron transporting layer between the cathode and the light emitting layer may be the same or different from an electron transporting co-host material. The electron transporting layer may include more than one electron transporting compound, deposited as a blend or divided into separate layers.

Preferred thin film-forming materials for use in constructing the electron transporting layer of the organic EL devices of this invention are metal-chelated oxinoid compounds, including chelates of oxine itself (also commonly referred to as 8-quinolinol or 8-hydroxyquinoline). Such compounds help to inject and transport electrons, exhibiting high levels of performance, and are readily fabricated in the form of thin films. Exemplary of contemplated oxinoid compounds are those satisfying structural formula (ET1) below:

(ET1)



wherein

M represents a metal;

n is an integer of from 1 to 4; and

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

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 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.

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.

Illustrative of useful chelated oxinoid compounds are the following:

CO-1: Aluminum trisoxine [alias, tris(8-quinolinolato)aluminum(III); Alq];

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

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

CO-4: Bis(2-methyl-8-quinolinolato)aluminum(III)-μ-oxo-bis(2-methyl-8-quinolinolato) aluminum(III);

CO-5: Indium trisoxine [alias, tris(8-quinolinolato)indium];

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

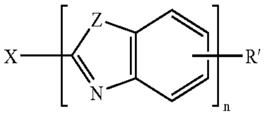
CO-7: Lithium oxine [alias, (8-quinolinolato)lithium(I)];

CO-8: Gallium oxine [alias, tris(8-quinolinolato)gallium (III)];

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

Other electron transporting materials suitable for use in the electron transporting layer 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. Benzazoles satisfying structural formula (ET2) are also useful electron transporting materials:

(ET2)



wherein

n is an integer of 3 to 8;

Z is O, NR or S; and

R and R' 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, quinolinyl and other heterocyclic systems; or halo such as chloro, fluoro; or atoms necessary to complete a fused aromatic ring; and

X is a linkage unit consisting of carbon, alkyl, aryl, substituted alkyl, or substituted aryl, which conjugately or unconjugately connects the multiple benzazoles together. An example of a useful benzazole is 2,2',2"-(1,3,5-phenylene)tris[1-phenyl-1H-benzimidazole] (TPBI) disclosed in Shi et al. in U.S. Pat. No. 5,766,779.

Other electron transporting materials suitable for use in the electron transporting layer may be selected from triazines, triazoles, imidazoles, oxazoles, thiazoles and their derivatives, polybenzobisazoles, pyridine- and quinoline-based materials, cyano-containing polymers, perfluorinated materials, and various substituted phenanthrolines.

The electron transporting layer or a portion of the electron transporting layer adjacent the cathode may further be doped with an alkali metal to reduce electron injection barriers and hence lower the drive voltage of the device. Suitable alkali metals for this purpose include lithium and cesium.

Cathode

When light emission is viewed solely through the anode **103**, the cathode used in this invention can be comprised of nearly any conductive material. Desirable materials have good film-forming properties to ensure good contact with the underlying organic layer, promote electron injection at low voltage, and have good stability. Useful cathode materials often contain a low work function metal (<4.0 eV) or metal alloy. One useful cathode material is comprised of a Mg:Ag alloy wherein the percentage of silver is in the range of 1 to 20%, as described in U.S. Pat. No. 4,885,221. Another suitable class of cathode materials includes bilayers comprising a thin electron-injection layer (EIL) in contact with an organic layer (e.g., an electron transporting layer (ETL)) which is capped with a thicker layer of a conductive metal. Here, the 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 is comprised of a thin layer of LiF followed by a thicker layer of Al as described in U.S. Pat. No. 5,677,572. An ETL material doped with an alkali metal, for example, Li-doped Alq, as disclosed in U.S. Pat. No. 6,013,384, is another example of a useful EIL. 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.

