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(54) **ORGANIC LIGHT EMITTING MATERIALS AND DEVICES**

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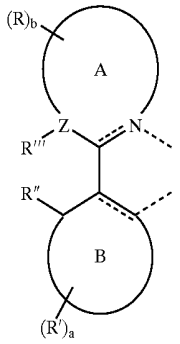
(57) **ABSTRACT**

An organic light emitting device is provided. The device has an anode, a cathode and an organic layer disposed between the anode and the cathode. The organic layer comprises a compound further comprising one or more arylimidazole, aryltriazole, or aryltetrazole derivative ligands coordinated to a metal center. The ligand has the structure:



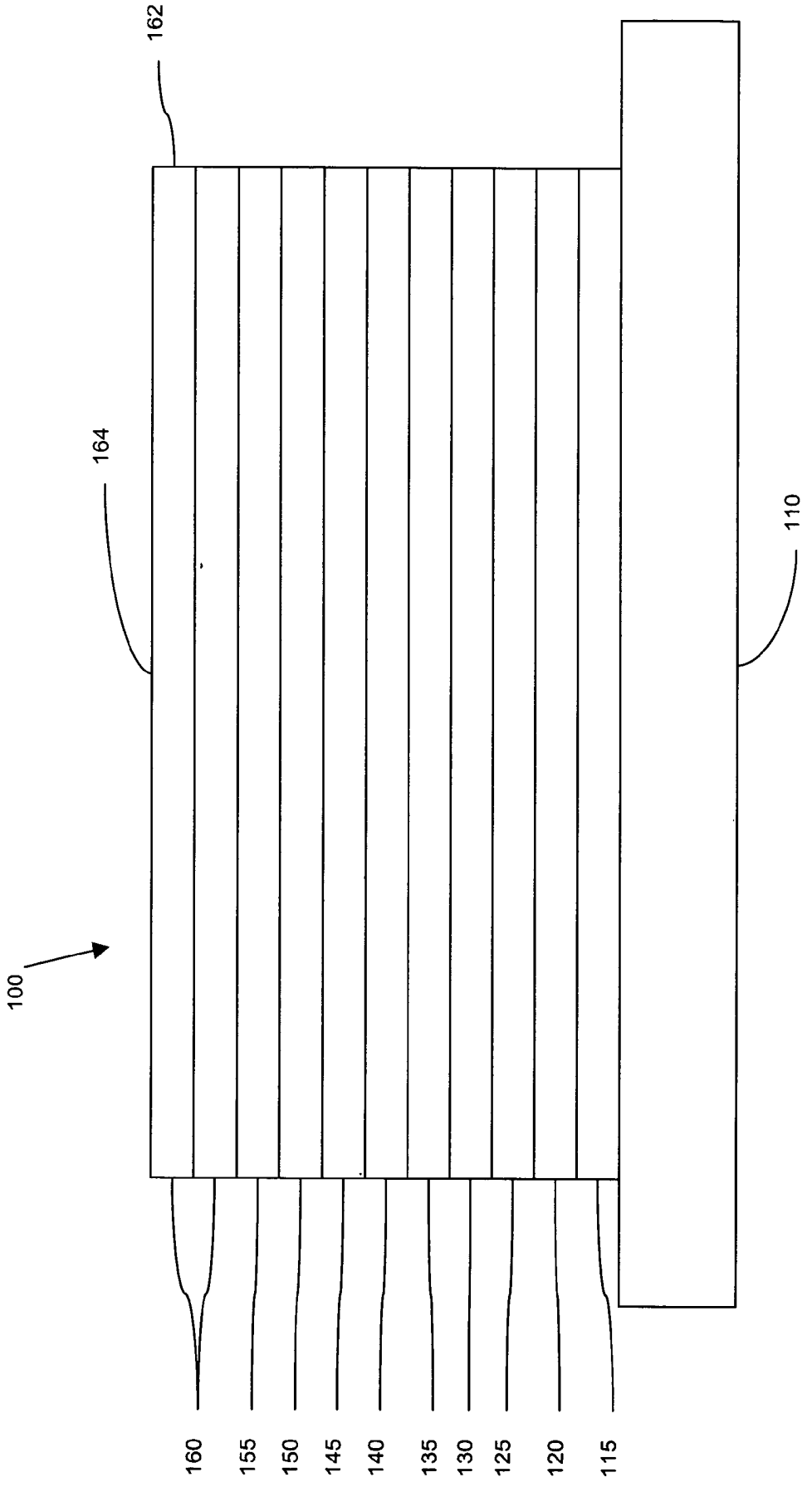


Figure 1

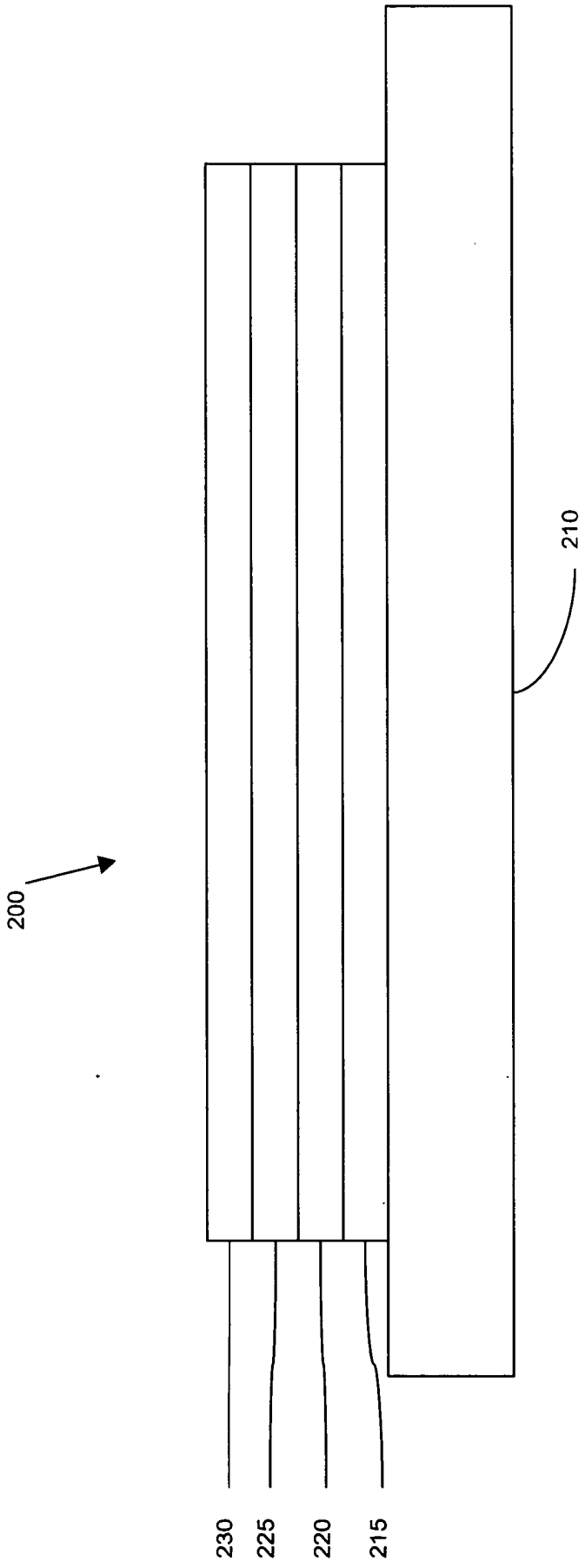


Figure 2

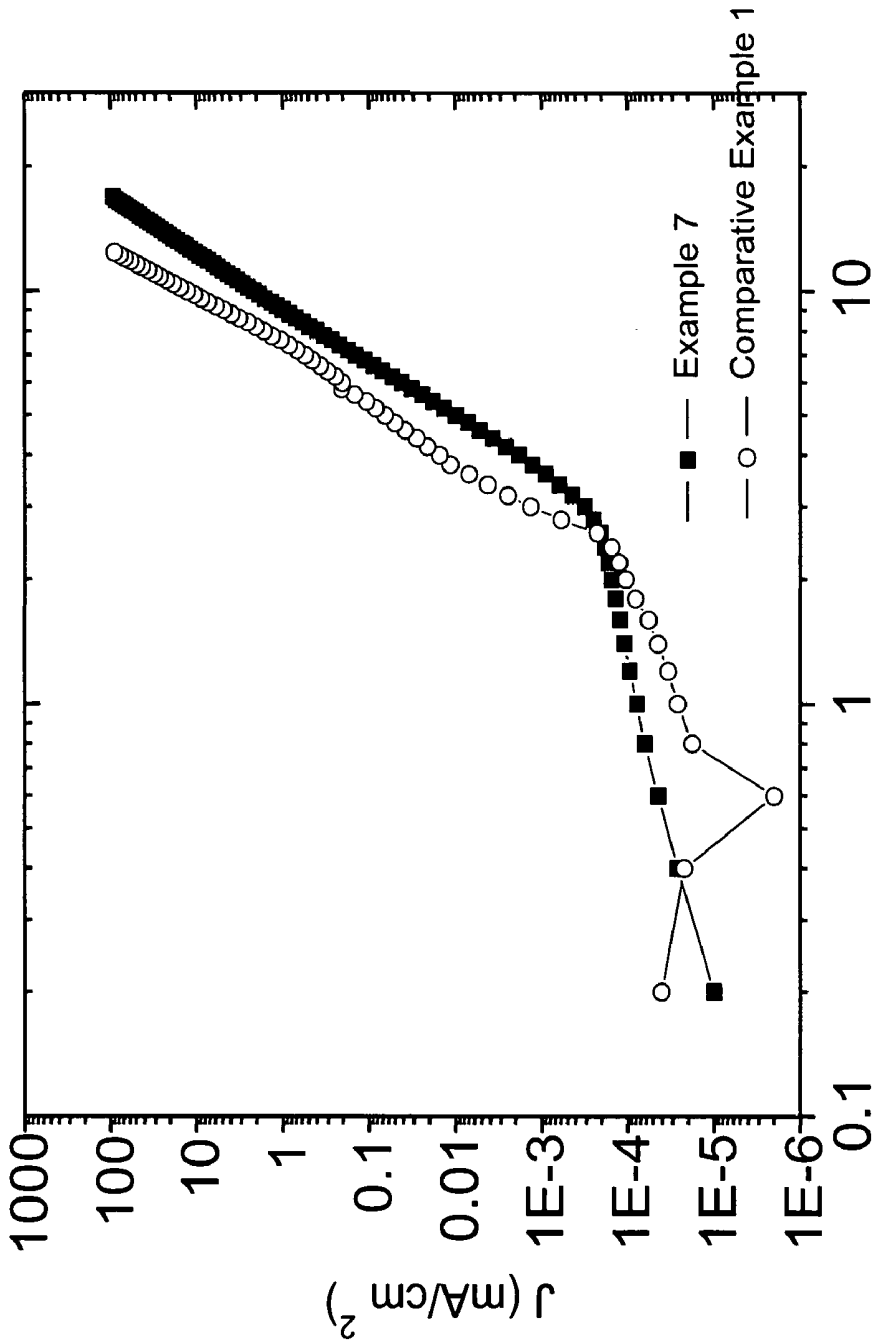

1000
100
10
1
0.1
0.01
1E-3
1E-4
1E-5
1E-6
J (mA/cm 2)
0.1
1
10
Voltage (V)
Example 7
Comparative Example 1

Figure 3

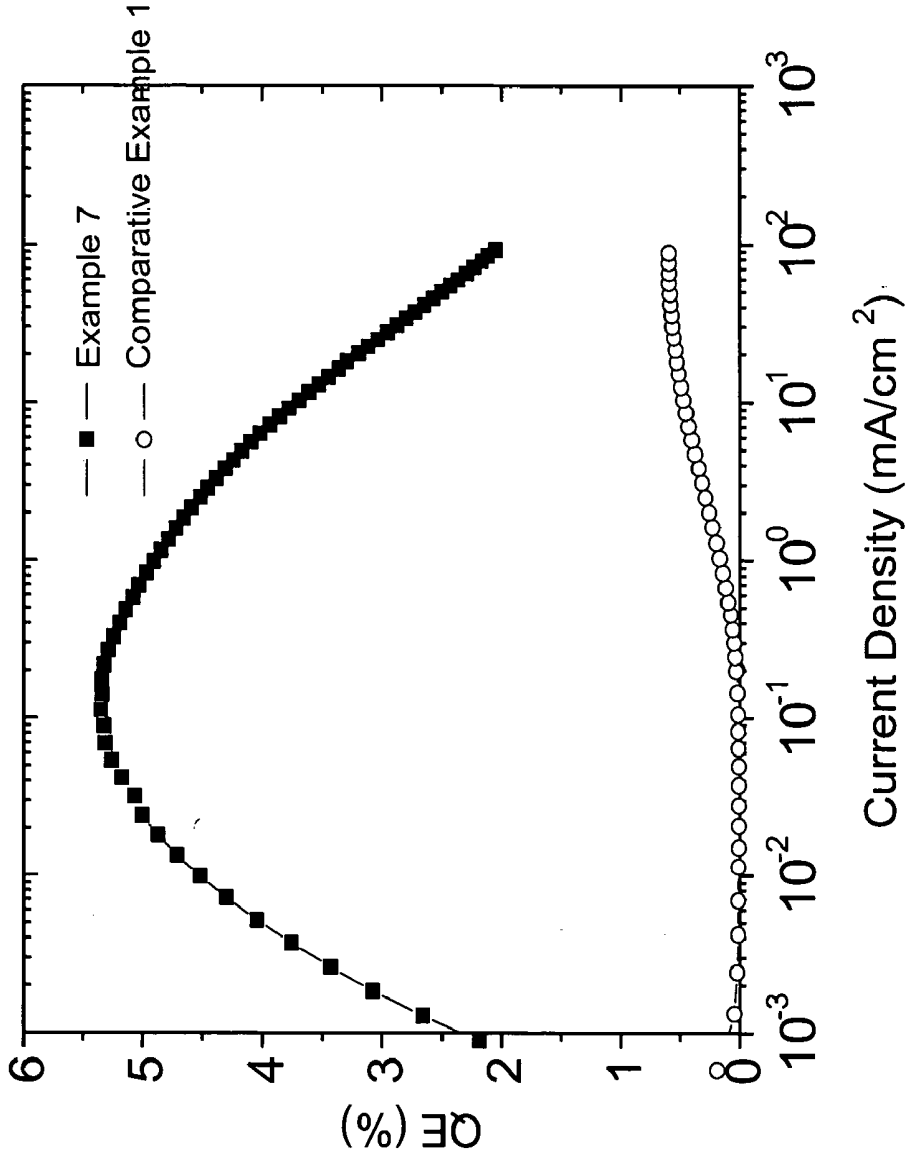

Example 7
Comparative Example 1
QE (%)
Current Density (mA/cm 2)
0
1
2
3
4
5
6
10-3
10-2
10-1
100
101
102
103

Figure 4

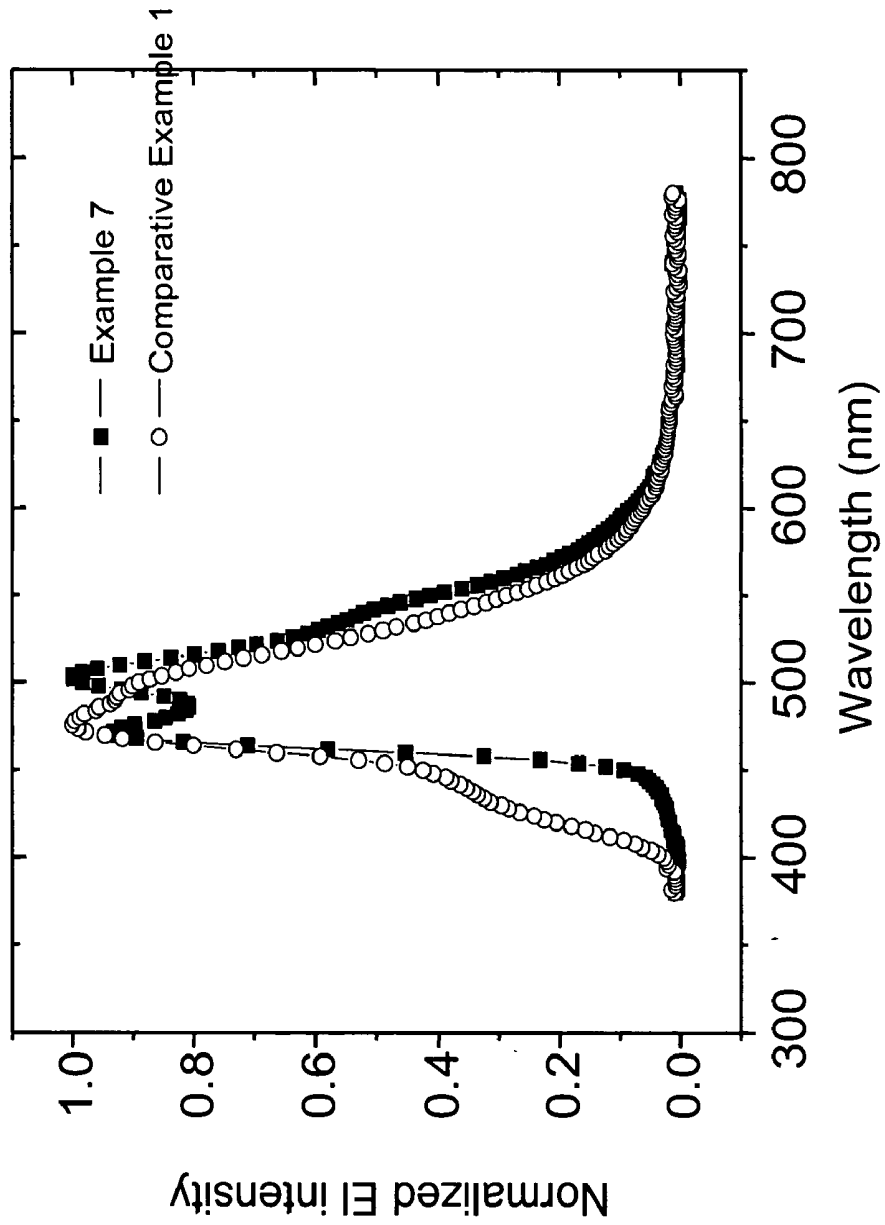

Example 7
Comparative Example 1
Normalized EI intensity
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
800

Figure 5

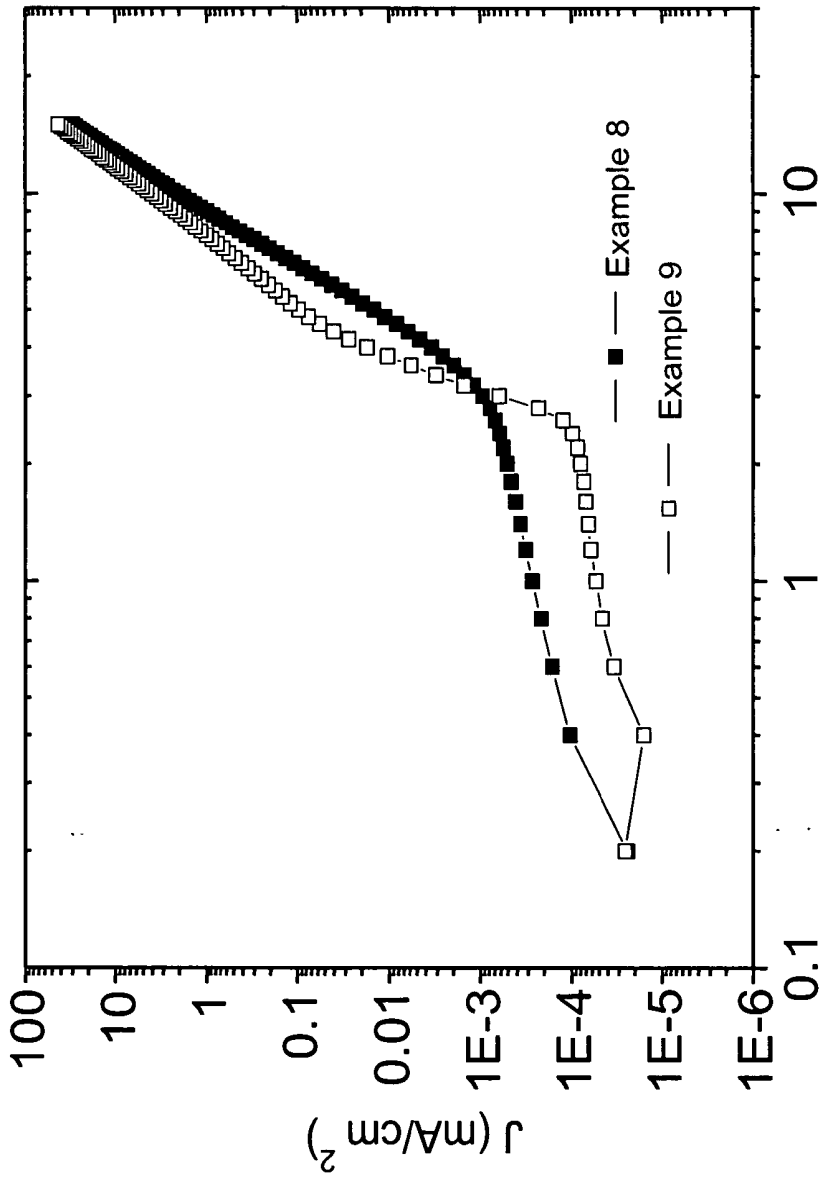

J (mA/cm 2)
100
10
1
0.1
0.01
1E-3
1E-4
1E-5
1E-6
0.1
1
10
Voltage (V)
Example 8
Example 9

