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(54) **Stable and efficient electroluminescent materials**

Stabile und leistungsstarke Elektrolumineszenzmaterialien

Matériaux électroluminescents stables et efficaces

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Description

[0001] The present invention relates to organic light emitting devices (OLEDs), and more specifically to phosphorescent organic materials used in such devices. More specifically, the present invention relates to phosphorescent emitting materials with improved electroluminescent efficiency when incorporated into an OLED.

Background

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

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

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

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

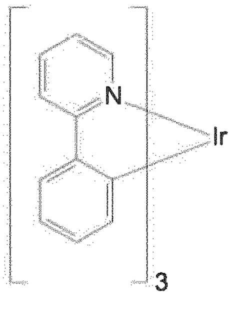
[0006] As used herein, "top" means furthest away from the substrate, while "bottom" means closest to the substrate. For example, for a device having two electrodes, the bottom electrode is the electrode closest to the substrate, and is generally the first electrode fabricated. The bottom electrode has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

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

[0008] As used herein, a first "Highest Occupied Molecular Orbital" (HOMO) or "Lowest Unoccupied Molecular Orbital" (LUMO) energy level is "greater 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 greater HOMO corresponds to an IP having a smaller absolute value (an IP that is less negative). Similarly, a greater LUMO 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 of a material is higher than the HOMO of the same material. A "greater" HOMO or LUMO appears closer to the top of such a diagram than a "lesser" HOMO or LUMO.

[0009] 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.

[0010] One example of a green emissive molecule is tris(2-phenylpyridine) iridium, denoted Ir(ppy)$_3$, which has the structure:



[0011] In this, and later figures herein, the dative bond from nitrogen to metal (here, Ir) is depicted in metal complexes as a straight line. Ir(ppy)$_3$ emits a spectrum at CIE 0.30, 0.63, and has a half-life of about 10,000 hours at an initial luminance of 500 cd/m^2, and a quantum efficiency of about 6 %. Kwong et al., Appl. Phys. Lett., 81, 162 (2002).

[0012] Industry standards call for the lifetime of full color displays to be at least about 5000 hours. In addition, high stability and efficiency are important characteristics of high quality displays. These requirements have helped generate a need for phosphorescent emissive materials that exhibit longer lifetimes, higher stability, and higher efficiency in the red, green and blue wavelength regimes than have been achieved in the prior art. Phosphorescent materials with improved device efficiency and stability are disclosed herein.

Summary of the Invention

[0013] An organic light emitting device is provided. The device has an anode, a cathode, and an emissive layer disposed between the anode and the cathode. The emissive layer further comprises an emissive material having the structure as defined in claim 1.

[0014] The emissive material itself is also provided. The emissive material may have improved efficiency and stability when incorporated into a light emitting device. In particular, the devices of the present invention may exhibit dramatically improved efficiency over known devices.

Brief Description of the Drawings

[0015]

Fig. 1 shows an organic light emitting device having separate electron transport, hole transport, and emissive layers, as well as other layers.

Fig. 2 shows an inverted organic light emitting device that does not have a separate electron transport layer.

Detailed Description

[0016] 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.

[0017] The initial OLEDs used emissive molecules that emitted light from their singlet states ("fluorescence") as disclosed, for example, in U.S. Patent No. 4,769,292. Fluorescent emission generally occurs in a time frame of less than 10 nanoseconds.

[0018] More recently, OLEDs having emissive materials that emit light from triplet states ("phosphorescence") have been demonstrated. Baldo et al., "Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices," Nature, vol. 395, 151-154, 1998; ("Baldo-I") and Baldo et al., "Very high-efficiency green organic light-emitting devices based on electrophosphorescence," Appl. Phys. Lett., vol. 75, No. 3, 4-6 (1999) ("Baldo-II"). Phosphorescence may be referred to as a "forbidden" transition because the transition requires a change in spin states, and quantum mechanics indicates that such a transition is not favored. As a result, phosphorescence generally occurs in a time frame exceeding at least 10 nanoseconds, and typically greater than 100 nanoseconds. If the natural radiative lifetime of phosphorescence is too long, triplets may decay by a non-radiative mechanism, such that no light is emitted. Organic phosphorescence is also often observed in molecules containing heteroatoms with unshared pairs of electrons at very low temperatures. 2,2’-bipyridine is such a molecule. Non-radiative decay mechanisms are typically temperature dependent, such that a material that exhibits phosphorescence at liquid nitrogen temperatures may not exhibit phosphorescence at room temperature. But, as demonstrated by Baldo, this problem may be addressed by selecting phosphorescent compounds that do phosphoresce at room temperature. Representative emissive layers include doped or un-doped phosphorescent organo-metallic materials such as disclosed in U.S. Patent Nos. 6,303,238 and 6,310,360; U.S. Patent Application Publication Nos. 2002-0034656; 2002-0182441; and 2003-0072964; and WO-02/074015.