When light emission is viewed through the cathode, the cathode must be transparent or nearly transparent. For such applications, metals must be thin or one must use transparent conductive oxides, or a combination of these materials. Optically transparent cathodes have been described in more detail in U.S. Pat. No. 4,885,211, U.S. Pat. No. 5,247,190, JP 3,234, 963, U.S. Pat. No. 5,703,436, U.S. Pat. No. 5,608,287, U.S. Pat. No. 5,837,391, U.S. Pat. No. 5,677,572, U.S. Pat. No. 5,776,622, U.S. Pat. No. 5,776,623, U.S. Pat. No. 5,714,838, U.S. Pat. No. 5,969,474, U.S. Pat. No. 5,739,545, U.S. Pat. No. 5,981,306, U.S. Pat. No. 6,137,223, U.S. Pat. No. 6,140, 763, U.S. Pat. No. 6,172,459, EP 1 076 368, U.S. Pat. No. 6,278,236, and U.S. Pat. No. 6,284,393. Cathode materials are typically deposited by any suitable methods such as evaporation, sputtering, or chemical vapor deposition. When needed, patterning can be achieved through many well known methods including, but not limited to, through-mask deposition, integral shadow masking as described in U.S. Pat. No. 5,276,380 and EP 0 732 868, laser ablation, and selective chemical vapor deposition.

Other Common Organic Layers and Device Architecture

In some instances, layers **109** and **111** can optionally be collapsed into a single layer that serves the function of supporting both light emission and electron transportation. It also known in the art that emitting dopants may be added to the hole-transporting layer, which may serve as a host. Multiple dopants may be added to one or more layers in order to create a white-emitting OLED, for example, by combining blue- and yellow-emitting materials, cyan- and red-emitting materials, or red-, green-, and blue-emitting materials. White-emitting devices are described, for example, in EP 1 187 235, EP 1 182 244, U.S. Pat. No. 5,683,823, U.S. Pat. No. 5,503, 910, U.S. Pat. No. 5,405,709, and U.S. Pat. No. 5,283,182, US 20020186214, US 20020025419, US 20040009367, and US 6627333.

Additional layers such as exciton, electron and hole-blocking layers as taught in the art may be employed in devices of this invention. Hole-blocking layers are commonly used to improve efficiency of phosphorescent emitter devices, for example, as in US 20020015859, WO 00/70655A2, WO 01/93642A1, US 20030068528 and US 20030175553 A1

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.

Deposition of Organic Layers

The organic materials mentioned above are suitably deposited through a vapor-phase method such as sublimation, but can be deposited from a fluid, for example, from a solvent with an optional binder to improve film formation. If the material is a polymer, solvent deposition is useful but other methods can be used, such as sputtering or thermal transfer from a donor sheet. The material to be deposited by sublimation can be vaporized from a sublimation "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 sublimation boats or the materials can be pre-mixed and coated from a single boat or donor sheet. Patterned deposition can be achieved using shadow masks, integral shadow masks (U.S. Pat. No. 5,294,870), spatially-defined thermal dye transfer from a donor sheet (U.S. Pat. Nos. 5,688,551, 5,851,709 and 6,066,357) and inkjet method (U.S. Pat. No. 6,066,357).

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

Most OLED devices are sensitive to moisture or oxygen, or both, so they are commonly sealed in an inert atmosphere such as nitrogen or argon. In sealing an OLED device in an inert environment, a protective cover can be attached using an organic adhesive, a metal solder, or a low melting temperature glass. Commonly, a getter or desiccant is also provided within the sealed space. Useful getters and desiccants include, alkali and alkaline metals, 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. In addition, barrier layers such as SiOx, Teflon, and alternating inorganic/polymeric layers are known in the art for encapsulation.

Optical Optimization

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 in functional relationship with the light emitting areas of the display. Filters, polarizers, and anti-glare or anti-reflection coatings can also be provided over a cover or as part of a cover.