Figure 6

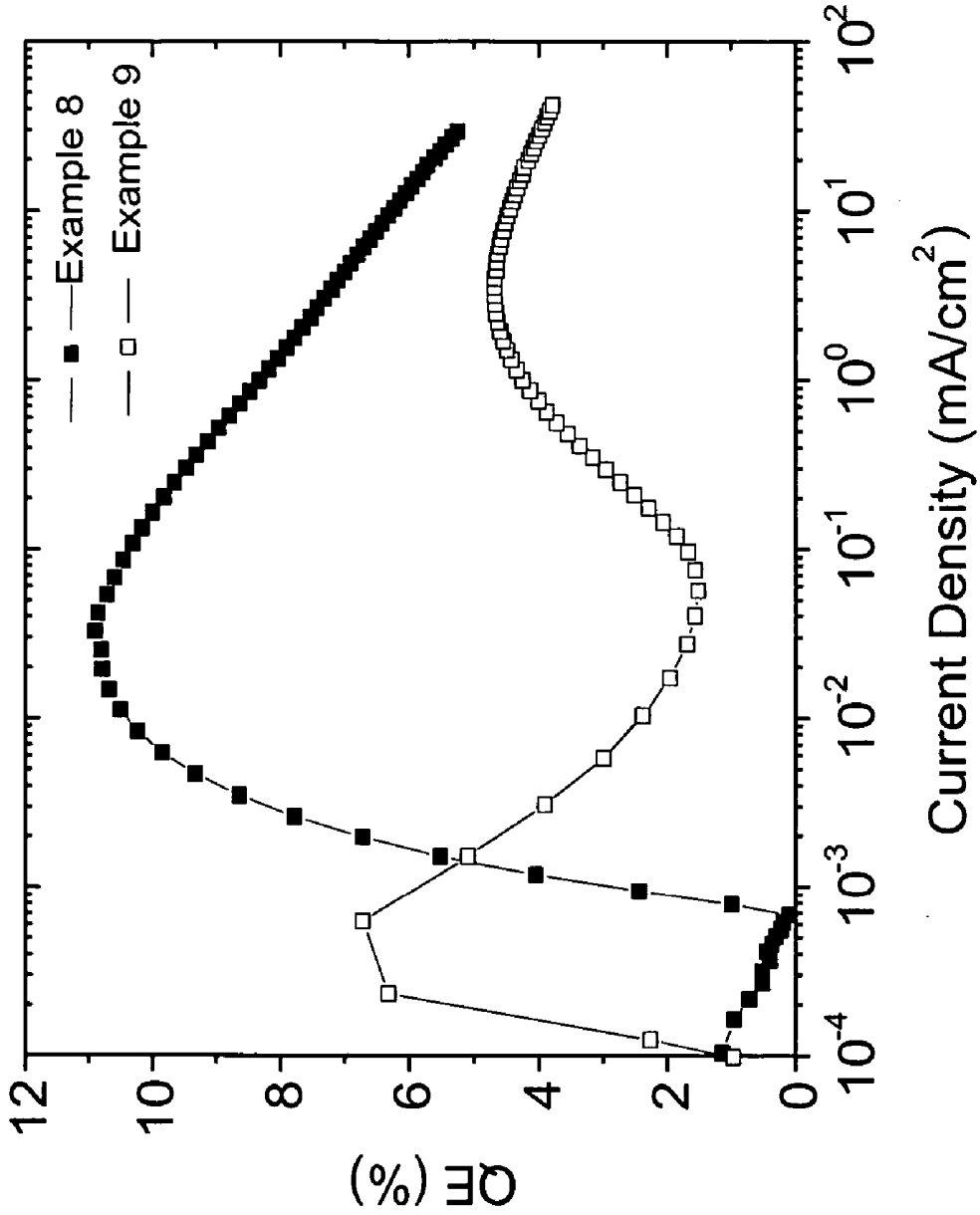

Example 8
Example 9
QE (%)
Current Density (mA/cm^2)
0
2
4
6
8
10
12
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}

Figure 7

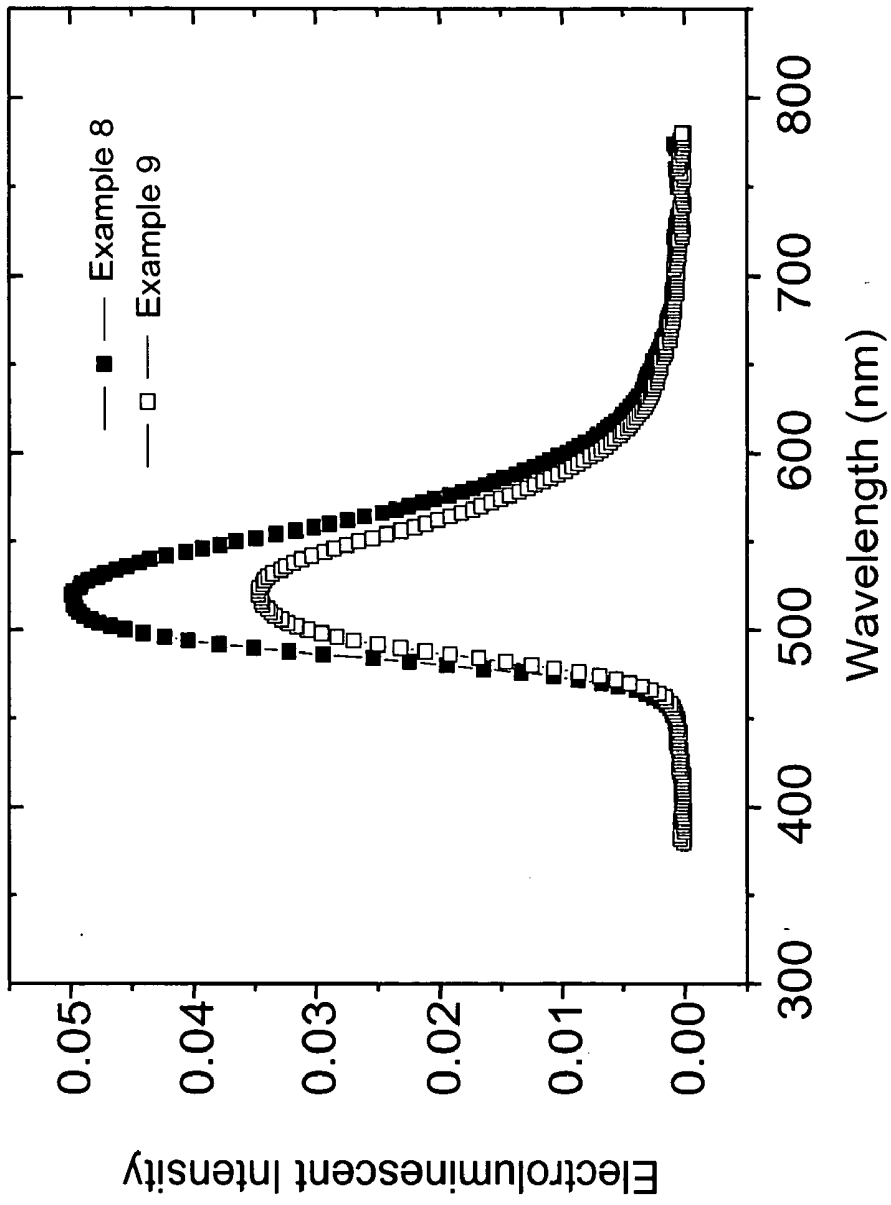

Example 8
Example 9
Electroluminescent Intensity
0.00
0.01
0.02
0.03
0.04
0.05
Wavelength (nm)
300
400
500
600
700
800

Figure 8

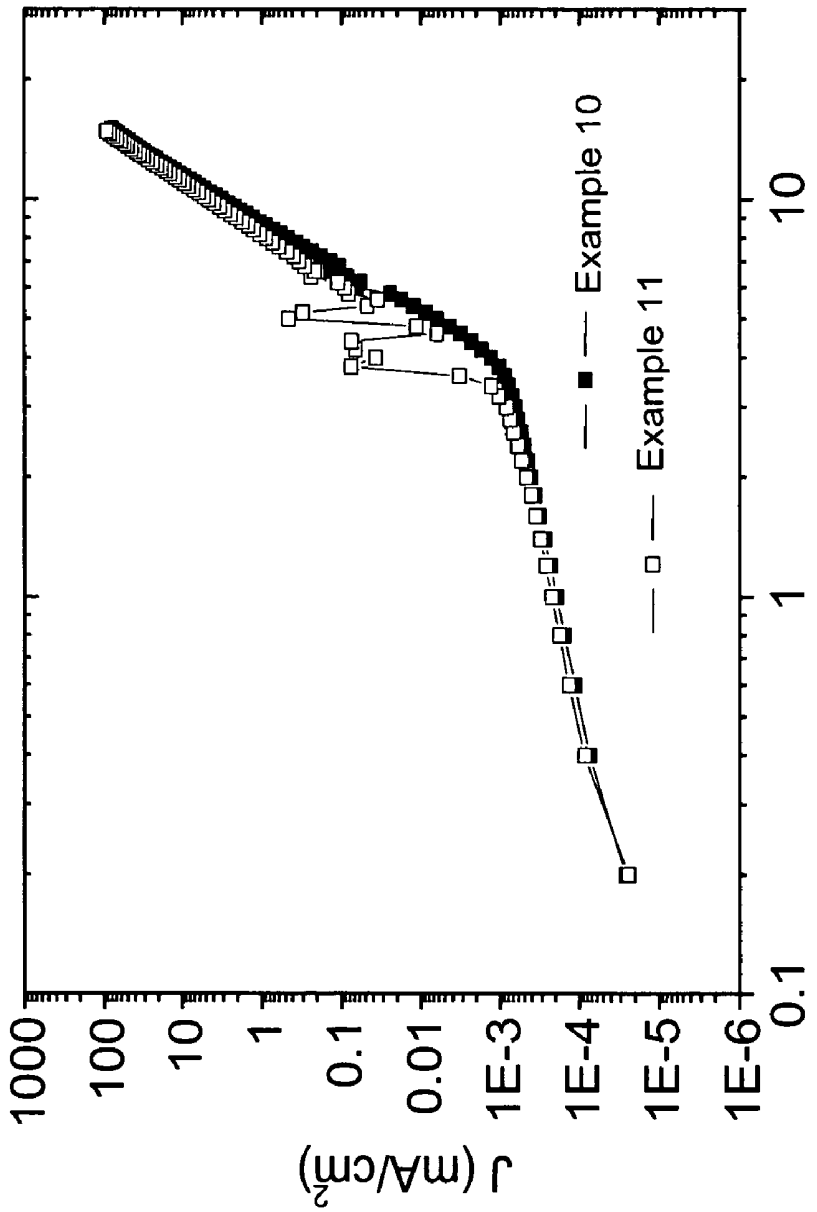

J (mA/cm²)
1000
100
10
1
0.1
0.01
1E-3
1E-4
1E-5
1E-6
0.1
1
10
Voltage (V)
Example 10
Example 11

Figure 9

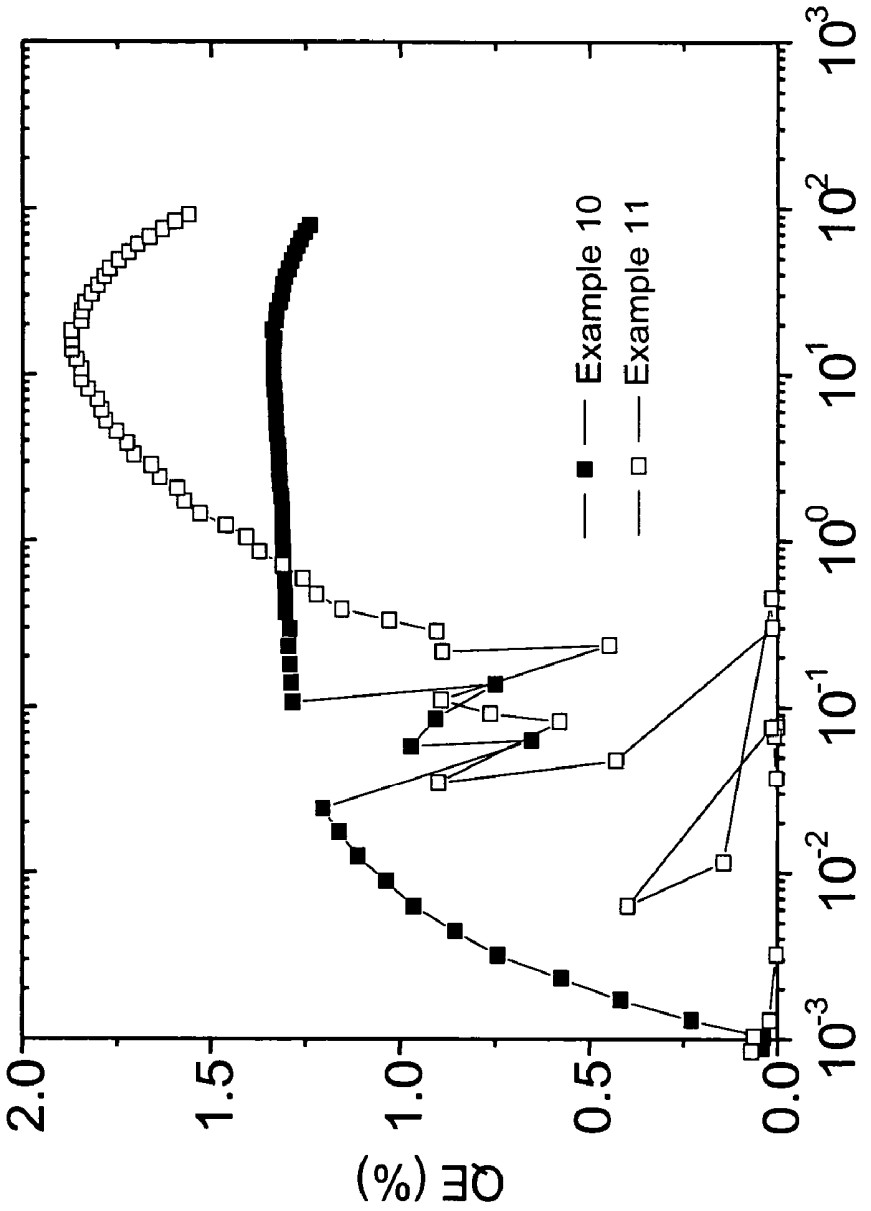

Example 10
Example 11
QE (%)
Current Density (mA/cm 2)
2.0
1.5
1.0
0.5
0.0
10-3
10-2
10-1
100
101
102
103

Figure 10

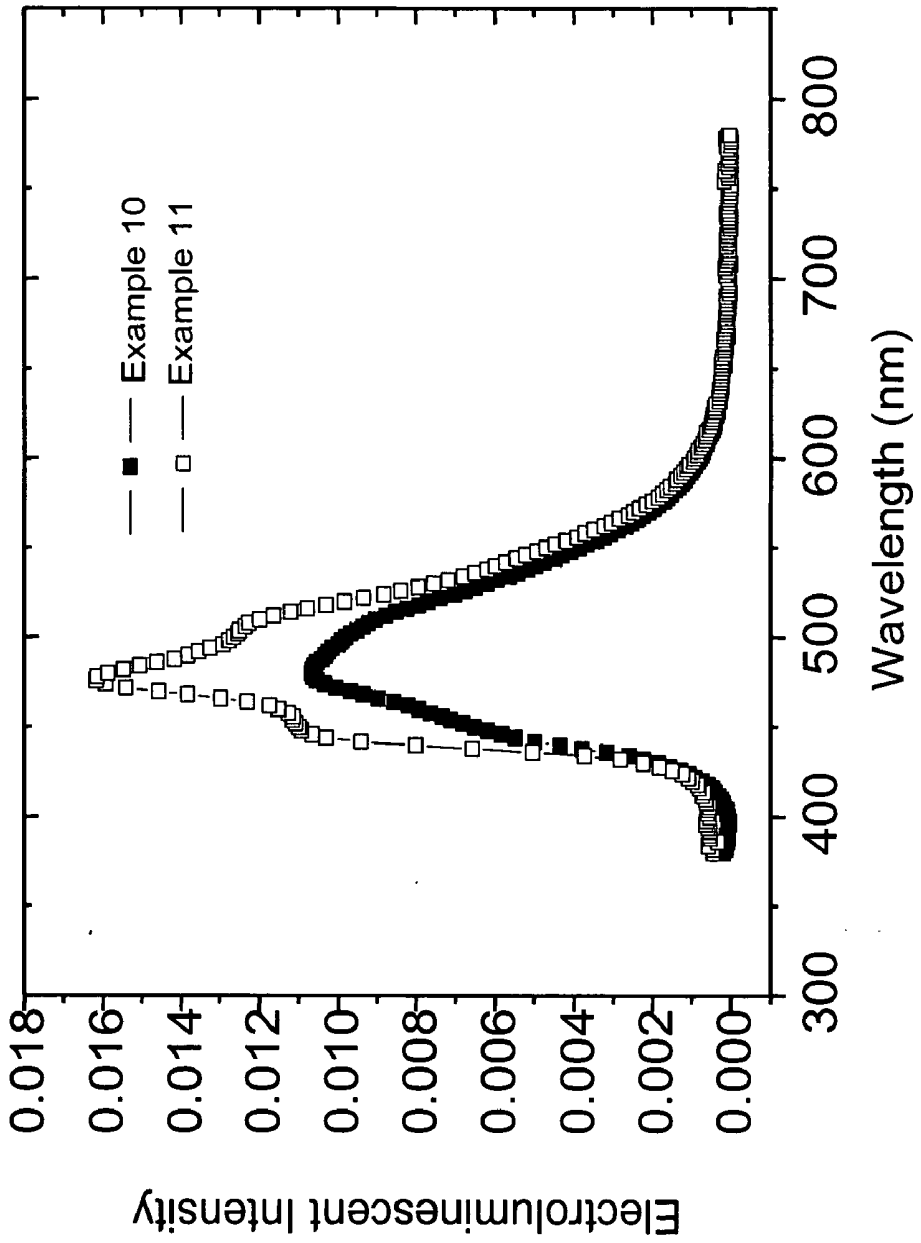

Example 10
Example 11
Electroluminescent Intensity
Wavelength (nm)
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
300
400
500
600
700
800

Figure 11

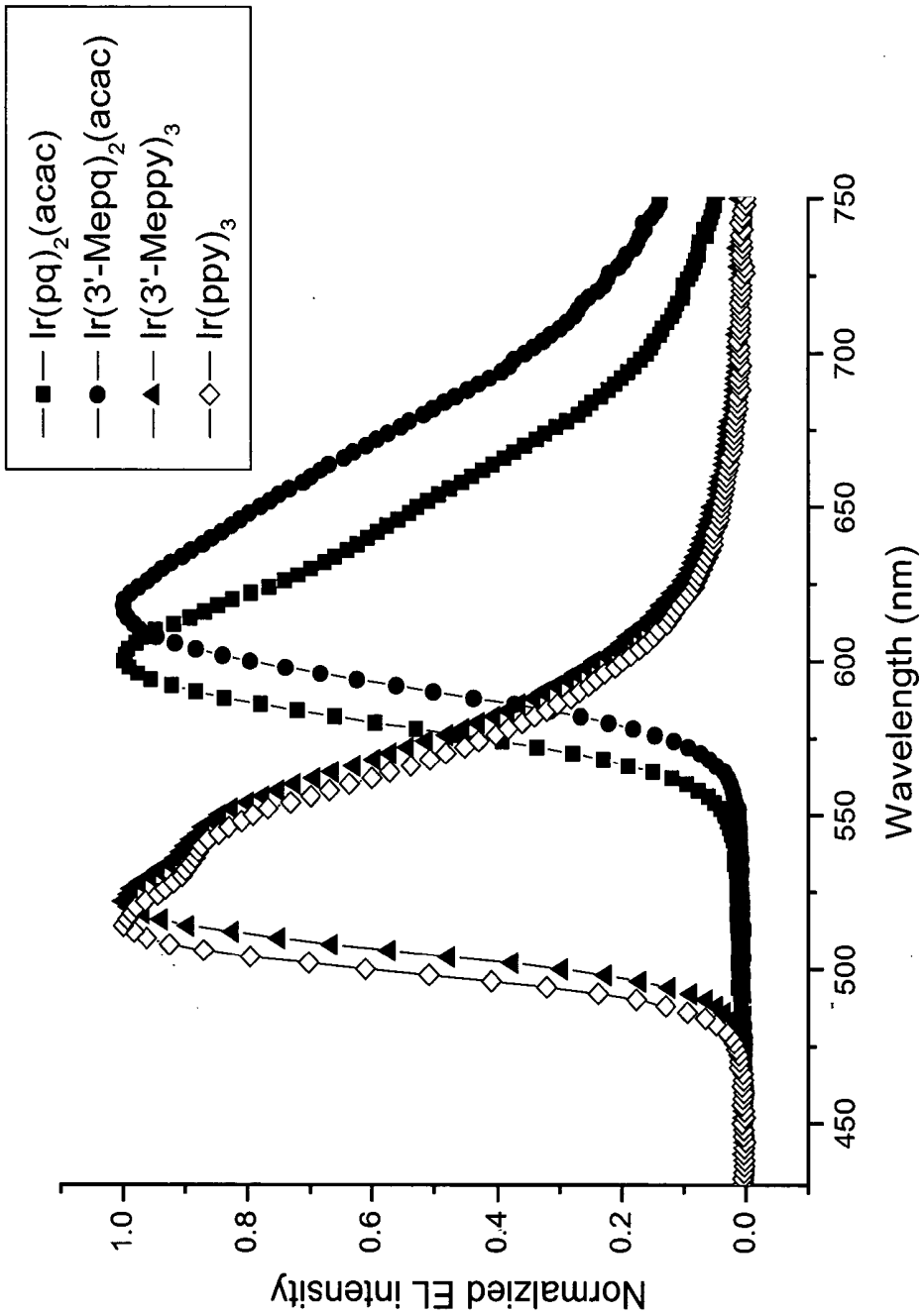

Ir(pq)2(acac)
Ir(3'-Mepq)2(acac)
Ir(3'-Meppy)3
Ir(ppy)3
Normalized EL Intensity
0.0
0.2
0.4
0.6
0.8
1.0
Wavelength (nm)
450
500
550
600
650
700
750

Figure 12

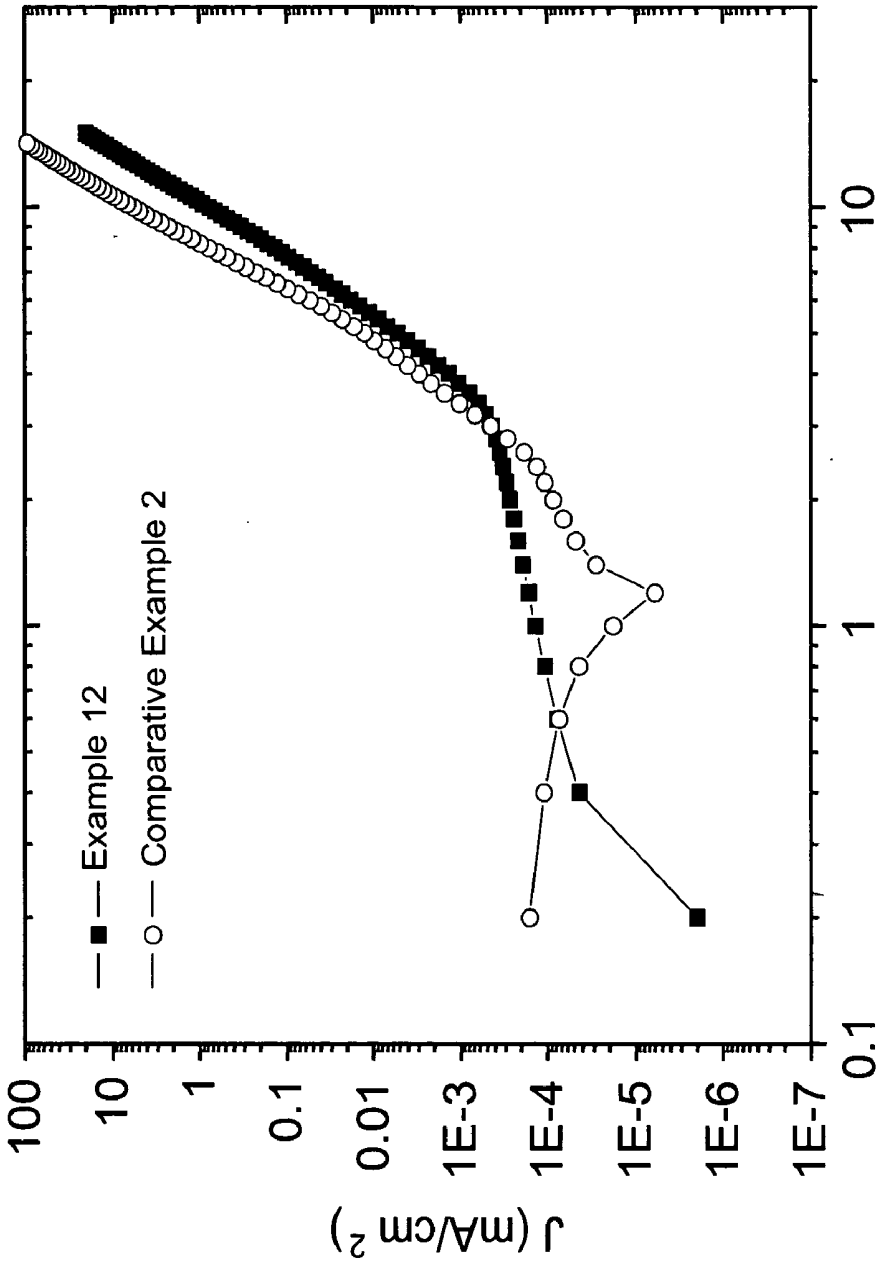

J (mA/cm 2)
100
10
1
0.1
0.01
1E-3
1E-4
1E-5
1E-6
1E-7
0.1
1
10
Voltage (V)
Example 12
Comparative Example 2