[0019] Generally, the excitons in an OLED are believed to be created in a ratio of about 3:1, *i.e.,* approximately 75% triplets and 25% singlets. See, Adachi et al., "Nearly 100% Internal Phosphorescent Efficiency In An Organic Light Emitting Device," J. Appl. Phys., 90, 5048 (2001). In many cases, singlet excitons may readily transfer their energy to triplet excited states via "intersystem crossing," whereas triplet excitons may not readily transfer their energy to singlet excited states. As a result, 100% internal quantum efficiency is theoretically possible with phosphorescent OLEDs. In a fluorescent device, the energy of triplet excitons is generally lost to radiationless decay processes that heat-up the device, resulting in much lower internal quantum efficiencies. OLEDs utilizing phosphorescent materials that emit from triplet excited states are disclosed, for example, in U.S. Patent No. 6,303,238.

[0020] Phosphorescence may be preceded by a transition from a triplet excited state to an intermediate non-triplet state from which the emissive decay occurs. For example, organic molecules coordinated to lanthanide elements often phosphoresce from excited states localized on the lanthanide metal. However, such materials do not phosphoresce directly from a triplet excited state but instead emit from an atomic excited state centered on the lanthanide metal ion. The europium diketonate complexes illustrate one group of these types of species.

[0021] Phosphorescence from triplets can be enhanced over fluorescence by confining, preferably through bonding, the organic molecule in close proximity to an atom of high atomic number. This phenomenon, called the heavy atom effect, is created by a mechanism known as spin-orbit coupling. Such a phosphorescent transition may be observed from an excited metal-to-ligand charge transfer (MLCT) state of an organometallic molecule such as tris(2-phenylpyridine)iridium(III).

[0022] As used herein, the term "triplet energy" refers to an energy corresponding to the highest energy feature discernable in the phosphorescence spectrum of a given material. The highest energy feature is not necessarily the peak having the greatest intensity in the phosphorescence spectrum, and could, for example, be a local maximum of a clear shoulder on the high energy side of such a peak.

[0023] The term "organometallic" as used herein is as generally understood by one of ordinary skill in the art and as given, for example, in "Inorganic Chemistry" (2nd Edition) by Gary L. Miessler and Donald A. Tarr, Pentice-Hall (1998). Thus, the term organometallic refers to compounds which have an organic group bonded to a metal through a carbon-metal bond. This class does not include per se coordination compounds, which are substances having only donor bonds from heteroatoms, such as metal complexes of anines, halides, pseudohalides (CN, etc.), and the like. In practice organometallic compounds generally comprise, in addition to one or more carbon-metal bonds to an organic species, one or more donor bonds from a heteroatom. The carbon-metal bond to an organic species refers to a direct bond between a metal and a carbon atom of an organic group, such as phenyl, alkyl, alkenyl, etc., but does not refer to a metal bond to an "inorganic carbon," such as the carbon of CN.

[0024] 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 (ETL) 145, an electron injection layer 150, a protective layer 155, and a cathode 160. Cathode 160 is a compound cathode having a first conductive layer 162 and a second conductive layer 164. Device 100 may be fabricated by depositing the layers described, in order.

[0025] Substrate 110 may be any suitable substrate that provides desired structural properties. Substrate 110 may be flexible or rigid. Substrate 110 may be transparent, translucent or opaque. Plastic and glass are examples of preferred rigid substrate materials. Plastic and metal foils are examples of preferred flexible substrate materials. Substrate 110 may be a semiconductor material in order to facilitate the fabrication of circuitry. For example, substrate 110 may be a silicon wafer upon which circuits are fabricated, capable of controlling OLEDs subsequently deposited on the substrate. Other substrates may be used. The material and thickness of substrate 110 may be chosen to obtain desired structural and optical properties.

[0026] Anode 115 may be any suitable anode that is sufficiently conductive to transport holes to the organic layers. The material of anode 115 preferably has a work function higher than about 4 eV (a "high work function material"). Preferred anode materials include conductive metal oxides, such as indium tin oxide (ITO) and indium zinc oxide (IZO), aluminum zinc oxide (AlZnO), and metals. Anode 115 (and substrate 110) may be sufficiently transparent to create a bottom-emitting device. A preferred transparent substrate and anode combination is commercially available ITO (anode) deposited on glass or plastic (substrate). A flexible and transparent substrate-anode combination is disclosed in United States Patent Nos. 5,844,363 and 6,602,540 B2. Anode 115 may be opaque and / or reflective. A reflective anode 115 may be preferred for some top-emitting devices, to increase the amount of light emitted from the top of the device. The material and thickness of anode 115 may be chosen to obtain desired conductive and optical properties. Where anode 115 is transparent, there may be a range of thickness for a particular material that is thick enough to provide the desired conductivity, yet thin enough to provide the desired degree of transparency. Other anode materials and structures may be used.