The OLED device may have a microcavity structure. In one useful example, one of the metallic electrodes is essentially opaque and reflective; the other one is reflective and semitransparent. The reflective electrode is preferably selected from Au, Ag, Mg, Ca, or alloys thereof. Because of the presence of the two reflecting metal electrodes, the device has a microcavity structure. The strong optical interference in this structure results in a resonance condition. Emission near the resonance wavelength is enhanced and emission away from the resonance wavelength is depressed. The optical path length can be tuned by selecting the thickness of the organic layers or by placing a transparent optical spacer between the electrodes. For example, an OLED device of this invention can have ITO spacer layer placed between a reflective anode and the organic EL media, with a semitransparent cathode over the organic EL media.

The following examples demonstrate the effects of the invention:

EXAMPLES

Example 1

An EL device (Sample 1) satisfying the requirements of the invention was constructed in the following manner:

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, degreased in toluene vapor and exposed to oxygen plasma for about 1 min.
2. Over the ITO was deposited a 1 nm fluorocarbon (CFx) hole-injecting layer (HIL) by plasma-assisted deposition of CHF_3.
3. A hole-transporting layer (HTL)of N,N'-di-1-naphthyl-N,N'-diphenyl-4,4'-diaminobiphenyl (NPB) having a thickness of 75 nm was then evaporated from a tantalum boat.
4. A 35 nm light-emitting layer (LEL) of 4,4'-N,N'-dicarbazole-biphenyl (CBP) and Inv-1 (1 wt %) were then deposited onto the hole-transporting layer. These materials were also evaporated from tantalum boats.
5. A hole-blocking layer of bis(2-methyl-quinolinolato)(2,4,6-triphenylphenolato)aluminum(III) (Balq) having a thickness of 10 nm was then evaporated from a tantalum boat.
6. A 40 nm electron-transporting layer (ETL) of tris(8-quinolinolato)aluminum (III) (AlQ_3) was then deposited onto the hole-blocking layer. This material was also evaporated from a tantalum boat.
7. On top of the AlQ_3 layer was deposited a cathode formed by first depositing a 1 nm layer of LiF followed by 150 nm of aluminum.

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

Samples 2-6 were fabricated in an identical manner to Sample 1 except the concentration of the emitter Inv-1 in the light emitting layer was increased to 2, 4, 6, 8, and 10 wt %, respectively. The sample cells thus formed were tested for efficiency and color. All samples displayed an electroluminescence spectrum very similar to the solution spectrum of Inv-1 and the λ_{max} of the electroluminance varied slightly with concentration of Inv-1 across the series from 495 to 509 nm. The luminance yield also increased steadily with concentration of Inv-1 until a maximum was reached at 8 wt % in Sample 5. The maximum luminance yield in Sample 5 was 28.9 cd/A with CIE (Commission Internationale de L'Eclairage) X,Y coordinates of 0.24, 0.59.

TABLE 1

Evaluation Results for EL devices.

Sample	Inv-1 (%)	Max. Luminance Yield (cd/A)	λmax (nm)	CIEx	CIEy
1	1	4.14	497	0.176	0.445
2	2	7.81	498	0.196	0.487
3	4	18.50	505	0.225	0.559
4	6	25.30	508	0.239	0.582
5	8	28.90	509	0.248	0.591
6	10	27.00	509	0.252	0.594

Example 2

An EL device (Sample 7) satisfying the requirements of the invention was constructed in the following manner:

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, degreased in toluene vapor and exposed to oxygen plasma for about 1 min.
2. Over the ITO was deposited a 1 nm fluorocarbon (CFx) hole-injecting layer (HIL) by plasma-assisted deposition of CHF_3.
3. A hole-transporting layer (HTL) of N,N'-di-1-naphthyl-N,N'-diphenyl-4,4'-diaminobiphenyl (NPB) having a thickness of 95 nm was then evaporated from a tantalum boat.
4. A 35 nm light-emitting layer (LEL) of 9,9'-(1,3-phenylene)bis-9H-carbazole (mCP) and Inv-1 (8 wt %) were then deposited onto the hole-transporting layer. These materials were also evaporated from tantalum boats.
5. A hole-blocking layer of bis(2-methyl-quinolinolato)(2,4,6-triphenylphenolato)aluminum(III) (Balq) having a thickness of 10 nm was then evaporated from a tantalum boat.
6. A 40 nm electron-transporting layer (ETL) of tris(8-quinolinolato)aluminum (III) (AlQ_3) was then deposited onto the light-emitting layer. This material was also evaporated from a tantalum boat.
7. On top of the AlQ_3 layer was deposited a cathode formed by first depositing a 1 nm layer of LiF followed by 150 nm of aluminum.

The above sequence completed the deposition of the EL device. The device was then hermetically packaged in a dry glove box for protection against ambient environment. The sample cell thus formed was tested for efficiency and color. The results are reported in Table 2 below.

TABLE 2

Evaluation Results for EL device Sample 7.

Sample	Max. Luminance Yield (cd/A)	λmax (nm)	CIEx	CIEy
7	30.0	510	0.242	0.607

Example 3

An EL device (Sample 8) satisfying the requirements of the invention was constructed in the following manner:

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, degreased in toluene vapor and exposed to oxygen plasma for about 1 min.
2. Over the ITO was deposited a 1 nm fluorocarbon (CFx) hole-injecting layer (HIL) by plasma-assisted deposition of CHF_3.
3. A hole-transporting layer (HTL) of N,N'-di-1-naphthyl-N,N'-diphenyl-4,4'-diaminobiphenyl (NPB) having a thickness of 95 nm was then evaporated from a tantalum boat.
4. A 35 nm light-emitting layer (LEL) of 4-(9H-carbazol-9-yl)-N,N-bis[4-(9H-carbazol-9-yl)phenyl]-benzenamine (TCTA) and Inv-1 (8 wt %) were then deposited onto the hole-transporting layer. These materials were also evaporated from tantalum boats.
5. A hole-blocking layer of bis(2-methyl-quinolinolato)(2,4,6-triphenylphenolato)aluminum(III) (Balq) having a thickness of 10 nm was then evaporated from a tantalum boat.

6. A 40 nm electron-transporting layer (ETL) of tris(8-quinolinolato)aluminum (III) (AlQ_3) was then deposited onto the hole-blocking layer. This material was also evaporated from a tantalum boat.
7. On top of the AlQ_3 layer was deposited a cathode formed by first depositing a 1 nm layer of LiF followed by 150 nm of aluminum.

Example 4

An EL device (Sample 9) satisfying the requirements of the invention was constructed in the following manner:

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, degreased in toluene vapor and exposed to oxygen plasma for about 1 min.
2. Over the ITO was deposited a 1 nm fluorocarbon (CFx) hole-injecting layer (HIL) by plasma-assisted deposition of CHF_3.
3. A hole-transporting layer (HTL) of N,N'-di-1-naphthyl-N,N'-diphenyl-4,4'-diaminobiphenyl (NPB) having a thickness of 85 nm was then evaporated from a tantalum boat.
4. An exciton blocking layer of 4-(9H-carbazol-9-yl)-N,N-bis[4-(9H-carbazol-9-yl)phenyl]-benzenamine (TCTA) having a thickness of 10 nm was evaporated from a tantalum boat.
5. A 35 nm light-emitting layer (LEL) of 4-(9H-carbazol-9-yl)-N,N-bis[4-(9H-carbazol-9-yl)phenyl]-benzenamine (TCTA) and Inv-1 (8 wt %) were then deposited onto the hole-transporting layer. These materials were also evaporated from tantalum boats.
6. A hole-blocking layer of bis(2-methyl-quinolinolato)(2,4,6-triphenylphenolato)aluminum(III) (Balq) having a thickness of 10 nm was then evaporated from a tantalum boat.
7. A 40 nm electron-transporting layer (ETL) of tris(8-quinolinolato)aluminum (III) (AlQ_3) was then deposited onto the hole-blocking layer. This material was also evaporated from a tantalum boat.
8. On top of the AlQ_3 layer was deposited a cathode formed by first depositing a 1 nm layer of LiF followed by 150 nm of aluminum.