Figure 13

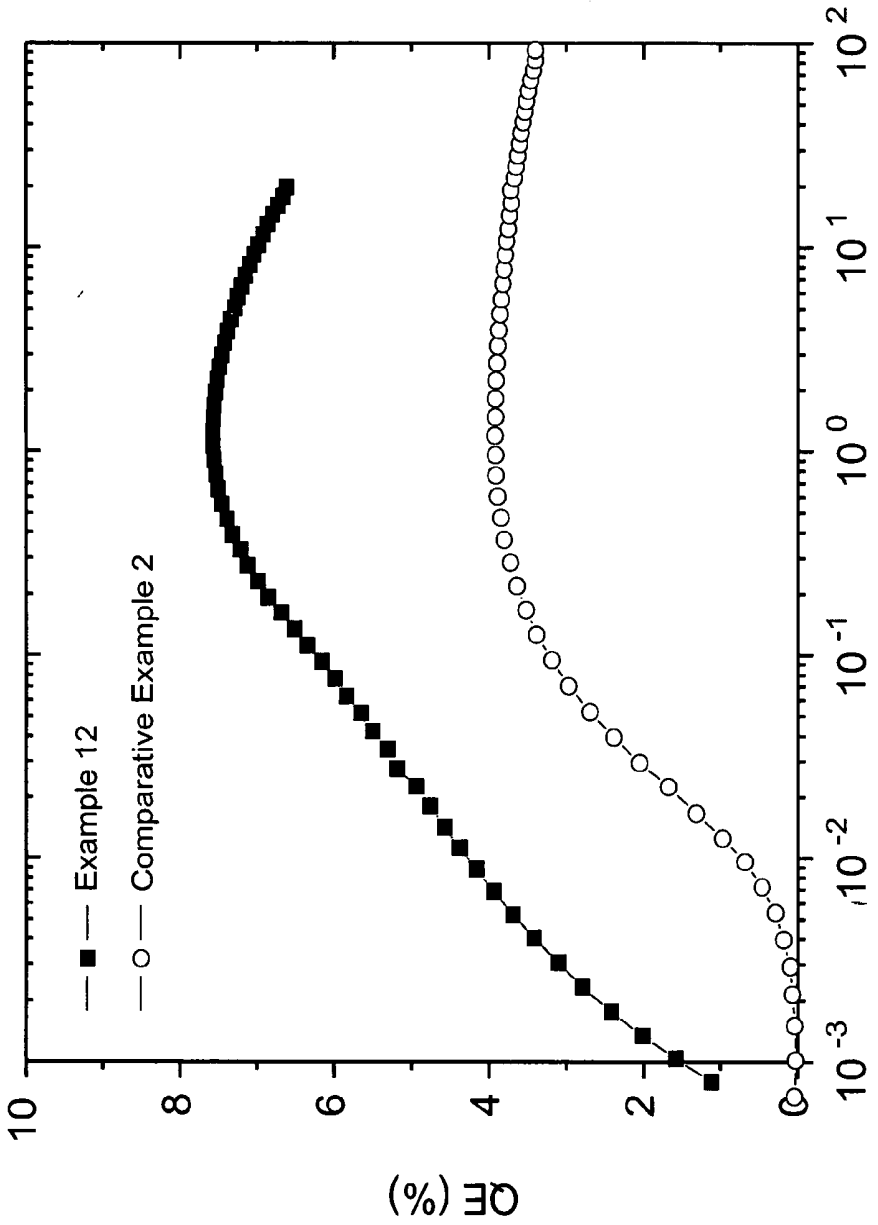

QE (%)
10
8
6
4
2
0
10^-3
10^-2
10^-1
10^0
10^1
10^2
Current Density (mA/cm^2)
Example 12
Comparative Example 2

Figure 14

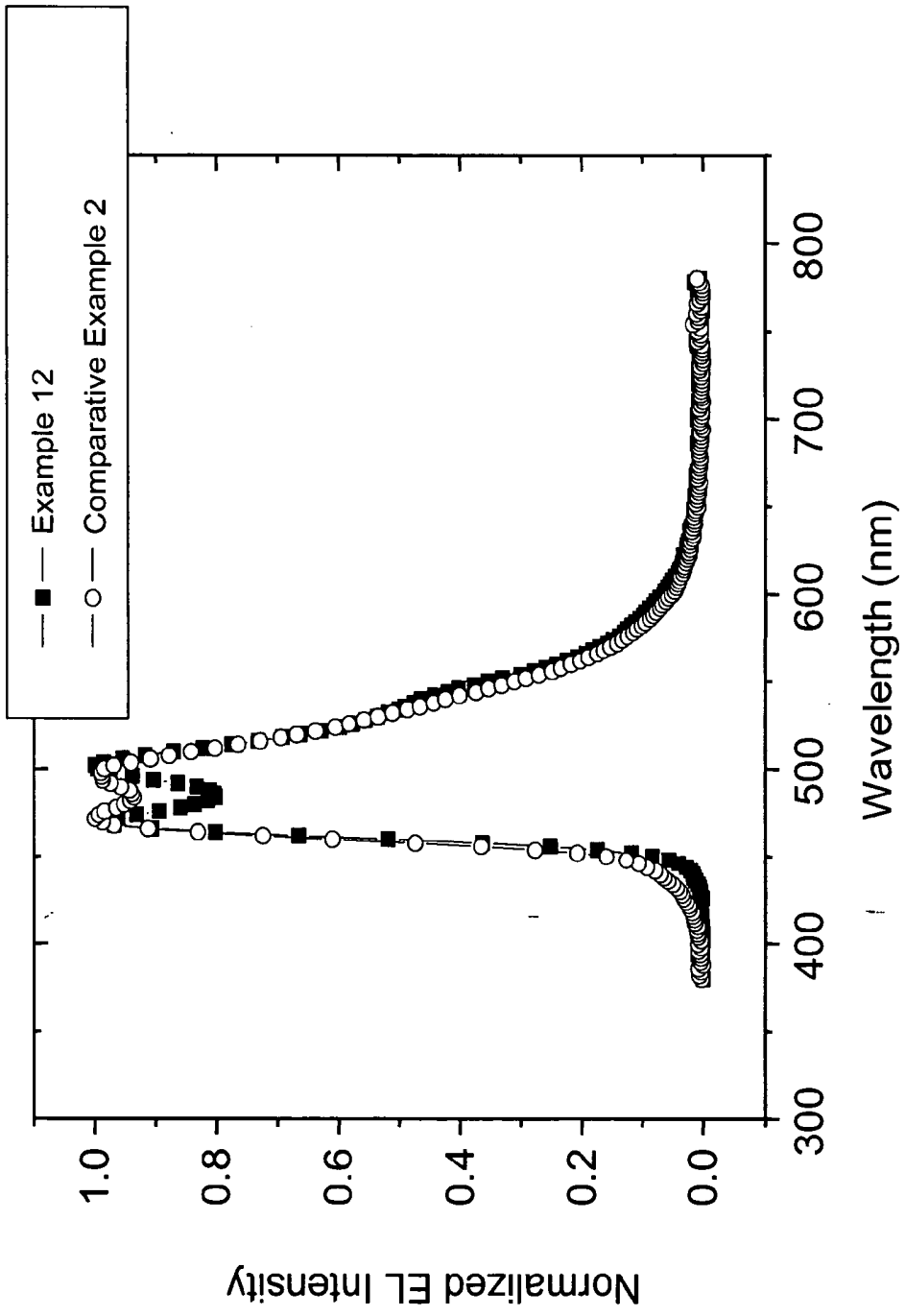

Example 12
Comparative Example 2
Normalized EL Intensity
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
800
Wavelength (nm)

Figure 15

ORGANIC LIGHT EMITTING MATERIALS AND DEVICES

FIELD OF THE INVENTION

[0001] The present invention relates to organic light emitting devices (OLEDs), and specifically to phosphorescent organic materials used in such devices. More specifically, the present invention relates to arylimidazole, aryltriazole, and aryltetrazole derivative complexes incorporated into OLEDs.

BACKGROUND

[0002] Opto-electronic devices that make use of organic materials are becoming increasingly desirable for a number of reasons. Many of the materials used to make such devices are relatively inexpensive, so organic opto-electronic devices have the potential for cost advantages over inorganic devices. In addition, the inherent properties of organic materials, such as their flexibility, may make them well suited for particular applications such as fabrication on a flexible substrate. Examples of organic opto-electronic devices include organic light emitting devices (OLEDs), organic phototransistors, organic photovoltaic cells, and organic photodetectors. For OLEDs, the organic materials may have performance advantages over conventional materials. For example, the wavelength at which an organic emissive layer emits light may generally be readily tuned with appropriate dopants.

[0003] As used herein, the term "organic" includes polymeric materials as well as small molecule organic materials that may be used to fabricate organic opto-electronic devices. "Small molecule" refers to any organic material that is not a polymer, and "small molecules" may actually be quite large. Small molecules may include repeat units in some circumstances. For example, using a long chain alkyl group as a substituent does not remove a molecule from the "small molecule" class. Small molecules may also be incorporated into polymers, for example as a pendent group on a polymer backbone or as a part of the backbone. Small molecules may also serve as the core moiety of a dendrimer, which consists of a series of chemical shells built on the core moiety. The core moiety of a dendrimer may be a fluorescent or phosphorescent small molecule emitter. A dendrimer may be a "small molecule," and it is believed that all dendrimers currently used in the field of OLEDs are small molecules. In general, a small molecule has a well-defined chemical formula with a single molecular weight, whereas a polymer has a chemical formula and a molecular weight that may vary from molecule to molecule.

[0004] OLEDs make use of thin organic films that emit light when voltage is applied across the device. OLEDs are becoming an increasingly interesting technology for use in applications such as flat panel displays, illumination, and backlighting. Several OLED materials and configurations are described in U.S. Pat. Nos. 5,844,363, 6,303,238, and 5,707,745, which are incorporated herein by reference in their entirety.

[0005] OLED devices are generally (but not always) intended to emit light through at least one of the electrodes, and one or more transparent electrodes may be useful in organic opto-electronic devices. For example, a transparent electrode material, such as indium tin oxide (ITO), may be used as the bottom electrode. A transparent top electrode, such as disclosed in U.S. Pat. Nos. 5,703,436 and 5,707,745, which are incorporated by reference in their entireties, may also be used. For a device intended to emit light only through the bottom electrode, the top electrode does not need to be transparent, and may be comprised of a thick and reflective metal layer having a high electrical conductivity. Similarly, for a device intended to emit light only through the top electrode, the bottom electrode may be opaque and/or reflective. Where an electrode does not need to be transparent, using a thicker layer may provide better conductivity, and using a reflective electrode may increase the amount of light emitted through the other electrode, by reflecting light back towards the transparent electrode. Fully transparent devices may also be fabricated, where both electrodes are transparent. Side emitting OLEDs may also be fabricated, and one or both electrodes may be opaque or reflective in such devices.

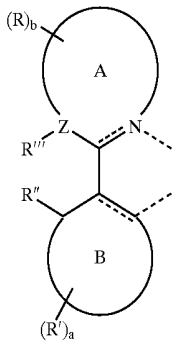
[0006] As used herein, "top" means furthest away from the substrate, while "bottom" means closest to the substrate. For example, for a device having two electrodes, the bottom electrode is the electrode closest to the substrate, and is generally the first electrode fabricated. The bottom electrode has two surfaces, a bottom surface closest to the substrate, and a top surface further away from the substrate. Where a first layer is described as "disposed over" a second layer, the first layer is disposed further away from substrate. There may be other layers between the first and second layer, unless it is specified that the first layer is "in physical contact with" the second layer. For example, a cathode may be described as "disposed over" an anode, even though there are various organic layers in between.

[0007] As used herein, "solution processible" means capable of being dissolved, dispersed, or transported in and/or deposited from a liquid medium, either in solution or suspension form.

[0008] As used herein, and as would be generally understood by one skilled in the art, a first "Highest Occupied Molecular Orbital" (HOMO) or "Lowest Unoccupied Molecular Orbital" (LUMO) energy level is "greater than" or "higher than" a second HOMO or LUMO energy level if the first energy level is closer to the vacuum energy level. Since ionization potentials (IP) are measured as a negative energy relative to a vacuum level, a higher HOMO energy level corresponds to an IP having a smaller absolute value (an IP that is less negative). Similarly, a higher LUMO energy level corresponds to an electron affinity (EA) having a smaller absolute value (an EA that is less negative). On a conventional energy level diagram, with the vacuum level at the top, the LUMO energy level of a material is higher than the HOMO energy level of the same material. A "higher" HOMO or LUMO energy level appears closer to the top of such a diagram than a "lower" HOMO or LUMO energy level.

SUMMARY OF THE INVENTION

[0009] An organic light emitting device is provided. The device has an anode, a cathode and an organic layer disposed between the anode and the cathode. The organic layer comprises a compound further comprising one or more arylimidazole, aryltriazole, or aryltetrazole derivative ligands coordinated to a metal center. The ligand has the structure:



wherein

the dotted lines inside the rings represent optional double bonds; Z is carbon or nitrogen; R" is H or F; each R, R' and R'" is independently selected from hydrogen, alkyl, alkenyl, alkynyl, alkylaryl, trialkylsilyl, cyano, trifluoromethyl, ester, keto, amino, nitro, alkoxy, halo, aryl, heteroaryl, substituted aryl, substituted heteroaryl, or a heterocyclic group; ring A is a 5-membered heterocyclic ring having at least 2 nitrogen atoms, with one nitrogen atom coordinated to metal M, wherein ring A can be optionally substituted with one or more substituents R, and additionally or alternatively, any two substituted positions on ring A together form, independently a cyclic ring, wherein the cyclic ring is not an aromatic ring, and the cyclic ring may be optionally substituted; ring B is an aromatic ring with at least one carbon atom coordinated to metal M, wherein ring B can be optionally substituted with one or more substituents R'; and additionally or alternatively, any two substituted positions on ring B together form, independently a fused 4-7-membered cyclic group, wherein said cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein the 4-7-membered cyclic group is optionally substituted; a is 0, 1, 2, 3, or 4; b is 0, 1, 2, or 3.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] **FIG. 1** shows an organic light emitting device having separate electron transport, hole transport, and emissive layers, as well as other layers.

[0011] **FIG. 2** shows an inverted organic light emitting device that does not have a separate electron transport layer.

[0012] **FIG. 3** shows plots of current density vs. voltage for example 7 and comparative example 1.

[0013] **FIG. 4** shows plots of external quantum efficiency vs. current density for example 7 and comparative example 1.

[0014] **FIG. 5** shows the normalized electroluminescence spectra of example 7 and comparative example 1 taken at a current density of 10 mA/cm^2.

[0015] **FIG. 6** shows plots of current density vs. voltage for example 8 and example 9.

[0016] **FIG. 7** shows plots of external quantum efficiency vs. current density for example 8 and example 9.

[0017] **FIG. 8** shows the normalized electroluminescence spectra of example 8 and example 9 taken at a current density of 10 mA/cm^2.

[0018] **FIG. 9** shows plots of current density vs. voltage for example 10 and example 11.

[0019] **FIG. 10** shows plots of external quantum efficiency vs. current density for example 10 and example 11

[0020] **FIG. 11** shows the normalized electroluminescence spectra for example 10 and example 11 at a current density of 10 mA/cm^2.

[0021] **FIG. 12** shows the normalized electroluminescence spectra for devices containing dopant emitters $Ir(pq)_2(acac)$, $Ir(3'\text{-}Mepq)_2(acac)$, $Ir(3'\text{-}Meppy)_3$, and $Ir(ppy)_3$.

[0022] **FIG. 13** shows plots of current density vs. voltage for example 12 and comparative example 2.

[0023] **FIG. 14** shows plots of external quantum efficiency vs. current density for example 12 and comparative example 2.

[0024] **FIG. 15** shows the normalized electroluminescence spectra of example 12 and comparative example 2 taken at a current density of 10 mA/cm^2.

DETAILED DESCRIPTION

[0025] Generally, an OLED comprises at least one organic layer disposed between and electrically connected to an anode and a cathode. When a current is applied, the anode injects holes and the cathode injects electrons into the organic layer(s). The injected holes and electrons each migrate toward the oppositely charged electrode. When an electron and hole localize on the same molecule, an "exciton," which is a localized electron-hole pair having an excited energy state, is formed. Light is emitted when the exciton relaxes via a photoemissive mechanism. In some cases, the exciton may be localized on an excimer or an exciplex. Non-radiative mechanisms, such as thermal relaxation, may also occur, but are generally considered undesirable.

[0026] The initial OLEDs used emissive molecules that emitted light from their singlet states ("fluorescence") as disclosed, for example, in U.S. Pat. No. 4,769,292, which is incorporated by reference in its entirety. Fluorescent emission generally occurs in a time frame of less than 10 nanoseconds.

[0027] More recently, OLEDs having emissive materials that emit light from triplet states ("phosphorescence") have been demonstrated. Baldo et al., "Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices," Nature, vol. 395, 151-154, 1998; ("Baldo-I") and Baldo et al., "Very high-efficiency green organic light-emitting devices based on electrophosphorescence," Appl. Phys. Lett., vol. 75, No. 3, 4-6 (1999) ("Baldo-II"), which are incorporated by reference in their entireties. Phosphorescence may be referred to as a "forbidden" transition because the transition requires a change in spin states, and quantum mechanics indicates that such a transition is not favored. As a result, phosphorescence generally occurs in a time frame exceeding at least 10 nanoseconds, and typically greater than 100 nanoseconds. If the natural radiative life-

time of phosphorescence is too long, triplets may decay by a non-radiative mechanism, such that no light is emitted. Organic phosphorescence is also often observed in molecules containing heteroatoms with unshared pairs of electrons at very low temperatures. 2,2'-bipyridine is such a molecule. Non-radiative decay mechanisms are typically temperature dependent, such that an organic material that exhibits phosphorescence at liquid nitrogen temperatures typically does not exhibit phosphorescence at room temperature. But, as demonstrated by Baldo, this problem may be addressed by selecting phosphorescent compounds that do phosphoresce at room temperature. Representative emissive layers include doped or un-doped phosphorescent organo-metallic materials such as disclosed in U.S. Pat. Nos. 6,303,238 and 6,310,360; U.S. patent application Publication Nos. 2002-0034656; 2002-0182441; 2003-0072964; and WO-02/074015.

[0028] Generally, the excitons in an OLED are believed to be created in a ratio of about 3:1, i.e., approximately 75% triplets and 25% singlets. See, Adachi et al., "Nearly 100% Internal Phosphorescent Efficiency In An Organic Light Emitting Device," J. Appl. Phys., 90, 5048 (2001), which is incorporated by reference in its entirety. In many cases, singlet excitons may readily transfer their energy to triplet excited states via "intersystem crossing," whereas triplet excitons may not readily transfer their energy to singlet excited states. As a result, 100% internal quantum efficiency is theoretically possible with phosphorescent OLEDs. In a fluorescent device, the energy of triplet excitons is generally lost to radiationless decay processes that heat-up the device, resulting in much lower internal quantum efficiencies. OLEDs utilizing phosphorescent materials that emit from triplet excited states are disclosed, for example, in U.S. Pat. No. 6,303,238, which is incorporated by reference in its entirety.

[0029] Phosphorescence may be preceded by a transition from a triplet excited state to an intermediate non-triplet state from which the emissive decay occurs. For example, organic molecules coordinated to lanthanide elements often phosphoresce from excited states localized on the lanthanide metal. However, such materials do not phosphoresce directly from a triplet excited state but instead emit from an atomic excited state centered on the lanthanide metal ion. The europium diketonate complexes illustrate one group of these types of species.

[0030] Phosphorescence from triplets can be enhanced over fluorescence by confining, preferably through bonding, the organic molecule in close proximity to an atom of high atomic number. This phenomenon, called the heavy atom effect, is created by a mechanism known as spin-orbit coupling. Such a phosphorescent transition may be observed from an excited metal-to-ligand charge transfer (MLCT) state of an organometallic molecule such as tris(2-phenylpyridine)iridium(III).

[0031] As used herein, the term "triplet energy" refers to an energy corresponding to the highest energy feature discernable in the phosphorescence spectrum of a given material. The highest energy feature is not necessarily the peak having the greatest intensity in the phosphorescence spectrum, and could, for example, be a local maximum of a clear shoulder on the high energy side of such a peak.

[0032] The term "organometallic" as used herein is as generally understood by one of ordinary skill in the art and as given, for example, in "Inorganic Chemistry" (2nd Edition) by Gary L. Miessler and Donald A. Tarr, Prentice Hall (1998). Thus, the term organometallic refers to compounds which have an organic group bonded to a metal through a carbon-metal bond. This class does not include per se coordination compounds, which are substances having only donor bonds from heteroatoms, such as metal complexes of amines, halides, pseudohalides (CN, etc.), and the like. In practice, organometallic compounds generally comprise, in addition to one or more carbon-metal bonds to an organic species, one or more donor bonds from a heteroatom. The carbon-metal bond to an organic species refers to a direct bond between a metal and a carbon atom of an organic group, such as phenyl, alkyl, alkenyl, etc., but does not refer to a metal bond to an "inorganic carbon," such as the carbon of CN or CO.

[0033] **FIG. 1** shows an organic light emitting device **100**. The figures are not necessarily drawn to scale. Device **100** may include a substrate **110**, an anode **115**, a hole injection layer **120**, a hole transport layer **125**, an electron blocking layer **130**, an emissive layer **135**, a hole blocking layer **140**, an electron transport layer **145**, an electron injection layer **150**, a protective layer **155**, and a cathode **160**. Cathode **160** is a compound cathode having a first conductive layer **162** and a second conductive layer **164**. Device **100** may be fabricated by depositing the layers described, in order.