[0027] Hole transport layer 125 may include a material capable of transporting holes. Hole transport layer 130 may be intrinsic (undoped), or doped. Doping may be used to enhance conductivity. α-NPD and TPD are examples of intrinsic hole transport layers. An example of a p-doped hole transport layer is m-MTDATA doped with F_4-TCNQ at a molar ratio of 50:1, as disclosed in United States Patent Application Publication No. 2002-0071963 A1 to Forrest et al., which is incorporated by reference in its entirety. Other hole transport layers may be used.

[0028] Emissive layer 135 may include an organic material capable of emitting light when a current is passed between anode 115 and cathode 160. Preferably, emissive layer 135 contains a phosphorescent emissive material, although fluorescent emissive materials may also be used. Phosphorescent materials are preferred because of the higher luminescent efficiencies associated with such materials. Emissive layer 135 may also comprise a host material capable of transporting electrons and / or holes, doped with an emissive material that may trap electrons, holes, and / or excitons, such that excitons relax from the emissive material via a photoemissive mechanism. Emissive layer 135 may comprise a single material that combines transport and emissive properties. Whether the emissive material is a dopant or a major constituent, emissive layer 135 may comprise other materials, such as dopants that tune the emission of the emissive material. Emissive layer 135 may include a plurality of emissive materials capable of, in combination, emitting a desired spectrum of light. Examples of phosphorescent emissive materials include $Ir(ppy)_3$. Examples of fluorescent emissive materials include DCM and DMQA. Examples of host materials include Alq_3, CBP and mCP. Examples of emissive and host materials are disclosed in U.S. Patent No. 6,303,238 to Thompson et al. Emissive material may be included in emissive layer 135 in a number of ways. For example, an emissive small molecule may be incorporated into a polymer. For example, an emissive small molecule may be incorporated into a polymer. This may be accomplished by several ways: by doping the small molecule into the polymer either as a separate and distinct molecular species; or by incorporating the small molecule into the backbone of the polymer, so as to form a co-polymer; or by bonding the small molecule as a pendant group on the polymer. Other emissive layer materials and structures may be used. For example, a small molecule emissive material may be present as the core of a dendrimer.

[0029] Many useful emissive materials include one or more ligands bound to a metal center. A ligand may be referred to as "photoactive" if it contributes directly to the photoactive properties of an organometallic emissive material. A "photoactive" ligand may provide, in conjunction with a metal, the energy levels from which and to which an electron moves when a photon is emitted. Other ligands may be referred to as "ancillary." Ancillary ligands may modify the photoactive properties of the molecule, for example by shifting the energy levels of a photoactive ligand, but ancillary ligands do not directly provide the energy levels directly involved in light emission. A ligand that is photoactive in one molecule may be ancillary in another. These definitions of photoactive and ancillary are intended as non-limiting theories.

[0030] Electron transport layer (ETL) 140 may include a material capable of transporting electrons. Electron transport layer 140 may be intrinsic (undoped), or doped. Doping may be used to enhance conductivity. Alq_3 is an example of an intrinsic electron transport layer. An example of an n-doped electron transport layer is BPhen doped with Li at a molar ratio of 1:1, as disclosed in United States Patent Application Publication No. 2002-0071963 A1 to Forrest et al. Other electron transport layers may be used.

[0031] The charge carrying component of the electron transport layer may be selected such that electrons can be efficiently injected from the cathode into the LUMO (Lowest Unoccupied Molecular Orbital) level of the electron transport layer. The "charge carrying component" is the material responsible for the LUMO that actually transports electrons. This component may be the base material, or it may be a dopant. The LUMO level of an organic material may be generally characterized by the electron affinity of that material and the relative electron injection efficiency of a cathode may be generally characterized in terms of the work function of the cathode material. This means that the preferred properties of an electron transport layer and the adjacent cathode may be specified in terms of the electron affinity of the charge carrying component of the ETL and the work function of the cathode material. In particular, so as to achieve high electron injection efficiency, the work function of the cathode material is preferably not greater than the electron affinity of the charge carrying component of the electron transport layer by more than about 0.75 eV, more preferably, by not more than about 0.5 eV. Similar considerations apply to any layer into which electrons are being injected.

[0032] Cathode 160 may be any suitable material or combination of materials known to the art, such that cathode 160 is capable of conducting electrons and injecting them into the organic layers of device 100. Cathode 160 may be transparent or opaque, and may be reflective. Metals and metal oxides are examples of suitable cathode materials. Cathode 160 may be a single layer, or may have a compound structure. Figure 1 shows a compound cathode 160 having a thin metal layer 162 and a thicker conductive metal oxide layer 164. In a compound cathode, preferred materials for the thicker layer 164 include ITO, IZO, and other materials known to the art. U.S. Patent Nos. 5,703,436, 5,707,745, 6,548,956 B2 and 6,576,134 B2 disclose examples of cathodes including compound cathodes having a thin layer of metal such as Mg:Ag with an overlying transparent, electrically-conductive, sputter-deposited ITO layer. The part of cathode 160 that is in contact with the underlying organic layer, whether it is a single layer cathode 160, the thin metal layer 162 of a compound cathode, or some other part, is preferably made of a material having a work function lower than about 4 eV (a "low work function material"). Other cathode materials and structures may be used.

