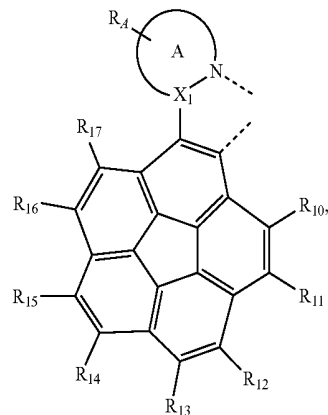




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(19) **United States**(12) **Patent Application Publication**
THOMPSON et al.(10) **Pub. No.: US 2015/0060830 A1**(43) **Pub. Date: Mar. 5, 2015**(54) **ORGANIC ELECTROLUMINESCENT
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DJUROVICH**, Long Beach, CA (US)(21) Appl. No.: **14/475,257**(22) Filed: **Sep. 2, 2014****Related U.S. Application Data**(60) Provisional application No. 61/872,871, filed on Sep.
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CPC **H01L 51/0085** (2013.01); **H01L 51/0087**
(2013.01); **H01L 51/5012** (2013.01)USPC **257/40**; 546/4(57) **ABSTRACT**A compound comprising a ligand L_A according to formula (I)

as well as, a first device and a formulation including the same are disclosed. In the structure of formula (I): ring A is a 5- or 6-membered heteroaryl ring; X_1 is C or N; R_A is mono-, bi-, tri-, tetradentate, or unsubstituted; R_A , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , R_{16} , and R_{17} are independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof, any adjacent substituents of R_A , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , R_{16} , and R_{17} are optionally joined to form a fused ring; the dashed lines represent bonds to a metal M; and metal M has an atomic number greater than 40.

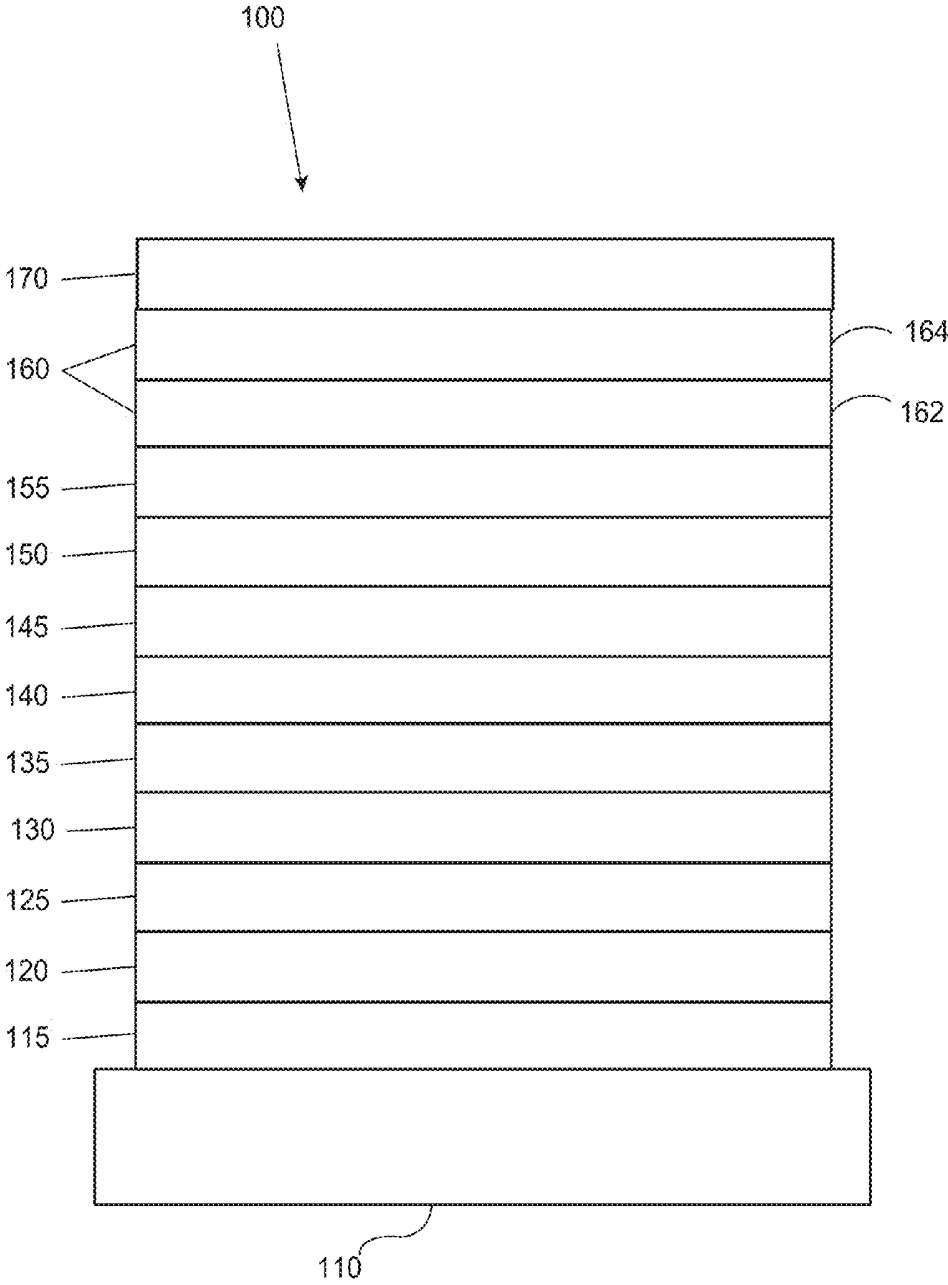


FIGURE 1

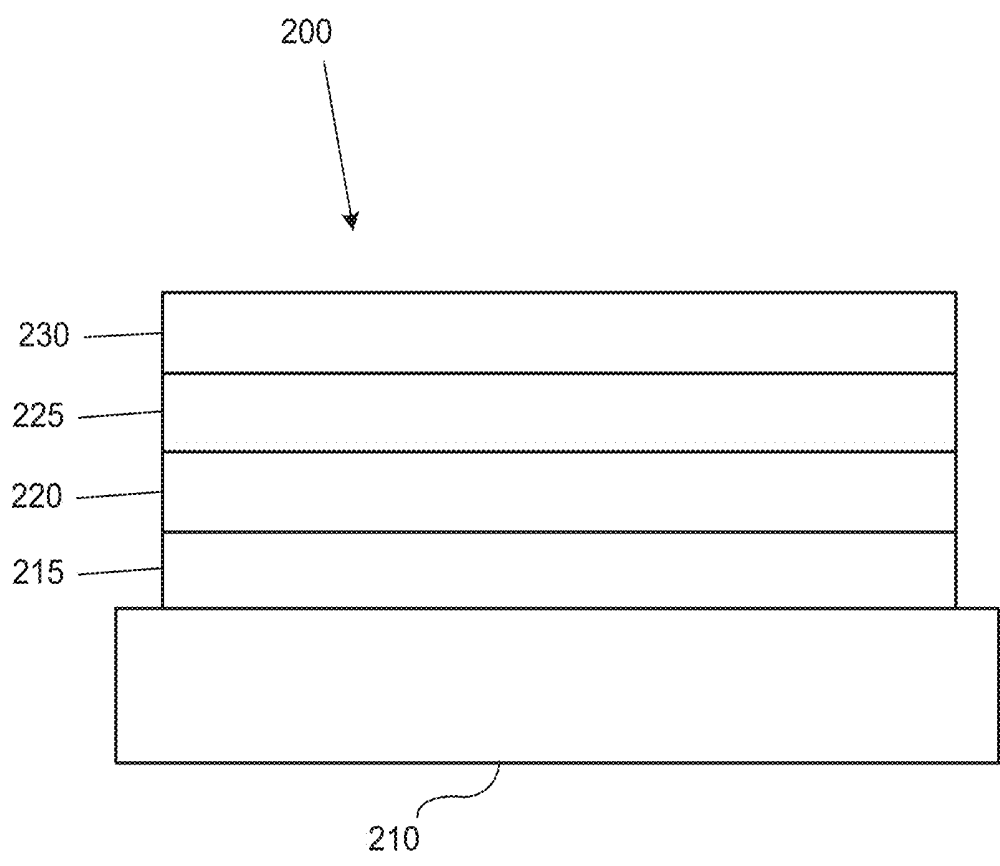
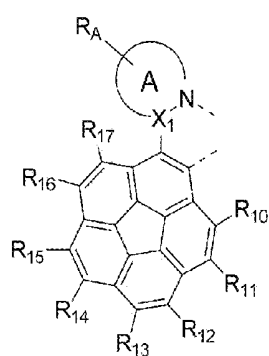
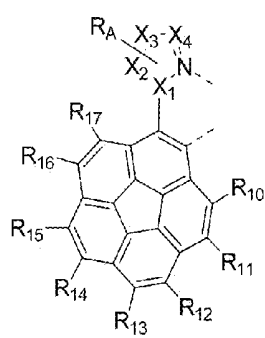


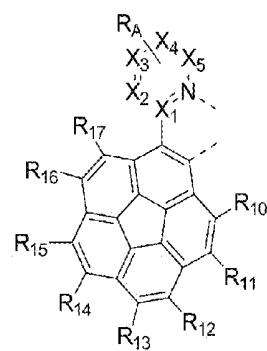
FIGURE 2



Formula (I)



Formula (II)



Formula (III)

FIGURE 3

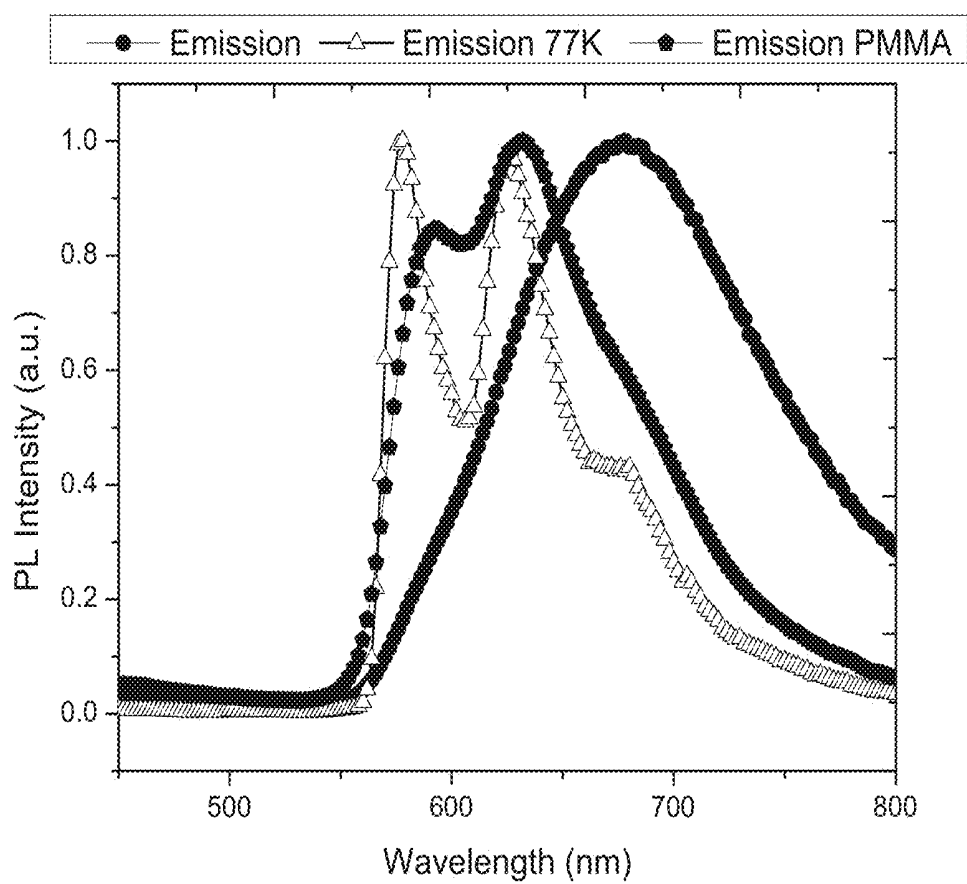


FIGURE 4

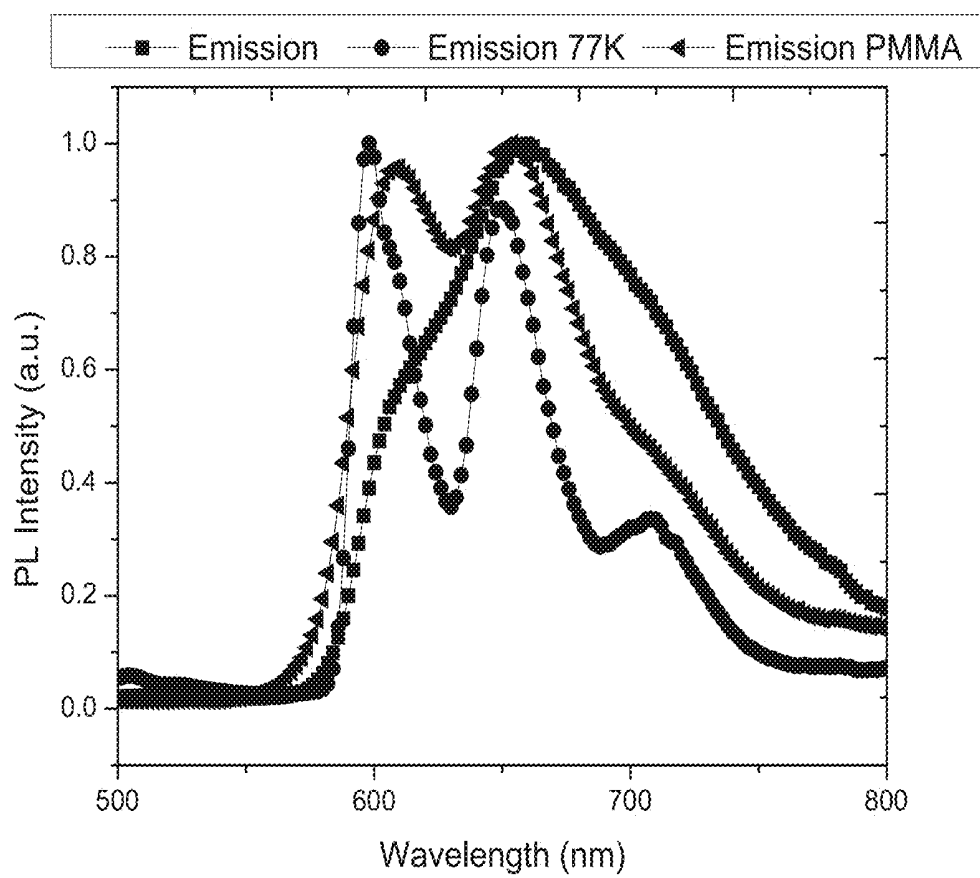


FIGURE 5

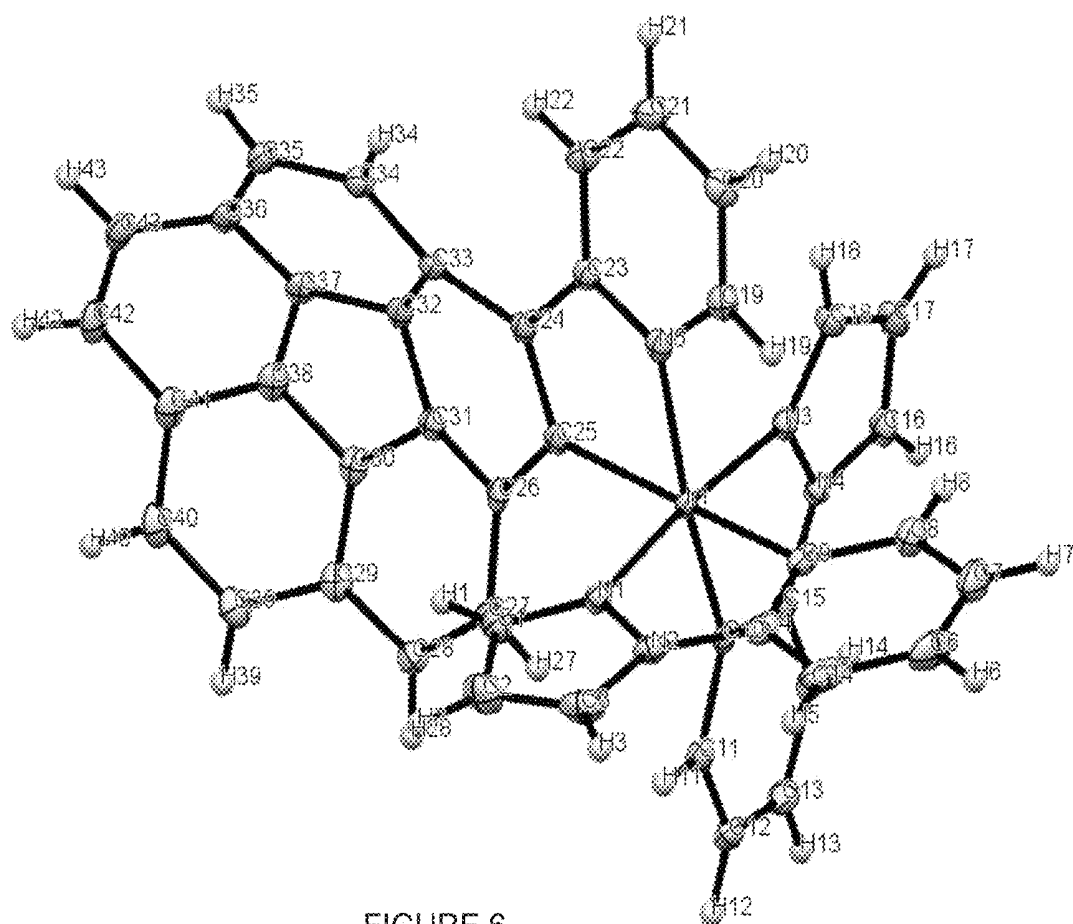


FIGURE 6

FIGURE 7

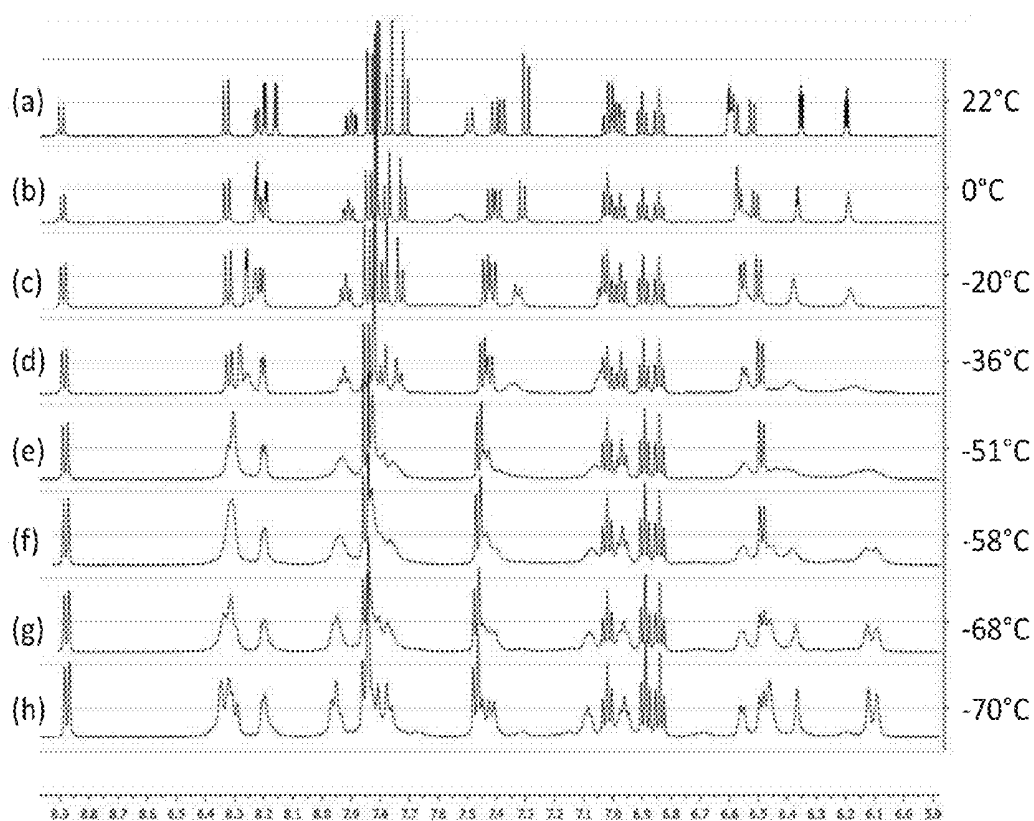


FIGURE 8

ORGANIC ELECTROLUMINESCENT MATERIALS AND DEVICES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application Ser. No. 61/872,871, filed Sep. 3, 2013, the entire content of which is incorporated herein by reference.

PARTIES TO A JOINT RESEARCH AGREEMENT

[0002] The claimed invention was made by, on behalf of, and/or in connection with one or more of the following parties to a joint university corporation research agreement: Regents of the University of Michigan, Princeton University, University of Southern California, and the Universal Display Corporation. The agreement was in effect on and before the date the claimed invention was made, and the claimed invention was made as a result of activities undertaken within the scope of the agreement.

FIELD OF THE INVENTION

[0003] The present invention relates to compounds for use as emitters and devices, such as organic light emitting diodes, including the same.

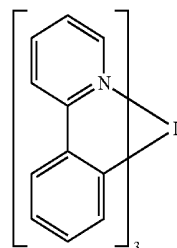
BACKGROUND

[0004] 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.

[0005] 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.

[0006] One application for phosphorescent emissive molecules is a full color display. Industry standards for such a display call for pixels adapted to emit particular colors, referred to as “saturated” colors. In particular, these standards call for saturated red, green, and blue pixels. Color may be measured using CIE coordinates, which are well known to the art.

[0007] One example of a green emissive molecule is tris(2-phenylpyridine)iridium, denoted Ir(ppy)₃, which has the following structure:



[0008] In this, and later figures herein, we depict the dative bond from nitrogen to metal (here, Ir) as a straight line.

[0009] 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.

[0010] As used herein, “top” means furthest away from the substrate, while “bottom” means closest to 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 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.

[0011] As used herein, “solution processable” means capable of being dissolved, dispersed, or transported in and/or deposited from a liquid medium, either in solution or suspension form.

[0012] A ligand may be referred to as “photoactive” when it is believed that the ligand directly contributes to the photoactive properties of an emissive material. A ligand may be referred to as “ancillary” when it is believed that the ligand does not contribute to the photoactive properties of an emissive material, although an ancillary ligand may alter the properties of a photoactive ligand.

[0013] 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

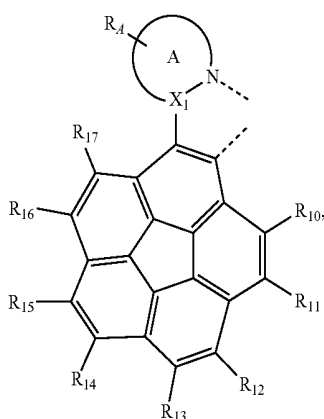
energy level of the same material. A “higher” HOMO or LUMO energy level appears closer to the top of such a diagram than a “lower” HOMO or LUMO energy level.

[0014] As used herein, and as would be generally understood by one skilled in the art, a first work function is “greater than” or “higher than” a second work function if the first work function has a higher absolute value. Because work functions are generally measured as negative numbers relative to vacuum level, this means that a “higher” work function is more negative. On a conventional energy level diagram, with the vacuum level at the top, a “higher” work function is illustrated as further away from the vacuum level in the downward direction. Thus, the definitions of HOMO and LUMO energy levels follow a different convention than work functions.