[0034] Substrate **110** may be any suitable substrate that provides desired structural properties. Substrate **110** may be flexible or rigid. Substrate **110** may be transparent, translucent or opaque. Plastic and glass are examples of preferred rigid substrate materials. Plastic and metal foils are examples of preferred flexible substrate materials. Substrate **110** may be a semiconductor material in order to facilitate the fabrication of circuitry. For example, substrate **110** may be a silicon wafer upon which circuits are fabricated, capable of controlling OLEDs subsequently deposited on the substrate. Other substrates may be used. The material and thickness of substrate **110** may be chosen to obtain desired structural and optical properties.

[0035] Anode **115** may be any suitable anode that is sufficiently conductive to transport holes to the organic layers. The material of anode **115** preferably has a work function higher than about 4 eV (a "high work function material"). Preferred anode materials include conductive metal oxides, such as indium tin oxide (ITO) and indium zinc oxide (IZO), aluminum zinc oxide (AlZnO), and metals. Anode **115** (and substrate **110**) may be sufficiently transparent to create a bottom-emitting device. A preferred transparent substrate and anode combination is commercially available ITO (anode) deposited on glass or plastic (substrate). A flexible and transparent substrate-anode combination is disclosed in U.S. Pat. Nos. 5,844,363 and 6,602,540 B2, which are incorporated by reference in their entireties. Anode **115** may be opaque and/or reflective. A reflective anode **115** may be preferred for some top-emitting devices, to increase the amount of light emitted from the top of the device. The material and thickness of anode **115** may be chosen to obtain desired conductive and optical properties. Where anode **115** is transparent, there may be a range of thickness for a particular material that is thick enough to provide the desired conductivity, yet thin enough to provide the desired degree of transparency. Other anode materials and structures may be used.

[0036] Hole transport layer **125** may include a material capable of transporting holes. Hole transport layer **130** may be intrinsic (undoped), or doped. Doping may be used to enhance conductivity. α-NPD and TPD are examples of intrinsic hole transport layers. An example of a p-doped hole transport layer is m-MTDATA doped with F_4-TCNQ at a molar ratio of 50:1, as disclosed in U.S. patent application Publication No. 2002-0071963 A1 to Forrest et al., which is incorporated by reference in its entirety. Other hole transport layers may be used.

[0037] Emissive layer **135** may include an organic material capable of emitting light when a current is passed between anode **115** and cathode **160**. Preferably, emissive layer **135** contains a phosphorescent emissive material, although fluorescent emissive materials may also be used. Phosphorescent materials are preferred because of the higher luminescent efficiencies associated with such materials. Emissive layer **135** may also comprise a host material capable of transporting electrons and/or holes, doped with an emissive material that may trap electrons, holes, and/or excitons, such that excitons relax from the emissive material via a photoemissive mechanism. Emissive layer **135** may comprise a single material that combines transport and emissive properties. Whether the emissive material is a dopant or a major constituent, emissive layer **135** may comprise other materials, such as dopants that tune the emission of the emissive material. Emissive layer **135** may include a plurality of emissive materials capable of, in combination, emitting a desired spectrum of light. Examples of phosphorescent emissive materials include $Ir(ppy)_3$. Examples of fluorescent emissive materials include DCM and DMQA. Examples of host materials include Alq_3, CBP and mCP. Examples of emissive and host materials are disclosed in U.S. Pat. No. 6,303,238 to Thompson et al., which is incorporated by reference in its entirety. Emissive material may be included in emissive layer **135** in a number of ways. For example, an emissive small molecule may be incorporated into a polymer. This may be accomplished by several ways: by doping the small molecule into the polymer either as a separate and distinct molecular species; or by incorporating the small molecule into the backbone of the polymer, so as to form a co-polymer; or by bonding the small molecule as a pendant group on the polymer. Other emissive layer materials and structures may be used. For example, a small molecule emissive material may be present as the core of a dendrimer.

[0038] Many useful emissive materials include one or more ligands bound to a metal center. A ligand may be referred to as "photoactive" if it contributes directly to the luminescent properties of an organometallic emissive material. A "photoactive" ligand may provide, in conjunction with a metal, the energy levels from which and to which an electron moves when a photon is emitted. Other ligands may be referred to as "ancillary." Ancillary ligands may modify the photoactive properties of the molecule, for example by shifting the energy levels of a photoactive ligand, but ancillary ligands do not directly provide the energy levels directly involved in light emission. A ligand that is photoactive in one molecule may be ancillary in another. These definitions of photoactive and ancillary are intended as non-limiting theories.

[0039] Electron transport layer **140** may include a material capable of transporting electrons. Electron transport layer **140** may be intrinsic (undoped), or doped. Doping may be used to enhance conductivity. Alq_3 is an example of an intrinsic electron transport layer. An example of an n-doped electron transport layer is BPhen doped with Li at a molar ratio of 1:1, as disclosed in U.S. patent application Publication No. 2002-0071963 A1 to Forrest et al., which is incorporated by reference in its entirety. Other electron transport layers may be used.

[0040] The charge carrying component of the electron transport layer may be selected such that electrons can be efficiently injected from the cathode into the LUMO (Lowest Unoccupied Molecular Orbital) energy level of the electron transport layer. The "charge carrying component" is the material responsible for the LUMO energy level that actually transports electrons. This component may be the base material, or it may be a dopant. The LUMO energy level of an organic material may be generally characterized by the electron affinity of that material and the relative electron injection efficiency of a cathode may be generally characterized in terms of the work function of the cathode material. This means that the preferred properties of an electron transport layer and the adjacent cathode may be specified in terms of the electron affinity of the charge carrying component of the ETL and the work function of the cathode material. In particular, so as to achieve high electron injection efficiency, the work function of the cathode material is preferably not greater than the electron affinity of the charge carrying component of the electron transport layer by more than about 0.75 eV, more preferably, by not more than about 0.5 eV. Similar considerations apply to any layer into which electrons are being injected.

[0041] Cathode **160** may be any suitable material or combination of materials known to the art, such that cathode **160** is capable of conducting electrons and injecting them into the organic layers of device **100**. Cathode **160** may be transparent or opaque, and may be reflective. Metals and metal oxides are examples of suitable cathode materials. Cathode **160** may be a single layer, or may have a compound structure. **FIG. 1** shows a compound cathode **160** having a thin metal layer **162** and a thicker conductive metal oxide layer **164**. In a compound cathode, preferred materials for the thicker layer **164** include ITO, IZO, and other materials known to the art. U.S. Pat. Nos. 5,703,436, 5,707,745, 6,548,956 B2, and 6,576,134 B2, which are incorporated by reference in their entireties, disclose examples of cathodes including compound cathodes having a thin layer of metal such as Mg:Ag with an overlying transparent, electrically-conductive, sputter-deposited ITO layer. The part of cathode **160** that is in contact with the underlying organic layer, whether it is a single layer cathode **160**, the thin metal layer **162** of a compound cathode, or some other part, is preferably made of a material having a work function lower than about 4 eV (a "low work function material"). Other cathode materials and structures may be used.

[0042] Blocking layers may be used to reduce the number of charge carriers (electrons or holes) and/or excitons that leave the emissive layer. An electron blocking layer **130** may be disposed between emissive layer **135** and the hole transport layer **125**, to block electrons from leaving emissive layer **135** in the direction of hole transport layer **125**. Similarly, a hole blocking layer **140** may be disposed between emissive layer **135** and electron transport layer **145**, to block holes from leaving emissive layer **135** in the

direction of electron transport layer **140**. Blocking layers may also be used to block excitons from diffusing out of the emissive layer. The theory and use of blocking layers is described in more detail in U.S. Pat. No. 6,097,147 and U.S. patent application Publication No. 2002-0071963 A1 to Forrest et al., which are incorporated by reference in their entireties.

[**0043**] As used herein, and as would be understood by one of skill in the art, the term "blocking layer" means that the layer provides a barrier that significantly inhibits transport of charge carriers and/or excitons through the device, without suggesting that the layer necessarily completely blocks the charge carriers and/or excitons. The presence of such a blocking layer in a device may result in substantially higher efficiencies as compared to a similar device lacking a blocking layer. Also, a blocking layer may be used to confine emission to a desired region of an OLED.

[**0044**] Generally, injection layers are comprised of a material that may improve the injection of charge carriers from one layer, such as an electrode or an organic layer, into an adjacent organic layer. Injection layers may also perform a charge transport function. In device **100**, hole injection layer **120** may be any layer that improves the injection of holes from anode **115** into hole transport layer **125**. CuPc is an example of a material that may be used as a hole injection layer from an ITO anode **115**, and other anodes. In device **100**, electron injection layer **150** may be any layer that improves the injection of electrons into electron transport layer **145**. LiF/Al is an example of a material that may be used as an electron injection layer into an electron transport layer from an adjacent layer. Other materials or combinations of materials may be used for injection layers. Depending upon the configuration of a particular device, injection layers may be disposed at locations different than those shown in device **100**. More examples of injection layers are provided in U.S. patent application Ser. No. 09/931,948 to Lu et al., which is incorporated by reference in its entirety. A hole injection layer may comprise a solution deposited material, such as a spin-coated polymer, e.g., PEDOT:PSS, or it may be a vapor deposited small molecule material, e.g., CuPc or MTDATA.

[**0045**] A hole injection layer (HIL) may planarize or wet the anode surface so as to provide efficient hole injection from the anode into the hole injecting material. A hole injection layer may also have a charge carrying component having HOMO (Highest Occupied Molecular Orbital) energy levels that favorably match up, as defined by their herein-described relative ionization potential (IP) energies, with the adjacent anode layer on one side of the HIL and the hole transporting layer on the opposite side of the HIL. The "charge carrying component" is the material responsible for the HOMO energy level that actually transports holes. This component may be the base material of the HIL, or it may be a dopant. Using a doped HIL allows the dopant to be selected for its electrical properties, and the host to be selected for morphological properties such as wetting, flexibility, toughness, etc. Preferred properties for the HIL material are such that holes can be efficiently injected from the anode into the HIL material. In particular, the charge carrying component of the HIL preferably has an IP not more than about 0.7 eV greater that the IP of the anode material. More preferably, the charge carrying component has an IP not more than about 0.5 eV greater than the anode material. Similar considerations apply to any layer into which holes are being injected. HIL materials are further distinguished from conventional hole transporting materials that are typically used in the hole transporting layer of an OLED in that such HIL materials may have a hole conductivity that is substantially less than the hole conductivity of conventional hole transporting materials. The thickness of the HIL of the present invention may be thick enough to help planarize or wet the surface of the anode layer. For example, an HIL thickness of as little as 10 nm may be acceptable for a very smooth anode surface. However, since anode surfaces tend to be very rough, a thickness for the HIL of up to 50 nm may be desired in some cases.

[**0046**] A protective layer may be used to protect underlying layers during subsequent fabrication processes. For example, the processes used to fabricate metal or metal oxide top electrodes may damage organic layers, and a protective layer may be used to reduce or eliminate such damage. In device **100**, protective layer **155** may reduce damage to underlying organic layers during the fabrication of cathode **160**. Preferably, a protective layer has a high carrier mobility for the type of carrier that it transports (electrons in device **100**), such that it does not significantly increase the operating voltage of device **100**. CuPc, BCP, and various metal phthalocyanines are examples of materials that may be used in protective layers. Other materials or combinations of materials may be used. The thickness of protective layer **155** is preferably thick enough that there is little or no damage to underlying layers due to fabrication processes that occur after organic protective layer **160** is deposited, yet not so thick as to significantly increase the operating voltage of device **100**. Protective layer **155** may be doped to increase its conductivity. For example, a CuPc or BCP protective layer **160** may be doped with Li. A more detailed description of protective layers may be found in U.S. patent application Ser. No. 09/931,948 to Lu et al., which is incorporated by reference in its entirety.

[**0047**] **FIG. 2** shows an inverted OLED **200**. The device includes a substrate **210**, an cathode **215**, an emissive layer **220**, a hole transport layer **225**, and an anode **230**. Device **200** may be fabricated by depositing the layers described, in order. Because the most common OLED configuration has a cathode disposed over the anode, and device **200** has cathode **215** disposed under anode **230**, device **200** may be referred to as an "inverted" OLED. Materials similar to those described with respect to device **100** may be used in the corresponding layers of device **200**. **FIG. 2** provides one example of how some layers may be omitted from the structure of device **100**.

[**0048**] The simple layered structure illustrated in **FIGS. 1 and 2** is provided by way of non-limiting example, and it is understood that embodiments of the invention may be used in connection with a wide variety of other structures. The specific materials and structures described are exemplary in nature, and other materials and structures may be used. Functional OLEDs may be achieved by combining the various layers described in different ways, or layers may be omitted entirely, based on design, performance, and cost factors. Other layers not specifically described may also be included. Materials other than those specifically described may be used. Although many of the examples provided herein describe various layers as comprising a single material, it is understood that combinations of materials, such as

a mixture of host and dopant, or more generally a mixture, may be used. Also, the layers may have various sublayers. The names given to the various layers herein are not intended to be strictly limiting. For example, in device **200**, hole transport layer **225** transports holes and injects holes into emissive layer **220**, and may be described as a hole transport layer or a hole injection layer. In one embodiment, an OLED may be described as having an "organic layer" disposed between a cathode and an anode. This organic layer may comprise a single layer, or may further comprise multiple layers of different organic materials as described, for example, with respect to **FIGS. 1 and 2**.

[**0049**] Structures and materials not specifically described may also be used, such as OLEDs comprised of polymeric materials (PLEDs) such as disclosed in U.S. Pat. No. 5,247,190, Friend et al., which is incorporated by reference in its entirety. By way of further example, OLEDs having a single organic layer may be used. OLEDs may be stacked, for example as described in U.S. Pat. No. 5,707,745 to Forrest et al, which is incorporated by reference in its entirety. The OLED structure may deviate from the simple layered structure illustrated in **FIGS. 1 and 2**. For example, the substrate may include an angled reflective surface to improve out-coupling, such as a mesa structure as described in U.S. Pat. No. 6,091,195 to Forrest et al., and/or a pit structure as described in U.S. Pat. No. 5,834,893 to Bulovic et al., which are incorporated by reference in their entireties.

[**0050**] Unless otherwise specified, any of the layers of the various embodiments may be deposited by any suitable method. For the organic layers, preferred methods include thermal evaporation, ink-jet, such as described in U.S. Pat. Nos. 6,013,982 and 6,087,196, which are incorporated by reference in their entireties, organic vapor phase deposition (OVPD), such as described in U.S. Pat. No. 6,337,102 to Forrest et al., which is incorporated by reference in its entirety, and deposition by organic vapor jet printing (OVJP), such as described in U.S. patent application Ser. No. 10/233,470, which is incorporated by reference in its entirety. Other suitable deposition methods include spin coating and other solution based processes. Solution based processes are preferably carried out in nitrogen or an inert atmosphere. For the other layers, preferred methods include thermal evaporation. Preferred patterning methods include deposition through a mask, cold welding such as described in U.S. Pat. Nos. 6,294,398 and 6,468,819, which are incorporated by reference in their entireties, and patterning associated with some of the deposition methods such as ink-jet and OVJD. Other methods may also be used. The materials to be deposited may be modified to make them compatible with a particular deposition method. For example, substituents such as alkyl and aryl groups, branched or unbranched, and preferably containing at least 3 carbons, may be used in small molecules to enhance their ability to undergo solution processing. Substituents having 20 carbons or more may be used, and 3-20 carbons is a preferred range. Materials with asymmetric structures may have better solution processibility than those having symmetric structures, because asymmetric materials may have a lower tendency to recrystallize. Dendrimer substituents may be used to enhance the ability of small molecules to undergo solution processing.

[**0051**] The molecules disclosed herein may be substituted in a number of different ways without departing from the scope of the invention. For example, substituents may be added to a compound having three bidentate ligands, such that after the substituents are added, one or more of the bidentate ligands are linked together to form, for example, a tetradentate or hexadentate ligand. Other such linkages may be formed. It is believed that this type of linking may increase stability relative to a similar compound without linking, due to what is generally understood in the art as a "chelating effect."

[**0052**] Devices fabricated in accordance with embodiments of the invention may be incorporated into a wide variety of consumer products, including flat panel displays, computer monitors, televisions, billboards, lights for interior or exterior illumination and/or signaling, heads up displays, fully transparent displays, flexible displays, laser printers, telephones, cell phones, personal digital assistants (PDAs), laptop computers, digital cameras, camcorders, viewfinders, micro-displays, vehicles, a large area wall, theater or stadium screen, or a sign. Various control mechanisms may be used to control devices fabricated in accordance with the present invention, including passive matrix and active matrix. Many of the devices are intended for use in a temperature range comfortable to humans, such as 18 degrees C. to 30 degrees C., and more preferably at room temperature (20-25 degrees C.).

[**0053**] The materials and structures described herein may have applications in devices other than OLEDs. For example, other optoelectronic devices such as organic solar cells and organic photodetectors may employ the materials and structures. More generally, organic devices, such as organic transistors, may employ the materials and structures.

[**0054**] The term "halo" or "halogen" as used herein includes fluorine, chlorine, bromine and iodine.

[**0055**] The term "alkyl" as used herein contemplates both straight and branched chain alkyl radicals. Preferred alkyl groups are those containing from one to fifteen carbon atoms and includes methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, and the like. Additionally, the alkyl group may be optionally substituted with one or more substituents selected from halo, CN, CO_2R, C(O)R, NR_2, cyclic-amino, NO_2, and OR.

[**0056**] The term "cycloalkyl" as used herein contemplates cyclic alkyl radicals. Preferred cycloalkyl groups are those containing 3 to 7 carbon atoms and includes cyclopropyl, cyclopentyl, cyclohexyl, and the like. Additionally, the cycloalkyl group may be optionally substituted with one or more substituents selected from halo, CN, CO_2R, C(O)R, NR_2, cyclic-amino, NO_2, and OR.

[**0057**] The term "alkenyl" as used herein contemplates both straight and branched chain alkene radicals. Preferred alkenyl groups are those containing two to fifteen carbon atoms. Additionally, the alkenyl group may be optionally substituted with one or more substituents selected from halo, CN, CO_2R, C(O)R, NR_2, cyclic-amino, NO_2, and OR.

[**0058**] The term "alkynyl" as used herein contemplates both straight and branched chain alkyne radicals. Preferred alkyl groups are those containing two to fifteen carbon atoms. Additionally, the alkynyl group may be optionally substituted with one or more substituents selected from halo, CN, CO_2R, C(O)R, NR_2, cyclic-amino, NO_2, and OR.

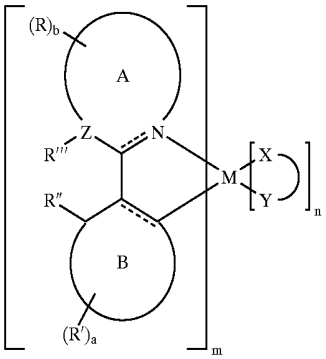
[0059] The terms "alkylaryl" as used herein contemplates an alkyl group that has as a substituent an aromatic group. Additionally, the alkylaryl group may be optionally substituted on the aryl with one or more substituents selected from halo, CN, CO_2R, C(O)R, NR_2, cyclic-amino, NO_2, and OR.

[0060] The term "heterocyclic group" as used herein contemplates non-aromatic cyclic radicals. Preferred heterocyclic groups are those containing 3 or 7 ring atoms which includes at least one hetero atom, and includes cyclic amines such as morpholino, piperdino, pyrrolidino, and the like, and cyclic ethers, such as tetrahydrofuran, tetrahydropyran, and the like.

[0061] The term "aryl" or "aromatic group" as used herein contemplates single-ring groups and polycyclic ring systems. The polycyclic rings may have two or more rings in which two atoms are common by two adjoining rings (the rings are "fused") wherein at least one of the rings is aromatic, e.g., the other rings can be cycloalkyls, cycloalkenyls, aryl, heterocycles and/or heteroaryls.

[0062] The term "heteroaryl" as used herein contemplates single-ring hetero-aromatic groups that may include from one to four heteroatoms, for example, pyrrole, furan, thiophene, imidazole, oxazole, thiazole, triazole, tetrazole, pyrazole, pyridine, pyrazine and pyrimidine, and the like. The term heteroaryl also includes polycyclic hetero-aromatic systems having two or more rings in which two atoms are common to two adjoining rings (the rings are "fused") wherein at least one of the rings is a heteroaryl, e.g., the other rings can be cycloalkyls, cycloalkenyls, aryl, heterocycles and/or heteroaryls.

[0063] A compound having the following structure is provided:



wherein

[0064] M is a metal having an atomic weight greater than 40;

[0065] the dotted lines inside the rings represent optional double bonds;

[0066] Z is carbon or nitrogen;

[0067] each R, R' and R''' is independently selected from hydrogen, alkyl, alkenyl, alkynyl, alkylaryl, trialkylsilyl, cyano, trifluoromethyl, ester, keto, amino, nitro, alkoxy, halo, aryl, heteroaryl, substituted aryl, substituted heteroaryl, or a heterocyclic group;

[0068] R" is H or F;

[0069] ring A is a 5-membered heterocyclic ring having at least 2 nitrogen atoms, with one nitrogen atom coordinated to metal M, wherein ring A can be optionally substituted with one or more substituents R, and additionally or alternatively, any two substituted positions on ring A together form, independently a cyclic ring, wherein the cyclic ring is not an aromatic ring, and the cyclic ring may be optionally substituted;

[0070] ring B is an aromatic ring with at least one carbon atom coordinated to metal M, wherein ring B can be optionally substituted with one or more substituents R'; and additionally or alternatively, any two substituted positions on ring B together form, independently a fused 4-7-membered cyclic group, wherein said cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein the 4-7-membered cyclic group is optionally substituted;

[0071] a is 0, 1, 2, 3, or 4;

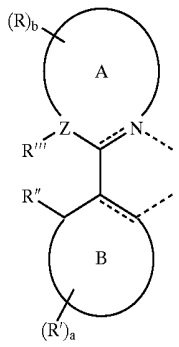
[0072] b is 0, 1, 2, or 3;

[0073] (X-Y) is an ancillary ligand;

[0074] m is the number of photoactive ligands and may be any integer from 1 to the maximum number of ligands that may be attached to the metal; and

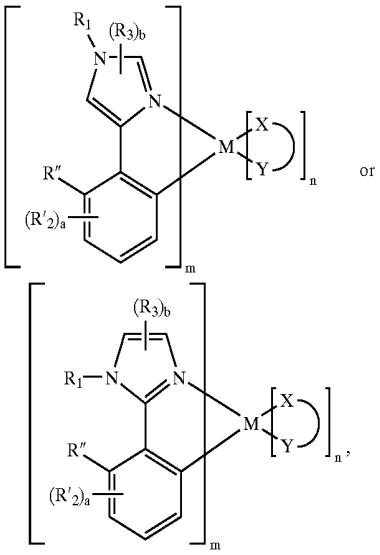
[0075] m+n is the number of ligands that may be attached to the metal.

[0076] The above compound includes a photoactive ligand having the following structure:



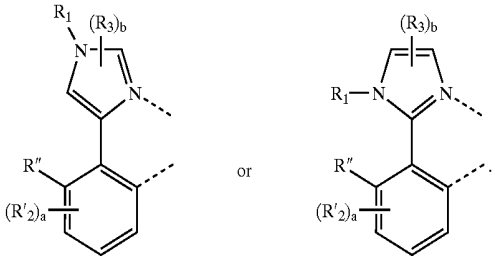
[0077] M may be any metal having an atomic weight greater than 40. Preferred metals include Ir, Pt, Pd, Rh, Re, Os, Ti, Pb, Bi, In, Sn, Sb, Te, Au, and Ag. More preferably, the metal is Ir or Pt. Most preferably, the metal is Ir.