[0033] Blocking layers may be used to reduce the number of charge carriers (electrons or holes) and / or excitons that leave the emissive layer. An electron blocking layer 130 may be disposed between emissive layer 135 and the hole transport layer 125, to block electrons from leaving emissive layer 135 in the direction of hole transport layer 125. Similarly, a hole blocking layer 140 maybe disposed between emissive layer 135 and electron transport layer 145, to block holes from leaving emissive layer 135 in the direction of electron transport layer 140. Blocking layers may also be used to block excitons from diffusing out of the emissive layer. The theory and use of blocking layers is described in more detail in United States Patent No. 6,097,147 and United States Patent Application Publication No. 2002-0071963 A1 to Forrest et al.

[0034] As used herein, the term "blocking layer" means that the layer provides a barrier that significantly inhibits transport of charge carriers and/or excitons through the device, without suggesting that the layer necessarily completely blocks the charge carriers and/or excitons. The presence of such a blocking layer in a device may result in substantially higher efficiencies as compared to a similar device lacking a blocking layer. Also, a blocking layer may be used to confine emission to a desired region of an OLED.

[0035] Generally, injection layers are comprised of a material that may improve the injection of charge carriers from one layer, such as an electrode or an organic layer, into an adjacent organic layer. Injection layers may also perform a charge transport function. In device 100, hole injection layer 120 may be any layer that improves the injection of holes from anode 115 into hole transport layer 125. CuPc is an example of a material that may be used as a hole injection layer from an ITO anode 115, and other anodes. In device 100, electron injection layer 150 may be any layer that improves the injection of electrons into electron transport layer 145. LiF / A1 is an example of a material that may be used as an electron injection layer into an electron transport layer from an adjacent layer. Other materials or combinations of materials may be used for injection layers. Depending upon the configuration of a particular device, injection layers may be disposed at locations different than those shown in device 100. More examples of injection layers are provided in U.S. Patent Application Serial No. 09/931,948 to Lu et al. A hole injection layer may comprise a solution deposited material, such as a spin-coated polymer, e.g., PEDOT:PSS, or it may be a vapor deposited small molecule material, e.g., CuPc or MTDATA.

[0036] A hole injection layer (HIL) may planarize or wet the anode surface so as to provide efficient hole injection from the anode into the hole injecting material. A hole injection layer may also have a charge carrying component having HOMO (Highest Occupied Molecular Orbital) energy levels that favorably match up, as defined by their herein-described relative ionization potential (IP) energies, with the adjacent anode layer on one side of the HIL and the hole transporting layer on the opposite side of the HIL. The "charge carrying component" is the material responsible for the HOMO that actually transports holes. This component may be the base material of the HIL, or it may be a dopant. Using a doped HIL allows the dopant to be selected for its electrical properties, and the host to be selected for morphological properties such as wetting, flexibility, toughness, etc. Preferred properties for the HIL material are such that holes can be efficiently injected from the anode into the HIL material. In particular, the charge carrying component of the HIL preferably has an IP not more than about 0.7 eV greater that the IP of the anode material. More preferably, the charge carrying component has an IP not more than about 0.5 eV greater than the anode material. Similar considerations apply to any layer into which holes are being injected. HIL materials are further distinguished from conventional hole transporting materials that are typically used in the hole transporting layer of an OLED in that such HIL materials may have a hole conductivity that is substantially less than the hole conductivity of conventional hole transporting materials. The thickness of the HIL of the present invention may be thick enough to help planarize or wet the surface of the anode layer. For example, an HIL thickness of as little as 10 nm may be acceptable for a very smooth anode surface. However, since anode surfaces tend to be very rough, a thickness for the HIL of up to 50 nm may be desired in some cases.

[0037] A protective layer may be used to protect underlying layers during subsequent fabrication processes. For example, the processes used to fabricate metal or metal oxide top electrodes may damage organic layers, and a protective layer may be used to reduce or eliminate such damage. In device 100, protective layer 155 may reduce damage to underlying organic layers during the fabrication of cathode 160. Preferably, a protective layer has a high carrier mobility for the type of carrier that it transports (electrons in device 100), such that it does not significantly increase the operating voltage of device 100. CuPc, BCP, and various metal phthalocyanines are examples of materials that may be used in protective layers. Other materials or combinations of materials may be used. The thickness of protective layer 155 is preferably thick enough that there is little or no damage to underlying layers due to fabrication processes that occur after organic protective layer 160 is deposited, yet not so thick as to significantly increase the operating voltage of device 100. Protective layer 155 may be doped to increase its conductivity. For example, a CuPc or BCP protective layer 160 may be doped with Li. A more detailed description of protective layers may be found in U.S. Patent Application Serial No. 09/931,948 to Lu et al.