[0015] More details on OLEDs, and the definitions described above, can be found in U.S. Pat. No. 7,279,704, which is incorporated herein by reference in its entirety.

SUMMARY OF THE INVENTION

[0016] According to one embodiment, a compound comprising a ligand L_A according to formula (I)



is provided. In the structure of formula (I):

[0017] ring A is a 5- or 6-membered heteroaryl ring;

[0018] X₁ is C or N;

[0019] R₄ is mono-, bi-, tri-, tetradentate, or unsubstituted;

[0020] R₄, R₁₀, R₁₁, R₁₂, R₁₃, R₁₄, R₁₅, R₁₆, and R₁₇ are independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof;

[0021] any adjacent substituents of R₄, R₁₀, R₁₁, R₁₂, R₁₃, R₁₄, R₁₅, R₁₆, and R₁₇ are optionally joined to form a fused ring;

[0022] the dashed lines represent bonds to a metal M; and

[0023] metal M has an atomic number greater than 40.

[0024] According to another embodiment, a first device comprising a first organic light emitting device is also provided. The first organic light emitting device can include an anode, a cathode, and an organic layer, disposed between the anode and the cathode. The organic layer can include a compound comprising a ligand L_A according to formula (I). The first device can be a consumer product, an organic light-emitting device, and/or a lighting panel.

[0025] In still another embodiment, a formulation that includes a ligand L_A according to formula (I) is also provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] FIG. 1 shows an organic light emitting device.

[0027] FIG. 2 shows an inverted organic light emitting device that does not have a separate electron transport layer.

[0028] FIG. 3 shows Formula (I), Formula (II), and Formula (III) as disclosed herein.

[0029] FIG. 4 is a graph of photoluminescent intensity versus wavelength for compound 1.

[0030] FIG. 5 is a graph of photoluminescent intensity versus wavelength for compound 2.

[0031] FIG. 6 is an Oak Ridge Thermal Ellipsoid Plot (ORTEP) drawing of compound 1.

[0032] FIG. 7 is an ORTEP drawing of compound 2.

[0033] FIG. 8 is a initial variable temperature NMR plot for compound 1 at (a) 22° C., (b) 0° C., (c) -20° C., (d) -36° C., (e) -51° C., (f) -58° C., (g) -68° C., and (h) -70° C.

DETAILED DESCRIPTION

[0034] 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.

[0035] 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.

[0036] 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-1”) 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 is described in more detail in U.S. Pat. No. 7,279,704 at cols. 5-6, which are incorporated by reference.

[0037] 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, a cathode 160, and a barrier layer 170. 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. The properties and functions of these various layers, as well as

example materials, are described in more detail in U.S. Pat. No. 7,279,704 at cols. 6-10, which are incorporated by reference.

[0038] More examples for each of these layers are available. For example, a flexible and transparent substrate-anode combination is disclosed in U.S. Pat. No. 5,844,363, which is incorporated by reference in its entirety. An example of a p-doped hole transport layer is m-MTDATA doped with F₄-TCNQ at a molar ratio of 50:1, as disclosed in U.S. Patent Application Publication No. 2003/0230980, which is incorporated by reference in its entirety. 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. 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. 2003/0230980, which is incorporated by reference in its entirety. U.S. Pat. Nos. 5,703,436 and 5,707,745, 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 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. 2003/0230980, which are incorporated by reference in their entireties. Examples of injection layers are provided in U.S. Patent Application Publication No. 2004/0174116, which is incorporated by reference in its entirety. A description of protective layers may be found in U.S. Patent Application Publication No. 2004/0174116, which is incorporated by reference in its entirety.

[0039] FIG. 2 shows an inverted OLED 200. The device includes a substrate 210, a 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.

[0040] 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.

[0041] 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 to 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.

[0042] 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. Pat. No. 7,431,968, 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 processability 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.

[0043] Devices fabricated in accordance with embodiments of the present invention may further optionally comprise a barrier layer. One purpose of the barrier layer is to protect the electrodes and organic layers from damaging exposure to harmful species in the environment including moisture, vapor and/or gases, etc. The barrier layer may be deposited over, under or next to a substrate, an electrode, or over any other parts of a device including an edge. The barrier layer may comprise a single layer, or multiple layers. The barrier layer may be formed by various known chemical vapor deposition techniques and may include compositions having a single phase as well as compositions having multiple phases. Any suitable material or combination of materials

may be used for the barrier layer. The barrier layer may incorporate an inorganic or an organic compound or both. The preferred barrier layer comprises a mixture of a polymeric material and a non-polymeric material as described in U.S. Pat. No. 7,968,146, PCT Pat. Application Nos. PCT/US2007/023098 and PCT/US2009/042829, which are herein incorporated by reference in their entireties. To be considered a "mixture", the aforesaid polymeric and non-polymeric materials comprising the barrier layer should be deposited under the same reaction conditions and/or at the same time. The weight ratio of polymeric to non-polymeric material may be in the range of 95:5 to 5:95. The polymeric material and the non-polymeric material may be created from the same precursor material. In one example, the mixture of a polymeric material and a non-polymeric material consists essentially of polymeric silicon and inorganic silicon.

[0044] 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, medical 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, 3-D 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.), but could be used outside this temperature range, for example, from -40 degree C. to +80 degree C.

[0045] 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.

[0046] The term "halo" or "halogen" as used herein includes fluorine, chlorine, bromine, and iodine.

[0047] 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.

[0048] 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.

[0049] 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.

[0050] The term "alkynyl" as used herein contemplates both straight and branched chain alkyne radicals. Preferred alkynyl groups are those containing two to fifteen carbon atoms. Additionally, the alkynyl group may be optionally substituted.

[0051] The terms "aralkyl" or "arylalkyl" as used herein are used interchangeably and contemplate an alkyl group that has as a substituent an aromatic group. Additionally, the aralkyl group may be optionally substituted.

[0052] The term "heterocyclic group" as used herein contemplates aromatic and non-aromatic cyclic radicals. Hetero-aromatic cyclic radicals also means heteroaryl. Preferred hetero-non-aromatic cyclic groups are those containing 3 or 7 ring atoms which includes at least one hetero atom, and includes cyclic amines such as morpholino, piperidino, pyrrolidino, and the like, and cyclic ethers, such as tetrahydrofuran, tetrahydropyran, and the like. Additionally, the heterocyclic group may be optionally substituted.

[0053] 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 carbons are common to 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. Additionally, the aryl group may be optionally substituted.

[0054] The term "heteroaryl" as used herein contemplates single-ring hetero-aromatic groups that may include from one to three heteroatoms, for example, pyrrole, furan, thiophene, imidazole, oxazole, thiazole, triazole, 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. Additionally, the heteroaryl group may be optionally substituted.

[0055] The alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl, heterocyclic group, aryl, and heteroaryl may be optionally substituted with one or more substituents selected from the group consisting of hydrogen, deuterium, halogen, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, cyclic amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acid, ether, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof.

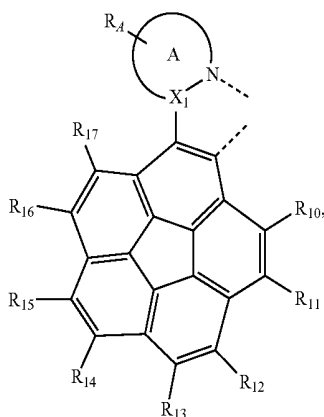
[0056] As used herein, "substituted" indicates that a substituent other than H is bonded to the relevant position, such as carbon. Thus, for example, where R¹ is mono-substituted, then one R¹ must be other than H. Similarly, where R¹ is di-substituted, then two of R¹ must be other than H. Similarly, where R¹ is unsubstituted, R¹ is hydrogen for all available positions.

[0057] The "aza" designation in the fragments described herein, i.e. aza-dibenzofuran, aza-dibenzothiophene, etc. means that one or more of the C—H groups in the respective fragment can be replaced by a nitrogen atom, for example, and without any limitation, azatriphenylene encompasses both dibenzo[f,h]quinoxaline and dibenzo[f,h]quinoline. One of ordinary skill in the art can readily envision other nitrogen analogs of the aza-derivatives described above, and all such analogs are intended to be encompassed by the terms as set forth herein.

[0058] It is to be understood that when a molecular fragment is described as being a substituent or otherwise attached to another moiety, its name may be written as if it were a fragment (e.g. phenyl, phenylene, naphthyl, dibenzofuryl) or as if it were the whole molecule (e.g. benzene, naphthalene,

dibenzofuran). As used herein, these different ways of designating a substituent or attached fragment are considered to be equivalent.

[0059] A compound comprising a ligand L_A according to formula (I)



is described. In the structure of formula (I):

[0060] ring A is a 5- or 6-membered heteroaryl ring;

[0061] X_1 is C or N;

[0062] R_A is mono-, bi-, tri-, tetradentate, or unsubstituted;

[0063] R_A , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , R_{16} , and R_{17} are independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof;

[0064] any adjacent substituents of R_A , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , R_{16} , and R_{17} are optionally joined to form a fused ring;

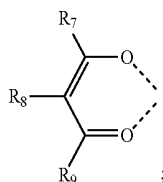
[0065] the dashed lines represent bonds to a metal M; and

[0066] metal M has an atomic number greater than 40.

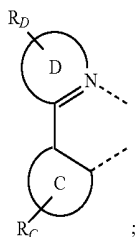
[0067] In some embodiments, the metal M is selected from the group consisting of Ir, Rh, Re, Ru, Os, Pt, Au, and Cu.

[0068] In some embodiments, the compound has the structure $M(L_A)_x(L_B)_y(L)_z$, where:

[0069] ligand L_B is



[0070] ligand L_C is



[0071] x is 1, 2, or 3;

[0072] y is 0, 1, or 2;

[0073] z is 0, 1, or 2;

[0074] $x+y+z$ is the oxidation state of the metal M;

[0075] R_7 and R_9 are independently selected from group consisting of hydrogen, alkyl, cycloalkyl, aryl, and heteroaryl;

[0076] R_8 is selected from group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof;

[0077] rings C and D are each independently a 5- or 6-membered carbocyclic or heterocyclic ring;

[0078] R_C and R_D each independently represent mono, di, tri, or tetra substitution, or no substitution;

[0079] each of R_C and R_D are independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof; and

[0080] any adjacent substituents of R_C and R_D are optionally joined to form a ring.

[0081] In some embodiments, at least one of R_7 , R_8 , and R_9 has at least two C atoms. In some embodiments, two or three of R_7 , R_8 , and R_9 have at least two C atoms.

[0082] In some embodiments, at least one of R_7 , R_8 , and R_9 has at least three C atoms. In some embodiments, two or three of R_7 , R_8 , and R_9 have at least three C atoms.

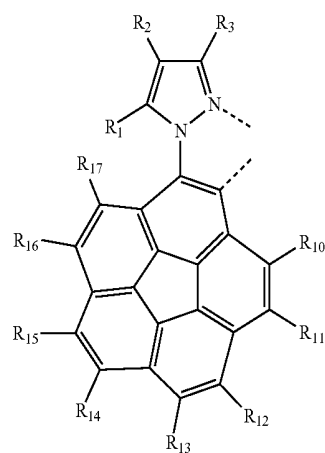
[0083] In some embodiments, at least one of R_7 , R_8 , and R_9 has at least four C atoms. In some embodiments, two or three of R_7 , R_8 , and R_9 have at least four C atoms.

[0084] In some embodiments, y is 1 or 2.

[0085] In some embodiments, the compound is homoleptic. In other embodiments, the compound is heteroleptic.

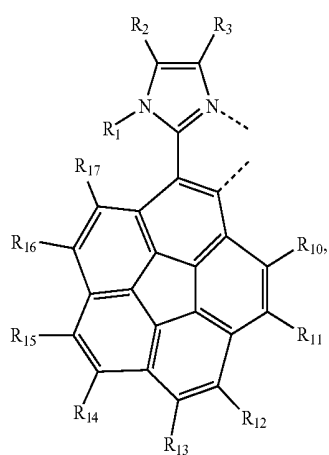
[0086] In some embodiments, each R_A is independently selected from the group consisting of hydrogen, alkyl, aryl, and combinations thereof. In some embodiments, at least one R_A is selected from the group consisting of methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, cyclobutyl, cyclopentyl, cyclohexyl, partially or fully deuterated variants thereof, and combinations thereof.

[0087] In some more specific embodiments, ligand L_A is selected from the group consisting of:

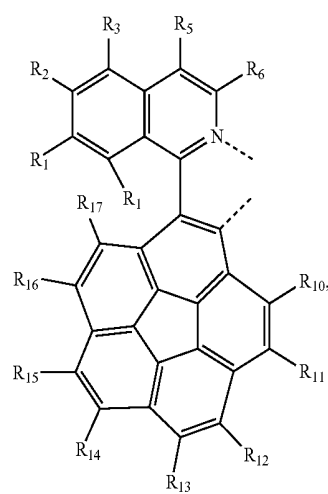
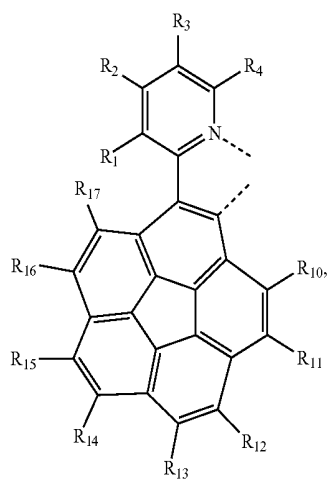
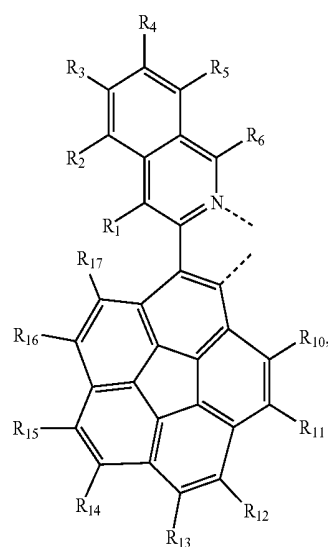
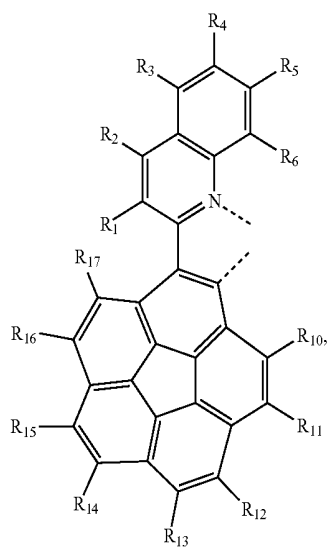
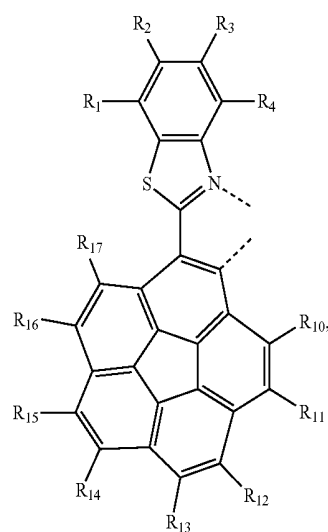


L_{A1}

-continued

L₄₂

-continued

L₄₅L₄₃L₄₆L₄₄L₄₇

where:

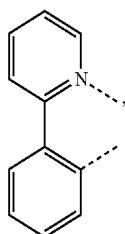
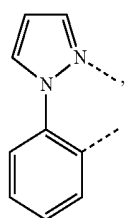
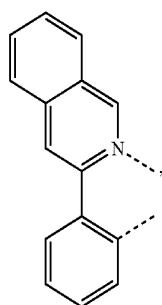
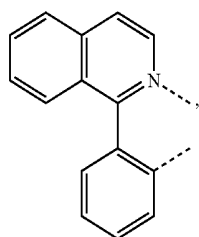
[0088] R₁, R₂, R₃, R₄, R₅, and R₆ are independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, ary-

loxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof; and

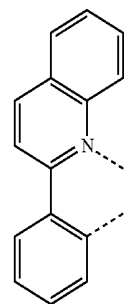
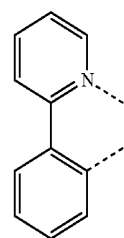
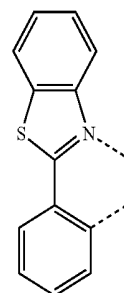
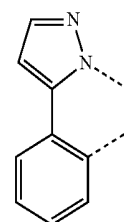
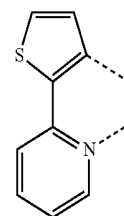
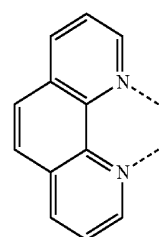
[0089] any adjacent substituents of R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are optionally joined to form a fused ring.

[0090] In some embodiments, at least one of R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 is selected from the group consisting of ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, cyclobutyl, cyclopentyl, cyclohexyl, partially or fully deuterated variants thereof, and combinations thereof.

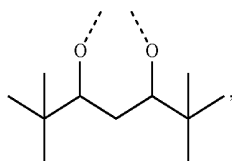
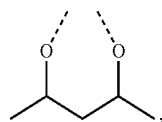
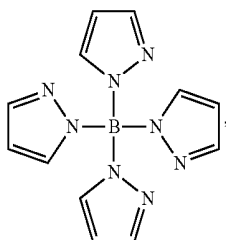
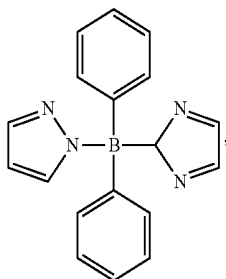
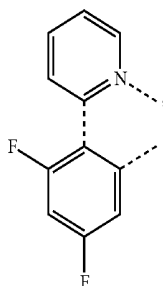
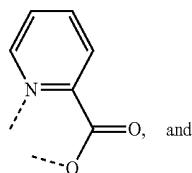
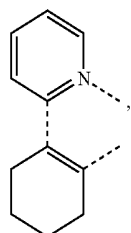
[0091] In some embodiments, the compound comprises a ligand L_D bonded to the metal M, wherein the ligand L_D is selected from the group consisting of:

 L_{D1}  L_{D2}  L_{D3}  L_{D4}

-continued

 L_{D5}  L_{D6}  L_{D7}  L_{D8}  L_{D9}  L_{D10}

-continued

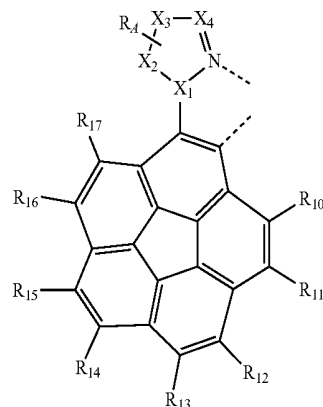
L_{D11}L_{D12}L_{D13}L_{D14}L_{D15}L_{D16}L_{D17}

[0092] where L_{D13} is bonded to metal M by two, three or four of the N atoms that are ortho to boron to form a bidentate, tridentate, or tetradentate ligand, and

[0093] where L_{D14} is bonded to metal M by the two N atoms ortho to boron to form a bidentate ligand.

[0094] In some embodiments, the compound includes one or two ligands independently selected from ligand L_D.

[0095] In some embodiments, ligand L_A has a structure according to formula (II):



where:

[0096] X₂, X₃, and X₄ are each independently C or N;

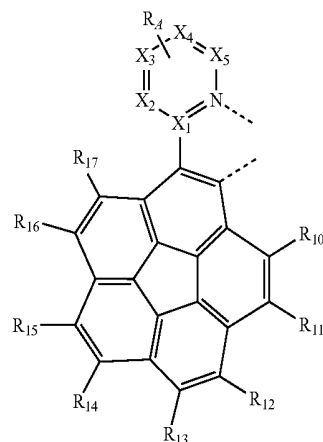
[0097] R₁, R₂, and R₃ are independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof;

[0098] any adjacent substituents of R₁, R₂, and R₃ are optionally joined to form a fused ring; and

[0099] R_A is mono-, bi-, tridentate, or unsubstituted.

[0100] In some embodiments, at least one of X₁ to X₄ is N. In some embodiments, at least two of X₁ to X₄ are N. In some embodiments, three of X₁ to X₄ are N. In some embodiments, three of X₁ to X₄ are C.

[0101] In some embodiments, ligand L_A has a structure according to formula (III):



where:

[0102] X₂, X₃, X₄, and X₅ are each independently C or N;

[0103] R₁, R₂, R₃, and R₄ are independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, het-

eroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof; and

[0104] any adjacent substituents of R_1 , R_2 , R_3 , and R_4 are optionally joined to form a fused ring.

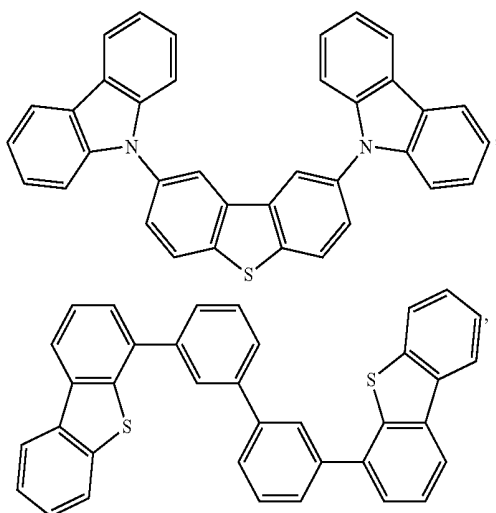
[0105] In some embodiments, at least one of X_1 to X_5 is N. In some embodiments, at least two of X_1 to X_5 are N, while at least three of X_1 to X_5 are N in other embodiments. In some embodiments, four of X_1 to X_5 are N.

[0106] According to another aspect of the present disclosure, a first device is also provided. The first device includes a first organic light emitting device, that includes an anode, a cathode, and an organic layer disposed between the anode and the cathode. The organic layer may include a host and a phosphorescent dopant. The organic layer can include a compound including a ligand L_A according to formula (I), and its variations as described herein.

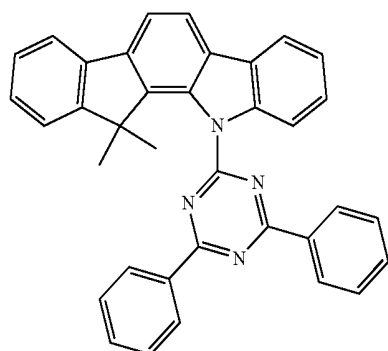
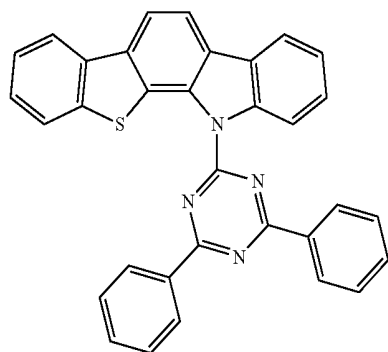
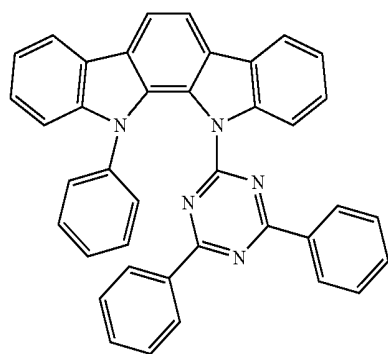
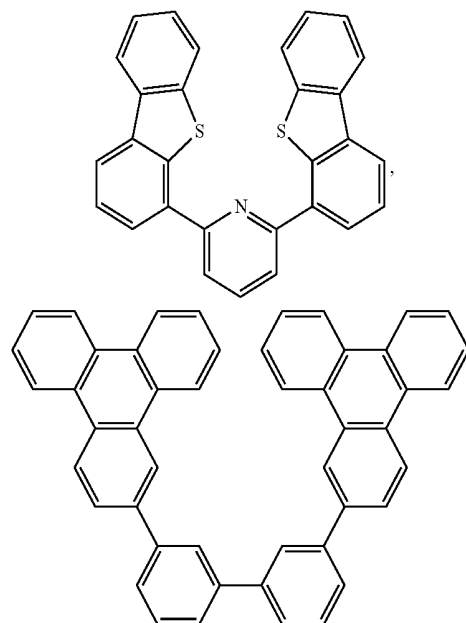
[0107] The first device can be one or more of a consumer product, an organic light-emitting device and a lighting panel. The organic layer can be an emissive layer and the compound can be an emissive dopant in some embodiments, while the compound can be a non-emissive dopant in other embodiments.