[0078] In particularly preferred embodiments, ring A is an imidazole ring. More preferred embodiments include compounds having one of the following structures:



or

in which the ligand has the corresponding structures:



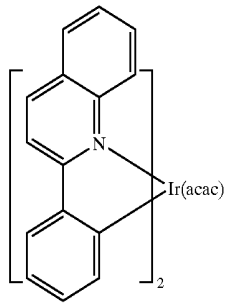
[0079] It is believed that 2-phenylimidazole and 4-phenylimidazole have higher triplet energy than the most commonly used ligand, 2-phenylpyridine, in phosphorescent organometallic complexes. When coordinated to a metal, such as iridium, the unsubstituted iridium 2-phenylimidazole and 4-phenylimidazole complexes exhibit higher triplet energy (i.e., bluer phosphorescence), and higher LUMO energy (i.e., harder to reduce) when compared to the unsubstituted iridium 2-phenylpyridine complex. This is believed to be partly due to that fact that in the former, the nitrogen atom not bound to the metal (i.e., the nitrogen atom single-bonded to 3 carbon atoms) is electron donating. For example, in one embodiment, tris(N-methyl-2-phenylimidazole)iridium(III), has a peak wavelength of 470 nm in a dilute CH_2Cl_2 solution. Tris(2-phenylpyridine)iridium(III), on the other hand, has a peak wavelength of 515 nm in a dilute CH_2Cl_2 solution.

[0080] These complexes may be highly phosphorescent at room temperature. When incorporated into an OLED, these complexes may exhibit high light emitting efficiency.

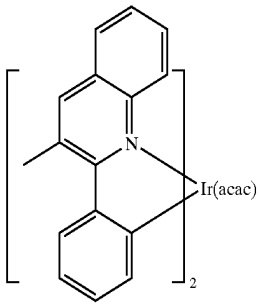
[0081] **FIGS. 3-5** compare device data for a tris(N-methyl-2-phenylimidazole)iridium(III) dopant and an existing blue emitting Ir[2-(4,6-difluorophenyl)pyridine]$_3$, abbreviated as Ir(F_2ppy)$_3$. **FIG. 5** shows that these two compounds have similar triplet energy (highest energy emission peak) corresponding to similar wavelengths in the electroluminescence spectra. The compounds were used as dopants in the same device structure, which is ITO/CuPc(100 Å)/NPD(300 Å)/CBP:dopant(6%, 300 Å)/BAlQ(400 Å)/LiF(10 Å)/Al(1000 Å). As shown in **FIG. 4**, the tris(N-methyl-2-phenylimidazole)iridium(III) device, which exhibited an external quantum efficiency of about 5%, is significantly more efficient than the Ir(F_2ppy)$_3$ device, which has an external quantum efficiency of less than 1%.

[0082] Substitutions of certain groups and modifications to the photoactive ligand may lower the triplet energy of the complex, which in some cases may be undesirable in certain OLED applications. For example, the most relevant application for this invention may be towards blue phosphorescence. A most preferred embodiment, the unsubstituted tris(N-methyl-2-phenylimidazole)iridium(III), already phosphoresces as blue as Ir(F_2ppy)$_3$, in which the phosphorescence is blue-shifted from the unsubstituted Ir(ppy)$_3$ by strongly electron withdrawing fluoro groups. Thus, it is believed that suitable substitutions on the tris(N-methyl-2-phenylimidazole)iridium(III) or similar compounds could provide much deeper blue phosphorescence than Ir(F_2ppy)$_3$. In addition, in order to achieve a blue emission, fusing a benzene ring or other aromatic rings to ring A, which delocalizes the electrons in the ligand and leads to a lower triplet energy for the organometallic complex (i.e., a red-shift in the phosphorescence), may be undesirable. Moreover, twisting rings A and B out of the same plane also lowers triplet energy (i.e., a red-shift in the phosphorescence) and may be undesirable. This is demonstrated in a pair of red and green emitting compounds. In **FIG. 12**, the normalized electroluminescence spectra are shown for the devices (i) CuPc(100 Å)/α-NPD(500 Å)/CBP:Ir(pq)$_2$(acac)(300 Å, 6%)/BAlq(150 Å)/Alq$_3$(500 Å)/LiF(10 Å)/Ai(1000 Å), (ii) CuPc(100 Å)/α-NPD(400 Å)/CBP:Ir(3'-Mepq)$_2$(acac)(300 Å, 12%)/BAlq(150 Å)/Alq$_3$(400 Å)/LiF(10 Å)/Al(1000 Å), (iii) CuPc(100 Å)/α-NPD(300 Å)/CBP:Ir(ppy)$_3$(300 Å, 6%)/BAlq(100 Å)/Alq$_3$(400 Å)/LiF(10 Å)/Al(1000 Å), and (iv) CuPc(100 Å)/α-NPD(300 Å)/CBP:Ir(3'-Meppy)$_3$(300 Å, 6%)/BAlq(100 Å)/Alq$_3$(400 Å)/LiF(10 Å)/Al(1000 Å). The structures of the red and green dopants are shown below.

Red:



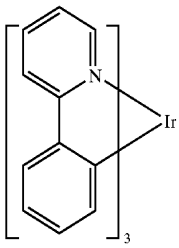
Ir(pq)$_2$(acac)



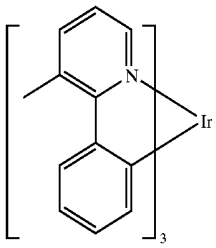
Ir(3'-Mepq)$_2$(acac)

-continued

Green:

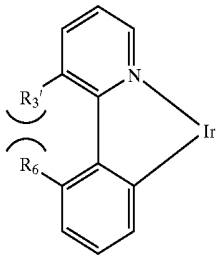


$Ir(ppy)_3$

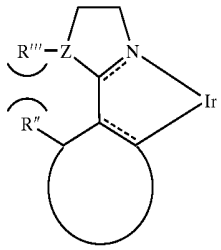


$Ir(3'\text{-}Meppy)_3$

The emission peaks for $Ir(pq)_2(acac)$ and $Ir(3'\text{-}Mepq)_2(acac)$ are 600 nm and 618 nm respectively, whereas the emission peaks for $Ir(ppy)_3$ and $Ir(3'\text{-}Meppy)_3$ are 514 nm and 522 nm respectively. The structural difference within the red pair and the green pair of compounds is only the absence and presence of the 3'-methyl group in the top ring. It is believed that the presence of the methyl group, which is a weak electron donating group, at the 3-position does not by itself account for the red-shifting effect in the phosphorescence. It is further believed that the red-shift in the phosphorescence may be partially due to the twisting between the top and bottom rings exerted by the steric hindrance from the presence of a bulky substituent at the 3'-methyl group such as a methyl group. Similar effect is expected when the 6-position of the bottom ring is substituted by a bulky group as shown in a generic structure below.



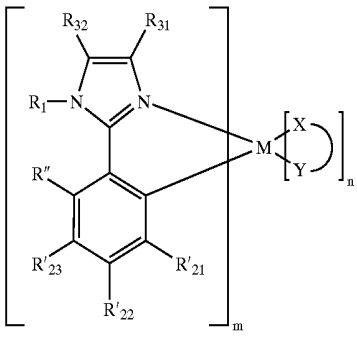
In order to maintain blue and achieve deeper blue emission of the invention compounds, it is believed that minimizing such twisting is essential. In the present compounds, the top ring is a 5-membered ring. The steric bulkiness of the R'" group, therefore, may have less effect on the twisting. As a result, R'" may be groups other than H and F (H and F are believed to be the smallest possible substituents). However, the R" is most preferably H or F to minimize the twisting.



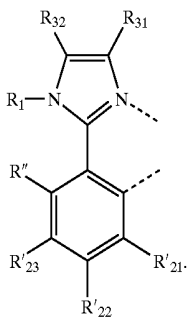
[0083] In other circumstances, it may be desirable to decrease triplet energy. For example, certain compounds may have triplet energies that are slightly higher than the energy corresponding to e.g. a saturated green emission. In this particular example, it would be desirable to lower the energy to obtain a compound that would emit at a wavelength corresponding to saturated green.

[0084] Preferably, R_1 is H, phenyl, or methyl. The phenyl may be substituted or unsubstituted. In preferred embodiments, M is iridium and the compound has a tris configuration wherein m is 3 and n is zero.

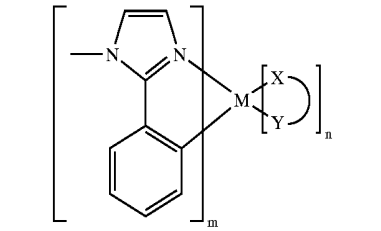
[0085] In another preferred embodiment, the compound has the structure

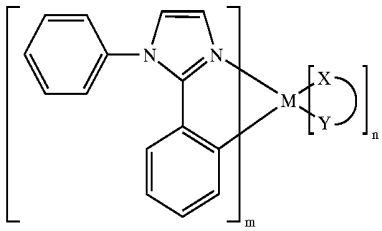


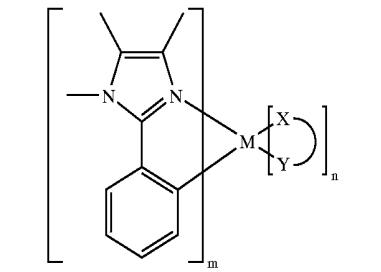
and the ligand has the structure

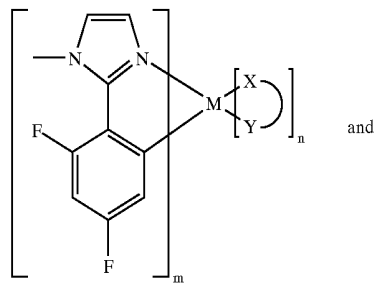


[0086] More preferred embodiments include compounds having the following structures:

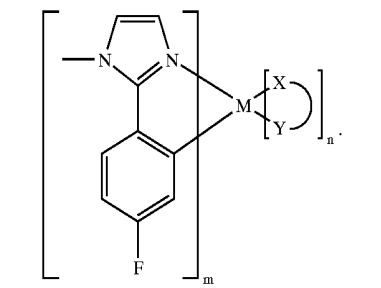




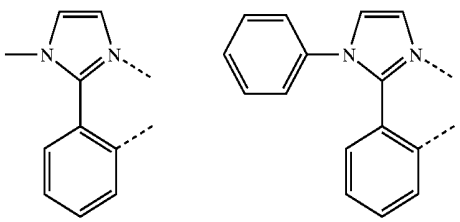




and



The ligands for these embodiments have the corresponding structures:



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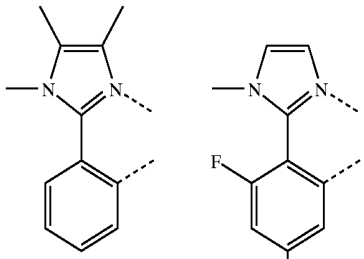
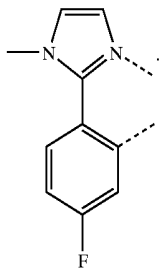
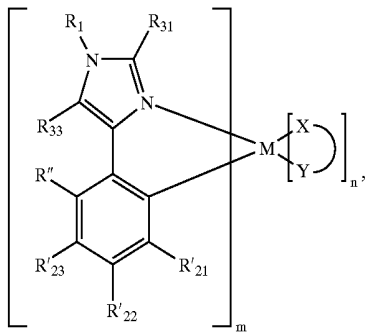


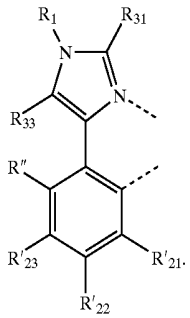
and



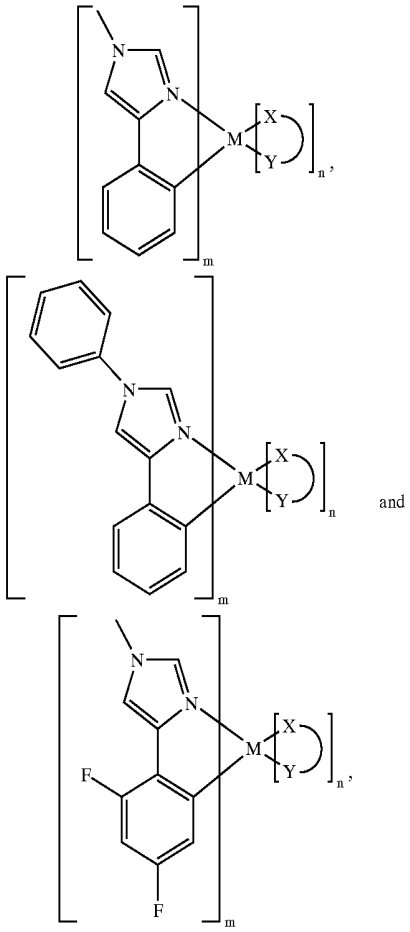
[0087] In another embodiment, the imidazole compound has the structure:



in which the ligand has the structure

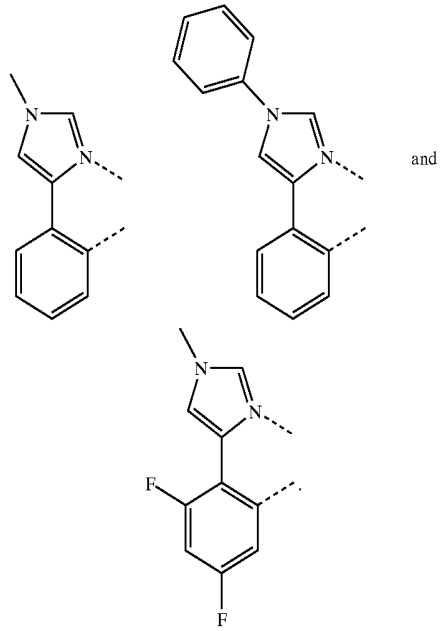


[0088] Preferred embodiments include compounds with the following structures:



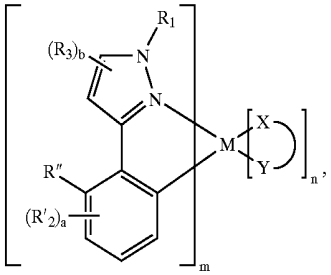
and

in which the ligands have the structure:

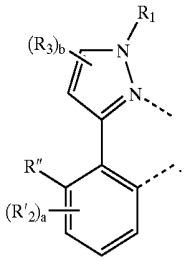


and

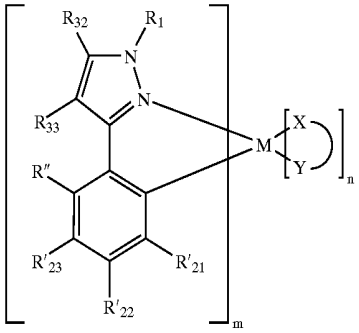
[0089] In one embodiment, the compound has the structure



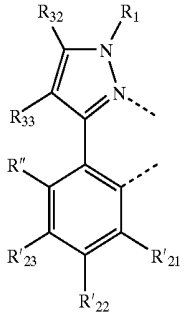
in which the ligand has the structure



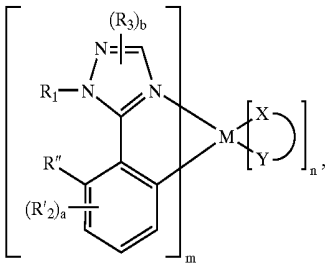
[0090] One embodiment has a compound with the structure

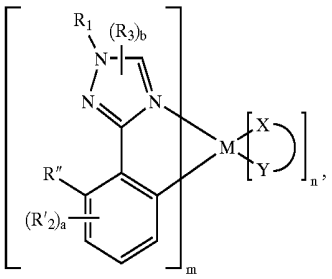


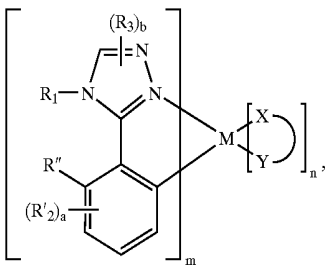
in which the ligand has the structure

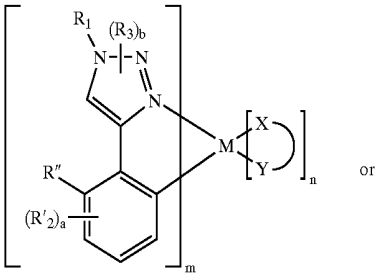


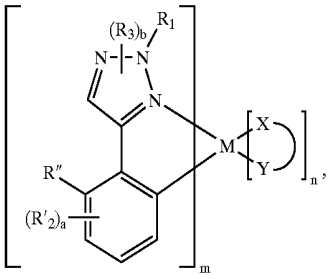
[0091] In another embodiment, the compound is a triazole having one of the following structures:



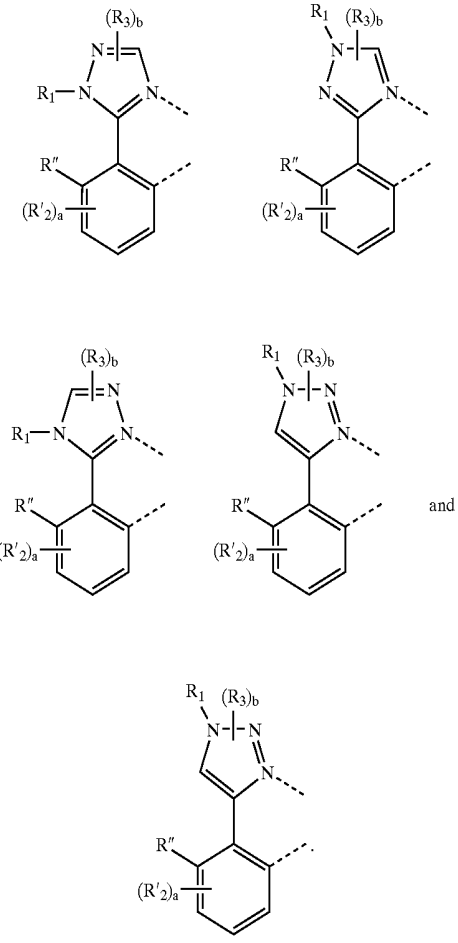





or

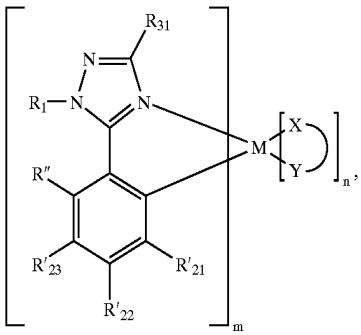


and the ligand has a structure selected from:


and

[0092] Preferably, R_1 is H, phenyl, or methyl. The phenyl may be substituted or unsubstituted. In preferred embodiments, M is Iridium and the compound has a tris configuration wherein m is 3 and n is zero.

[0093] In other embodiments, the triazole compounds have the following structures:



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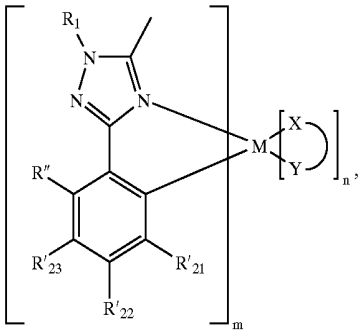
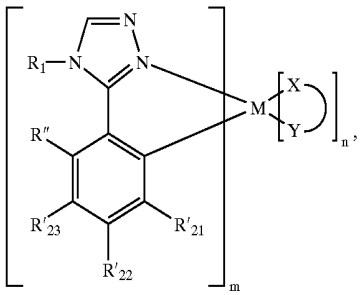
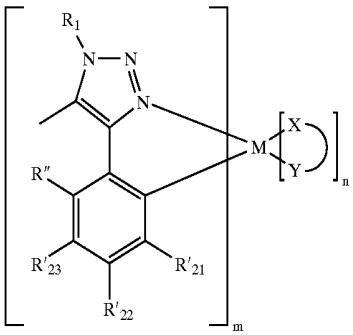
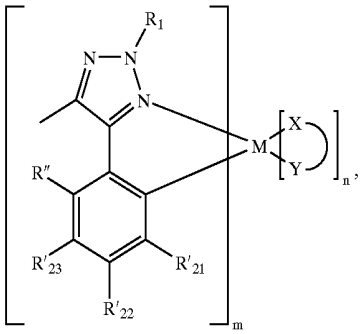


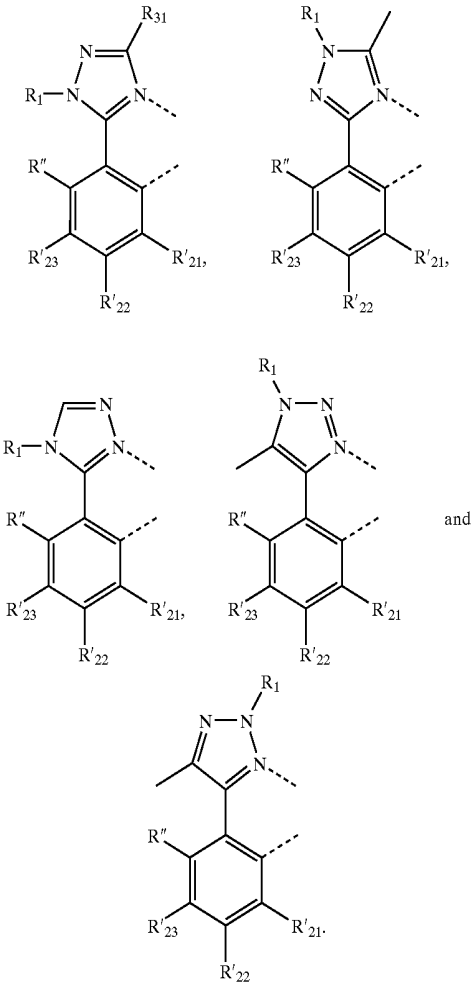




and

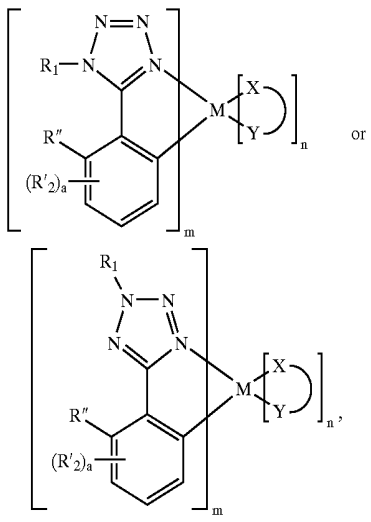


, in which the ligands have the following structures:



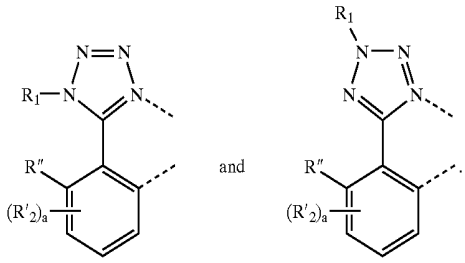
and

[0094] In another embodiment, the compound is a tetrazole having one of the following structures:



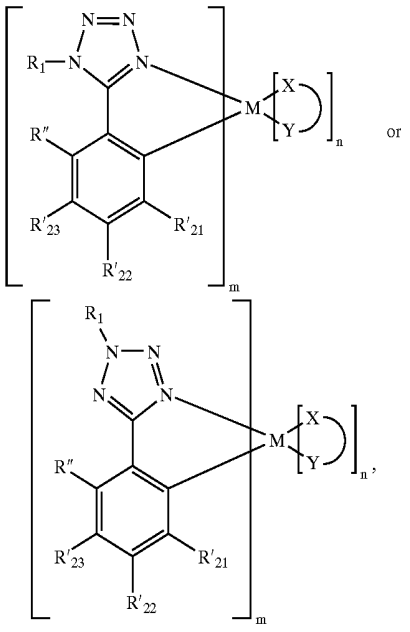
or

in which the ligand has a structure selected from the following structures:



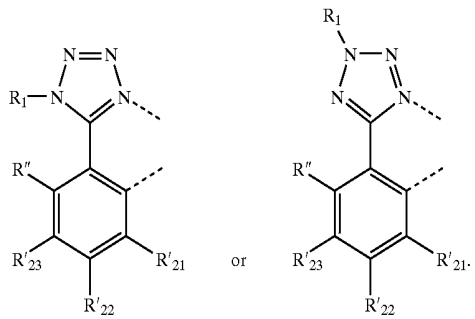
[0095] Preferably, R_1 is H, phenyl, or methyl. The phenyl may be substituted or unsubstituted. In preferred embodiments, M is Iridium and the compound has a tris configuration wherein m is 3 and n is zero.