An EL device (Sample 10) satisfying the requirements of the invention was constructed in the same manner as Sample 9, except the thickness of the light emitting layer was reduced to 20 nm.

The above sequences completed the deposition of the EL device Samples 8, 9, and 10. The devices were then hermetically packaged in a dry glove box for protection against ambient environment.

The sample cells thus formed were tested for efficiency and color. The results are reported in Table 3 below and show good efficiency and green color for all three of the devices.

TABLE 3

Evaluation Results for EL devices.

Sample	Max. Luminance Yield (cd/A)	λmax (nm)	CIEx	CIEy
8	35.7	510	0.247	0.601
9	37.7	510	0.247	0.597
10	31.7	508	0.227	0.588

Embodiments of the invention can provide advantageous features such as operating efficiency, higher luminance, color hue, low drive voltage, and improved operating stability. Embodiments of the metallic compounds useful in the invention can provide a wide range of hues including those useful in the emission of white light (directly or through filters to provide multicolor displays).

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 entire contents of the patents and other publications referred to in this specification are incorporated herein by reference.

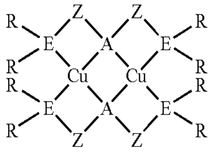
PARTS LIST

101 Substrate
103 Anode
105 Hole-Injecting layer (HIL)
107 Hole-Transporting layer (HTL)
108 Exciton Blocking Layer (EBL)
109 Light-Emitting layer (LEL)
110 Hole Blocking Layer (HBL)
111 Electron-Transporting layer (ETL)
113 Cathode
150 Current/Voltage source
160 Electrical conductors

The invention claimed is:

1. An OLED device comprising an anode, a cathode and therebetween a light emitting layer containing a phosphorescent compound represented by Formula I below:

Formula I

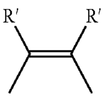


wherein:

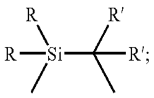
each A is independently selected from N and P;

each E is independently selected from N, P, and As;

each Z is a radical independently selected from the group consisting of



and



each R is an independently selected substituent; and

each R' is independently selected from H and a substituent;

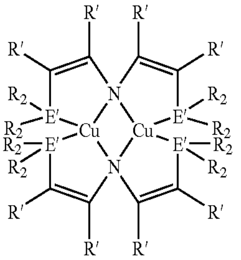
provided that two substituent groups can join to form a ring.

2. An OLED device of claim **1** wherein A represents N.

3. An OLED device of claim **2** wherein E represents P or As.

4. An OLED device of claim **1** wherein the compound is represented by Formula II below:

Formula II



wherein:

each E' is independently selected from P and As;

each R' is independently selected from H and a substituent; and

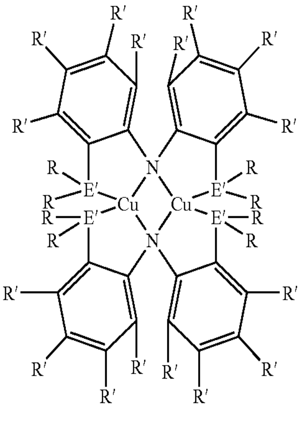
each R_2 is independently selected from alkyl, aryl, heteroaryl and cyano substituents;

provided two substituent groups can join to form a ring.

5. An OLED device of claim **4** wherein E' represents P.

6. An OLED device of claim **4** wherein the compound is represented by Formula III below:

Formula III



wherein:

each E' is independently selected from P and As;

each R is an independently selected substituent; and

each R' is independently selected from H or a substituent;

provided two substituent groups can join to form a ring.