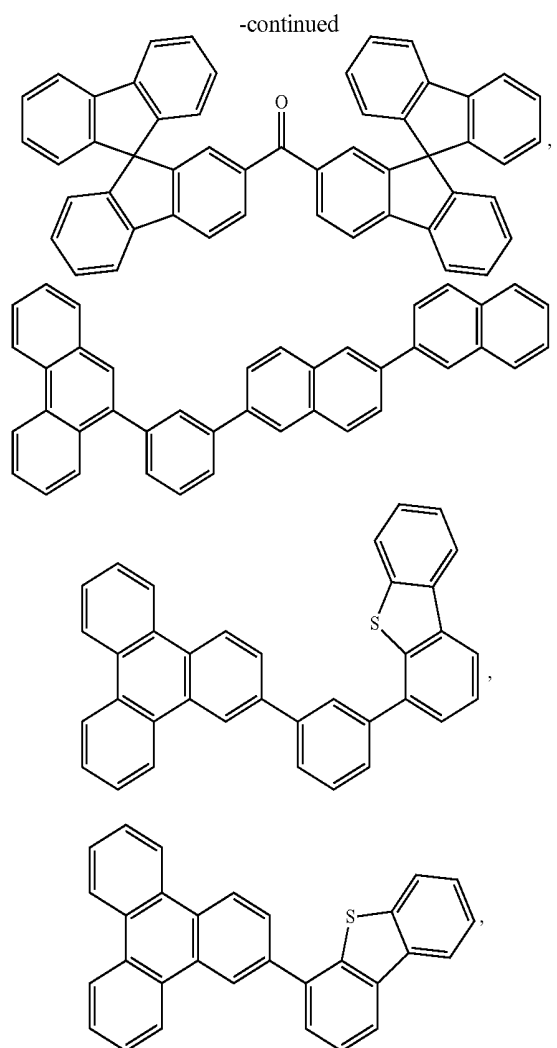
[0108] The organic layer can also include a host. In some embodiments, the host can include a metal complex. The host can be a triphenylene containing benzo-fused thiophene or benzo-fused furan. Any substituent in the host can be an unfused substituent independently selected from the group consisting of C_nH_{2n+1} , OC_nH_{2n+1} , OAr_1 , $N(C_nH_{2n+1})_2$, $N(Ar_1)(Ar_2)$, $CH=CH-C_nH_{2n+1}$, $C\equiv C-C_nH_{2n+1}$, Ar_1 , Ar_1-Ar_2 , and $C_nH_{2n}-Ar_1$, or no substitution. In the preceding substituents n can range from 1 to 10; and Ar_1 and Ar_2 can be independently selected from the group consisting of benzene, biphenyl, naphthalene, triphenylene, carbazole, and heteroaromatic analogs thereof.

[0109] The host can be a compound comprising at least one chemical group selected from the group consisting of triphenylene, carbazole, dibenzothiophene, dibenzofuran, dibenzoselenophene, azatriphenylene, azacarbazole, aza-dibenzothiophene, aza-dibenzofuran, and aza-dibenzoselenophene. The host can include a metal complex. The host can be a specific compound selected from the group consisting of:



-continued





and combinations thereof.

[0110] In yet another aspect of the present disclosure, a formulation that comprises a compound including a ligand L_A according to formula (I), and its variations as described herein. The formulation can include one or more components selected from the group consisting of a solvent, a host, a hole injection material, hole transport material, and an electron transport layer material, disclosed herein.

Combination with Other Materials

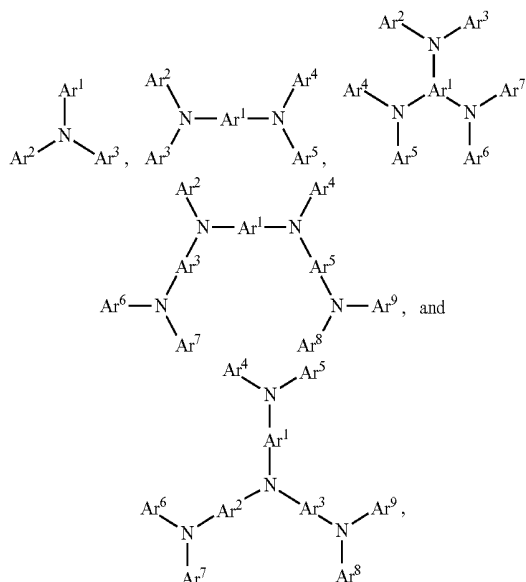
[0111] The materials described herein as useful for a particular layer in an organic light emitting device may be used in combination with a wide variety of other materials present in the device. For example, emissive dopants disclosed herein may be used in conjunction with a wide variety of hosts, transport layers, blocking layers, injection layers, electrodes and other layers that may be present. The materials described or referred to below are non-limiting examples of materials that may be useful in combination with the compounds disclosed herein, and one of skill in the art can readily consult the literature to identify other materials that may be useful in combination.

HIL/HTL:

[0112] A hole injecting/transporting material to be used in the present invention is not particularly limited, and any com-

pound may be used as long as the compound is typically used as a hole injecting/transporting material. Examples of the material include, but not limit to: a phthalocyanine or porphyrin derivative; an aromatic amine derivative; an indolocarbazole derivative; a polymer containing fluorohydrocarbon; a polymer with conductivity dopants; a conducting polymer, such as PEDOT/PSS; a self-assembly monomer derived from compounds such as phosphonic acid and silane derivatives; a metal oxide derivative, such as MoO_x ; a p-type semiconducting organic compound, such as 1,4,5,8,9,12-Hexaazatriphenylenehexacarbonitrile; a metal complex, and a cross-linkable compounds.

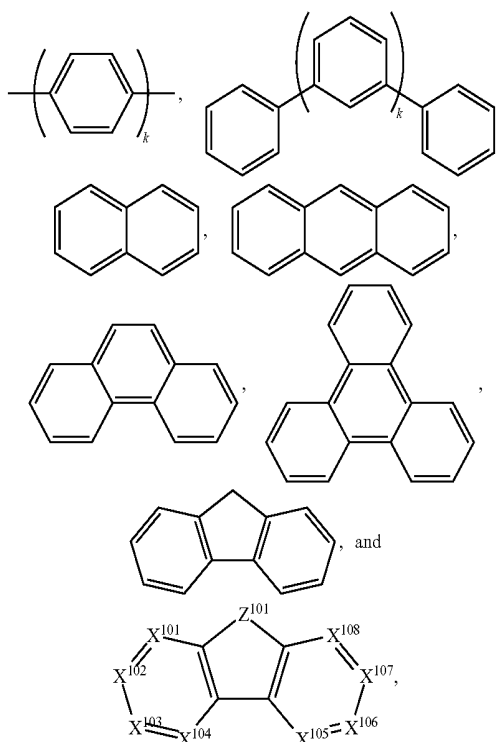
[0113] Examples of aromatic amine derivatives used in HIL or HTL include, but not limit to the following general structures:



[0114] Each of Ar^1 to Ar^9 is selected from the group consisting of aromatic hydrocarbon cyclic compounds such as benzene, biphenyl, triphenyl, triphenylene, naphthalene, anthracene, phenalene, phenanthrene, fluorene, pyrene, chrysene, perylene, and azulene; the group consisting of aromatic heterocyclic compounds such as dibenzothiophene, dibenzofuran, dibenzoselenophene, furan, thiophene, benzofuran, benzothiophene, benzoselenophene, carbazole, indolocarbazole, pyridylindole, pyrrolodipyridine, pyrazole, imidazole, triazole, oxazole, thiazole, oxadiazole, oxatriazole, dioxazole, thiadiazole, pyridine, pyridazine, pyrimidine, pyrazine, triazine, oxazine, oxathiazine, oxadiazine, indole, benzimidazole, indazole, indoxazine, benzoxazole, benzisoxazole, benzothiazole, quinoline, isoquinoline, cinoline, quinoxaline, naphthyridine, phthalazine, pteridine, xanthene, acridine, phenazine, phenothiazine, phenoxazine, benzofuopyridine, furodipyridine, benzothienopyridine, thienodipyridine, benzoselenophenopyridine, and selenophenodipyridine; and the group consisting of 2 to 10 cyclic structural units which are groups of the same type or different types selected from the aromatic hydrocarbon cyclic group and the aromatic heterocyclic group and are bonded to each other directly or via at least one of oxygen atom, nitrogen atom, sulfur atom, silicon atom, phosphorus atom, boron atom, chain structural unit and the aliphatic

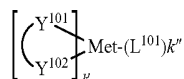
cyclic group. Wherein each Ar is further substituted by a substituent selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof.

[0115] In one aspect, Ar¹ to Ar⁹ is independently selected from the group consisting of:



wherein k is an integer from 1 to 20; X¹⁰¹ to X¹⁰⁸ is C (including CH) or N; Z¹⁰¹ is NAr¹, O, or S; Ar¹ has the same group defined above.

[0116] Examples of metal complexes used in HIL or HTL include, but not limit to the following general formula:



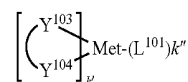
wherein Met is a metal, which can have an atomic weight greater than 40; (Y¹⁰¹-Y¹⁰²) is a bidentate ligand, Y¹⁰¹ and Y¹⁰² are independently selected from C, N, O, P, and S; L¹⁰¹ is an ancillary ligand; k' is an integer value from 1 to the maximum number of ligands that may be attached to the metal; and k'+k'' is the maximum number of ligands that may be attached to the metal.

[0117] In one aspect, (Y¹⁰¹-Y¹⁰²) is a 2-phenylpyridine derivative. In another aspect, (Y¹⁰¹-Y¹⁰²) is a carbene ligand. In another aspect, Met is selected from Ir, Pt, Os, and Zn. In a further aspect, the metal complex has a smallest oxidation potential in solution vs. Fc⁺/Fc couple less than about 0.6 V.

Host:

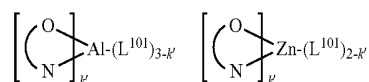
[0118] The light emitting layer of the organic EL device of the present invention preferably contains at least a metal complex as light emitting material, and may contain a host material using the metal complex as a dopant material. Examples of the host material are not particularly limited, and any metal complexes or organic compounds may be used as long as the triplet energy of the host is larger than that of the dopant. While the Table below categorizes host materials as preferred for devices that emit various colors, any host material may be used with any dopant so long as the triplet criteria is satisfied.

[0119] Examples of metal complexes used as host are preferred to have the following general formula:



wherein Met is a metal; (Y¹⁰³-Y¹⁰⁴) is a bidentate ligand, Y¹⁰³ and Y¹⁰⁴ are independently selected from C, N, O, P, and S; L¹⁰¹ is an another ligand; k' is an integer value from 1 to the maximum number of ligands that may be attached to the metal; and k'+k'' is the maximum number of ligands that may be attached to the metal.

[0120] In one aspect, the metal complexes are:



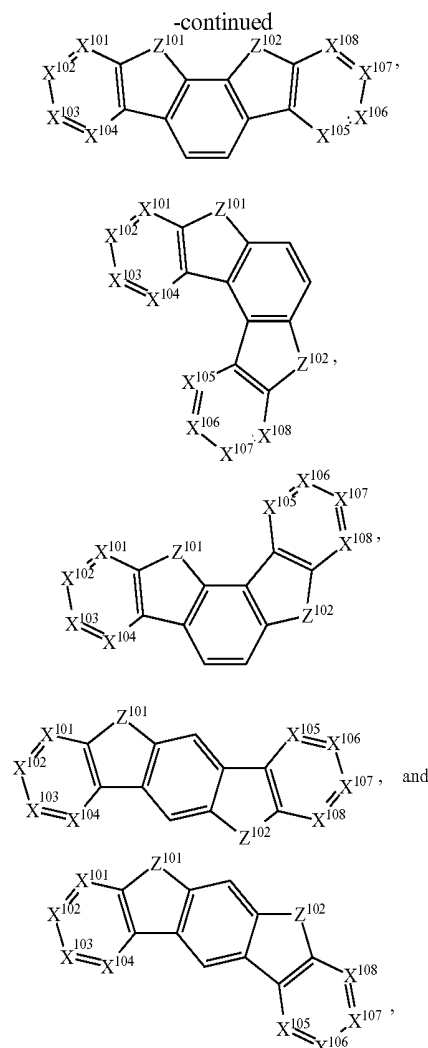
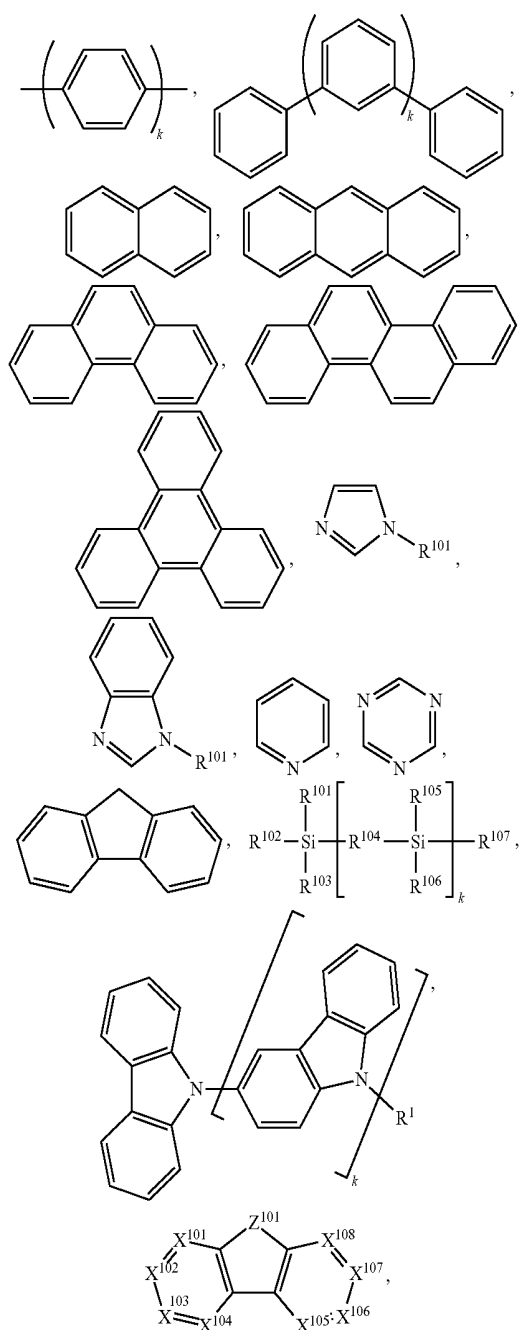
wherein (O—N) is a bidentate ligand, having metal coordinated to atoms O and N.

[0121] In another aspect, Met is selected from Ir and Pt. In a further aspect, (Y¹⁰³-Y¹⁰⁴) is a carbene ligand.

[0122] Examples of organic compounds used as host are selected from the group consisting of aromatic hydrocarbon cyclic compounds such as benzene, biphenyl, triphenyl, triphenylene, naphthalene, anthracene, phenalene, phenanthrene, fluorene, pyrene, chrysene, perylene, and azulene; the group consisting of aromatic heterocyclic compounds such as dibenzothiophene, dibenzofuran, dibenzoselenophene, furan, thiophene, benzofuran, benzothiophene, benzoselenophene, carbazole, indolocarbazole, pyridylindole, pyrrolo-dipyridine, pyrazole, imidazole, triazole, oxazole, thiazole, oxadiazole, oxatriazole, dioxazole, thiadiazole, pyridine, pyridazine, pyrimidine, pyrazine, triazine, oxazine, oxathiazine, oxadiazine, indole, benzimidazole, indazole, indoxazine, benzoxazole, benzisoxazole, benzothiazole, quinoline, isoquinoline, cinnoline, quinazoline, quinoxaline, naphthyridine, phthalazine, pteridine, xanthene, acridine, phenazine, phenothiazine, phenoxazine, benzofuopyridine, furodipyridine, benzothienopyridine, thienodipyridine, benzoselenophenopyridine, and selenophenodipyridine; and the group consisting of 2 to 10 cyclic structural units which are groups of the same type or different types selected from the aromatic

hydrocarbon cyclic group and the aromatic heterocyclic group and are bonded to each other directly or via at least one of oxygen atom, nitrogen atom, sulfur atom, silicon atom, phosphorus atom, boron atom, chain structural unit and the aliphatic cyclic group. Wherein each group is further substituted by a substituent selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof.

[0123] In one aspect, the host compound contains at least one of the following groups in the molecule:



wherein R^{101} to R^{107} is independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof, when it is aryl or heteroaryl, it has the similar definition as Ar's mentioned above. k is an integer from 0 to 20 or 1 to 20; k'' is an integer from 0 to 20. X^{101} to X^{108} is selected from C (including CH) or N. Z^{101} and Z^{102} is selected from NR^{101} , O, or S.

HBL:

[0124] A hole blocking layer (HBL) may be used to reduce the number of holes and/or excitons that leave the emissive layer. 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.

[0125] In one aspect, compound used in HBL contains the same molecule or the same functional groups used as host described above.

TABLE A

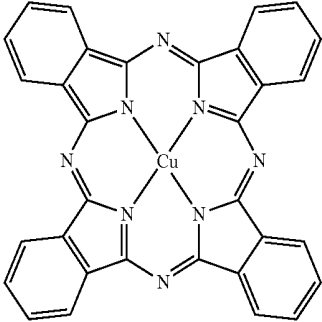
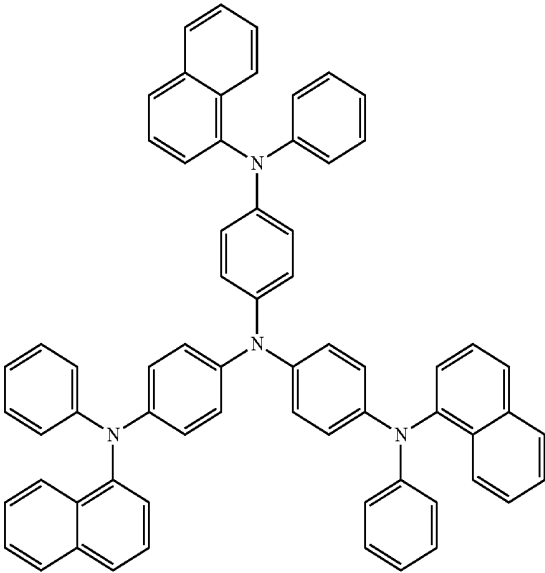
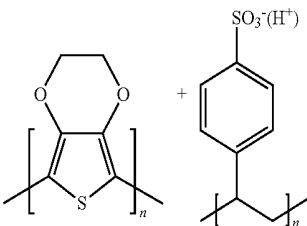
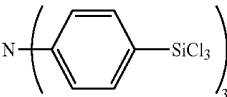
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Hole injection materials		
Phthalocyanine and porphyrin compounds		Appl. Phys. Lett. 69, 2160 (1996)
Starburst triarylamines		J. Lumin. 72-74, 985 (1997)
CF _x Fluorohydrocarbon polymer	$\text{---}[\text{CH}_x\text{F}_y]_n\text{---}$	Appl. Phys. Lett. 78, 673 (2001)
Conducting polymers (e.g., PEDOT:PSS, polyaniline, polythiophene)		Synth. Met. 87, 171 (1997) WO2007002683
Phosphonic acid and silane SAMS		US20030162053

TABLE A-continued

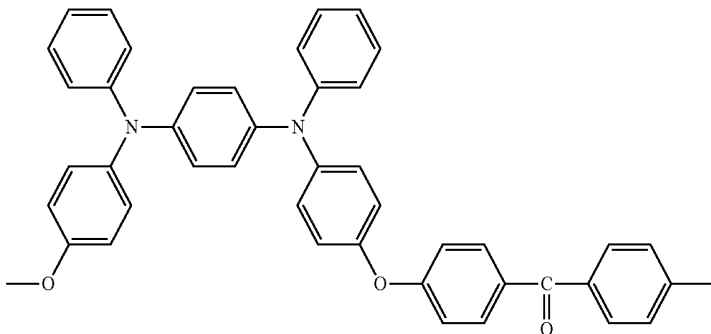
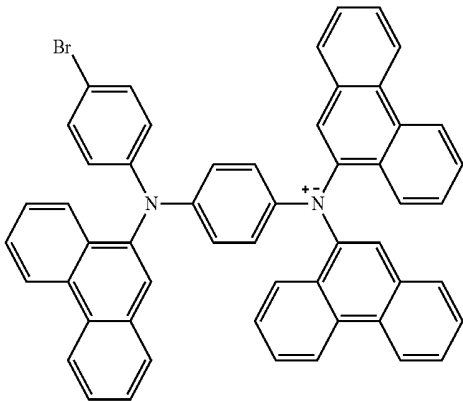
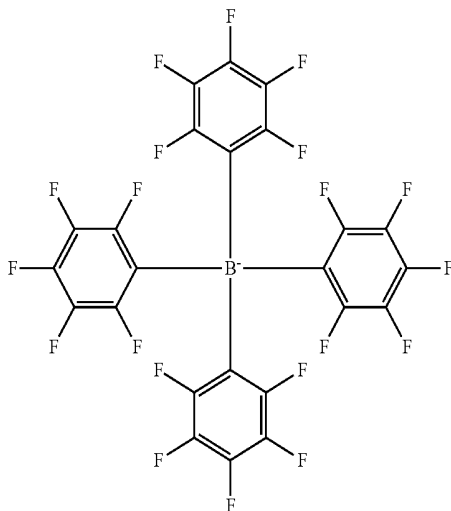
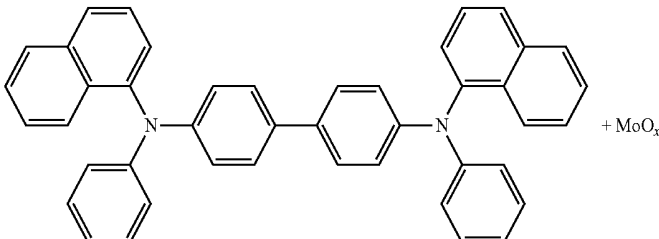
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Triarylamine or polythiophene polymers with conductivity dopants		EP1725079A1
	and	
		
Organic compounds with conductive inorganic compounds, such as molybdenum and tungsten oxides		US20050123751 SID Symposium Digest, 37, 923 (2006) WO2009018009
		