[0038] Figure 2 shows an inverted OLED 200. The device includes a substrate 210, an cathode 215, an emissive layer 220, a hole transport layer 225, and an anode 230. Device 200 may be fabricated by depositing the layers described, in order. Because the most common OLED configuration has a cathode disposed over the anode, and device 200 has cathode 215 disposed under anode 230, device 200 may be referred to as an "inverted" OLED. Materials similar to those described with respect to device 100 may be used in the corresponding layers of device 200. Figure 2 provides one example of how some layers may be omitted from the structure of device 100.

[0039] The simple layered structure illustrated in Figures 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 Figures 1 and 2.

[0040] Structures and materials not specifically described may also be used, such as OLEDs comprised of polymeric materials (PLEDs) such as disclosed in U.S. Pat. No. 5,247,190, Friend et al. 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. Patent No. 5,707,745 to Forrest et al. The OLED structure may deviate from the simple layered structure illustrated in Figures 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. Patent No. 6,091,195 to Forrest et al., and / or a pit structure as described in U.S. Patent No. 5,834,893 to Bulovic et al.

[0041] 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. Patent Nos. 6,013,982 and 6,087,196, organic vapor phase deposition (OVPD), such as described in U.S. Patent No. 6,337,102 to Forrest et al., and deposition by organic vapor jet printing (OVJP), such as described in U.S. Patent Application No. 10/233,470. 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. Patent Nos. 6,294,398 and 6,468,819, and patterning associated with some of the deposition methods such as ink-jet and OVJD. Other methods may also be used. The materials to be deposited may be modified to make them compatible with a particular deposition method. For example, substituents such as alkyl and aryl groups, branched or unbranched, and preferably containing at least 3 carbons, may be used in small molecules to enhance their ability to undergo solution processing. Substituents having 20 carbons or more may be used, and 3-20 carbons is a preferred range. Materials with asymmetric structures may have better solution processibility than those having symmetric structures, because asymmetric materials may have a lower tendency to recrystallize. Dendrimer substituents may be used to enhance the ability of small molecules to undergo solution processing.

[0042] Devices fabricated in accordance with embodiments of the invention may be incorporated into a wide variety of consumer products, including flat panel displays, computer monitors, televisions, billboards, lights for interior or exterior illumination and / or signaling, heads up displays, fully transparent displays, flexible displays, laser printers, telephones, cell phones, personal digital assistants (PDAs), laptop computers, digital cameras, camcorders, viewfinders, micro-displays, vehicles, a large area wall, theater or stadium screen, or a sign. Various control mechanisms may be used to control devices fabricated in accordance with the present invention, including passive matrix and active matrix. Many of the devices are intended for use in a temperature range comfortable to humans, such as 18 degrees C to 30 degrees C, and more preferably at room temperature (20 - 25 degrees C).

[0043] 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.

[0044] Phosphorescent OLEDs with unexpected and exceptionally high device efficiency are disclosed herein. In some embodiments, the phosphorescent dopants used are Ir(5'-alkyl-2-phenylpyridine) type metal complexes. Many alkyl substituted on Ir(2-phenylpyridine) complexes are known. However, we have found that 5'-alkyl substituted analogs have unexpected properties such that, when they are incorporated into an organic light emitting device, unexpected results are attained. By incorporating the phosphorescent materials of the present invention into organic light emitting devices (OLEDs), unexpected and exceptionally high device efficiencies have been demonstrated.

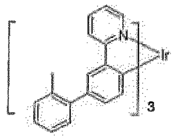
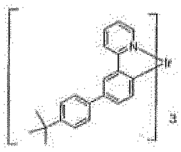
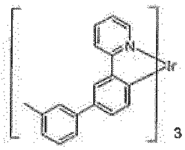
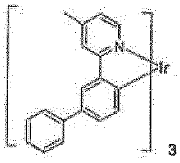
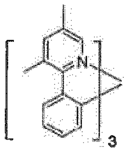
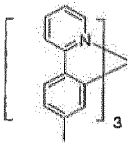
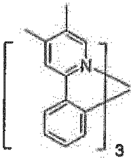
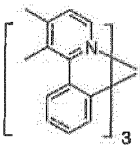
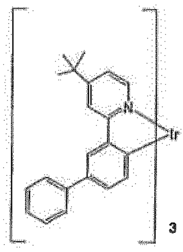
[0045] As used herein, the term "external quantum efficiency" refers to the percentage of charge carriers injected into a device that result in the emission of a photon from the device in the forward direction. A number of factors can affect the external quantum efficiency, including the "internal quantum efficiency," which is the percentage of charge carriers injected into a device that result in the creation of a photon, and the "outcoupling efficiency," which is the percentage of photons created that are emitted from a device towards a viewer. In some embodiments of the present invention an organic layer comprising a 5'alkyl substituted dopant (with and without an aromatic hydrocarbon layer (HPT) that is in direct contact with an emissive layer) may enhance the internal quantum efficiency and thus the external quantum efficiency of the device. Because external quantum efficiency is more readily and directly measured than internal quantum efficiency, it may be desirable to describe certain aspects of the invention with respect to external quantum efficiency. But, in order to determine whether an enhanced external quantum efficiency is due to the use of an alkyl substituent at position 5', it is preferable to account for other factors that affect external quantum efficiency. The term "unmodified external quantum efficiency" as used herein refers to the external quantum efficiency of a device, after multiplication by a factor to account for any differences in the outcoupling efficiency of that device and the outcoupling efficiency of the devices described experimentally herein. For example, a device having an external quantum efficiency of 5%, but having an outcoupling efficiency 3 times better than the devices described herein, would have an "unmodified external quantum efficiency" of 1.33% (one third of 5%). A typical outcoupling efficiency for the types of devices described herein is about 20-30%. There are device structures having better outcoupling efficiencies than the devices described herein, and it is anticipated that improvements to outcoupling efficiency will be made over time. Such improvements would enhance external quantum efficiency, but should not affect "unmodified" external quantum efficiency, and devices having such improvements may fall within the scope of the present invention.