[0096] In one embodiment, the compound has the structure:



in which the ligand

[0097] has the corresponding structure



[0098] It is understood that the various embodiments described herein are by way of example only, and are not intended to limit the scope of the invention. For example, many of the materials and structures described herein may be substituted with other materials and structures without deviating from the spirit of the invention. It is understood that various theories as to why the invention works are not intended to be limiting. For example, theories relating to charge transfer are not intended to be limiting.

Material Definitions:

[0099] As used herein, abbreviations refer to materials as follows:—

[0100] CBP: 4,4'-N,N-dicarbazole-biphenyl

[0101] m-MTDATA 4,4',4"-tris(3-methylphenylphenylamino)triphenylamine

[0102] Alq_3: 8-tris-hydroxyquinoline aluminum

[0103] Bphen: 4,7-diphenyl-1,10-phenanthroline

[0104] n-BPhen: n-doped BPhen (doped with lithium)

[0105] F_4-TCNQ: tetrafluoro-tetracyano-quinodimethane

[0106] p-MTDATA: p-doped m-MTDATA (doped with F_4-TCNQ)

[0107] $Ir(Ppy)_3$: tris(2-phenylpyridine)-iridium

[0108] $Ir(ppz)_3$: tris(1-phenylpyrazoloto,N,C(2')iridium(III)

[0109] BCP: 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline

[0110] TAZ: 3-phenyl-4-(1'-naphthyl)-5-phenyl-1,2,4-triazole

[0111] CuPc: copper phthalocyanine.

[0112] ITO: indium tin oxide

[0113] NPD: N,N'-diphenyl-N-N'-di(1-naphthyl)-benzidine

[0114] TPD: N,N'-diphenyl-N-N'-di(3-toly)-benzidine

[0115] BAlq: aluminum(III)bis(2-methyl-8-hydroxyquinolinato)4-phenylphenolate

[0116] mCP: 1,3-N,N-dicarbazole-benzene

[0117] DCM: 4-(dicyanoethylene)-6-(4-dimethylaminostyryl-2-methyl)-4H-pyran

[0118] DMQA: N,N'-dimethylquinacridone

[0119] PEDOT:PSS: an aqueous dispersion of poly(3,4-ethylenedioxythiophene) with polystyrenesulfonate (PSS)

[0120] F_2ppy: 2-(4',6'-difluorophenyl)pyridine

[0121] $Ir(F_2ppy)_3$: tris[2-(4,6-difluorophenyl)pyridine]iridium(III)

[0122] HPT: 2,3,6,7,10,11-hexaphenyltriphenylene

[0123] $Ir(3'\text{-}Meppy)_3$: tris(3-methyl-2-phenylpyridine) iridium(III)

[0124] $Ir(pq)_2(acac)$: bis(2-phenylquinoline) iridium(III) acetylacetonate

[0125] $Ir(3'\text{-}Mepq)_2(acac)$: bis(3-methyl-2-phenylquinoline) iridium(III) acetylacetonate

Experimental:

[0126] Specific representative embodiments of the invention will now be described, including how such embodiments may be made. It is understood that the specific methods, materials, conditions, process parameters, apparatus and the like do not necessarily limit the scope of the invention.

[0127] Certain of the iridium complexes may be subject to photo-oxidation in air and therefore should be protected from light and/or air during synthesis, isolation, and subsequent use in fabricating devices.

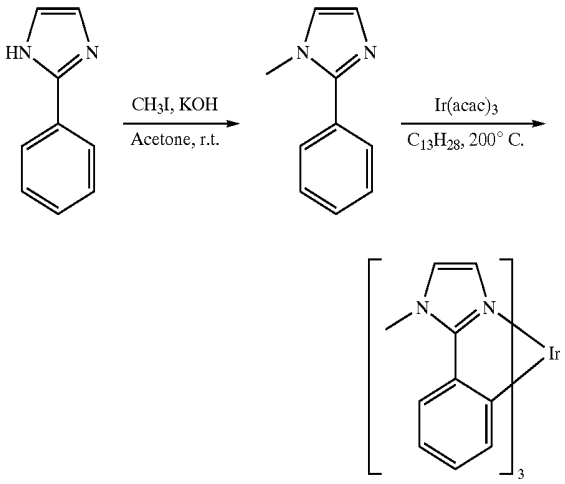
Synthesis of fac-tris[arylimidazolato-N,$C^{2'}$]iridium(III) Complexes

EXAMPLE 1

Synthesis of fac-tris(2-phenyl-N-methylimidazolato-N,$C^{2'}$)iridium(III)

[0128]

Step 1:



Potassium hydroxide (14.03 g, 250 mmol) was added to a stirred solution of 2-phenylimidazole (7.20 g, 50 mmol) in 100 mL of acetone. After 10 min, iodomethane (7.80g, 55 mmol) was added with vigorous stirring. After an additional 20 min, 200 mL of CH_2Cl_2 was added, followed by 200 mL of water. The organic layer was separated and dried with sodium sulfate, then filtered and the filtrate concentrated under reduced pressure. The residue was distilled under reduced pressure (0.1 torr) at 150° C. to yield clear, colorless oil (6.64 g, 84 % yield). ^{1}H-NMR and MS results showed this material to be N-methyl-2-phenylimidazole.

Step 2:

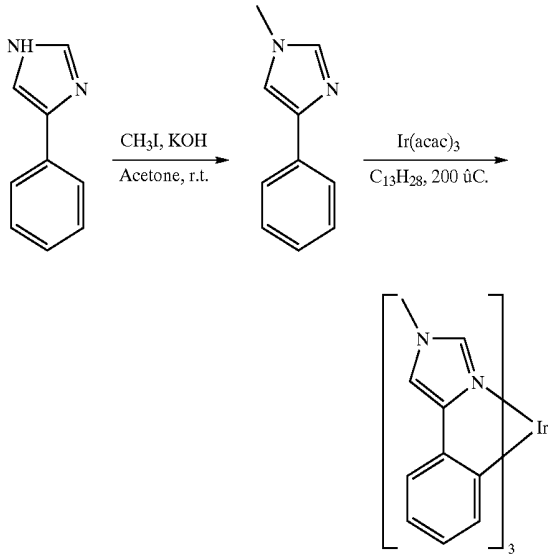
N-Methyl-2-phenylimidazole (9.30 g, 59 mmol) and tris(acetylacetonate)iridium(III) (4.90 g, 10 mmol) were added to a flask containing 20 mL of tridecane. The mixture was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. After cooling, the precipitate which formed was filtered and washed with absolute ethanol followed by hexane. The residue was further purified by a silica gel column chromatography to give fac-tris[N-methyl-2-phenylimidazolato-N,$C^{2'}$]iridium(III) (2.60 g), which was further purified by vacuum sublimation and characterized by ^{1}H-NMR, cylic voltammetry, UV-Vis and mass spectrometry. λ_{max} of emission=468, 498 nm, CIE=(0.20, 0.37), E_{ox}=−0.05 V, E_{red}=−3.27 V (vs. Fc^+/Fc).

EXAMPLE 2

Synthesis of fac tris(N-methyl-4-phenylimidazolato-N,$C^{2'}$)iridium(III)

[0129] Although this compound has not been synthesized, it is believed, based on other synthesized compounds, that the following synthetic scheme produces fac-tris(N-methyl-4-phenylimidazolato-N,$C^{2'}$)iridium(III):

Step 1:



Potassium hydroxide (19.0 g, 339 mmol) is added to a stirred solution of 4-Phenylimidazole (10.0 g, 67 mmol) in 200 mL of acetone. After 10 min, iodomethane (10.9 g, 74 mmol) is added with vigorous stirring. After additional 20 min, the mixture is filtered and the solvents of filtrate is removed under reduced pressure. The residue is distilled at 180° C. to yield N-methyl-4-phenylimidazole as a white solid (7.0 g, 66 % yield), as confirmed by ^{1}H-NMR and mass spectrometry.

Step 2:

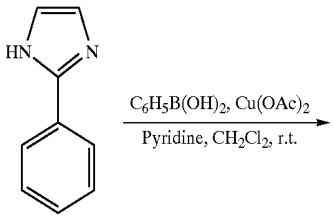
N-Methyl-4-phenylimidazole (930 mg, 6 mmol) and tris(acetylacetonate)iridium(III) (490 mg, 1 mmol) are added to a flask containing 5 mL of tridecane. The reaction mixture is heated to reflux and stirred under a nitrogen atmosphere for 24 hours. After cooling, the precipitate which forms is filtered and washed with absolute ethanol followed by hexane. The residue is further purified by a silica gel column to give fac-tris[N-methyl-4-phenylimidazolato-N,$C^{2'}$]iridium(III).

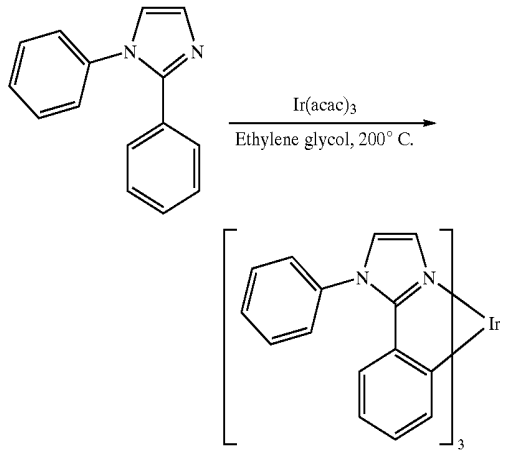
EXAMPLE 3

Synthesis of fac-tris[N-phenyl-2-phenylimidazolato-N,C$^{2'}$]iridium(III)

[0130]

Step 1:





To a 500 mL round flask was added phenylboronic acid (6.10 g, 50 mmol), 1-H-2-phenylimidazole (3.60 g, 25 mmol), pyridine (3.95 g, 50 mmol), anhydrous cupric acetate (6.65 g, 37 mmol), and 125 mL dichloromethane. The reaction is stirred under air at ambient temperature for 2 days. The mixture is filtered through a short silica plug, washed with ethyl acetate and purified by silica gel column chromatography. Distillation of the product at 240° C. gave colorless solid of N-phenyl-2-phenylimidazole (2.37 g, 43 % yield), characterized by ^{1}H-NMR and mass spectrometry.

Step 2:

N-Phenyl-2-phenylimidazole (0.44 g, 2.0 mmol) and tris(acetylacetonate)iridium(III) (0.25 g, 0.5 mmol) were added to a flask containing 5 mL of ethyleneglycol. The reaction mixture was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. After cooling, the precipitate formed was filtered and washed first with absolute ethanol followed by hexane. The residue was further purified by a silica gel column chromatography to give fac-tris[N-phenyl-2-phenylimidazolato-N,C$^{2'}$]iridium(III) (0.15 g). ^{1}H-NMR and mass spectrometry results confirmed the desired compound. λ_{max} of emission=520 nm, CIE=(0.32, 0.56), E_{ox}=0.06 V (r), E_{red}=−2.79 V (i) (vs. Fc^+/Fc).

EXAMPLE 4

Synthesis of fac-tris[N-methyl-2-(2,4-difluorophenyl)imidazolato-N,C$^{2'}$]iridium(III)

Step 1:

[0131] To a solution of 1-H-imidazole (8.20 g, 100 mmol) in dry THF (210 mL) at −78° C. was added n-butyllithium (1.6M in hexane, 75 mL, 120 mmol) dropwise. The solution was gradually warmed up to room temperature and further stirred for 2 h. The mixture was then cooled to −78° C., and tetrabromomethane (33.2 g, 100 mmol) in 30 mL of dry THF was added dropwise. After the addition, the mixture continued to stir for 15 min and was quenched by water. The mixture was extracted with ether and purified by a silica gel column with ethyl acetate as eluent. Distillation of the product gave N-methyl-2-bromoimidazole as a colorless oil (7.40 g, 46% yield), characterized by ^{1}H-NMR and MS.

Step 2:

[0132] To a 500 mL round flask was added N-methyl-2-bromoimidazole (6.50 g, 40 mmol),2,4-difluorophenylboronic acid (7.89g, 50 mmol), palladium(II) acetate (0.28 g, 1.25 mmol), triphenylphosphine (1.31 g, 5 mmol), sodium carbonate (14.31 g, 135 mmol), and 200 mL of DME and 100 mL of water. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 12 hours. The mixture was extracted with ethyl acetate and further purified by a silica gel column. Distillation of the product at 150° C. gave N-methyl-2-(2,4-difluorophenyl)imidazole as a colorless oil (6.60 g, 85% yield), characterized by ^{1}H-NMR and MS.

Step 3:

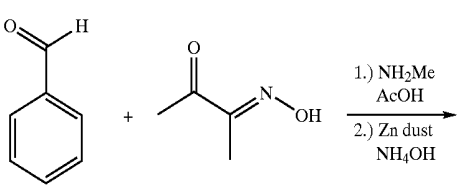
[0133] N-methyl-2-(2,4-difluorophenyl)imidazole (0.39 g, 2.0 mmol) and tris(acetylacetonate)iridium(III) (0.25 g, 0.5 mmol) were added to a flask containing 5 mL of tridecane. The reaction mixture was heated to reflux and stirred under a nitrogen atmosphere for 24 hours. After cooling, the precipitate formed was filtered and washed first with absolute ethanol followed by hexane. The residue was further purified by a silica gel column chromatography to give fac-tris[N-methyl-2-(2,4-difluorophenyl)imidazolato-N,C$^{2'}$] iridium(III) (0.02 g). ^{1}H-NMR and mass spectrometry results confirmed the desired compound. λ_{max} of emission= 446, 474 nm, CIE=(0.18, 0.26), E_{ox}=0.42 V (r), E_{red}=−3.15 V (i) (vs. Fc^+/Fc).

EXAMPLE 5

Synthesis of fac-tris(1,4,5-trimethyl-2-phenyl)imidazolato-N,C$^{2'}$iridium (III)

[0134]

Step 1:



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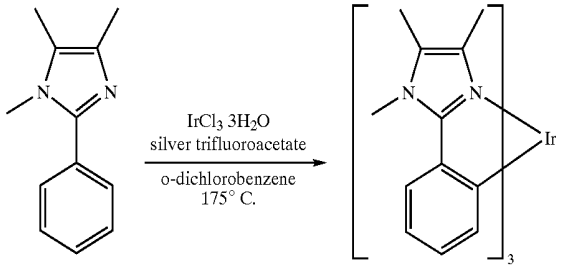


To a 3-neck 1L flask filled with 280 mL acetic acid was added benzaldehyde (25.0 g, 236mmol), butanedione monoxime (23.8 g, 236 mmol), and 40% v/v methylamine (18.3 g, 236 mmol). The solution stirred at reflux for 2 hours and then was cooled to room temperature.

Step 2:

The resultant product was loaded into a 3-neck flask equipped with a mechanical stir arm, cooled in an ice bath and zinc dust (47 g) was added slowly. The solution was allowed to stir at reflux for 1 hour and then continued for 16 hours at room temperature. The mixture was then filtered via suction to remove the zinc acetate. The filtrate was basified with the slow addition of ammonium hydroxide and monitored by pH paper. The aqueous layer was thrice extracted with toluene and the organic layer dried with $MgSO_4$, filtered and evaporated of solvent. The residue was twice distilled under reduced pressure (0.1 torr) (Kugelrohr 160° C.) and the distillate recrystallized to yield white solids (13 g, 29.5% after rinse with hexanes and drying).

Step 3:

To a 100 mL flask was added 30 mL o-dichlorobenzene. The solvent was purged with N_2 at 180° C. for 30 minutes. The solvent was then cooled to room temperature and the 1,4,5-trimethyl-2-phenylimidazole (1.5 g, 8.1 mmol), $IrCl_3.3H_2O$, (0.58 g, 1.6 mmol), and silver trifluoroacetate (1.42 g, 6.44 mmol) were added. The mixture was heated @175° C. for 20 hours under a stream of N_2. The solution was cooled to room temperature, enriched with CH_2Cl_2 and purified on a silica gel plug with CH_2Cl_2 to give a low yield of tris(1,4,5-trimethyl-2-phenylimidazolato-N,$C^{2'}$)iridium (III), characterized by mass spectrometry and UV-Vis spectroscopy. λ_{max} of emission is 478 nm, 498 nm. CIE=(0.23, 0.40)

EXAMPLE 6

Synthesis of fac-tris[N-phenyl-2-(2,4-diflurophenyl)imidazolato-N,$C^{2'}$]iridium(III)

[0135] N-Phenyl-2-(2,4-diflurophenyl)imidazole (6.80 g, 26.5 mmol) and tris(acetylacetonate)iridium(III) (3.25 g, 6.6 mmol) were added to a flask containing 35 mL of ethylene glycol. The reaction mixture was heated to reflux and stirred under a nitrogen atmosphere for 48 hours. After cooling, the precipitate formed was filtered and washed first with absolute ethanol followed by hexane. The residue was further purified by a silica gel column chromatography to give fac-tris[N-phenyl-2-(2,4-diflurophenyl)imidazolato-N,$C^{2'}$] iridium(III) (1.05 g). The product was further purified by vacuum sublimation. ^{1}H-NMR and mass spectrometry results confirmed the desired compound. λ_{max} of emission= 498 nm, CIE=(0.25, 0.45), E_{ox}=0.49 V (r), E_{red}=−2.80 V (i) (vs. Fc^+/Fc).

Device Fabrication and Measurement

[0136] All devices were fabricated by high vacuum ($<10^{-7}$ Torr) thermal evaporation. The anode electrode was ~1200 Å of indium tin oxide (ITO). The cathode consisted of 10 Å of LiF followed by 1,000 Å of Al. All devices were encapsulated with a glass lid sealed with an epoxy resin in a nitrogen glove box (<1 ppm of H_2O and O_2) immediately after fabrication, and a moisture getter was incorporated inside the package. The devices consisted of either one electron transporting layer layer (ETL2) or 2 ETL layers (ETL2 and ETL1). ETL2 refers to the ETL adjacent to the emissive layer (EML) and ETL1 refers to the ETL adjacent to ETL2.

TABLE 1

	Device Characteristics				
	Compounds	ETL2	ETL1	External quantum efficiency at 10 mA/cm^2 (%)	CIE
Example 7	Tris(N-methyl-2-phenylimidazolato-N,$C^{2'}$)iridium(III)	BAlq (400 Å)	none	3.7	(0.185, 0.413)
Comparative example 1	Tris[2-(4,6-difluorophenyl)pyridine]iridium(III)	BAlq (400 Å)	none	0.46	(0.167, 0.296)
Example 8	Tris(N-phenyl-2-phenylimidazole)iridium(III)	BAlq (400 Å)	none	6.2	(0.270, 0.581)
Example 9	Tris(N-phenyl-2-phenylimidazole)iridium(III)	HPT (100 Å)	BAlq (300 Å)	4.4	(0.277, 0.582)
Example 10	Tris[N-methyl-2-(4,6-difluorophenyl)imidazole]iridium(III)	BAlq (400 Å)	none	1.3	(0.174, 0.312)
Example 11	Tris[N-methyl-2-(4,6-difluorophenyl)imidazole]iridium(III)	HPT (100 Å)	BAlq (300 Å)	1.8	(0.167, 0.280)

TABLE 1-continued

	Device Characteristics				
	Compounds	ETL2	ETL1	External quantum efficiency at 10 mA/cm^2 (%)	CIE
Example 12	Tris(N-methyl-2-phenylimidazolato-N,C$^{2'}$)iridium(III)	BAlq (400 Å)	none	7.0	(0.17, 0.40)
Comparative example 2	Tris[2-(4,6-difluorophenyl)pyridine]iridium(III)	BAlq (400 Å)	none	3.8	(0.16, 0.36)

EXAMPLE 7

[0137] The organic stack consisted of sequentially, from the ITO surface, 100 Å thick of copper phthalocyanine (CuPc) as the hole injection layer (HIL), 300 Å of 4,4'-bis [N-(1-naphthyl)-N-phenylamino]biphenyl (cc-NPD) as the hole transporting layer (HTL), 300 Å of 4,4'-bis(N-carbazolyl)biphenyl (CBP) doped with 6 wt % of the dopant emitter tris(N-methyl-2-phenylimidazolato-N, C$^{2'}$)iridium(III) as the emissive layer (EML), 400 Å of aluminum(III)bis(2-methyl-8-hydroxyquinolinato)4-phenylphenolate (BAlq) as the ETL2. There was no ETL1.

COMPARATIVE EXAMPLE 1

[0138] The organic stack consisted of sequentially, from the ITO surface, 100 Å thick of copper phthalocyanine (CuPc) as the hole injection layer (HIL), 300 Å of 4,4'-bis [N-(1-naphthyl)-N-phenylamino]biphenyl (α-NPD) as the hole transporting layer (HTL), 300 Å of 4,4'-bis(N-carbazolyl)biphenyl (CBP) doped with 6 wt % of the dopant emitter tris(2-(4,6-difluorophenyl)pyridine)iridium(III) [Ir(F_2ppy)$_3$] as the emissive layer (EML), 400 Å of aluminum(III)bis(2-methyl-8-hydroxyquinolinato)4-phenylphenolate (BAlq) as the ETL2. There was no ETL1.

EXAMPLE 8

[0139] The organic stack consisted of sequentially, from the ITO surface, 100 Å thick of copper phthalocyanine (CuPc) as the hole injection layer (HIL), 300 Å of 4,4'-bis [N-(1-naphthyl)-N-phenylamino]biphenyl (α-NPD),as the hole transporting layer (HTL), 300 Å of 4,4'-bis(N-carbazolyl)biphenyl (CBP) doped with 6 wt % of the dopant emitter tris(N-phenyl-2-phenylimidazolato-N, C$^{2'}$)iridium(III) as the emissive layer (EML), 400 Å of aluminum(III)bis(2-methyl-8-hydroxyquinolinato)4-phenylphenolate (BAlq) as the ETL2. There was no ETL1.