TABLE A-continued

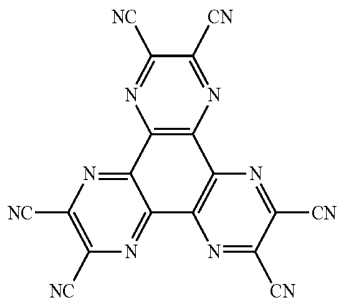
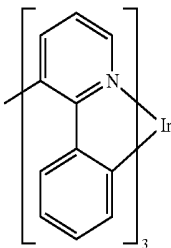
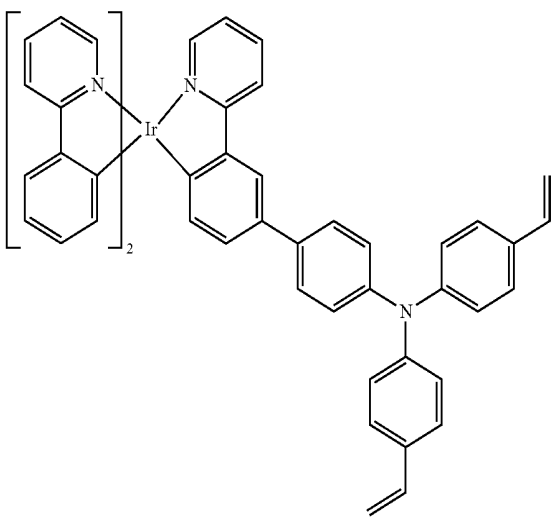
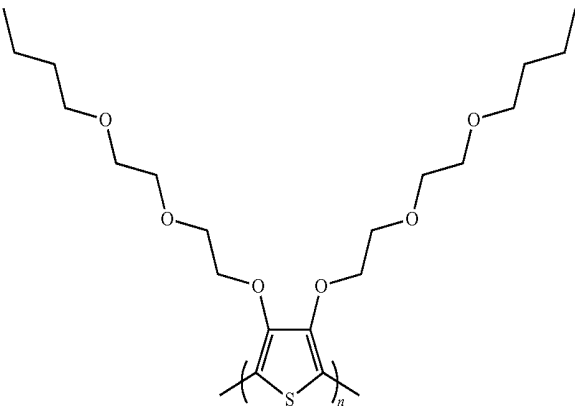
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
n-type semiconducting organic complexes		US20020158242
Metal organometallic complexes		US20060240279
Cross-linkable compounds		US20080220265
Polythiophene based polymers and copolymers		WO2011075644 EP2350216

TABLE A-continued

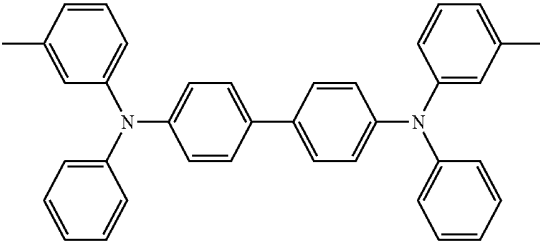
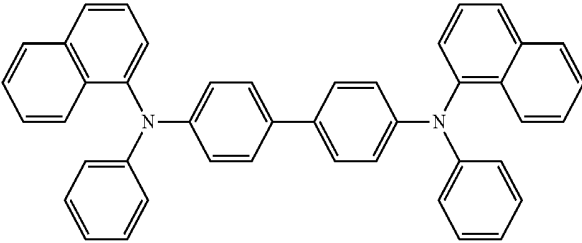
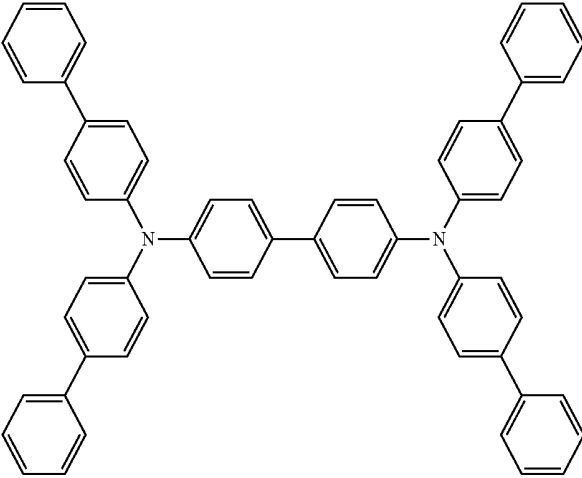
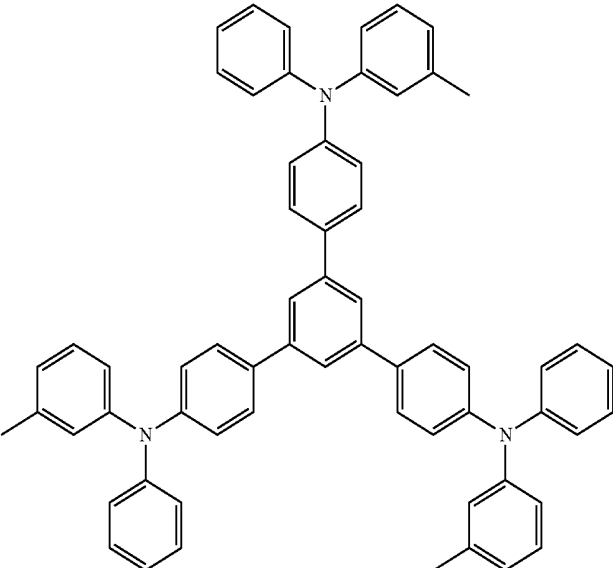
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Hole transporting materials		
Triarylamines (e.g., TPD, α -NPD)		Appl. Phys. Lett. 51, 913 (1987)
		U.S. Pat. No. 5,061,569
		EP650955
		J. Mater. Chem. 3, 319 (1993)

TABLE A-continued

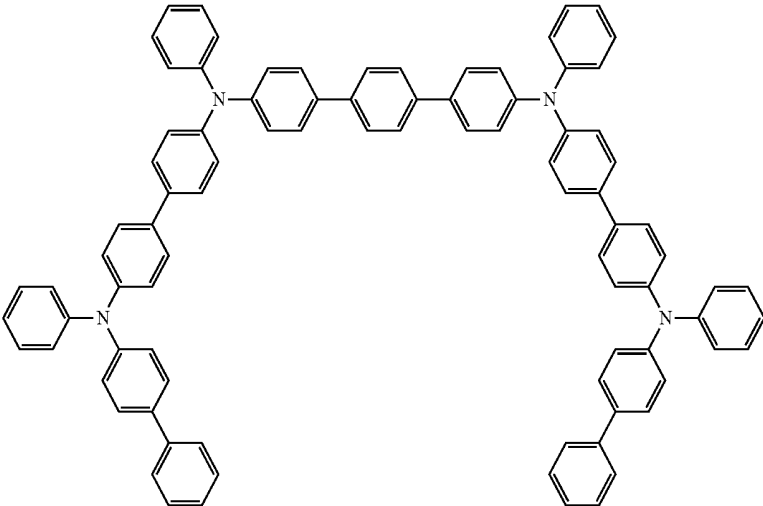
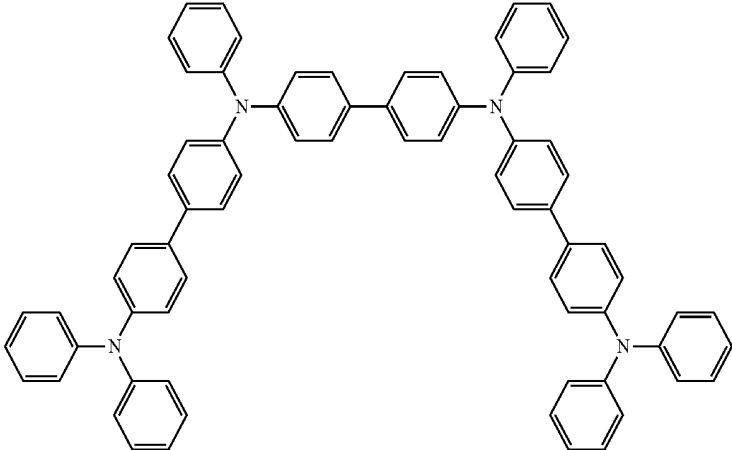
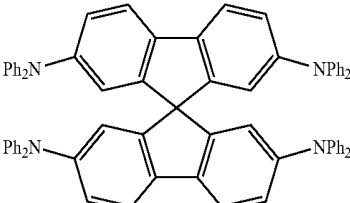
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		Appl. Phys. Lett. 90, 183503 (2007)
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Triaylamine on spirofluorene core		Synth. Met. 91, 209 (1997)

TABLE A-continued

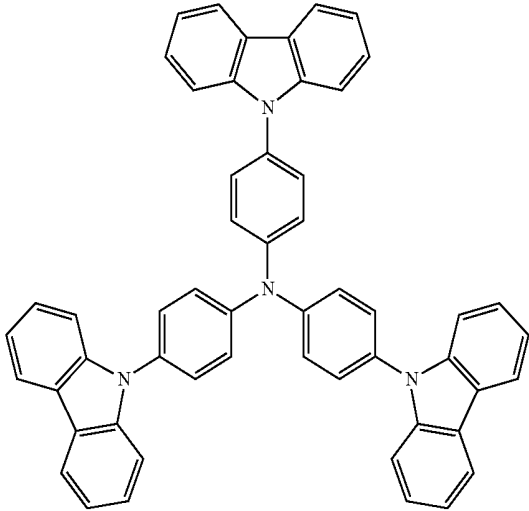
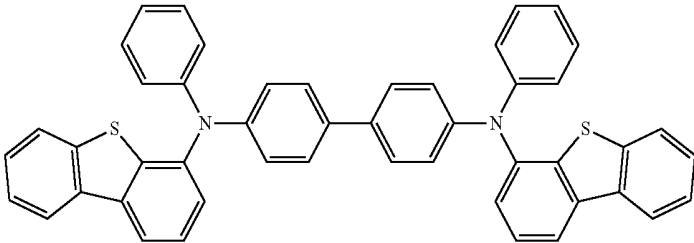
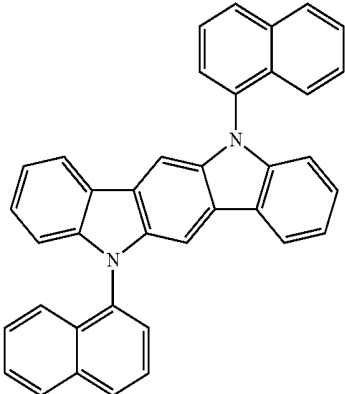
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Arylamine carbazole compounds		Adv. Mater. 6, 677 (1994), US20080124572
Triarylamine with (di)benzothiophene/ (di)benzofuran		US20070278938, US20080106190 US20110163302
Indolocarbazoles		Synth. Met, 111, 421 (2000)

TABLE A-continued

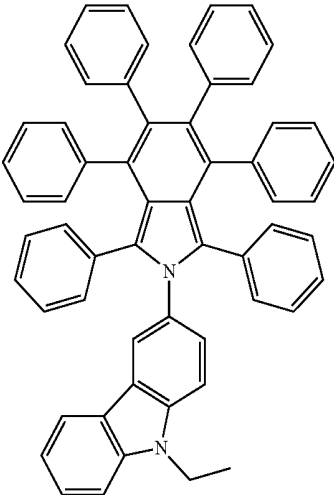
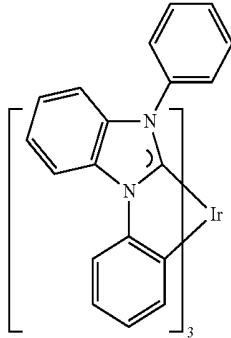
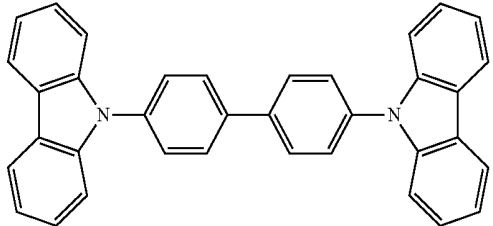
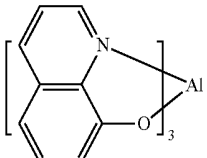
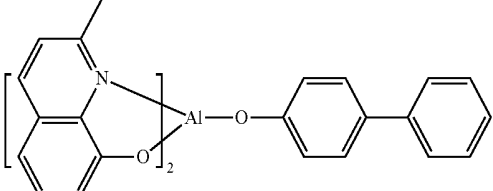
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Isoindole compounds		Chem. Mater. 15, 3148 (2003)
Metal carbene complexes		US20080018221
Phosphorescent OLED host materials		
Red hosts		
Arylcarbazoles		Appl. Phys. Lett. 78, 1622 (2001)
Metal 8-hydroxy-quinolates (e.g., Alq ₃ , BAlq)		Nature 395, 151 (1998)
		US20060202194

TABLE A-continued

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Metal phenoxy- benzothiazole compounds		WO2005014551
		WO2006072002
		Appl. Phys. Lett. 90, 123509 (2007)
Conjugated oligomers and polymers (e.g., polyfluorene)		Org. Electron. 1, 15 (2000)
Aromatic fused rings		WO2009066779, WO2009066778, WO2009063833, US20090045731, US20090045730, WO2009008311, US20090008605, US20090009065
Zinc complexes		WO2010056066

TABLE A-continued

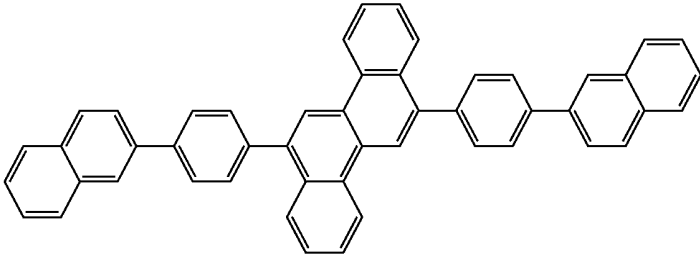
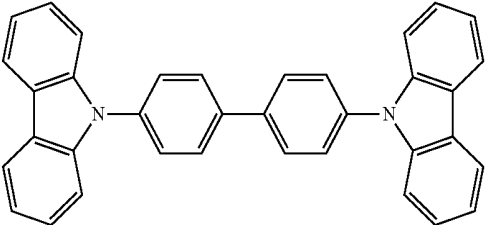
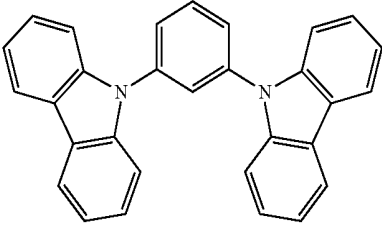
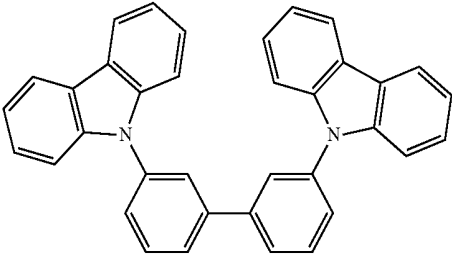
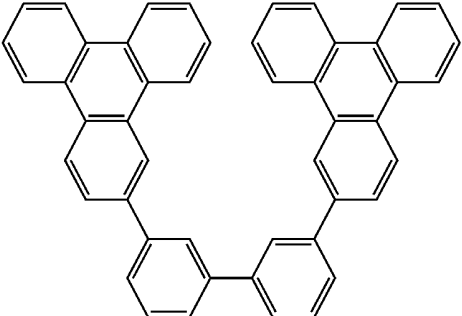
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Chrysene based compounds		WO2011086863
Green hosts		
Arylcarbazoles		Appl. Phys., Lett. 78, 1622 (2001)
		US20030175553
		WO2001039234
Aryltriphenylene compounds		US20060280965

TABLE A-continued

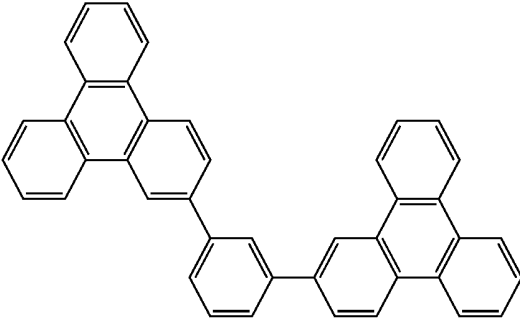
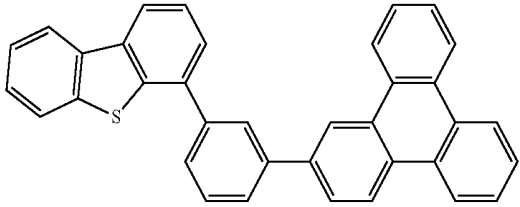
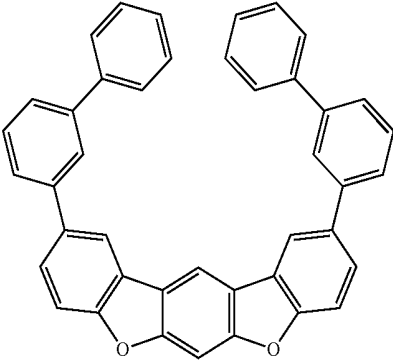
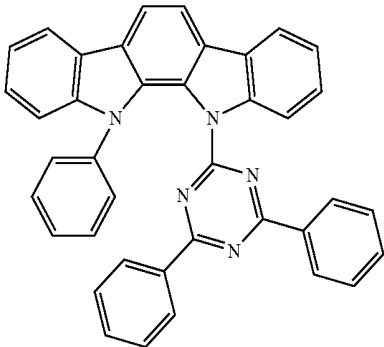
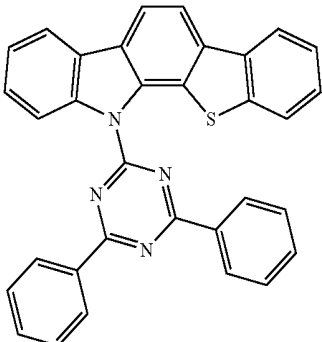
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Poly-fused heteroaryl compounds		US20060280965
		WO2009021126
		US20090309488 US20090302743 US20100012931
		WO2008056746
Donor acceptor type molecules		WO2010107244

TABLE A-continued

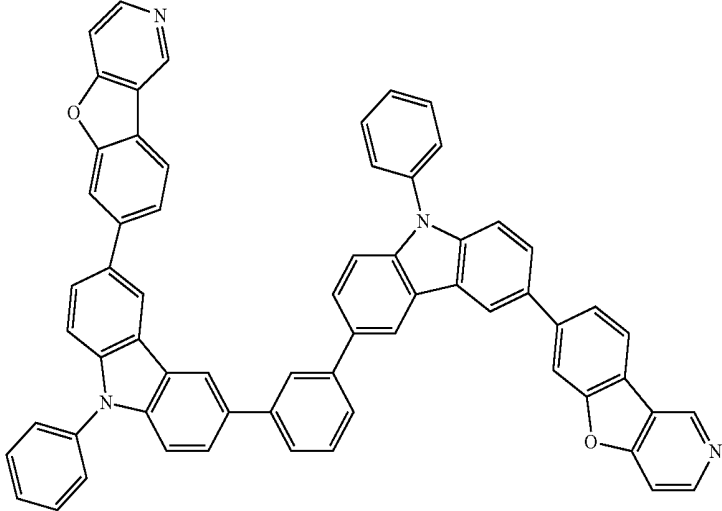
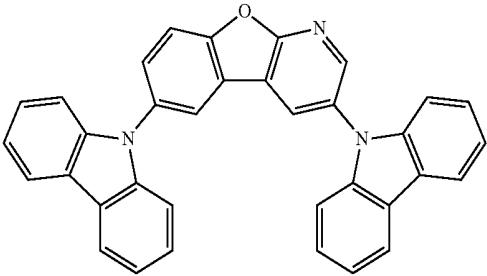
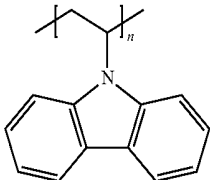
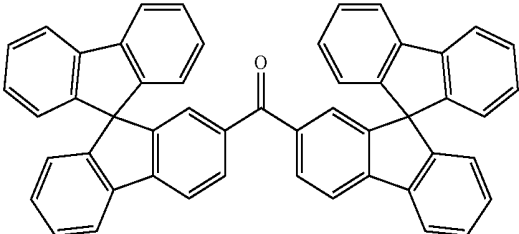
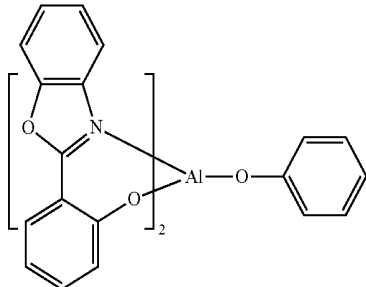
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Aza-carbazole/ DBT/DBF		JP2008074939
		US20100187984
Polymers (e.g., PVK)		Appl. Phys. Lett. 77, 2280 (2000)
Spirofluorene compounds		WO2004093207
Metal phenoxy- benzoxazole compounds		WO2005089025

TABLE A-continued

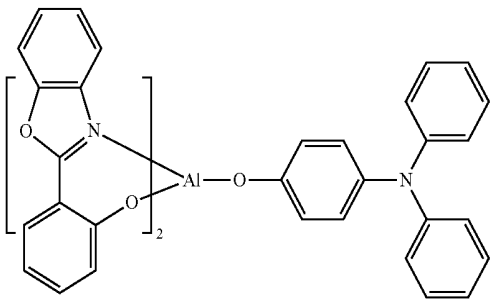
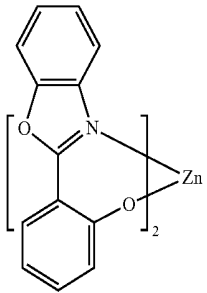
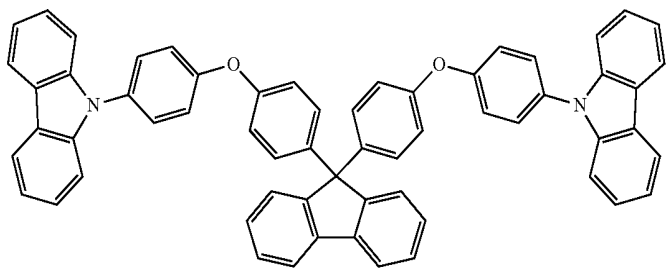
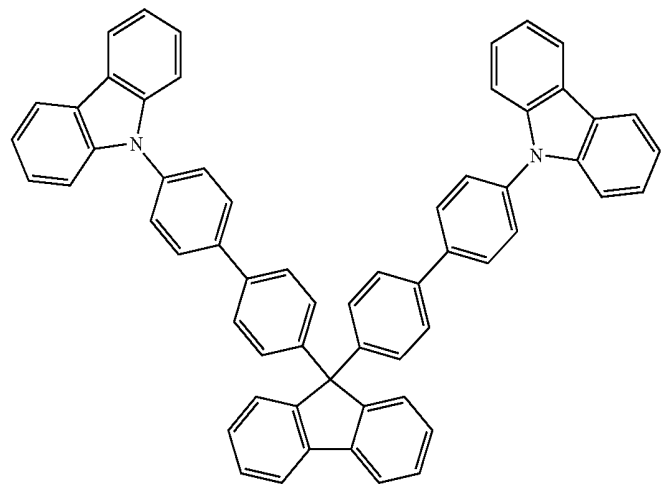
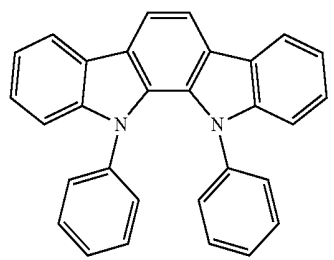
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
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		JP200511610
Spirofluorene-carbazole compounds		JP2007254297
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Indolocabazoles		WO2007063796