[0046] "Stability" may be measured in a number of ways. One stability measurement is the operational stability of the electroluminescent device which can be measured in terms of operational half-life. The operational half-life is the time required for the luminance of the device to decay from the initial luminance (L_0) to 50% of its initial luminance ($L_{0.5}$) under constant current and at room temperature unless otherwise noted. Operational half-life depends upon luminance at which the device is operated, because a higher luminance generally corresponds to a faster decay in a particular device. Luminance may be measured in cd/m^2. Devices in accordance with embodiments of the present invention can advantageously have an operational half-life in excess of about 50 hours, preferably about 100 hours, more preferably about 200 hours at initial luminance of about 10,700 cd/m^2 preferably about 12,000 cd/m^2, more preferably about 16,000 cd/m^2, most preferably about 17,000 cd/m^2 or higher.

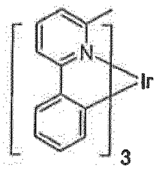
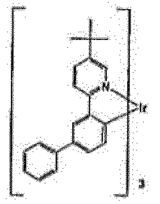
[0047] The emissive material of the present invention may comprise a compound as claimed such that the device has an unmodified external quantum efficiency of at least about 10% at current densities between about 0.1 to about 1000 mA/cm^2; and a lifetime of at least about 50 hours at an initial luminance of at least about 10700 cd/m^2. In another embodiment, the emissive material may comprise a compound as claimed such that the device has an unmodified external quantum efficiency of at least about 15%, preferably at least about 20 % at current densities from about 0.1 to about 1000 mA/cm^2; and a lifetime of at least about 50 hours at an initial luminance of at least about 10,700 cd/m^2. In yet another embodiment, the emissive layer may be in direct contact with an electron transport layer comprising a material having a molecular dipole moment less than about 2.0 debyes, such that the device has an external quantum efficiency of at least about 10% at about at current densities between about 0.1 to about 1000 mA/cm^2.

[0048] In one embodiment, it is believed that the use of a second electron transport layer (ETL2) including an aromatic hydrocarbon having a zero or low molecular dipole moment (TPD) adjacent to the emissive layer may further enhance device performance, as disclosed in U.S. patent application serial number 10/785, 287. Without intending to limit all embodiments with a particular theory of how the invention works, it is believed that this symmetric energy structure may improve electron injection from ETL2 into the emissive layer. The (ETL2) may be in direct contact with the cathode, or there may be a separate organic layer between the organic enhancement layer and the cathode. Other aromatic hydrocarbon materials may be used.

[0049] Various alkyl and aryl substitutions offer a wide range of tunability in terms of evaporation temperature, solubility, energy levels, device efficiency, and are stable functional groups chemically and in device operation. For example, by appropriately substituting one or more alkyl groups (i.e. methyl, ethyl, t-butyl) on either (or in combination) the pyridine or phenyl rings of a phenyl pyridine ligand and then cyclometallated onto a metal center to give dopant emitters for OLED devices, the properties observed gave unexpected improvements in material and device properties including sublimability (lower depositions temperatures and remaining residue in the boat), solubility, color tunability, device stability, and device efficiencies. The color of emission can be fine-tuned to give greater saturation and more desired CIE color requirements. For example, a 4',5'-dimethyl substituted PPY tris Iridium emitter, exhibited a 15 nm blue shift in emission when compared with the unsubstitued $Ir(ppy)_3$ and a and aryl substituted emissive materials have chemical structures as follows:

Compound	Structure
XIV (not claimed)	
XV (not claimed)	
XVI	
XVII	
XVIII	
XIX (not claimed)	
XX	
XXI	
XXII	

(continued)

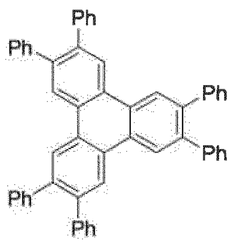
Compound	Structure
XXIII	
XXIV	

Material Definitions:

[0050] As used herein, abbreviations refer to materials as follows:

CBP:	4,4'-N,N-dicarbazole-biphenyl
m-MTDATA	4,4',4"-tris(3-methylphenylphenlyamino)triphenylamine
Alq_3:	8-tris-hydroxyquinoline aluminum
Bphen:	4,7-diphenyl-1,10-phenanthroline
n-BPhen:	n-doped BPhen (doped with lithium)
F_4-TCNQ:	tetrafluoro-tetracyano-quinodimethane
p-MTDATA:	p-doped m-MTDATA (doped with F_4-TCNQ)
$Ir(ppy)_3$:	tris(2-phenylpyridine)-iridium
$Ir(ppz)_3$:	tris(1-phenylpyrazoloto,N,C(2')iridium(III)
BCP:	2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline
TAZ:	3-phenyl-4-(1'-naphthyl)-5-phenyl-1,2,4-triazole
CuPc:	copper phthalocyanine.
ITO:	indium tin oxide
NPD:	N,N'-diphenyl-N-N'-di(1-naphthyl)-benzidine
TPD:	N,N'-diphenyl-N-N'-di(3-toly)-benzidine
BAlq:	aluminum(III)bis(2-methyl-8-hydroxyquinolinato)4-phenylphenolate
mCP:	1,3-N,N-dicarbazole-benzene
DCM:	4-(dicyanoethylene)-6-(4-dimethylaminostyryl-2-methyl)-4H-pyran [00058]
DMQA:	N,N'-dimethylquinacridone
PEDOT:PSS :	an aqueous dispersion of poly(3,4-ethylenedioxythiophene) with polystyrenesulfonate (PSS)
HPT:	2,3,6,7,10,11-hexaphenyltriphenylene

HPT



EXPERIMENTAL:

[0051] Specific representative embodiments of the invention will now be described, including how such embodiments may be made. It is understood that the specific methods, materials, conditions, process parameters, apparatus and the like do not necessarily limit the scope of the invention.

[0052] In order to study different alkyl and aryl substitution patterns to establish a structure-property relationship in the material processibility and device characteristics of Ir(ppy)$_3$ type phosphorescent materials and their PHOLEDs, numerous alkyl and aryl substituted Ir(ppy)$_3$ phosphorescent materials were synthesized and OLEDs incorporating them as the dopant emitters were fabricated by vacuum thermal evaporation. Alkyl and aryl substitutions are of particular importance because they offer a wide range of tunability in terms of evaporation temperature, solubility, energy levels, device efficiency, and that they are stable functional groups chemically and in device operation.

Compound XV:*fac*-tris[2-(4'-tertbutylbiphenyl-3-yl)pyridine] Ir(III)

Step 1: 2-(3-bromophenyl)pyridine

[0053] 14.2 g (0.088 mol) of 2-bromopyridine was added to 19.6 g (0.098 mol) of 3-bromophenylboronic acid, 5.2 g (0.0044mol) of Pd(Ph$_3$)$_4$, 31.0 g (0.23 mol) of K_2CO_3, 50 mL of DME and 50 mL of water. The reaction mixture was refluxed for 20 hours and separated on silica gel column. MS confirmed the desired product.

Step 2: 2-(4'-*tert*-butylbiphenyl-3-yl)pyridine

[0054] 13.7 g (0.058 mol) of 2-(3-bromophenyl)pyridine was added to 12.5 g (0.070 mol) of 4-*tert*-butylphenylboronic acid, 3.4 g (0.003 mol) of Pd(Ph$_3$)$_4$, 22.0 g (0.16 mol) of K_2CO_3, 50 mL of DME and 50 mL of water. The reaction mixture was refluxed for 20 hours and separated on silica gel column. MS confirmed the desired product.

Step 3: *fac*-tris[2-(4'-tert-butylbiphenyl-3-yl)pyridine] Ir(III)

[0055] 9.0 g (0.03 mol) of 2-(5-(4-tert-butylphenyl) phenyl)pyridine and 3.8 g (0.0077 mol) of Ir(acac)$_3$ were mixed with 15 mL of ethylene glycol and heated to reflux under nitrogen for 24 hours. The reaction mixture was cooled down. The product was separated on silica gel column and further purified by zone sublimation. MS and NMR both confirmed the desired product.

Compound XVI: *fac-tris* [2-(3'-methylbiphenyl-3-yl)pyridine] iridium(III)

[0056] The synthesis of above title complex was conducted in the same fashion as Compound XV. The difference is in **Step 2** that instead of using 4-tert-butylphenylboronic acid, 3-methylphenylboronic acid was used for the Suzuki coupling.

Compound XVII: *fac*-tris[2-(biphenyl-3-yl)-4-methylpyridine] Ir(III)

Step 1: 2-(biphenyl-3-yl)-4-methylpyridine

[0057] 9.0 g (0.05 mol) of 2-bromo-4-methylpyridine, 12.0 g (0.06 mol) of 3-biphenylboronic acid, 1.7 g (0.0015 mol) of Pd(Ph$_3$)$_4$, 19.0 g (0.135 mol) of K_2CO_3, 50 mL of DME and 50 mL of water. The reaction mixture was refluxed for 20 hours and separated on silica gel column. MS confirmed the desired product.