EXAMPLE 9

[0140] The organic stack consisted of sequentially, from the ITO surface, 100 Å thick of copper phthalocyanine (CuPc) as the hole injection layer (HIL), 300 Å of 4,4'-bis [N-(1-naphthyl)-N-phenylamino]biphenyl (α-NPD), as the hole transporting layer (HTL), 300 Å of 4,4'-bis(N-carbazolyl)biphenyl (CBP) doped with 6 wt % of the dopant emitter tris(N-phenyl-2-phenylimidazolato-N, C$^{2'}$)iridium(III) as the emissive layer (EML), 100 Å of HPT as the ETL2, 300 Å of aluminum(III)bis(2-methyl-8-hydroxyquinolinato)4-phenylphenolate (BAlq) as the ETL1.

EXAMPLE 10

[0141] The organic stack consisted of sequentially, from the ITO surface, 100 Å thick of copper phthalocyanine (CuPc) as the hole injection layer (HIL), 300 Å of 4,4'-bis [N-(1-naphthyl)-N-phenylamino]biphenyl (α-NPD), as the hole transporting-layer (HTL), 300 Å of 4,4'-bis(N-carbazolyl)biphenyl (CBP) doped with 6 wt % of the dopant emitter tris[N-methyl-2-(4,6-difluorophenyl)imidazolato-N, C$^{2'}$]iridium(III) as the emissive layer (EML), 400 Å of aluminum(M)bis(2-methyl-8-hydroxyquinolinato)4-phenylphenolate (BAlq) as the ETL2. There was no ETL1.

EXAMPLE 11

[0142] The organic stack consisted of sequentially, from the ITO surface, 100 Å thick of copper phthalocyanine (CuPc) as the hole injection layer (HIL), 300 Å of 4,4'-bis [N-(1-naphthyl)-N-phenylamino]biphenyl (α-NPD), as the hole transporting layer (HTL), 300 Å of 4,4'-bis(N-carbazolyl)biphenyl (CBP) doped with 6 wt % of the dopant emitter tris[N-methyl-2-(4,6-difluorophenyl)imidazolato-N, C$^{2'}$]iridium(III) as the emissive layer (EML), 100 Å of HPT as the ETL2, 300 Å of aluminum(III)bis(2-methyl-8-hydroxyquinolinato)4-phenylphenolate (BAlq) as the ETL1.

EXAMPLE 12

[0143] The organic stack consisted of sequentially, from the ITO surface, 100 Å thick of copper phthalocyanine (CuPc) as the hole injection layer (HIL), 300 Å of 4,4'-bis [N-(1-naphthyl)-N-phenylamino]biphenyl (α-NPD) as the hole transporting layer (HTL), 300 Å of 1,3-N,N-dicarbazole-benzene (mCP) doped with 6 wt % of the dopant emitter tris(N-methyl-2-phenylimidazolato-N, C$^{2'}$)iridium(III) as the emissive layer (EML), 400 Å of aluminum(III)bis(2-methyl-8-hydroxyquinolinato)4-phenylphenolate (BAlq) as the ETL2. There is no ETL1.

COMPARATIVE EXAMPLE 2

[0144] The organic stack consisted of sequentially, from the ITO surface, 100 Å thick of copper phthalocyanine (CuPc) as the hole injection layer (HIL), 300 Å of 4,4'-bis [N-(1-naphthyl)-N-phenylamino]biphenyl (α-NPD) as the hole transporting layer (HTL), 300 Å of 1,3-N,N-dicarbazole-benzene (mCP) doped with 6 wt % of the dopant emitter tris(2-(4,6-difluorophenyl)pyridine)iridium(III) [Ir(F_2ppy)$_3$] as the emissive layer (EML), 400 Å of aluminum(III)bis(2-methyl-8-hydroxyquinolinato)4-phenylphenolate (BAlq) as the ETL2. There is no ETL1.

[0145] **FIG. 3** shows plots of current density vs. voltage for example 7 and comparative example 1. The current-voltage characteristics are similar, with example 1 driving at slightly higher voltage at the same current density.

[0146] **FIG. 4** shows plots of external quantum efficiency vs. current density for example 7 and comparative example 1. **FIG. 5** shows the normalized electroluminescence spectra of example 7 and comparative example 1 taken at a current density of 10 mA/cm^2. While the electroluminescence spectra are similar, the maximum external quantum efficiency of example 7 is 5.4% whereas that of comparative example 1 is <1%. It demonstrates that the invention compounds are advantageously much more efficient in this device architecture. Without being limited to how it works, the better efficiency of example 7 may be partially due to the improved charge trapping, particularly hole trapping, of tris(N-methyl-2-phenylimidazolato-N,C$^{2'}$)iridium(III) than Ir(F_2ppy)$_3$. Tris(N-methyl-2-phenylimidazolato-N,C$^{2'}$)iridium(III) is about 0.8 V easier to oxidize than Ir(F_2ppy)$_3$ in cylic voltammetry in the same solvent system. This may lead to better a hole trapping behavior of the former when used as a dopant at the same concentration in the same host (6% of dopant in CBP in this case), thus improving device efficiency.

[0147] **FIG. 6** shows plots of current density vs. voltage for example 8 and example 9. The current-voltage characteristics are similar in examples 8 and 9 which respectively has BAlq as the only ETL and HTP/BAlq as the ETL2 /ETL1.

[0148] **FIG. 7** shows plots of external quantum efficiency vs. current density for example 8 and example 9.

[0149] **FIG. 8** shows the normalized electroluminescence spectra of example 8 and example 9 taken at a current density of 10 mA/cm^2. Example 8 has a maximum external quantum efficiency of 11% whereas example 9 has a maximum external quantum efficiency of 6.8%. It suggests, although the EML is the same in examples 8 and 9, the ETLs may have a significant effect on the device efficiency due to the electron injection, hole blocking and exciton blocking properties of the ETLs.

[0150] **FIG. 9** shows plots of current density vs. voltage for example 10 and example 11. The current-voltage characteristics are similar in examples 10 and 11 which respectively has BAlq as the only ETL and HTP/BAlq as the ETL2/ETL1.

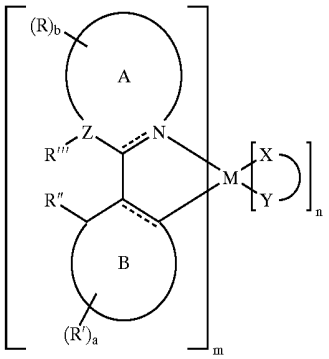
[0151] **FIG. 10** shows plots of external quantum efficiency vs. current density for example 10 and example 11.

[0152] **FIG. 11** shows the normalized electroluminescence spectra of example 10 and example 11 taken at a current density of 10 mA/cm^2. Example 10 has a maximum external quantum efficiency of 1.3% whereas example 11 has a maximum external quantum efficiency of 1.8%. Again, it suggests, although the EML is the same in examples 10 and 11, the ETLs may have a significant effect on the device efficiency due to the electron injection, hole blocking and exciton blocking proerties of the ETLs.

[0153] **FIG. 13** shows plots of current density vs. voltage for example 12 and comparative example 2. **FIG. 14** shows plots of external quantum efficiency vs. current density for example 12 and comparative example 2. **FIG. 15** shows the normalized electroluminescence spectra of example 12 and comparative example 2 taken at a current density of 10 mA/cm^2. While the electroluminescence spectra are similar, the maximum external quantum efficiency of example 12 is 7.5% whereas that of comparative example is 4.0%. Without being limited to how it works, the better efficiency of example 12 may be partially due to the improved charge trapping, particularly hole trapping, of tris(N-methyl-2-phenylimidazolato-N,C$^{2'}$)iridium(III) than Ir(F_2ppy)$_3$. Tris(N-methyl-2-phenylimidazolato-N,C$^{2'}$)iridium(III) is about 0.8 V easier to oxidize than Ir(F_2ppy)$_3$ in cylic voltammetry in the same solvent system. This may lead to better a hole trapping behavior of the former when used as a dopant at the same concentration in the same host (6% of dopant in mCP in this case), thus improving device efficiency. The efficiency of example 12 (7.5%) is better than that of example 7 (3.7%). The difference between the two devices is only the host material. Example 12 consists of mCP as the host, whereas example 7 consists of CBP as the host. Again, without being limited to how it works, it is believed that mCP is more suitable as a host than CBP in this case because of the higher triplet energy of the former which leads to reduced or no phosphorescence quenching of the dopant emitter tris(N-methyl-2-phenylimidazolato-N, C$^{2'}$)iridium(III).

[0154] While the present invention is described with respect to particular examples and preferred embodiments, it is understood that the present invention is not limited to these examples and embodiments. The present invention as claimed therefore includes variations from the particular examples and preferred embodiments described herein, as will be apparent to one of skill in the art. For example, structural isomers may exist in the invention compounds (facial and meridional). In the examples, the facial isomers are described. However, it is believed that the meridional isomers may also be synthesized and utilized in devices.

1. A compound, having the structure:



wherein

M is a metal having an atomic weight greater than 40;

the dotted lines inside the rings represent optional double bonds;

Z is carbon or nitrogen;

each R, R', and R'" is independently selected from hydrogen, alkyl, alkenyl, alkynyl, alkylaryl, trialkylsilyl,

cyano, trifluoromethyl, ester, keto, amino, nitro, alkoxy, halo, aryl, heteroaryl, substituted aryl, substituted heteroaryl, or a heterocyclic group;

R" is H or F;

ring A is a 5-membered heterocyclic ring having at least 2 nitrogen atoms, with one nitrogen atom coordinated to metal M, wherein ring A can be optionally substituted with one or more substituents R and additionally or alternatively, any two substituted positions on ring A together form, independently, a cyclic ring, wherein the cyclic ring is not an aromatic ring, and the cyclic ring may be optionally substituted;

ring B is an aromatic ring with at least one carbon atom coordinated to metal M, wherein ring B can be optionally substituted with one or more substituents R'; and additionally or alternatively, any two substituted positions on ring B together form, independently a fused 4-7-membered cyclic group, wherein said cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein the 4-7-membered cyclic group is optionally substituted;

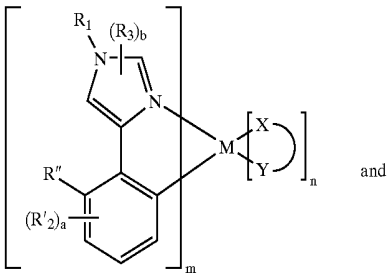
(X—Y) is an ancillary ligand;

a is 0, 1, 2, 3, or 4;

b is 0, 1, 2, or 3;

m is a value from 1 to the maximum number of ligands that may be attached to the metal; and m+n is the maximum number of ligands that may be attached to the metal.

2. The compound of claim 1, wherein the compound is selected from the group consisting of: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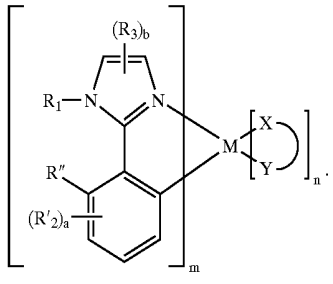
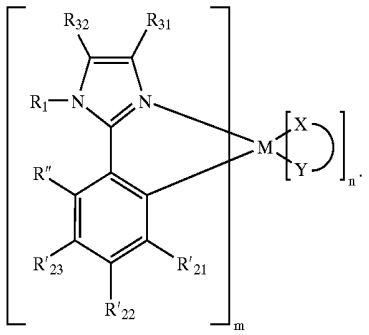
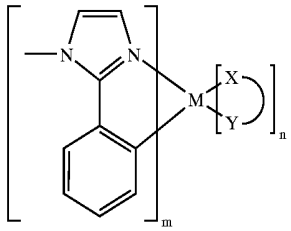
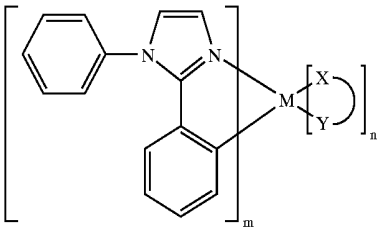
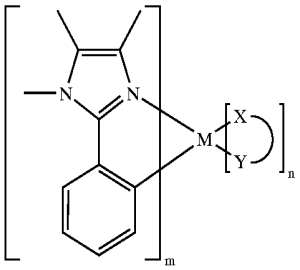
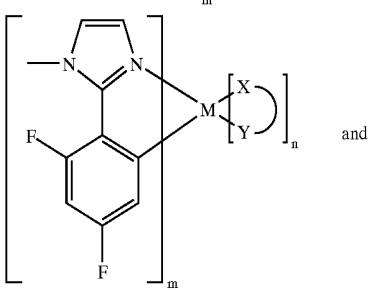


3. The compound of claim 2, having the structure:



4. The compound of claim 3, wherein R_1 is H, phenyl or methyl.

5. The compound of claim 3, wherein the compound is selected from the group consisting of: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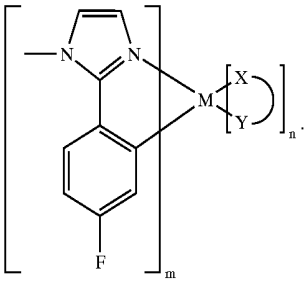
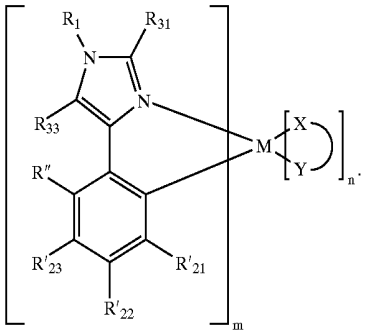


6. The compound of claim 5, wherein M is selected from the group consisting of Ir, Pt, Pd. Rh, Re, Ru, Os, T, Pb, Bi, In, Sn, Sb, Te, Au, and Ag.

7. The compound of claim 6, wherein M is Ir.

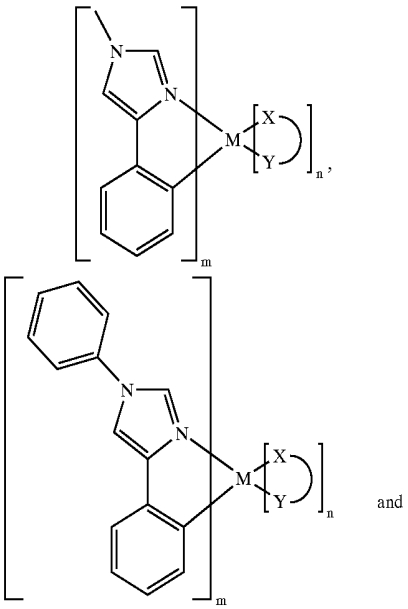
8. The compound of claim 7, wherein m is 3 and n is zero.

9. The compound of claim 2, having the structure:



10. The compound of claim 9, wherein R_1 is H, phenyl or methyl.

11. The compound of claim 9, wherein the compound is selected from the group consisting of:



and

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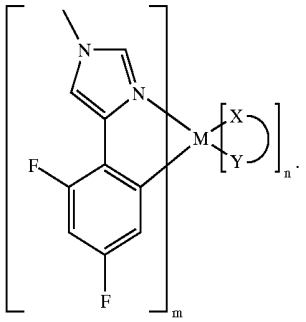
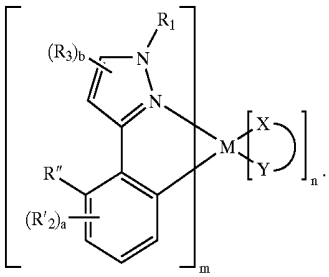


12. The compound of claim 11, wherein M is selected from the group consisting of Ir, Pt, Pd, Rh, Re, Ru, Os, Ti, Pb, Bi, In, Sn, Sb, Te, Au, and Ag.

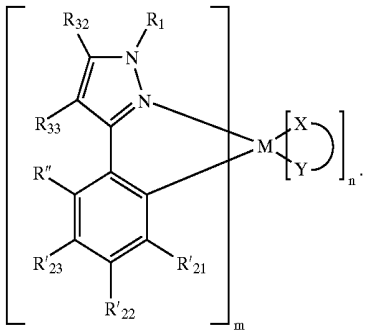
13. The compound of claim 12, wherein M is Ir.

14. The compound of claim 13, wherein m is 3 and n is zero.

15. The compound of claim 1, having the structure:



16. The compound of claim 15, having the structure:



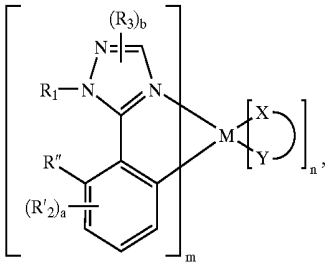
17. The compound of claim 16, wherein R_1 is H, phenyl or methyl.

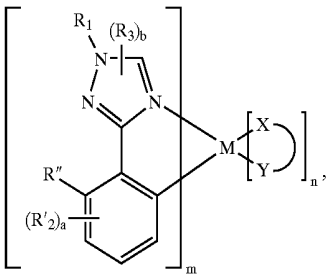
18. The compound of claim 17, wherein M is selected from the group consisting of Ir, Pt, Pd, Rh, Re, Ru, Os, Tl, Pb, Bi, In, Sn, Sb, Te, Au, and Ag.

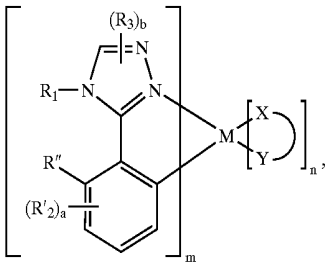
19. The compound of claim 18, wherein M is Ir.

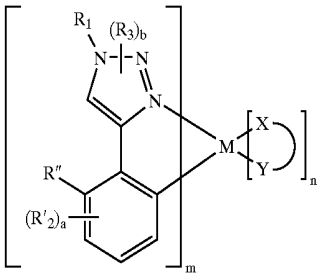
20. The compound of claim 19, wherein m is 3 and n is zero.

21. The compound of claim 1, wherein the compound is selected from the group consisting of:

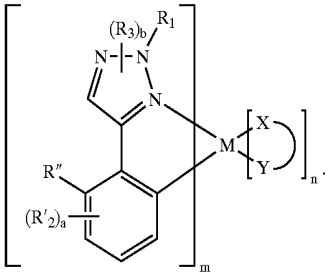




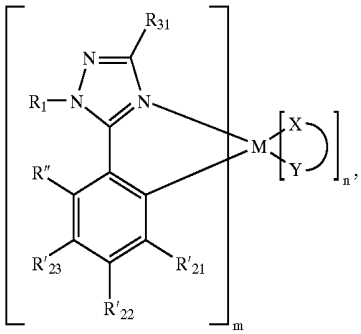


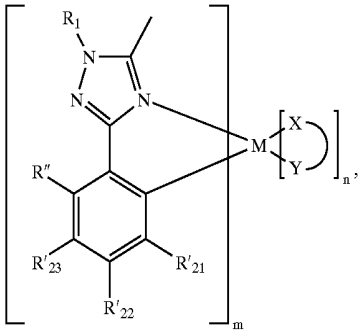


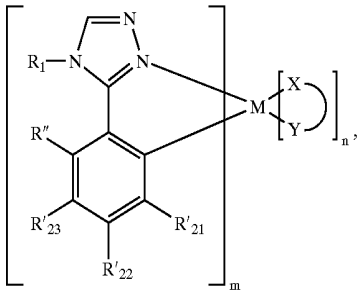
and

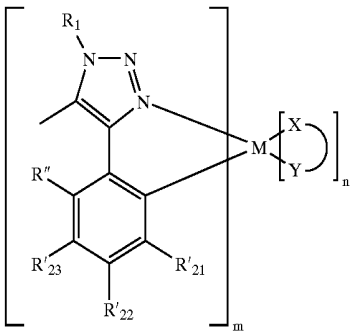


22. The compound of claim 21, wherein the compound is selected from the group consisting of:

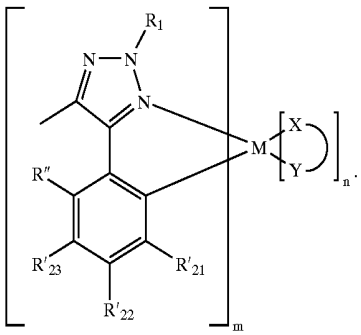








and



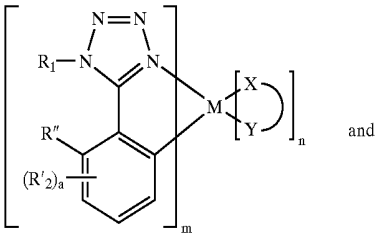
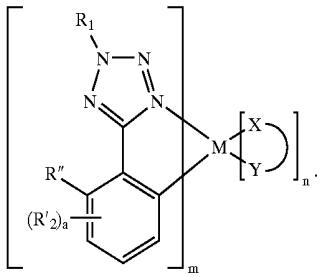
23. The compound of claim 22, wherein R_1 is H. phenyl or methyl.

24. The compound of claim 23, wherein M is selected from the group consisting of Ir, Pt, Pd. Rh, Re, Ru, Os, TI, Pb, Bi, In, Sn, Sb, Te, Au, and Ag.

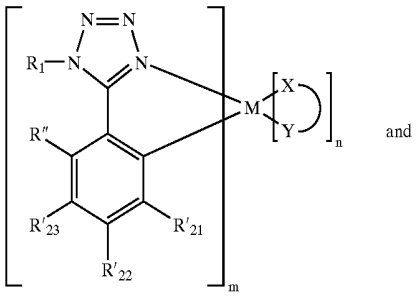
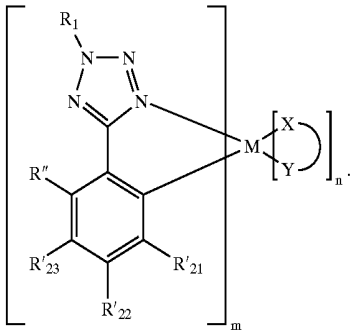
25. The compound of claim 24, wherein M is Ir.

26. The compound of claim 25, wherein m is 3 and n is zero.

27. The compound of claim 1, wherein the compound is selected from the group consisting of:


and


28. The compound of claim 27, wherein the compound is selected from the group consisting of:


and


29. The compound of claim 28, wherein R_1 is H, phenyl or methyl.

30. The compound of claim 29, wherein M is selected from the group consisting of Ir, Pt, Pd, Rh, Re, Ru, Os, TI, Pb, Bi, In, Sn, Sb, Te, Au, and Ag.

31. The compound of claim 30, wherein M is Ir.

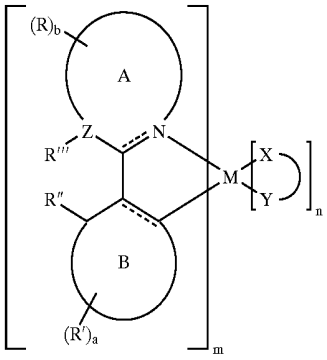
32. The compound of claim 31, wherein m is 3 and n is zero.