TABLE A-continued

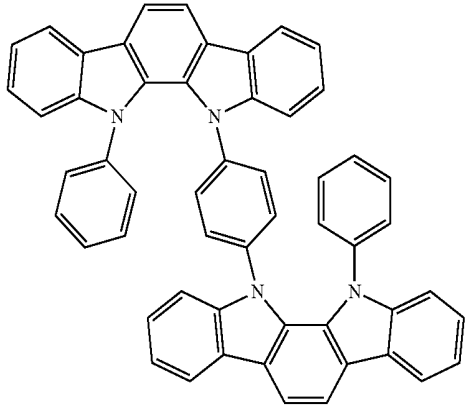
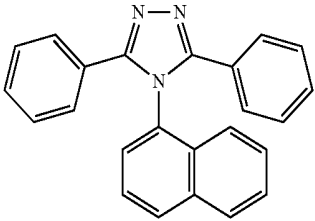
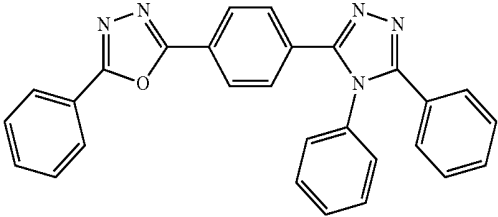
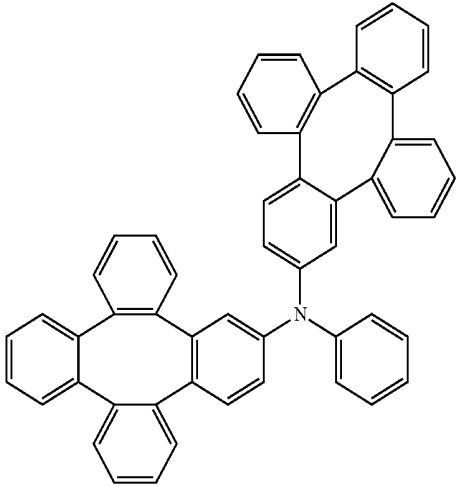
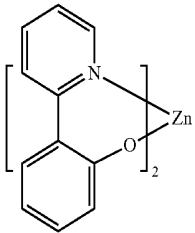
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		WO2007063754
5-member ring electron deficient heterocycles (e.g., triazole, oxadiazole)		J. Appl. Phys. 90, 5048 (2001)
		WO2004107822
Tetraphenylene complexes		US20050112407
Metal phenoxypyridine compounds		WO2005030900

TABLE A-continued

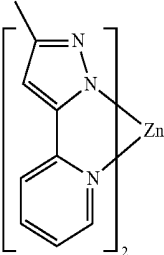
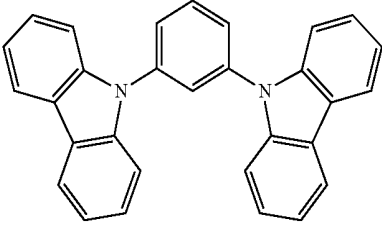
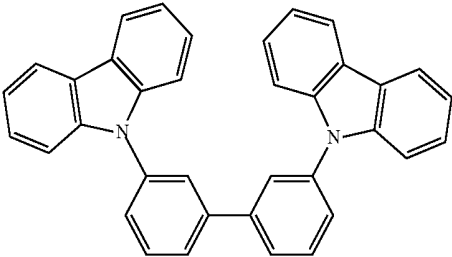
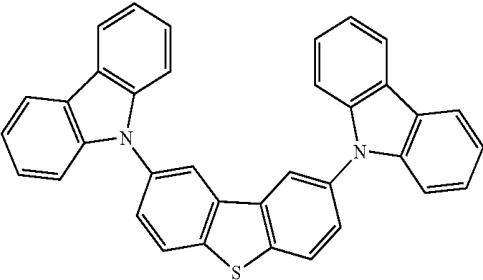
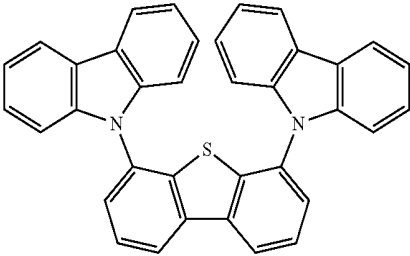
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Metal coordination complexes (e.g., Zn, Al with N-N ligands)		US20040137268, US20040137267
Blue hosts		
Arylcarbazoles		Appl. Phys. Lett., 82, 2422 (2003)
		US20070190359
Dibenzothiophene/ Dibenzofuran- carbazole compounds		WO2006114966, US20090167162
		US20090167162

TABLE A-continued

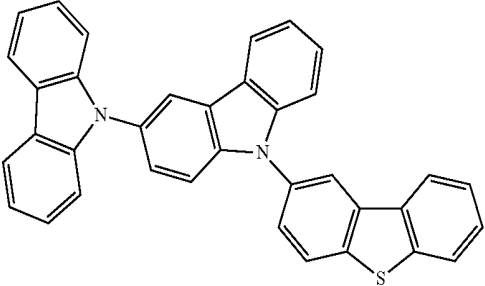
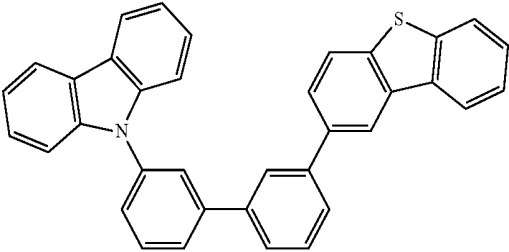
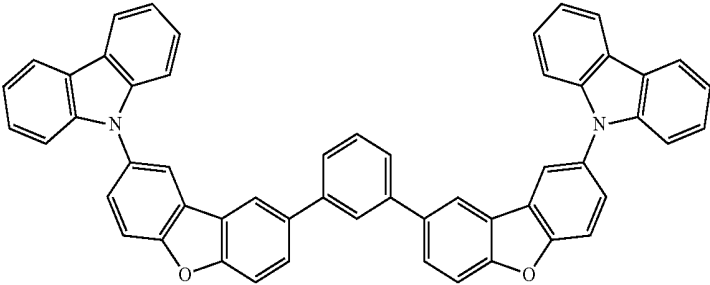
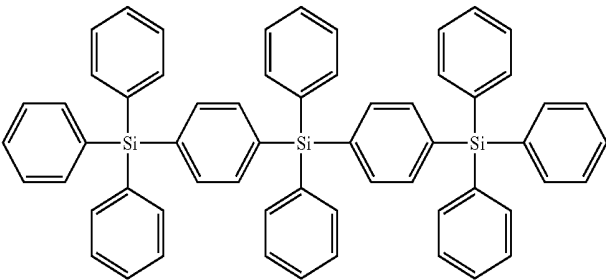
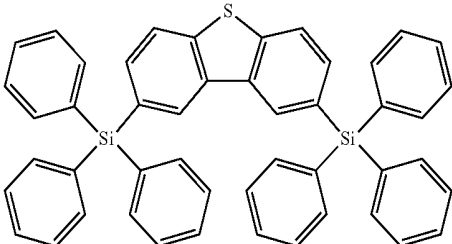
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
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		US20090030202, US20090017330
		US20100084966
Silicon aryl compounds		US20050238919
		WO2009003898

TABLE A-continued

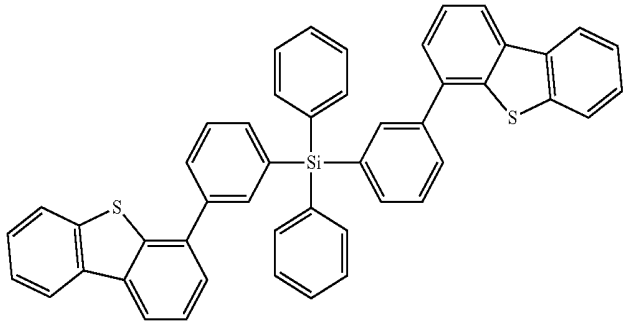
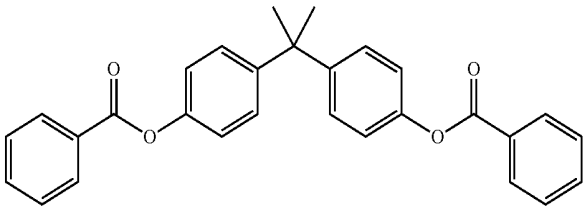
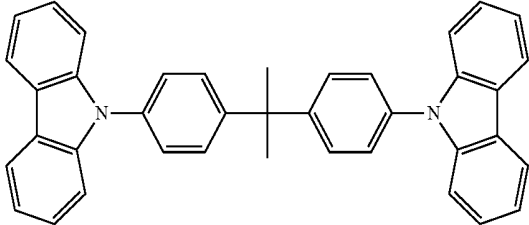
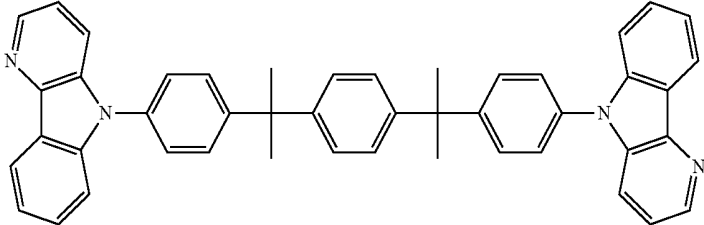
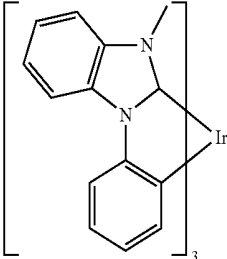
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Silicon/ Germanium aryl compounds		EP2034538A
Aryl benzoyl ester		WO2006100298
Carbazole linked by non- conjugated groups		US20040115476
Aza-carbazoles		US20060121308
High triplet metal organometallic complex		U.S. Pat. No. 7,154,114

TABLE A-continued

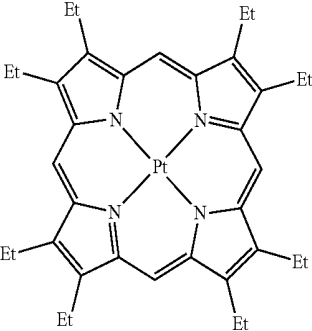
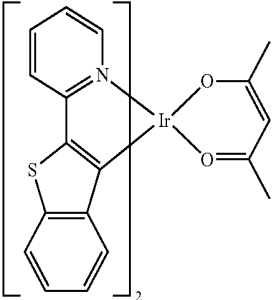
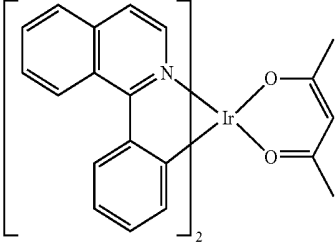
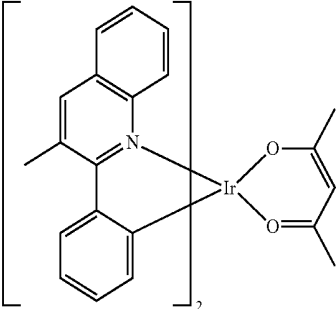
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Phosphorescent dopants		
Red dopants		
Heavy metal porphyrins (e.g., PtOEP)		Nature 395, 151 (1998)
Iridium(III) organometallic complexes		Appl. Phys. Lett. 78, 1622 (2001)
		US20030072964
		US20030072964

TABLE A-continued

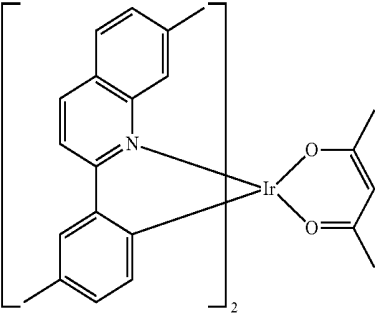
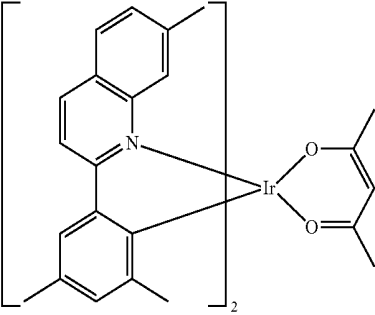
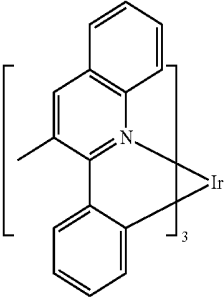
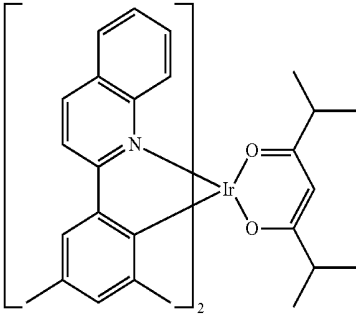
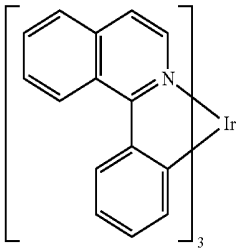
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		US20070087321
		US20080261076 US20100090591
		US20070087321

TABLE A-continued

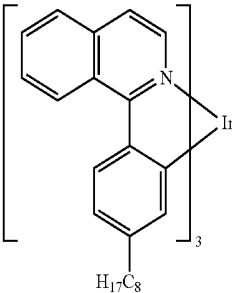
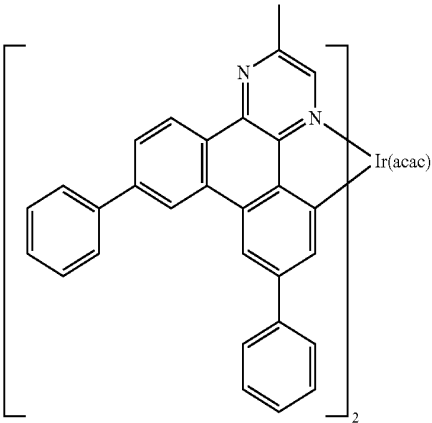
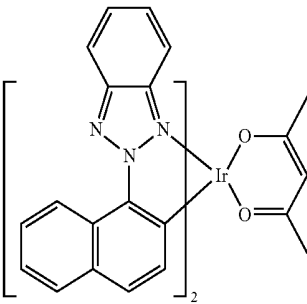
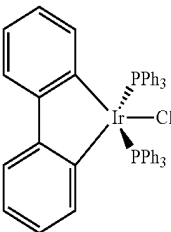
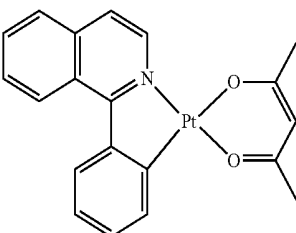
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		Adv. Mater. 19, 739 (2007)
		WO2009100991
		WO2008101842
		U.S. Pat. No. 7,232,618
Platinum(II) organometallic complexes		WO2003040257

TABLE A-continued

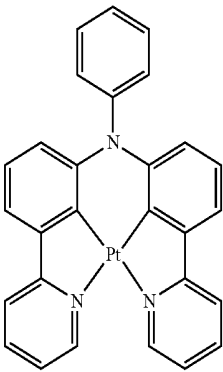
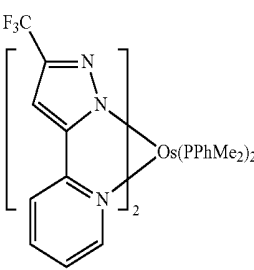
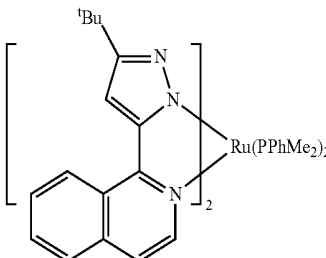
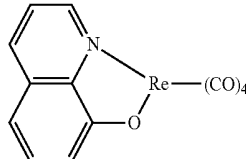
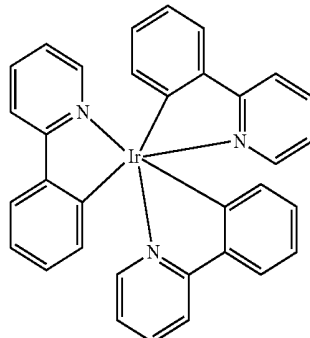
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		US20070103060
Osmium(III) complexes		Chem. Mater. 17, 3532 (2005)
Ruthenium(II) complexes		Adv. Mater. 17, 1059 (2005)
Rhenium (I), (II), and (III) complexes		US20050244673
Green dopants		
Iridium(III) organometallic complexes	 and its derivatives	Inorg. Chem. 40, 1704 (2001)

TABLE A-continued

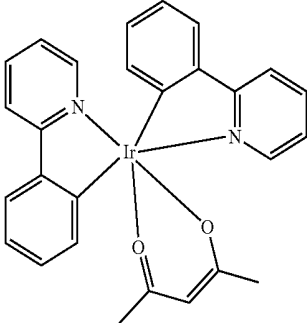
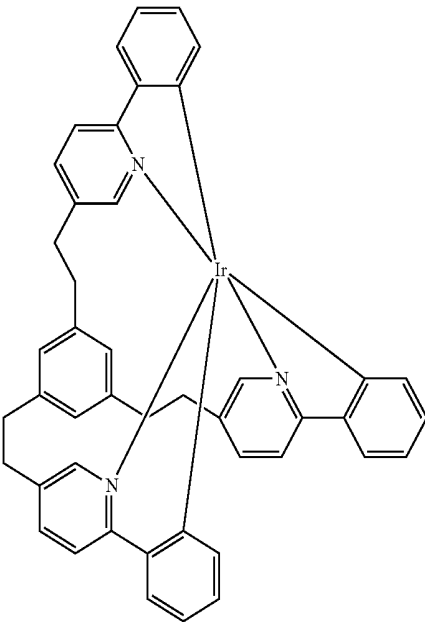
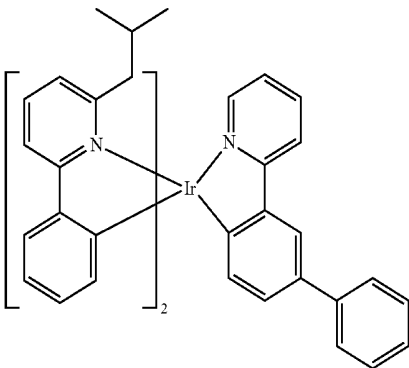
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		US20020034656
		U.S. Pat. No. 7,332,232
		US20090108737

TABLE A-continued

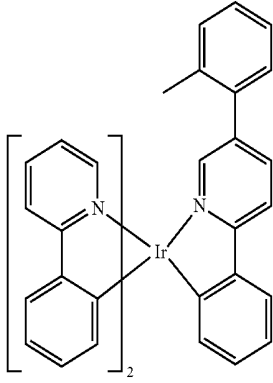
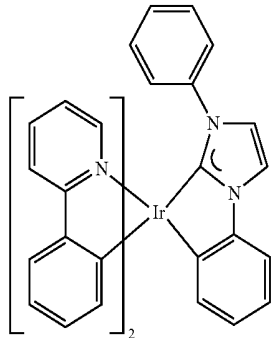
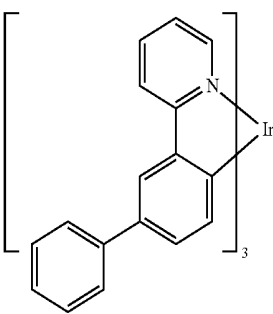
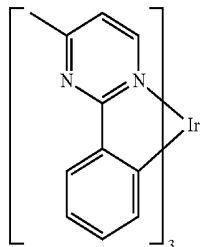
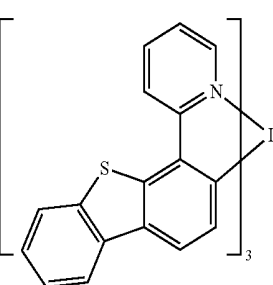
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		WO2010028151
		EP1841834B
		US20060127696
		US20090039776
		U.S. Pat. No. 6,921,915

TABLE A-continued

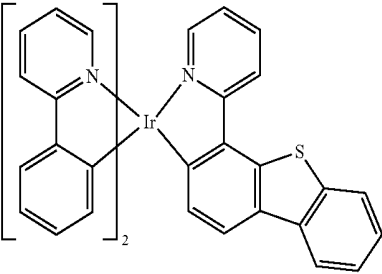
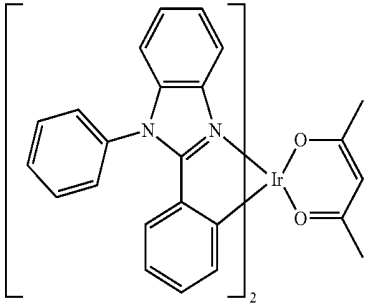
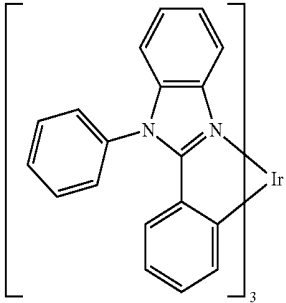
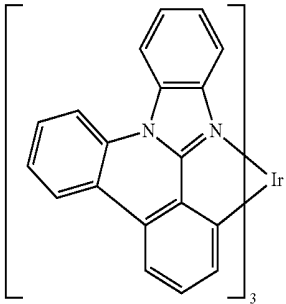
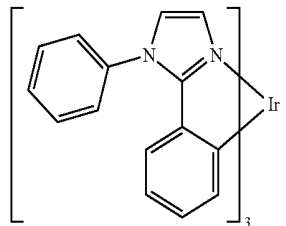
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		US20100244004
		U.S. Pat. No. 6,687,266
		Chem. Mater. 16, 2480 (2004)
		US20070190359
		US20060008670 JP2007123392

TABLE A-continued

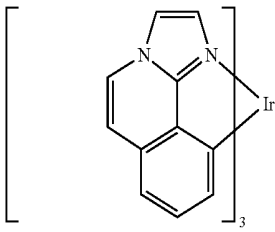
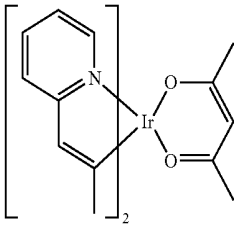
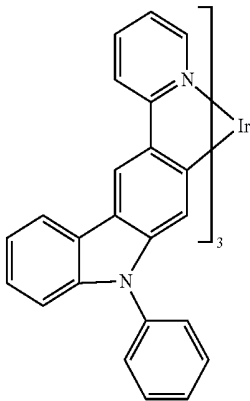
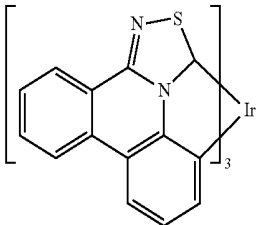
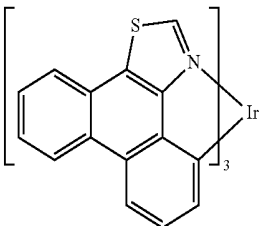
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		WO2010086089, WO2011044988
		Adv. Mater. 16, 2003 (2004)
		Angew. Chem. Int. Ed. 2006, 45, 7800
		WO2009050290
		US20090165846

TABLE A-continued

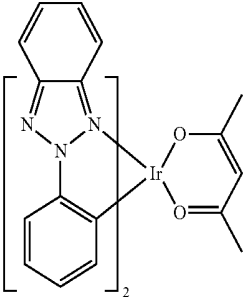
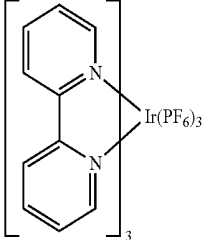
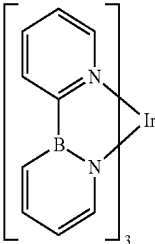
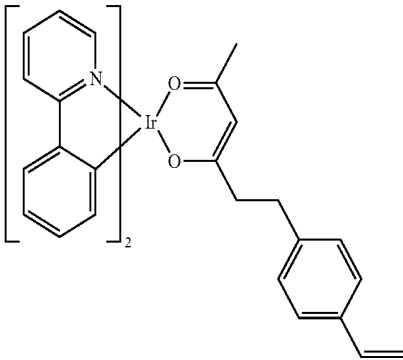
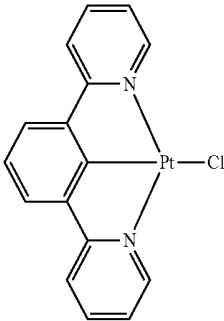
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		US20080015355
		US20010015432
		US20100295032
Monomer for polymeric metal organometallic compounds		U.S. Pat. No. 7,250,226, U.S. Pat. No. 7,396,598
Pt(II) organometallic complexes, including polydentate ligands		Appl. Phys. Lett. 86, 153505 (2005)