7. An OLED device of claim **6** wherein, R is selected from alkyl, aryl, heteroaryl, and CN.

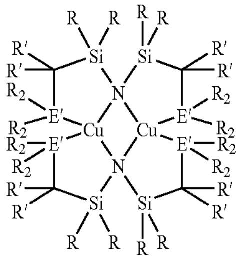
8. An OLED device of claim **6** wherein adjacent R' substituents join to form an aromatic ring.

9. An OLED device of claim **6** wherein E' represents P.

10. An OLED device of claim **6** wherein, R is selected from isobutyl and phenyl.

11. An OLED device of claim **1** wherein, the compound is represented by Formula IV below:

Formula IV



wherein:

each E' is independently selected from P and As;

each R is an independently selected substituent;

each R' is independently selected from H and a substituent;

each R_2 is independently selected from alkyl, aryl, heteroaryl and cyano substituents; and

provided two substituent groups on adjacent atoms can join to form a ring.

12. An OLED device of claim **11** wherein E' represents P.

13. An OLED device of claim **1** wherein the light emitting layer additionally comprises a carbazole.

14. An OLED device of claim **13** wherein the light emitting layer additionally comprises a compound selected from the group consisting of 4,4'-N,N'-dicarbazole-biphenyl (CBP), 9,9'-(1,3-phenylene)bis-9H-carbazole (mCP), 9,9'-(2,2'-dimethyl[1,1'-biphenyl]-4,4'-diyl)bis-9H-carbazole (CDBP), and 4-(9H-carbazol-9-yl)-N,N-bis[4-(9H-carbazol-9-yl)phenyl]-benzenamine (TCTA).

15. An OLED device of claim **1** wherein, the compound is from 1 to 15 wt % of the light emitting layer.

16. An OLED device of claim **1** including an exciton blocking layer adjacent to a phosphorescent light emitting layer, containing the phosphorescent compound of Formula (I) and a host material, on the anode side, and a hole-transporting layer adjacent to the exciton blocking layer on the anode side, the exciton blocking layer comprising a material having a triplet energy that exceeds that of the phosphorescent compound and is greater than 2.5 eV.

17. An OLED device of claim **16** wherein the material of said exciton blocking layer further comprises a material having a LUMO energy level greater by 0.2 eV or more than that of the host material of the light emitting layer.

18. An OLED device of claim **16** wherein the material in the exciton blocking layer is a triarylamine.

19. An OLED device of claim **18** wherein the triarylamine is selected from 1,1-Bis(4-(N,N-di-p-tolylamino)phenyl)cyclohexane and 2,2'-dimethyl-N,N,N',N'-tetrakis(4-methylphenyl)-1,1'-biphenyl-4,4'-diamine.

20. An OLED device of claim **16** wherein the host material of the light emitting layer is a carbazole.

21. An OLED device of claim **20** wherein the host material is selected from the group consisting of 9,9'-(2,2'-dimethyl[1,1'-biphenyl]-4,4'-diyl)bis-9H-carbazole; 9,9'-(1,3-phenylene)bis-9H-carbazole; and 4-(9H-carbazol-9-yl)-N,N-bis[4-(9H-carbazol-9-yl)phenyl]-benzenamine.

* * * * *

专利名称(译)	具有双核铜化合物的OLED器件		
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当前申请(专利权)人(译)	全球OLED科技有限责任公司		
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外部链接	Espacenet USPTO		

摘要(译)

OLED器件包括阳极，阴极和其间的发光层，该发光层含有由下式I表示的化合物： 其中：每个A独立地选自N和P;每个E独立地选自N，P和As;每个Z是独立地选自N，P和As的基团; 每个R是独立选择的取代基; an'和R'独立地选自H和取代基; 条件是两个取代基可以连接形成环。