33. An organic light emitting device, comprising:

(a) an anode;

(b) a cathode; and

(c) an emissive layer disposed between the anode and the cathode, wherein the emissive layer comprises a compound having the structure:



wherein

M is a metal having an atomic weight greater than 40;

the dotted lines inside the rings represent optional double bonds;

Z is carbon or nitrogen;

each R, R', and R''' is independently selected from hydrogen, alkyl, alkenyl, alkynyl, alkylaryl, trialkylsilyl, cyano, trifluoromethyl, ester, keto, amino, nitro, alkoxy, halo, aryl, heteroaryl, substituted aryl, substituted heteroaryl, or a heterocyclic group;

R" is H or F;

ring A is a 5-membered heterocyclic ring having at least 2 nitrogen atoms, with one nitrogen atom coordinated to metal M, wherein ring A can be optionally substituted with one or more substituents R, and additionally or alternatively, any two substituted positions on ring A together form, independently a cyclic ring, wherein the cyclic ring is not an aromatic ring, and the cyclic ring may be optionally substituted;

ring B is an aromatic ring with at least one carbon atom coordinated to metal M, wherein ring B can be optionally substituted with one or more substituents R'; and additionally or alternatively, any two substituted positions on ring B together form, independently a fused 4-7-membered cyclic group, wherein said cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein the 4-7-membered cyclic group is optionally substituted;

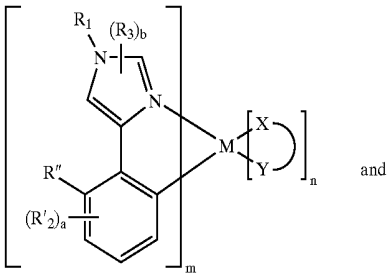
(X—Y) is an ancillary ligand;

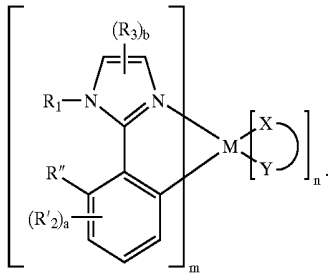
a is 0, 1, 2, 3, or 4;

b is 0, 1, 2, or 3;

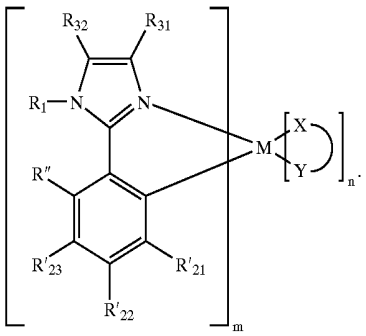
m is a value from 1 to the maximum number of ligands that may be attached to the metal; and m+n is the maximum number of ligands that may be attached to the metal.

34. The device of claim 33, wherein the compound is selected from the group consisting of:


and

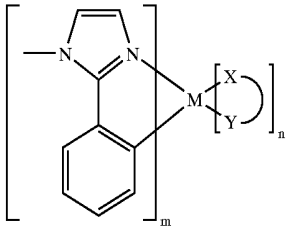


35. The device of claim 34, wherein the compound has the structure:



36. The device of claim 35, wherein R_1 is H, phenyl or methyl.

37. The device of claim 35, wherein the compound is selected from the group consisting of:



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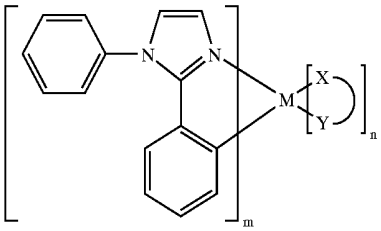
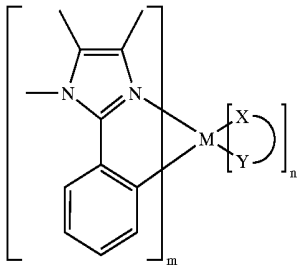
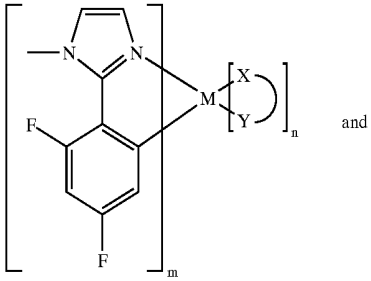
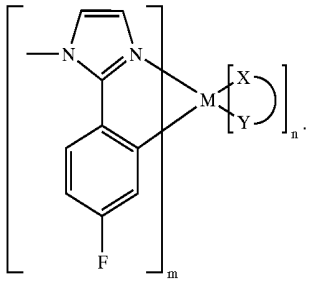





and

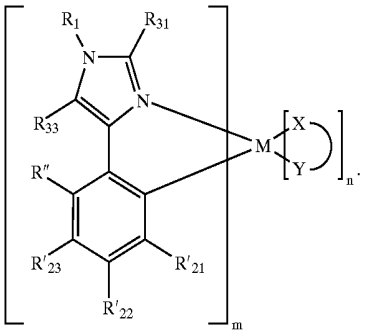


38. The device of claim 37, wherein M is selected from the group consisting of Ir, Pt, Pd, Rh, Re, Ru, Os, Tl, Pb, Bi, In, Sn, Sb, Te, Au, and Ag.

39. The device of claim 38, wherein M is Ir.

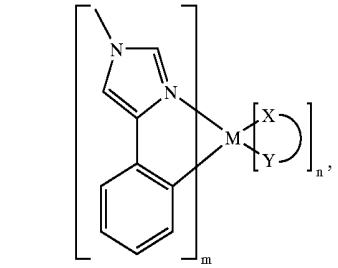
40. The device of claim 39, wherein m is 3 and n is zero.

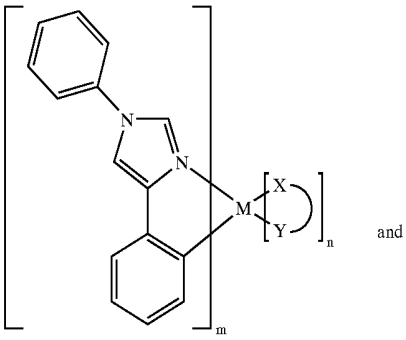
41. The device of claim 34, wherein the compound has the structure:



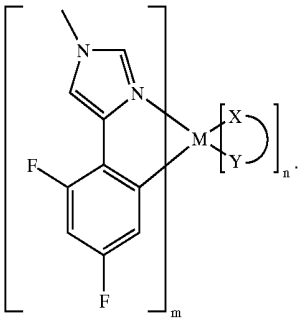
42. The device of claim 41, wherein R_1 is H, phenyl or methyl.

43. The device of claim 41, wherein the compound is selected from the group consisting of:





and

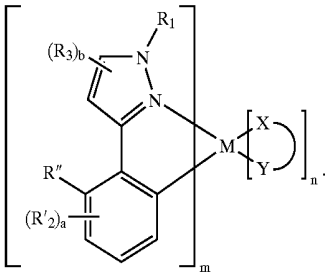


44. The device of claim 43, wherein M is selected from the group consisting of Ir, Pt, Pd, Rh, Re, Ru, Os, Ti, Pb, Bi, In, Sn, Sb, Te, Au, and Ag.

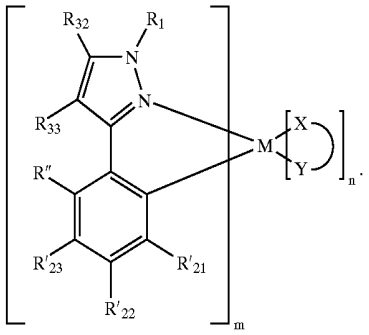
45. The device of claim 44, wherein M is Ir.

46. The device of claim 45, wherein m is 3 and n is zero.

47. The device of claim 33, wherein the compound has the structure:



48. The device of claim 47, wherein the compound has the structure:



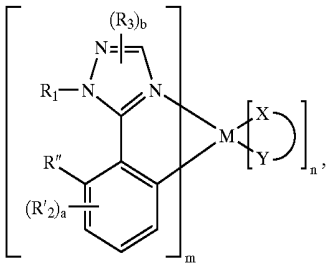
49. The device of claim 48, wherein R_1 is H, phenyl or methyl.

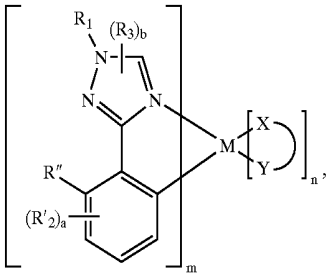
50. The device of claim 49, wherein M is selected from the group consisting of Ir, Pt, Pd, Rh, Re, Ru, Os, Tl, Pb, Bi, In, Sn, Sb, Te, Au, and Ag.

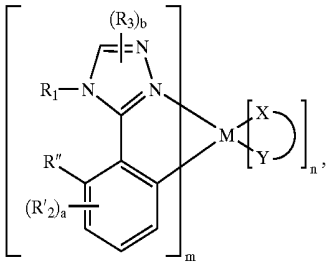
51. The device of claim 50, wherein M is Ir.

52. The device of claim 51, wherein m is 3 and n is zero.

53. The device of claim 33, wherein the compound is selected from the group consisting of:







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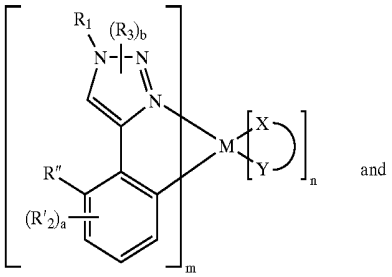
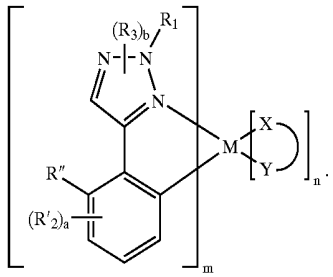
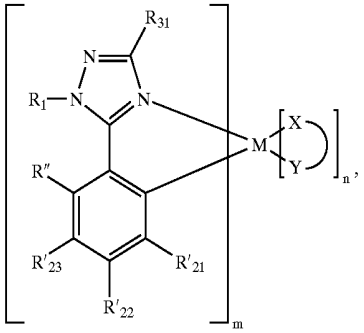
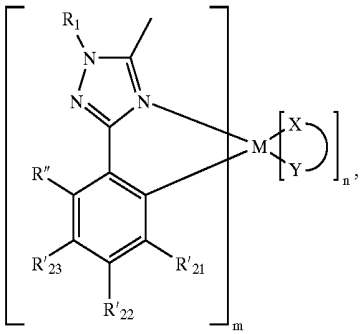


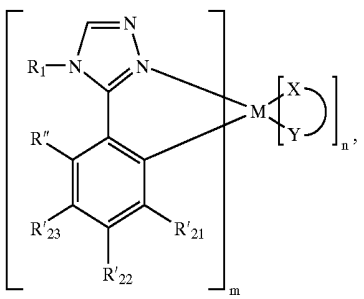
and



54. The device of claim 53, wherein the compound is selected from the group consisting of:







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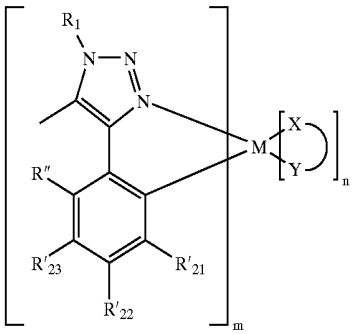
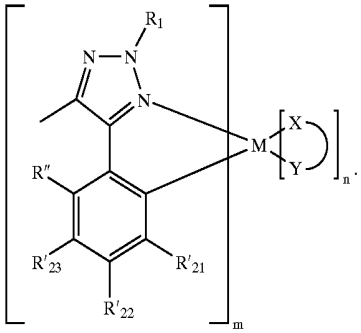


and



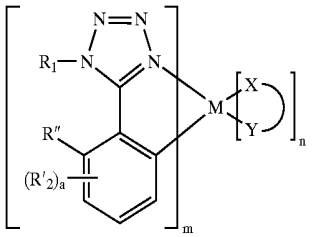
55. The device of claim 54, wherein R_1 is H, phenyl or methyl.

56. The device of claim 55, wherein M is selected from the group consisting of Ir, Pt, Pd, Rh, Re, Ru, Os, Ti, Pb, Bi, In, Sn, Sb, Te, Au, and Ag.

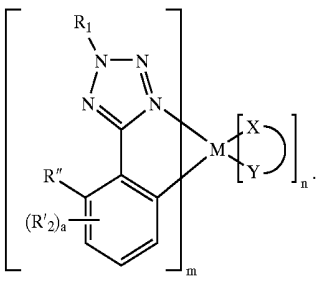
57. The device of claim 56, wherein M is Ir.

58. The device of claim 57, wherein m is 3 and n is zero.

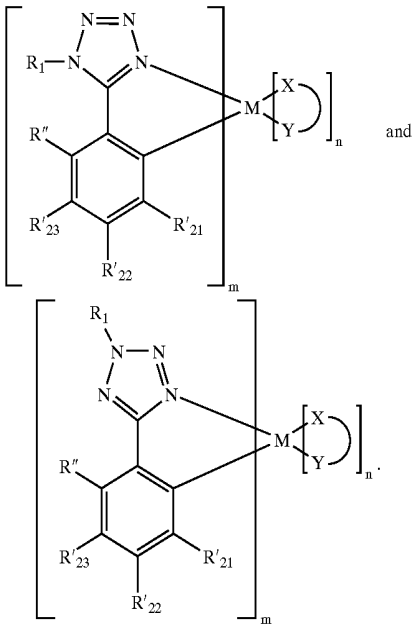
59. The device of claim 33, wherein the compound is selected from the group consisting of:



and



60. The device of claim 59, wherein the compound is selected from the group consisting of:



and

61. The device of claim 60, wherein R_1 is H, phenyl or methyl.

62. The device of claim 61, wherein M is selected from the group consisting of Ir, Pt, Pd, Rh, Re, Ru, Os, Tl, Pb, Bi, In, Sn, Sb, Te, Au, and Ag.

63. The device of claim 62, wherein M is Ir.

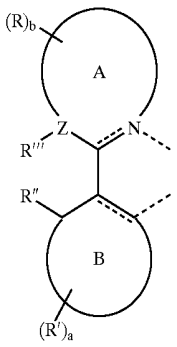
64. The device of claim 63, wherein m is 3 and n is zero.

65. An organic light emitting device, comprising:

(a) an anode;

(b) a cathode; and

(c) an emissive layer disposed between the anode and the cathode, wherein the emissive layer comprises a ligand having the structure:



wherein

the dotted lines inside the rings represent optional double bonds;

Z is carbon or nitrogen;

each R, R',and R'" is independently selected from hydrogen, alkyl, alkenyl, alkynyl, alkylaryl, trialkylsilyl, cyano, trifluoromethyl, ester, keto, amino, nitro, alkoxy, halo, aryl, heteroaryl, substituted aryl, substituted heteroaryl, or a heterocyclic group;

R" is H or F;

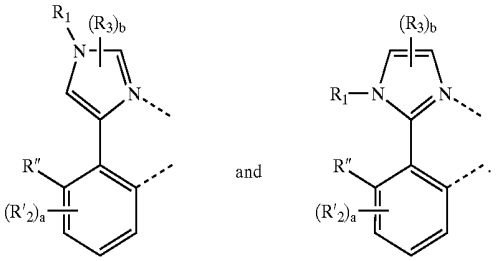
ring A is a 5-membered heterocyclic ring having at least 2 nitrogen atoms, with one nitrogen atom coordinated to metal M, wherein ring A can be optionally substituted with one or more substituents R_1 and additionally or alternatively, any two substituted positions on ring A together form, independently a cyclic ring, wherein the cyclic ring is not an aromatic ring, and the cyclic ring may be optionally substituted;

ring B is an aromatic ring with at least one carbon atom coordinated to metal M, wherein ring B can be optionally substituted with one or more substituents R'; and additionally or alternatively, any two substituted positions on ring B together form, independently a fused 4-7-membered cyclic group, wherein said cyclic group is cycloalkyl, cycloheteroalkyl, aryl, or heteroaryl, and wherein the 4-7-membered cyclic group is optionally substituted;

a is 0, 1, 2, 3, or 4;

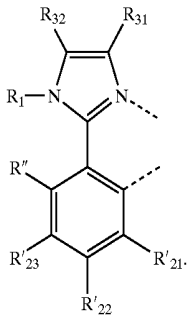
b is 0, 1, 2, or 3.

66. The device of claim 65, wherein the ligand is selected from the group consisting of:



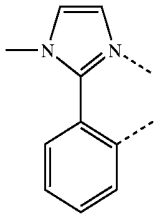
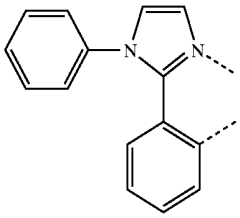
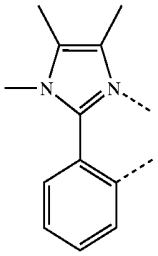
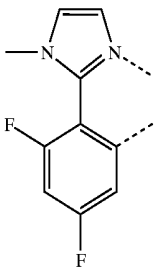
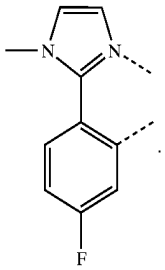
and

67. The device of claim 66, wherein the ligand has the structure:

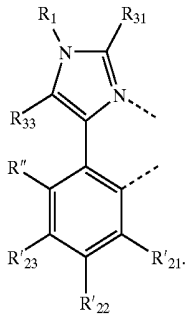


68. The device of claim 67, wherein R_1 is H, phenyl or methyl.

69. The device of claim 67, wherein the ligand is selected from the group consisting of:

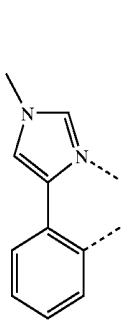
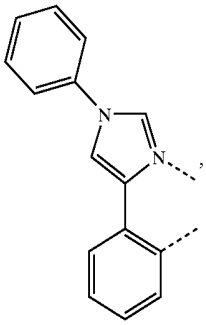
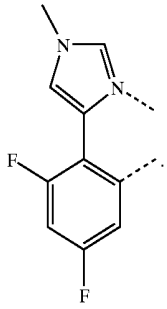




and


70. The device of claim 66, wherein the ligand has the structure:

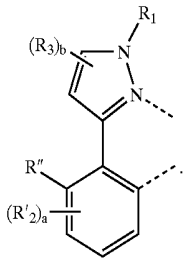


71. The device of claim 70, wherein R_1 is H, phenyl or methyl.

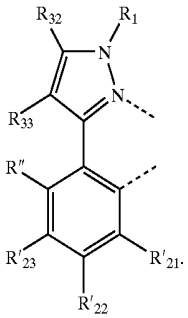
72. The device of claim 70, wherein the ligand is selected from the group consisting of:



, and


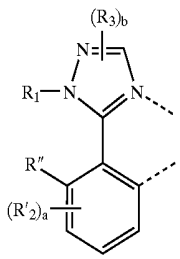
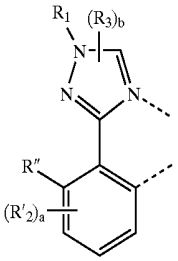
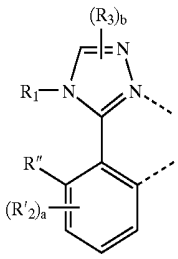
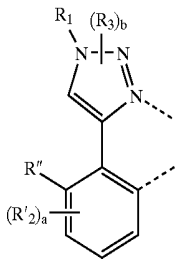
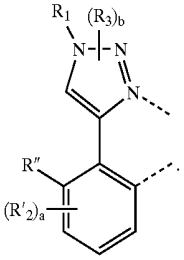
73. The device of claim 65, wherein the ligand has the structure:



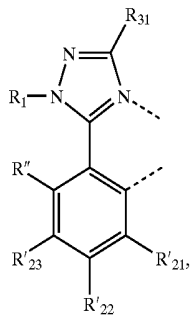
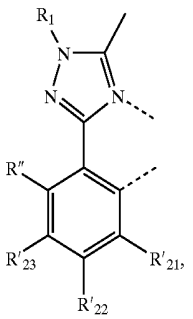
74. The device of claim 73, wherein the ligand has the structure:



75. The device of claim 65, wherein the ligand is selected from the group consisting of:





and


76. The device of claim 75, wherein the ligand is selected from the group consisting of:

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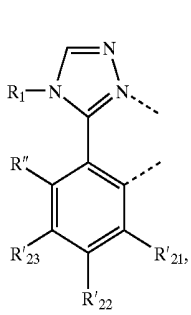
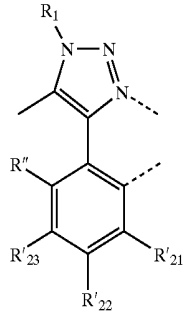
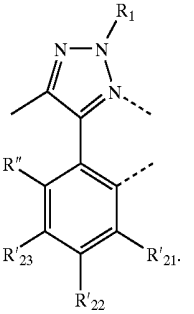
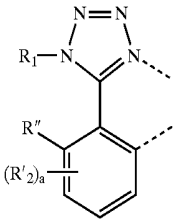
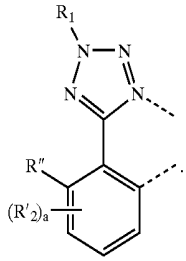
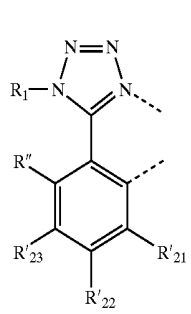
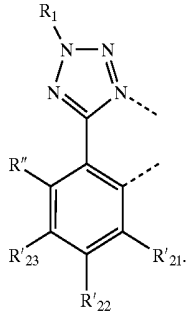


and


77. The device of claim 76, wherein R_1 is H, phenyl or methyl.

78. The device of claim 65, wherein the ligand is selected from the group consisting of:


and


79. The device of claim 78, wherein the ligand is selected from the group consisting of:


and


80. The device of claim 79, wherein R_1 is H, phenyl or methyl.

* * * * *

专利名称(译)	有机发光材料和器件		
公开(公告)号	US20060008670A1	公开(公告)日	2006-01-12
申请号	US10/886098	申请日	2004-07-06
[标]申请(专利权)人(译)	马斌 KNOWLES DAVID乙 BROOKS JASON 邝RAYMOND		
申请(专利权)人(译)	林春 马斌 KNOWLES DAVID乙 BROOKS JASON 邝RAYMOND		
当前申请(专利权)人(译)	通用显示器公司		
[标]发明人	LIN CHUN MA BIN KNOWLES DAVID B BROOKS JASON KWONG RAYMOND		
发明人	LIN, CHUN MA, BIN KNOWLES, DAVID B. BROOKS, JASON KWONG, RAYMOND		
IPC分类号	H05B33/14 C09K11/06 C07D231/00 C07D233/00 C07D249/00 C07D257/00		
CPC分类号	C07D231/12 C07D233/54 C07D249/06 C07D249/08 C07D257/04 H05B33/14 C09K11/06 C09K2211/185 H01L51/0085 H01L51/5016 C07F15/0033		
外部链接	Espacenet USPTO		

摘要(译)

提供一种有机发光器件。该器件具有阳极，阴极和设置在阳极和阴极之间的有机层。有机层包含化合物，其还包含与金属中心配位的一种或多种芳基咪唑，芳基三唑或芳基四唑衍生物配体。配体具有以下结构：