TABLE A-continued

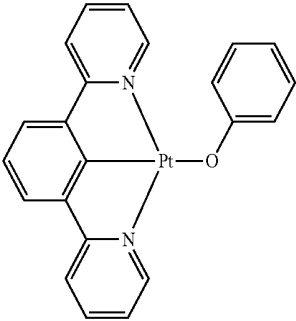
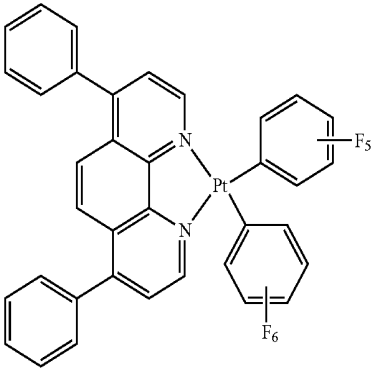
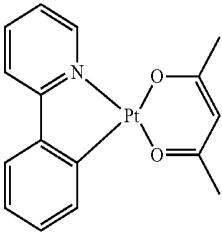
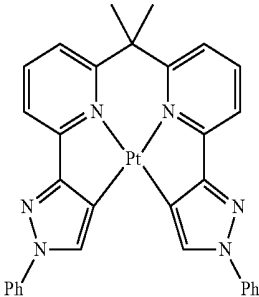
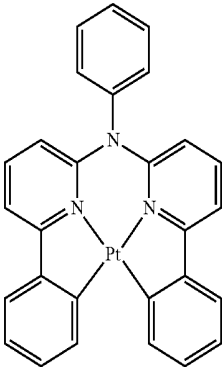
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		Appl. Phys. Lett. 86, 153505 (2005)
		Chem. Lett. 34, 592 (2005)
		WO2002015645
		US20060263635
		US20060182992 US20070103060

TABLE A-continued

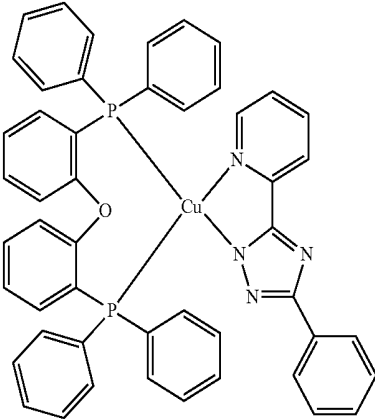
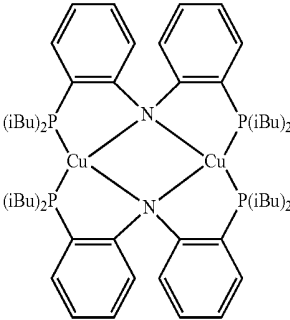
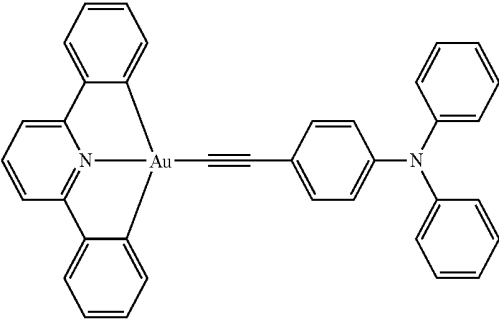
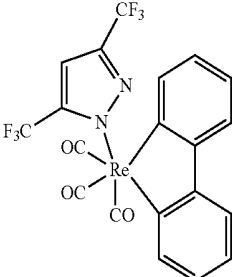
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Cu complexes		WO2009000673
		US20070111026
Gold complexes		Chem. Commun. 2906 (2005)
Rhenium(III) complexes		Inorg. Chem. 42, 1248 (2003)

TABLE A-continued

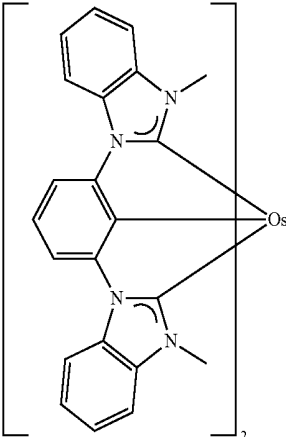
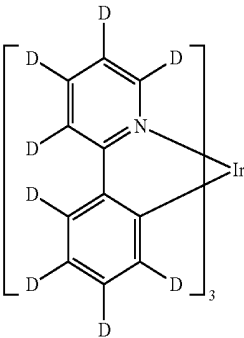
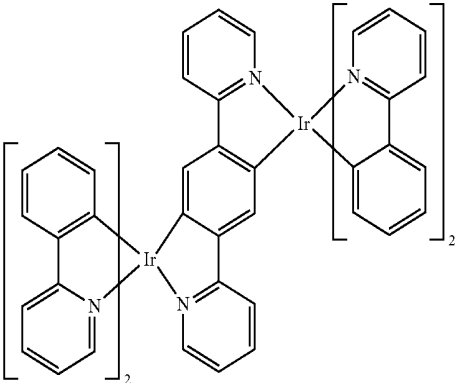
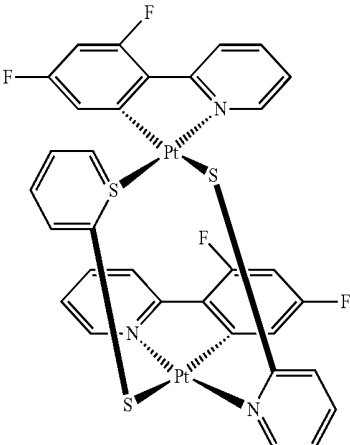
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Osmium(II) complexes		U.S. Pat. No. 7,279,704
Deuterated organometallic complexes		US20030138657
Organometallic complexes with two or more metal centers		US20030152802
		U.S. Pat. No. 7,090,928

TABLE A-continued

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Blue dopants		
Iridium(III) organometallic complexes		WO2002002714
		WO2006009024
		US20060251923 US20110057559 US20110204333
		U.S. Pat. No. 7,393,599, WO2006056418, US20050260441, WO2005019373
		U.S. Pat. No. 7,534,505

TABLE A-continued

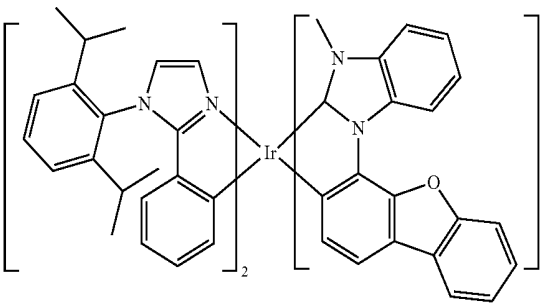
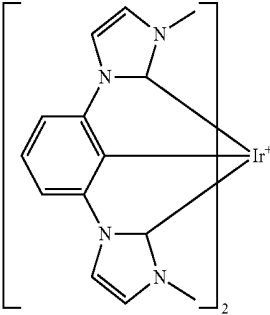
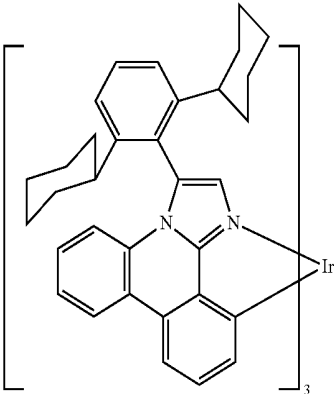
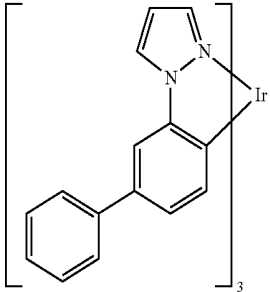
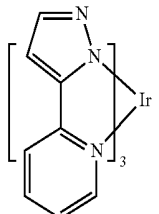
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		WO2011051404
		U.S. Pat. No. 7,445,855
		US20070190359, US20080297033 US20100148663
		U.S. Pat. No. 7,338,722
		US20020134984

TABLE A-continued

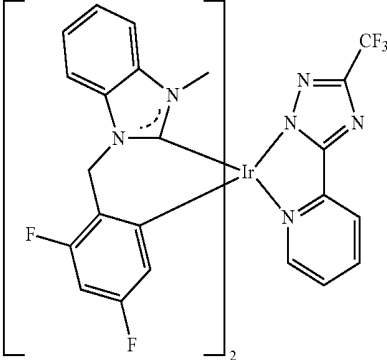
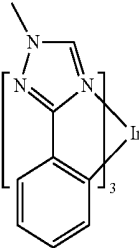
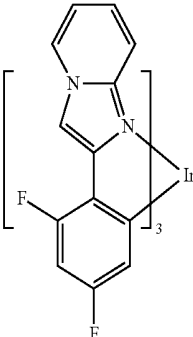
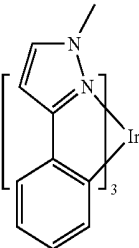
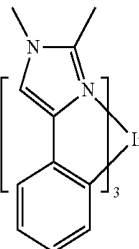
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		Chem. Mater. 18, 5119 (2006)
		Inorg. Chem, 46, 4308 (2007)
		WO2005123873
		WO2005123873

TABLE A-continued

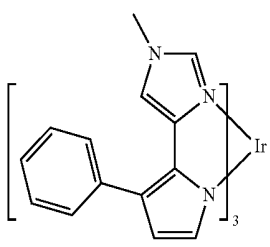
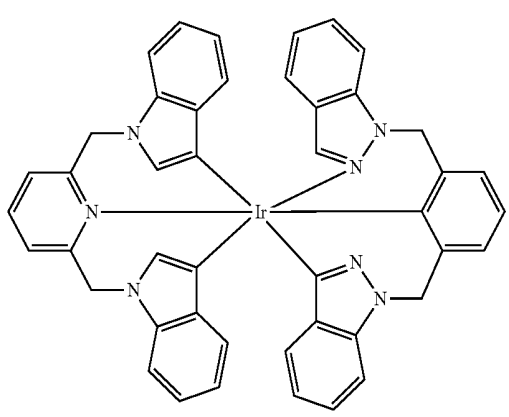
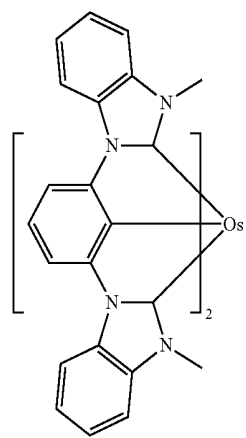
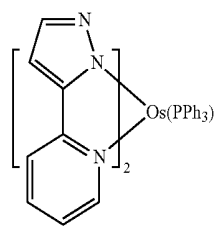
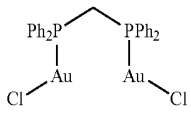
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		WO2007004380
		WO2006082742
Osmium(II) complexes		U.S. Pat. No. 7,279,704
		Organometallics 23, 3745 (2004)
Gold complexes		Appl. Phys. Lett. 74, 1361 (1999)

TABLE A-continued

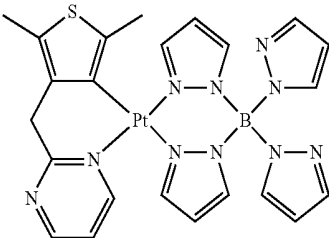
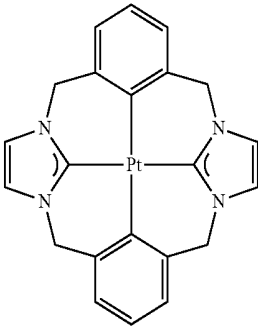
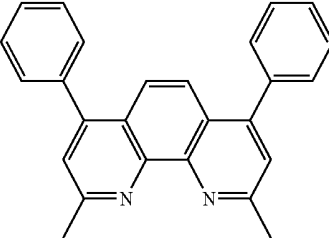
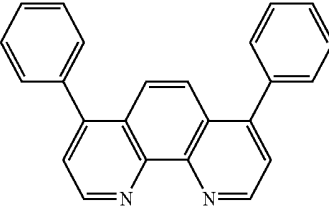
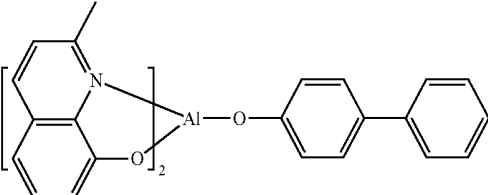
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Platinum(II) complexes		WO2006098120, WO2006103874
Pt tetradentate complexes with at least one metal-carbene bond		U.S. Pat. No. 7,655,323
Exciton/hole blocking layer materials		
Bathocuprine compounds (e.g., BCP, BPhen)		Appl. Phys. Lett. 75, 4 (1999)
		Appl. Phys. Lett. 79, 449 (2001)
Metal 8-hydroxy-quinolates (e.g., BAlq)		Appl. Phys. Lett. 81, 162 (2002)

TABLE A-continued

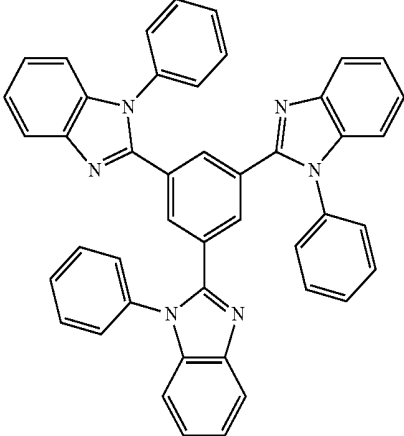
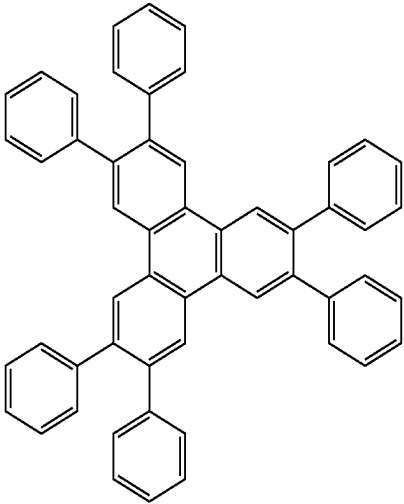
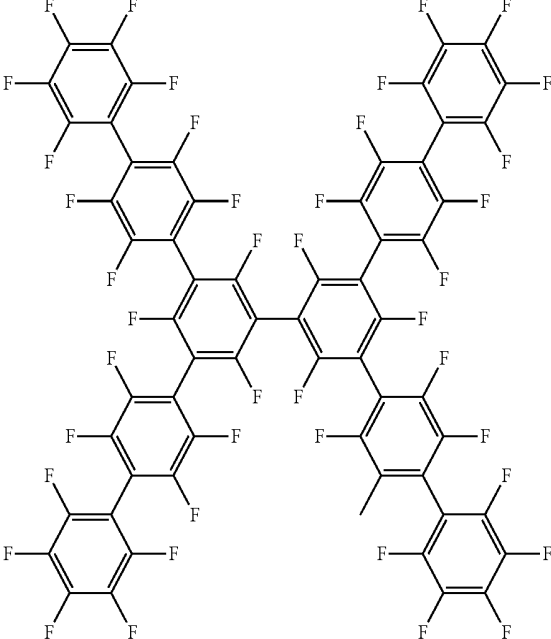
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
5-member ring electron deficient heterocycles such as triazole, oxadiazole, imidazole, benzimidazole		Appl. Phys. Lett. 81, 162 (2002)
Triphenylene compounds		US20050025993
Fluorinated aromatic compounds		Appl. Phys. Lett. 79, 156 (2001)

TABLE A-continued

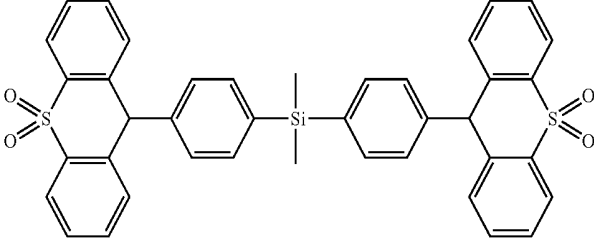
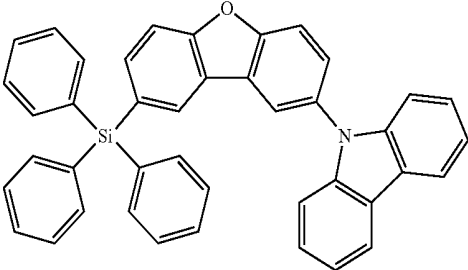
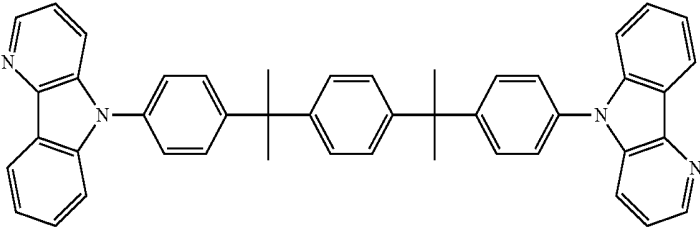
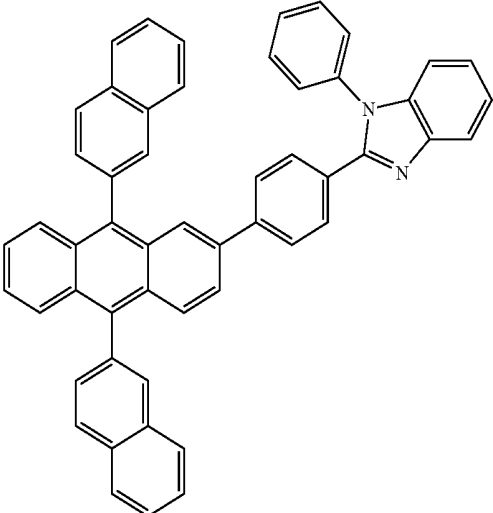
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Phenothiazine-S-oxide		WO2008132085
Silylated five-membered nitrogen, oxygen, sulfur or phosphorus dibenzo-heterocycles		WO2010079051
Aza-carbazoles		US20060121308
Electron transporting materials		
Anthracene-benzoimidazole compounds		WO2003060956

TABLE A-continued

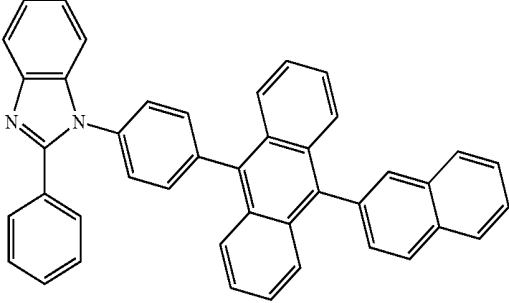
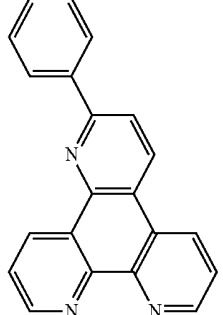
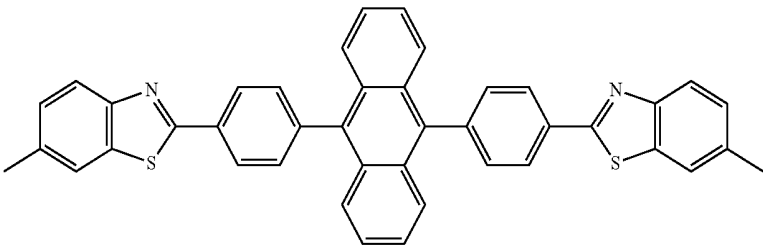
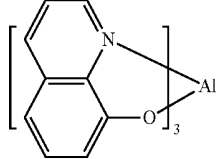
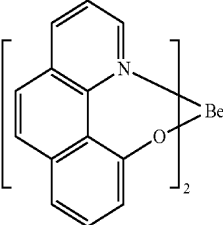
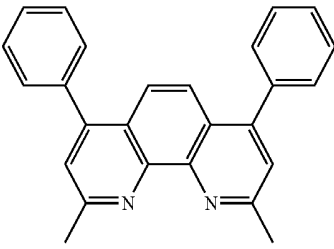
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		US20090179554
Aza triphenylene derivatives		US20090115316
Anthracene-benzothiazole compounds		Appl. Phys. Lett. 89, 063504 (2006)
Metal 8-hydroxy-quinolates (e.g., Alq ₃ , Zr _q ₄)		Appl. Phys. Lett. 51, 913 (1987) U.S. Pat. No. 7,230,107
Metal hydroxy-benzoquinolates		Chem. Lett. 5, 905 (1993)
Bathocuprine compounds such as BCP, BPhen, etc		Appl. Phys. Lett. 91, 263503 (2007)

TABLE A-continued

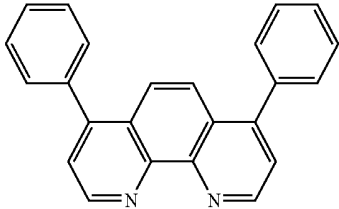
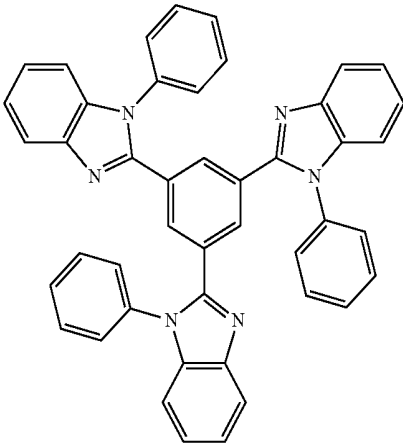
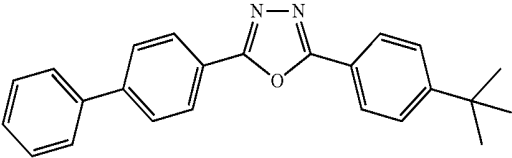
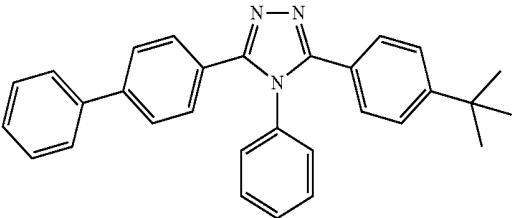
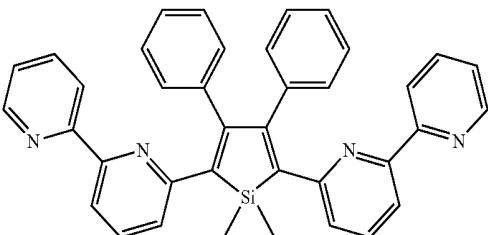
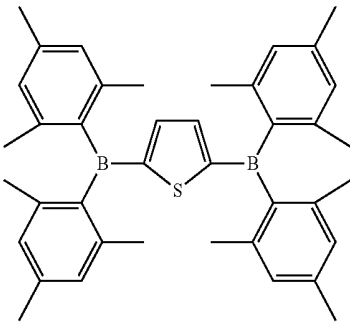
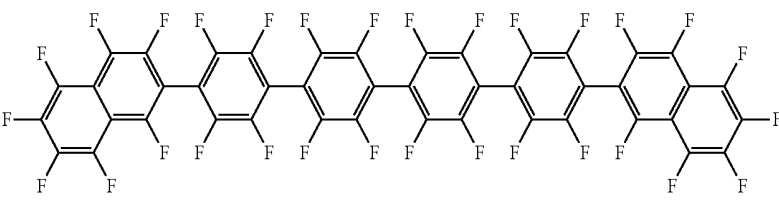
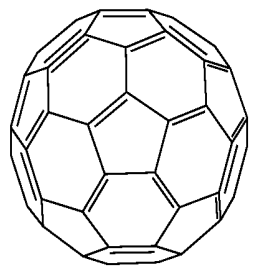
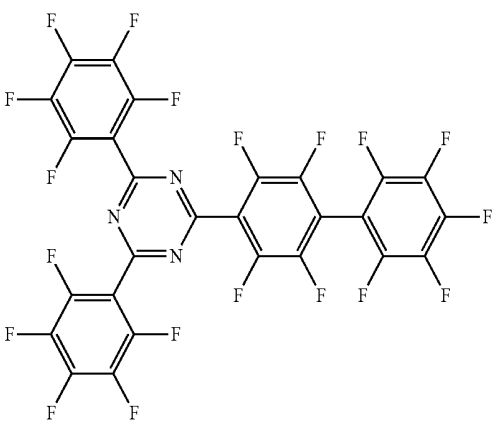
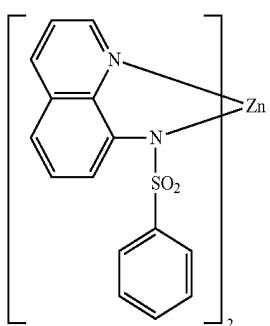
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		Appl. Phys. Lett. 79, 449 (2001)
5-member ring electron deficient heterocycles (e.g., triazole, oxadiazole, imidazole, benzoimidazole)		Appl. Phys. Lett. 74, 865 (1999)
		Appl. Phys. Lett. 55, 1489 (1989)
		Jpn. J. Apply. Phys. 32, L917 (1993)
Silole compounds		Org. Electron. 4, 113 (2003)

TABLE A-continued

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Arylborane compounds		J. Am. Chem. Soc. 120, 9714 (1998)
Fluorinated aromatic compounds		J. Am. Chem. Soc. 122, 1832 (2000)
Fullerene (e.g., C60)		US20090101870
Triazine complexes		US20040036077
Zn (N^N) complexes		U.S. Pat. No. 6,528,187

EXPERIMENTAL

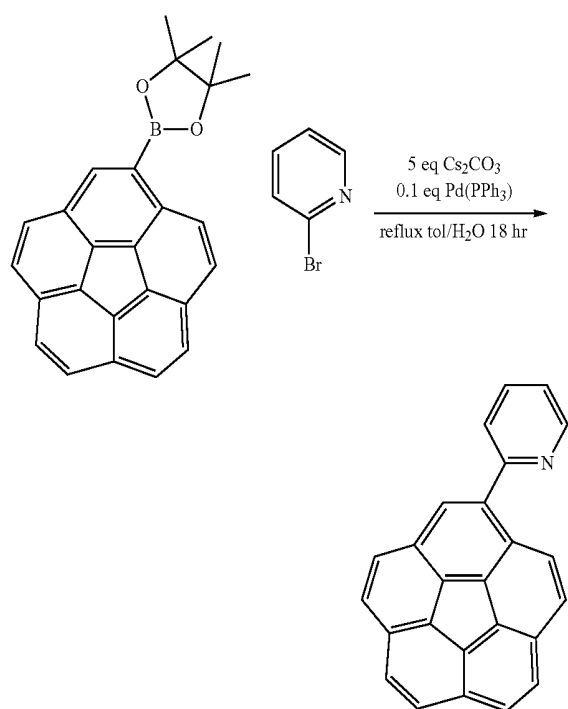
Synthesis of Compound 1

Step 1: Synthesis of 2-(dibenzo[ghi,mno]fluoranth-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

[0132] 2-(dibenzo[ghi,mno]fluoranth-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was synthesized following the procedure published by Wegner, H. A., Scott, L. T., Meijere, A., *J. Org. Chem.* 2003. 68 883-887.

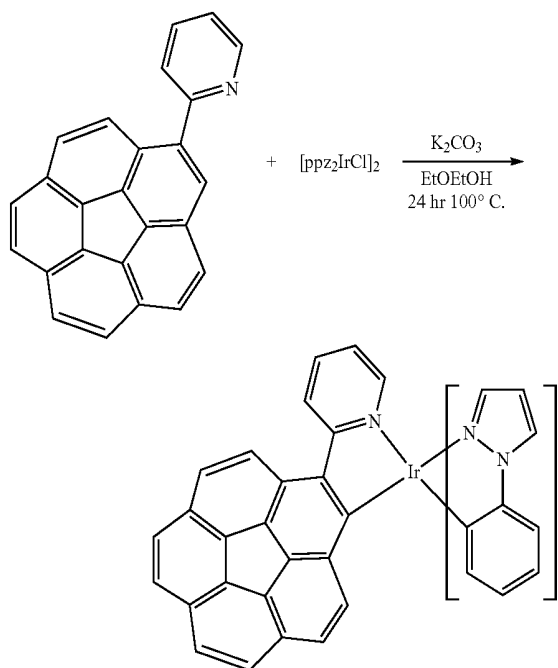
Step 2: Synthesis of 2-(dibenzo[ghi,mno]fluoranth-1-yl)pyridine

[0133]



[0134] A 3 neck flask was charged with 2-(dibenzo[ghi,mno]fluoranth-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (500 mg, 1.33 mmol), 2-bromopyridine (0.14 mL, 1.46 mmol), cesium carbonate (2.17 g, 6.66 mmol), and dissolved in 50 mL toluene and 6 mL water. A condenser was attached and the mixture was degassed for 40 minutes, then tetrakis(triphenylphosphine)palladium(0) (154 mg, 0.133 mmol) was added to the flask and the reaction mixture was heated to reflux for 18 hours. The mixture was then cooled to ambient temperature and concentrated in vacuo. Column chromatography on silica gel was performed on the resultant crude mixture using 85%:15% Hexanes:Ethyl Acetate, which yielded 2-(dibenzo[ghi,mno]fluoranth-1-yl)pyridine as a pale yellow solid (250 mg, 57% yield). The molecular weight was determined to be 327.35 g/mol by Matrix-assisted laser desorption/ionization. NMR results confirmed the presence of 2-(dibenzo[ghi,mno]fluoranth-1-yl)pyridine: ¹H NMR (400 MHz, chloroform-d₃, δ) 7.37 (m, 1H), 7.82 (m, 5H), 7.85 (d, 1H), 7.87 (d, 1H), 7.90 (m, 1H), 7.96 (m, 1H), 8.07 (d, 1H), 8.28 (s, 1H), 8.86 (m, 1H).

Step 3: Synthesis of Compound 1: [(corpy)Ir(ppz)₂]
[0135]

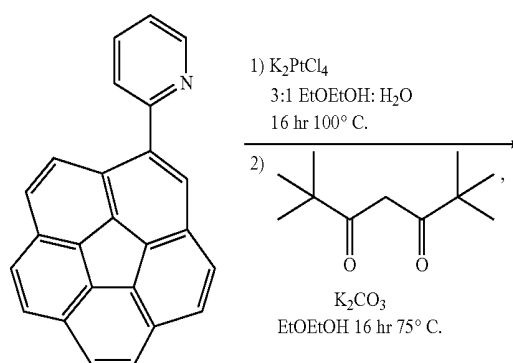


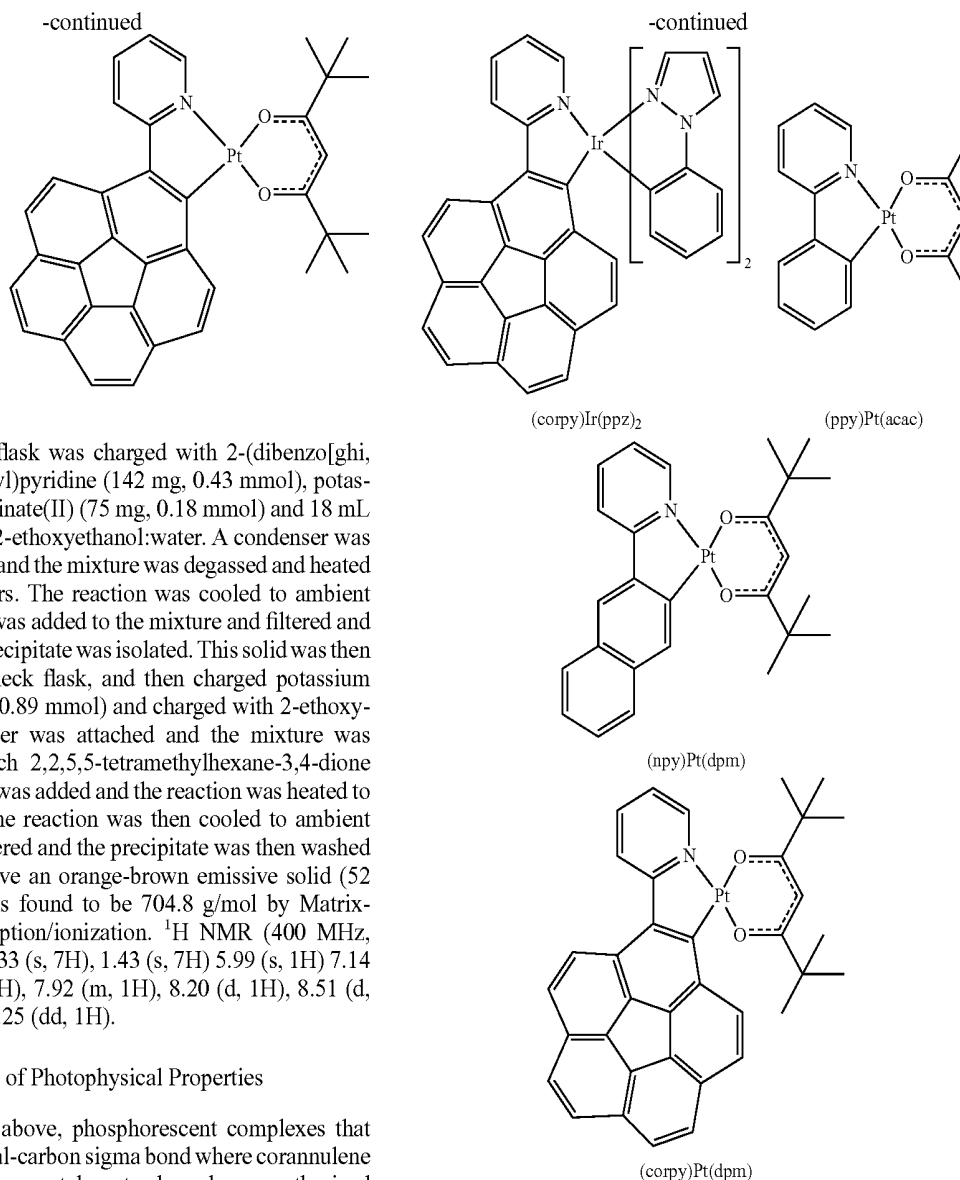
[0136] A 3-neck flask was charged with 2-(dibenzo[ghi,mno]fluoranth-1-yl)pyridine (65 mg, 0.20 mmol), [(ppz)₂Ir(μ-Cl)2Ir(ppz)₂] (100 mg, 0.1 mmol), potassium carbonate (116 mg, 0.84 mmol), and 12 mL of 2-ethoxyethanol. A condenser was attached to the flask and the reaction was degassed, then heated to 100° C. for 24 hrs. The reaction mixture was then cooled to ambient temperature and 10 mL of deionized water was added to dissolve excess potassium carbonate. An orange-red solid was vacuum filtered and washed with 10 mL of methanol and 10 mL hexanes, then air dried. Column chromatography on silica gel was performed on the resultant crude mixture (100% methylene chloride) to yield compound 1 as an orange-red emissive solid (36 mg, 75%). The molecular weight was determined to be 804.7 g/mol by Matrix-assisted laser desorption/ionization. NMR results confirmed the presence of compound 1: ¹H NMR (400 MHz, acetone-d₆, δ) 6.30 (dd, 1H), 6.43 (dd, 1H), 6.52 (dd, 1H), 6.57 (m, 2H), 6.68 (m, 1H), 6.80 (m, 1H), 6.87 (m, 1H), 6.94 (m, 1H), 6.99 (m, 1H), 7.13 (ddd, 1H), 7.32 (d, 1H), 7.51 (dd, 1H), 7.56 (m, 2H), 7.78 (d, 1H), 7.84 (d, 1H), 7.89 (m, 3H), 8.03 (m, 1H), 8.26 (m, 1H), 8.43 (m, 2H), 8.49 (dd, 1H), 8.99 (d, 1H).

Synthesis of Compound 2

Synthesis of Compound 2: [(corpy)Pt(dDm)]

[0137]





[0138] A 3 neck flask was charged with 2-(dibenzo[ghi, mno]fluoranthene-1-yl)pyridine (142 mg, 0.43 mmol), potassium tetrachloroplatinate(II) (75 mg, 0.18 mmol) and 18 mL of a 3:1 mixture of 2-ethoxyethanol:water. A condenser was attached to the flask and the mixture was degassed and heated to 100° C. for 16 hrs. The reaction was cooled to ambient temperature, water was added to the mixture and filtered and an orange-yellow precipitate was isolated. This solid was then added to a new 3 neck flask, and then charged potassium carbonate (124 mg, 0.89 mmol) and charged with 2-ethoxyethanol. A condenser was attached and the mixture was degassed after which 2,2,5,5-tetramethylhexane-3,4-dione (56 μ L, 0.27 mmol) was added and the reaction was heated to 75° C. for 16 hr. The reaction was then cooled to ambient temperature and filtered and the precipitate was then washed with methanol to give an orange-brown emissive solid (52 mg, 41%). MW was found to be 704.8 g/mol by Matrix-assisted laser desorption/ionization. ¹H NMR (400 MHz, chloroform-d₁, δ) 1.33 (s, 7H), 1.43 (s, 7H) 5.99 (s, 1H) 7.14 (m, 1H), 7.79 (m, 5H), 7.92 (m, 1H), 8.20 (d, 1H), 8.51 (d, 1H), 8.92 (d, 1H), 9.25 (dd, 1H).

Analysis of Photophysical Properties

[0139] As shown above, phosphorescent complexes that contain a single metal-carbon sigma bond where corannulene is cyclometalated to a metal center have been synthesized using techniques that provide the ability to synthesize a diverse set of corannulene ligands bonded to a metal center. These complexes have photophysical properties that are affected by bowl inversion of corannulene. By measuring the rate of bowl inversion, one can determine what amount of non-radiative decay is due to inversion, which has never been directly measured in metal complexes.

[0140] Examples of some corannulene complexes and comparative complexes are shown below:

[0141] These corannulene based ligands produce a smaller red shift than would be expected for the complexes. The conjugated π -system is greatly increased in the corannulene containing ligand compared to phenyl pyridine (ppy) and naphthyl pyridine (npv) complexes.

TABLE 1

Photophysical Data of Example Compounds			
Compound	λ_{max} (nm)	τ	QY
Compound 1: [(ppz) ₂ Ir(corpy)] in solution	678	1.64 μ s (64%)	0.022
[(ppz) ₂ Ir(corpy)] at 77K	578	9.42 μ s (36%)	—
		8.61 μ s (87%)	
		16.7 μ s (13%)	
Ir(ppy) ₃ in solution	508		
[(npv) ₂ Ir(acac)] in solution	600		
[(ppz) ₂ Ir(corpy)] in Poly(methyl methacrylate) (PMMA)	632	3.32 μ s (14%)	0.202
Compound 2: [(corpy)Pt(dpm)] in solution	660	8.17 μ s (86%)	0.053
		5.05 μ s	
[(corpy)Pt(dpm)] at 77k	598	14.1 μ s	—

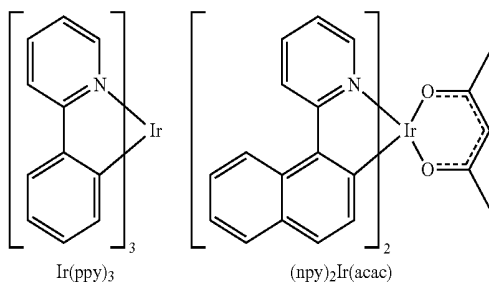


TABLE 1-continued

Photophysical Data of Example Compounds			
Compound	λ_{max} (nm)	τ	QY
[(corpy)Pt(dpm)] in PMMA	654	12.2 μ s	0.198
[(ppy)Pt(acac)] in solution	486		
[(npv)Pt(dpm)] in solution	560		

[0142] As shown in Table 1, the emission of corannulene pyridine complexes (corpy) is red shifted 50-100 nanometers from npy complexes. The modest size of this red shift relative to npy complexes is surprising, because the π -system of the corpy ligand is more than double the size of the npy ligand. The npy complexes have a single ring added, relative to ppy, and they give the same red shift of approximately 100 nm. The additional π -conjugation on corpy red shift the emission to nearly the same extent that a single fused ring did, on going from ppy to npy.

[0143] FIG. 4 shows a broad featureless red emission was observed for (corpy)Ir(ppz)₂ at room temperature in solution, with a biexponential decay of $\tau=1.64 \mu$ s (64%), 9.42 μ s (36%). At 77 K, (corpy)Ir(ppz)₂ produces a bright yellow emission shows distinct vibronic structure and the lifetime becomes a first order decay ($\tau=9.42 \mu$ s). In PMMA, (corpy)Ir(ppz)₂ produced an orange emission that was found to have relatively well defined band structure, again with a biexponential decay ($\tau=3.32 \mu$ s (14%), 8.17 μ s (86%)). The quantum yield is increased by an order of magnitude going from solution ($\Phi=0.02$) to a rigid matrix ($\Phi=0.20$) as the molecule becomes more constrained and less likely to non-radiatively decay.

[0144] FIG. 5 shows a broad featureless orange-red emission was observed for (corpy)Pt(dpm) at room temperature in solution, with a monoexponential lifetime of 5.05 μ s. At 77 K, (corpy)Pt(dpm) produced a bright yellow emission shows distinct vibronic structure ($\lambda_{max}=598$ nm, $\tau=14.1 \mu$ s) and the lifetime is almost triple in magnitude. In PMMA, (corpy)Pt(dpm) produced an orange emission found to have more ordered vibronic structure in between the spectra in solution and in 2-MeTHF glass ($\tau=12.2 \mu$ s). The quantum yield is increased by a factor of 4 going from solution ($\Phi=0.05$) to a rigid matrix ($\Phi=0.20$).

[0145] Although (corpy)Ir(ppz)₂ is slightly red-shifted from (corpy)Pt(dpm), the quantum yields of both platinum and iridium complexes are similar in both solution (5.3 vs 2.2) and PMMA (20 vs 20), which is not normally seen in heavy metal complexes with different metals and similar ligand sets. Non-radiative decay due to photoisomerization was ruled out as an explanation after the compound was irradiated by 252 nm light in acetonitrile and was found to show no change after 8 hrs. Thus, the property appears to be due to high non-radiative rates of the complexes that are both dictated by corannulene bowl inversion, leading to higher k_{nr} , resulting in low quantum yield in solution. However, their lifetimes differ in that (corpy)Ir(ppz)₂ is second order, while the platinum complex has a first order decay, which suggests two different emission states for (corpy)Ir(ppz)₂.

[0146] Crystals of (corpy)Pt(dpm) and (corpy)Ir(ppz)₂ were grown by slow diffusion of hexanes into dichloromethane of the metal complex. X ray diffraction analysis was carried out for both complexes. The unit cell of (corpy)Ir(ppz)₂ contains two (2) molecules of the complex, as well as, two dichloromethane molecules in a triclinic P1 space group. The structure is shown in FIG. 6. The iridium center has pseudo-octahedral geometry and the C¹N ligands are

found to coordinate in the mer orientation. Two diastereomers are observed within the crystal structure, i.e. Λ -P and the Δ -M where Λ and Δ describe the metal center and P and M describe the corannulene bowl chirality. The Ir—N(corpy) bond (2.1218(16) Å) is longer than the Ir—N(ppz) bonds (2.0147(16) and 2.0156(16) Å), but is comparable to other Ir—N (pyridyl) bonds in mer-complexes with phenyl pyridine ligands. Conversely, the Ir—C(corpy) bond (2.1033(18) Å) is longer than both Ir—C(ppz) bonds (2.0827(19) and 2.0184(19)) and other mer-complexes with phenyl pyridine, which average 2.087 Å. The C(corpy)—Ir—C(ppz) bond angle (170.86(7)°) and the N(ppz)—Ir—N(ppz) bond angle (174.19(6)°) are comparable to other mer-C¹N complexes.²

[0147] The structure of (corpy)Pt(dpm) is shown in FIG. 7. The unit cell of (corpy)Pt(dpm) contains 8 molecules in a monoclinic C 2/c space group. The corannulene bowl has a chirality of P as designated by the stereodescriptor system for chiral buckybowls based on fullerene nomenclature. The Pt complex has two chelating ligands in a pseudo-square planar geometry around the metal center, with deviations from ideal geometry most likely due to crystal packing forces. There are no metal-metal interactions, as the closest Pt—Pt distance is 5.65 Å. The bond lengths for Pt—C(1) (1.988(6) Å), Pt—N(1) (1.995(5) Å), Pt—O(1) (2.088(5) Å), and Pt—O(2) (2.021(4) Å) are slightly larger than the values reported for [(ppy)Pt(dpm)], and comparable with other Pt(β -ketonato derivatives). The bond angles for C(1)—Pt—N(1) (81.3(2)°) and O(1)—Pt—O(2) (89.98(18)°) were also found to be comparable with other cyclometalates of Pt. The bowl depth of corannulene was calculated to be 0.895 Å which is slightly deeper than the bowl depth of unsubstituted corannulene (0.87 Å).

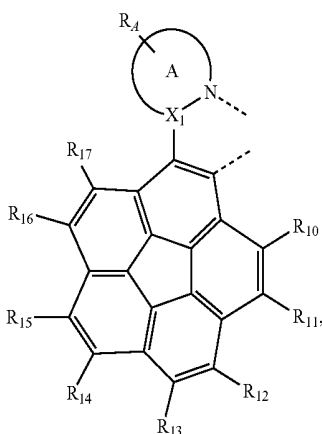
[0148] Variable temperature NMR was carried out on (corpy)Ir(ppz)₂ to determine the rate of inversion for the cyclometalated corannulene. The spectra at a range of temperatures, between room temperature and -70° C., are shown in FIG. 8. A combination of 2:1 deuterated dichloromethane: acetone was used for (corpy)Ir(ppz)₂, so that good separation of all proton peaks could be achieved while also maintaining solubility of the complex at lower temperatures. The (corpy)Ir(ppz)₂ sample exhibited a loss in coalescence not only at the most downfield corannulene resonances as the sample is cooled, but also at other proton resonances on the pyrazole ring. As shown in FIG. 8, VT NMR was performed between room temperature ($\sim 22^\circ$ C.) and $\sim 70^\circ$ C. As temperature decreases, the two most downfield resonances of corannulene broaden and then disappear into the baseline. The individual corannulene resonances are difficult to assign in the cold spectra due to extensive overlap. Kinetic analysis of the VT spectra was carried out using the pyrazole resonance at 6.3 ppm. This proton has an anisotropic chemical shift depending on the position of corannulene bowl. Corannulene has an intrinsic dipole where electron density is localized in the base of the corannulene bowl. Depending on whether the corannulene bowl is concave or convex to the pyrazole proton will dictate whether the proton is shielded due to the corannulene dipole or deshielded when the bowl is inverted. This fluxional behavior is seen as an average chemical shift at room temperature.

[0149] 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. The present invention as claimed may therefore include variations from the particular

examples and preferred embodiments described herein, as will be apparent to one of skill in the art. It is understood that various theories as to why the invention works are not intended to be limiting.

We claim:

1. A compound comprising a ligand L_A according to formula (I):



wherein ring A is a 5- or 6-membered heteroaryl ring;

wherein X_1 is C or N;

wherein R_A is mono-, bi-, tri-, tetradentate, or unsubstituted;

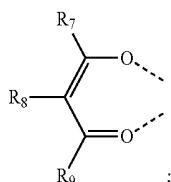
wherein R_A , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , R_{16} , and R_{17} are independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof;

wherein any adjacent substituents of R_A , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , R_{16} , and R_{17} are optionally joined to form a fused ring;

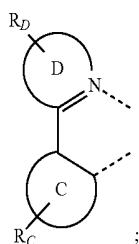
wherein the dashed lines represent bonds to a metal M; and wherein metal M has an atomic number greater than 40.

2. The compound of claim 1, wherein the compound has the structure $M(L_A)_x(L_B)_y(L_C)_z$:

wherein the ligand L_B is



wherein the ligand L_C is



wherein x is 1, 2, or 3;

wherein y is 0, 1, or 2;

wherein z is 0, 1, or 2;

wherein $x+y+z$ is the oxidation state of the metal M;

wherein R_7 and R_9 are independently selected from group consisting of hydrogen, alkyl, cycloalkyl, aryl, and heteroaryl;

wherein R_8 is selected from group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof;

wherein rings C and D are each independently a 5- or 6-membered carbocyclic or heterocyclic ring;

wherein R_C and R_D each independently represent mono, di, tri, or tetra substitution, or no substitution;

wherein each of R_C and R_D are independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof; and wherein any adjacent substituents of R_C and R_D are optionally joined to form a ring.

3. The compound of claim 2, wherein at least one of R_7 , R_8 , and R_9 has at least two C atoms.

4. The compound of claim 2, wherein y is 1 or 2.

5. The compound of claim 1, wherein the compound is homoleptic.

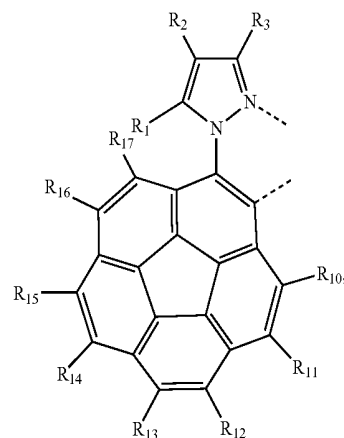
6. The compound of claim 1, wherein the compound is heteroleptic.

7. The compound of claim 1, wherein each R_A is independently selected from the group consisting of hydrogen, alkyl, aryl, and combinations thereof.

8. The compound of claim 1, wherein at least one R_A is selected from the group consisting of methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, cyclobutyl, cyclopentyl, cyclohexyl, partially or fully deuterated variants thereof, and combinations thereof.

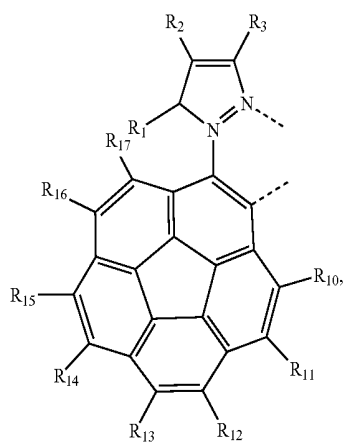
9. The compound of claim 1, wherein metal M is selected from the group consisting of Ir, Rh, Re, Ru, Os, Pt, Au, and Cu.

10. The compound of claim 1, wherein ligand L_A is selected from the group consisting of:

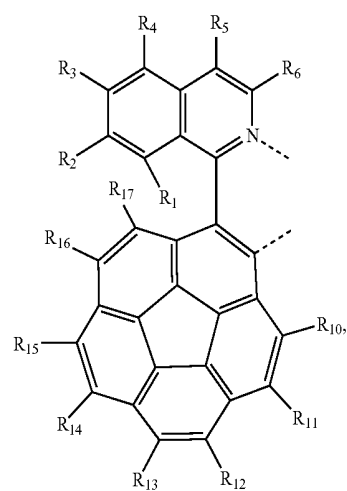
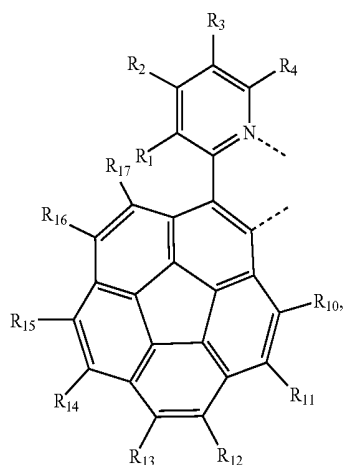
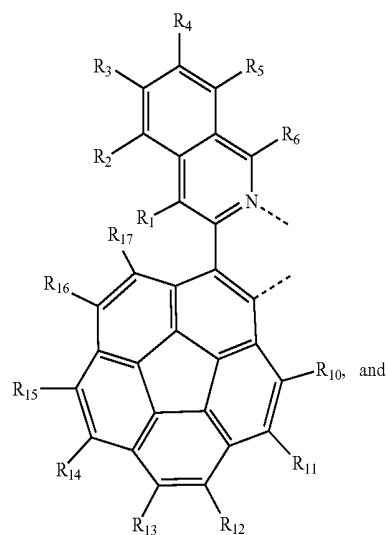
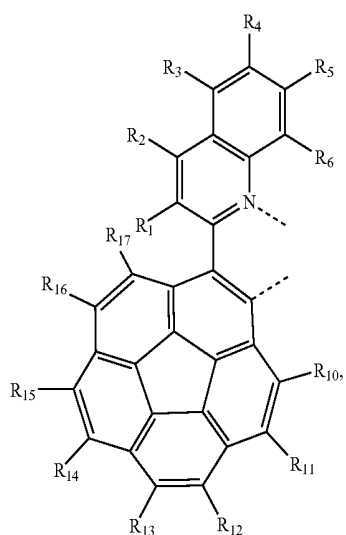
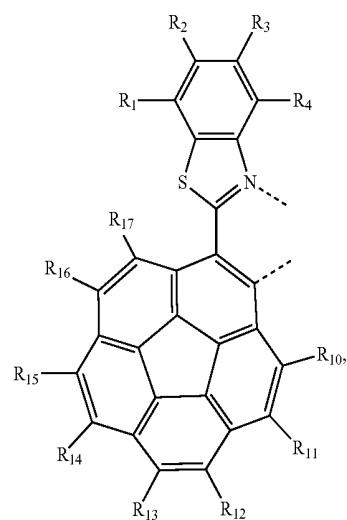


L_{A1}

-continued

L₄₂

-continued

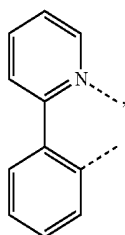
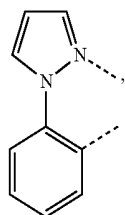
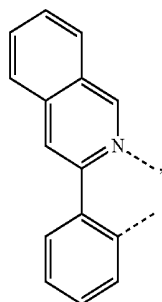
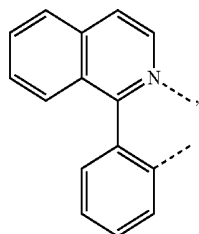
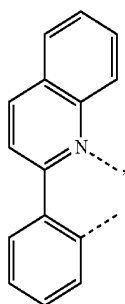
L₄₃L₄₄L₄₅L₄₆L₄₇

wherein R₁, R₂, R₃, R₄, R₅, and R₆ are independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, car-

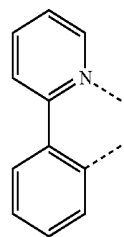
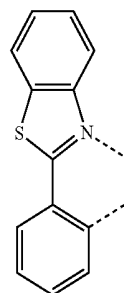
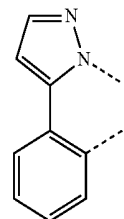
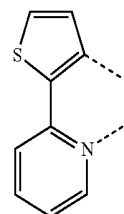
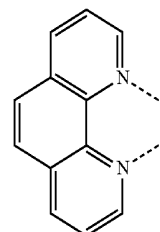
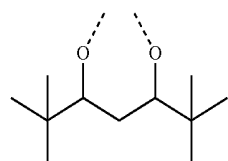
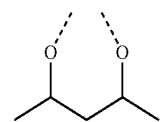
boxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof; and wherein any adjacent substituents of R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are optionally joined to form a fused ring.

11. The compound of claim **10**, wherein at least one of R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 is selected from the group consisting of ethyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, cyclobutyl, cyclopentyl, cyclohexyl, partially or fully deuterated variants thereof, and combinations thereof.

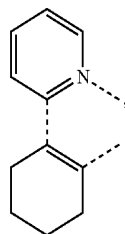
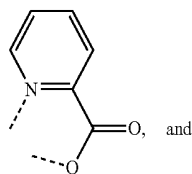
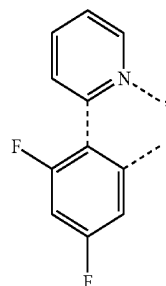
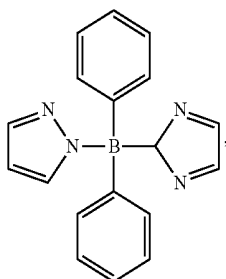
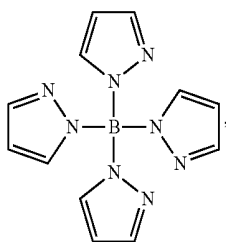
12. The compound of claim **1**, further comprising a ligand L_D bonded to the metal M, wherein the ligand L_D is selected from the group consisting of:

 L_{D1}  L_{D2}  L_{D3}  L_{D4}  L_{D5}

-continued

 L_{D6}  L_{D7}  L_{D8}  L_{D9}  L_{D10}  L_{D11}  L_{D12}

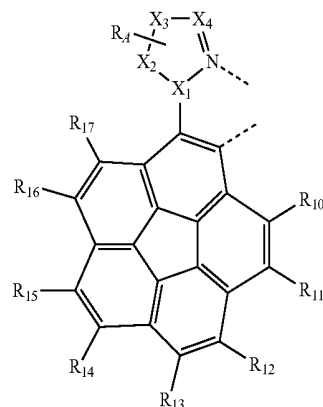
-continued



wherein L_{D13} is bonded to metal M by the N atoms ortho to boron to form a bidentate, tridentate, or tetradentate ligand, and

wherein L_{D14} is bonded to metal M by N atoms ortho to boron to form a bidentate ligand.

13. The compound of claim 1, wherein the ligand L_A has a structure according to formula (II):

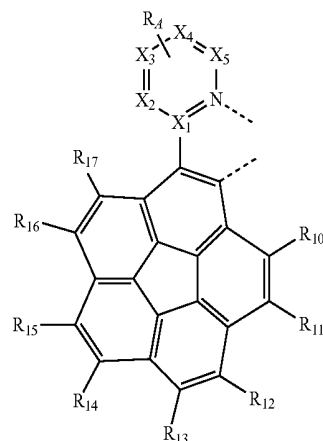
 L_{D13}  L_{D14}

wherein X_2 , X_3 , and X_4 are each independently C or N; wherein R_1 , R_2 , and R_3 are independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof;

 L_{D15}

wherein any adjacent substituents of R_1 , R_2 and R_3 are optionally joined to form a fused ring; and wherein R_A is mono-, bi-, tridentate, or unsubstituted.

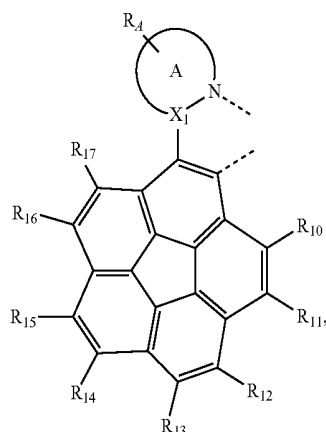
14. The compound of claim 1, wherein the ligand L_A has a structure according to formula (III):

 L_{D16}  L_{D17}

wherein X_2 , X_3 , X_4 , and X_5 are each independently C or N; wherein R_1 , R_2 , R_3 , and R_4 are independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof; and wherein any adjacent substituents of R_1 , R_2 , R_3 , and R_4 are optionally joined to form a fused ring.

15. A first device comprising a first organic light emitting device, the first organic light emitting device comprising:

an anode;
 a cathode; and
 an organic layer, disposed between the anode and the cathode, comprising a compound comprising a ligand L_A according to formula (I):



wherein ring A is a 5- or 6-membered heteroaryl ring;

wherein X_1 is C or N;

wherein R_A is mono-, bi-, tri-, tetradentate, or unsubstituted;

wherein R_A , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , R_{16} , and R_{17} are independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof;

wherein any adjacent substituents of R_A , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , R_{16} , and R_{17} are optionally joined to form a fused ring;

wherein the dashed lines represent bonds to a metal M; and
 wherein metal M has an atomic number greater than 40.

16. The first device of claim 15, wherein the first device is a consumer product.

17. The first device of claim 15, wherein the first device is an organic light emitting device.

18. The first device of claim 15, wherein the first device comprises a light panel.

19. The first device of claim 15, wherein the organic layer is an emissive layer and the compound is an emissive dopant.

20. The first device of claim 15, wherein the organic layer is an emissive layer and the compound is a non-emissive dopant.

21. The first device of claim 15, wherein the organic layer further comprises a host material.

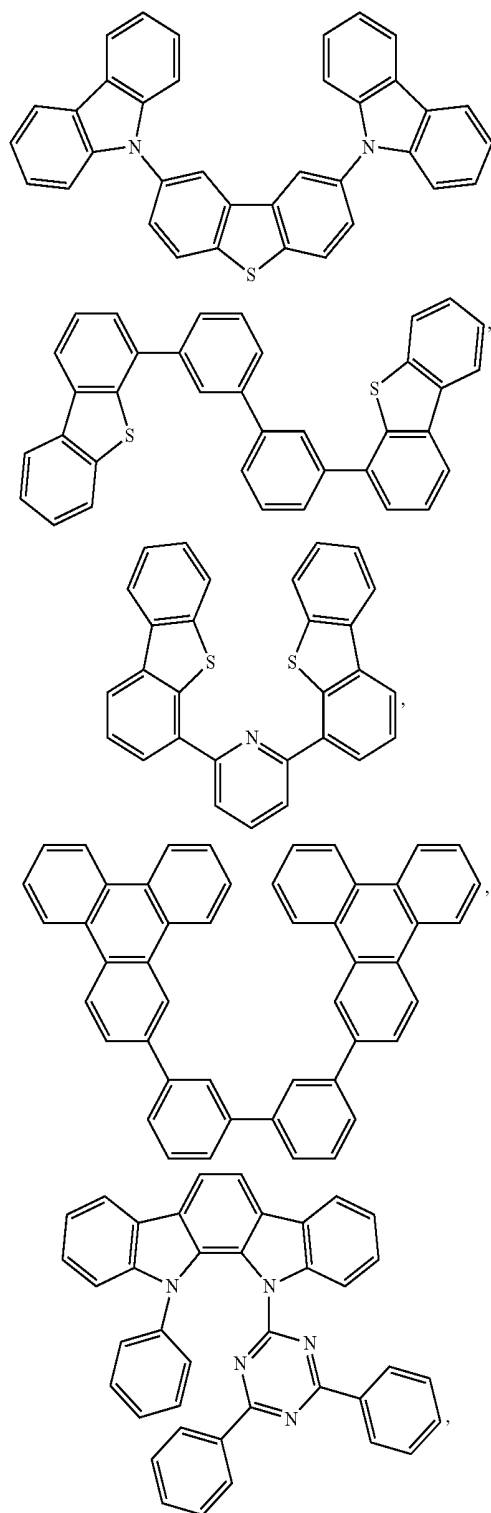
22. The first device of claim 21, wherein the host material comprises a triphenylene containing benzo-fused thiophene or benzo-fused furan;

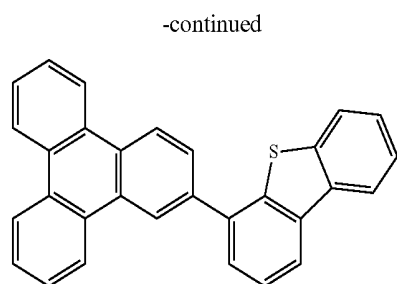
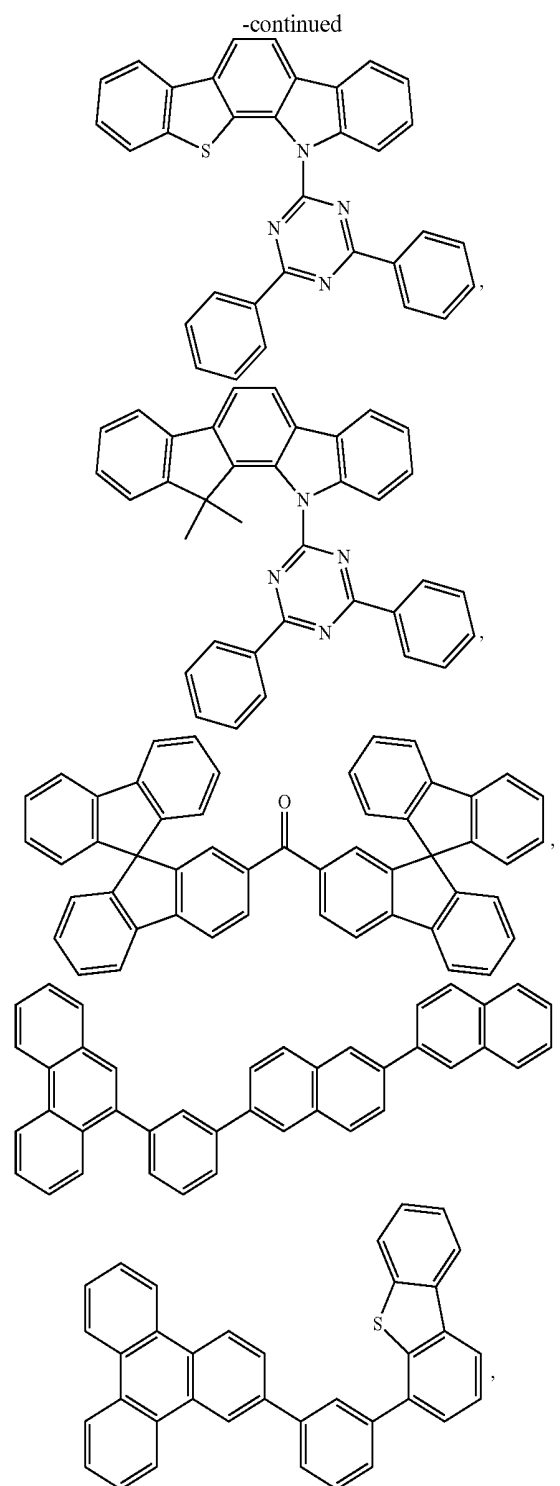
wherein any substituent in the host material is an unfused substituent independently selected from the group consisting of C_nH_{2n+1} , OC_nH_{2n+1} , OAr_1 , $N(C_nH_{2n+1})_2$, $N(Ar_1)(Ar_2)$, $CH=CH-C_nH_{2n+1}$, $C\equiv C-C_nH_{2n+1}$, Ar_1 , Ar_1-Ar_2 , and $C_nH_{2n}-Ar_1$, or no substitution; wherein n is from 1 to 10; and

wherein Ar_1 and Ar_2 are independently selected from the group consisting of benzene, biphenyl, naphthalene, triphenylene, carbazole, and heteroaromatic analogs thereof.

23. The first device of claim 21, wherein the host material comprises at least one chemical group selected from the group consisting of triphenylene, carbazole, dibenzothiophene, dibenzofuran, dibenzoselenophene, azatriphenylene, azacarbazole, aza-dibenzothiophene, aza-dibenzofuran, and aza-dibenzoselenophene.

24. The first device of claim 21, wherein the host material is selected from the group consisting of:

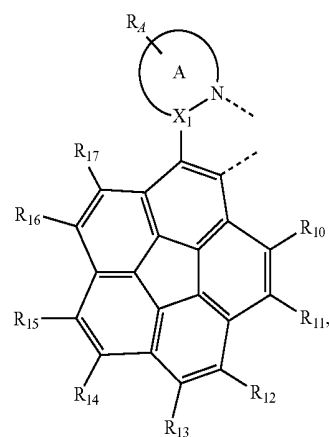




and combinations thereof.

25. The first device of claim **21**, wherein the host material comprises a metal complex.

26. A formulation comprising a compound comprising a ligand L_A according to formula (I):



wherein ring A is a 5- or 6-membered heteroaryl ring;

wherein X_1 is C or N;

wherein R_A is mono-, bi-, tri-, tetradentate, or unsubstituted;

wherein R_A , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , R_{16} , and R_{17} are independently selected from the group consisting of hydrogen, deuterium, halide, alkyl, cycloalkyl, heteroalkyl, arylalkyl, alkoxy, aryloxy, amino, silyl, alkenyl, cycloalkenyl, heteroalkenyl, alkynyl, aryl, heteroaryl, acyl, carbonyl, carboxylic acids, ester, nitrile, isonitrile, sulfanyl, sulfinyl, sulfonyl, phosphino, and combinations thereof;

wherein any adjacent substituents of R_A , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , R_{16} , and R_{17} are optionally joined to form a fused ring;

wherein the dashed lines represent bonds to a metal M; and wherein metal M has an atomic number greater than 40.

* * * * *

专利名称(译)	有机电致发光材料和器件		
公开(公告)号	US20150060830A1	公开(公告)日	2015-03-05
申请号	US14/475257	申请日	2014-09-02
[标]申请(专利权)人(译)	南加利福尼亚大学		
申请(专利权)人(译)	南加州大学		
当前申请(专利权)人(译)	南加州大学		
[标]发明人	THOMPSON MARK E FACENDOLA JOHN W DJUROVICH PETER I		
发明人	THOMPSON, MARK E. FACENDOLA, JOHN W. DJUROVICH, PETER I.		
IPC分类号	H01L51/00		
CPC分类号	H01L51/0085 H01L51/5024 H01L51/5012 H01L51/0087 C09K11/06 C09K2211/1011 C09K2211/1029 C09K2211/1037 C09K2211/1044 H01L51/5016 H05B33/14		
优先权	61/872871 2013-09-03 US		
其他公开文献	US10199582		
外部链接	Espacenet USPTO		

摘要(译)

包含根据式 (I) 的配体L A 的化合物 以及第一装置和包括其的配方公开了。在式 (I) 的结构中：环A是5-或6-元杂芳基环；X₁ 是C或N；R_A 是单 - ，双 - ，三 - ，四齿或未取代的；R_A ， R₁₀ ， R₁₁ ， R₁₂ ， R₁₃ ， R₁₄ ， R₁₅ ， R₁₆ ， R₁₇ 独立地选自氢，氘，卤化物，烷基，环烷基，杂烷基，芳烷基，烷氧基，芳氧基，氨基，甲硅烷基，链烯基，环烯基，杂烯基，炔基，芳基，杂芳基，酰基，羰基，羧酸，酯，腈，异腈，硫烷基，亚磺酰基，磺酰基，膦基及其组合，R_A ， R₁₀ ， R₁₁ ， R₁₂ 的任何相邻取代基，R₁₃ ， R₁₄ ， R₁₅ ， R₁₆ ， R₁₇ 任选地连接形成稠环；虚线表示与金属M的键合；金属M的原子序数大于40。