Step 2: *fac*-tris[2-(biphenyl-3-yl)-4-methylpyridine]

[0058] Ir(III) 3.6 g (0.014 mol) of 2-(biphenyl-3-yl)-4-methylpyridine was mixed with 2.1 g (0.004 mol) of Ir(acac)$_3$ and 12 mL of ethylene glycol. The mixture was heated to reflux for 24 hours. The product was separated on silica gel column and further purified by zone sublimation method. MS and NMR both confirmed the desired product.

Compound XVIII: *fac*-tris(2-phenyl-3,5-dimethylpyridine) Ir(III)

[0059] The synthesis of above title complex was conducted in the same fashion as Compound XX described below. Instead of using 3,4-lutidine, 3,5-lutidine was used as the starting material to make the ligand 2-phenyl-3,5-dimethylpyridine and *fac*-tris(2-phenyl-3,5-dimethylpyridine) Ir(III).

Compound XX and Compound XXI: *fac*-tris(2-phenyl-4,5-dimethylpyridine) Ir(III) and *fac*-tris(2-phenyl-3,4-dimethylpyridine) Ir(III)

[0060] Step 1: 2-amino-4,5-dimethylpyridine and 2-amino-3,4-dimethylpyridine To 100.0 g (0.94 mol) of 3,4-lutidine

(3,4-dimethylpyridine) and 40 g (1.0 mol) of sodium amide was added 237 mL (1.86 mol) of N,N-dimethylaniline. The reaction mixture was heated with stirring under nitrogen for 7 hours at 150°C. After cooling down, the reaction mixture was added to 400 mL of ice and ~250 mL of ethyl acetate was added to the mixture to extract the organic phase. The organic phase was evaporated and fractional distilled. About ~40 g (35% yield) of a white solid mixture of 2-amino-3,4-dimethylpyridine (~78%) and 2-amino-4,5-dimethylpyridine (~22%) was obtained for next step reaction without further purification. MS results confirmed the desired products.

[0061] Step 2: 2-bromo-4,5-dimethylpyridine and 2-bromo-3,4-dimethylpyridine 8.0 g (0.065 mol) of the Step 1 mixture was added to -25 mL of 60% HBr , then stirred at -10°C to - 17°C. 31.0 g (0.2 mol) of pre-cooled Br_2 (~0°C) was added dropwise and the mixture was stirred for 20 mins. Pre-cooled (0°C) $NaNO_2$ solution of 11.4 g (0.16 mol) of $NaNO_2$ dissolved in 18 - 20 mL of water was added dropwise into the reaction mixture at about -150C. After the addition, the reaction was stirred for one hour. Ice-cooled 25% NaOH solution was added slowly until the solution became basic. 200 mL of ethyl acetate was added to the mixture to extract the organic phase. The organic phase solvent was evaporated and distilled under vacuum. -10.7 g (88% yield) a solid mixture of 2-bromo-3,4-dimethylpyridine (~78%) and 2-bromo-4,5-dimethylpyridne (~22%) was obtained which confirmed by MS. The mixture was used for next step Suzuki coupling reaction without further purification.

Step 3: 2-phenyl-4,5-dimethylpyridine and 2-phenyl-3,4-dimethylpyridine

[0062] 12.0 g (0.0645 mol) of the **Step 2** mixture was added to 9.1 g (0.071 mol) of phenylboronic acid, 2.2 g (0.002mol) of $Pd(Ph_3)_4$, 24 g (0.174 mol) of K_2CO_3, 100 mL of DME and 100 mL of water. The reaction mixture was refluxed for 20 hours and separated on silica gel column with 10% ethyl acetate in hexane. - 7.5 g of 2-phenyl-3,4-dimethylpyridine and 2.5 g of 2-phenyl-4,5-dimethylpyridine were obtained which are confirmed by NMR and MS.

Step 4: *fac*-tris(2-phenyl-4,5-dimethylpyridine) Ir(III) and *fac*-tris(2-phenyl-3,4-dimethylpyridine) Ir(III)

[0063] 2.0 g (0.01 mol) of 2-phenyl-4,5-dimethylpyridine was added to 1.6 g (0.003 mol) of $Ir(acac)_3$ and 10 mL of ethylene glycol and heated to reflux under nitrogen for 20 hours. The reaction mixture was separated on silica gel column to obtain tris (2-phenyl-4,5-dimethylpyridine) Ir(III) as in Example 46. The complex was further purified by zone sublimation method and confirmed by both MS and NMR. 5.0 g (0.027 mol) of 2-phenyl-3,4-dimethylpyridine was added with 2.2 g (0.0045 mol) of $Ir(acac)_3$ and heated under nitrogen at high temperature for 24 hours. The reaction mixture was separated on silica gel column to obtain tris(2-phenyl-3,4-dimethylpyridine) Ir(III) complex as Compound XX. The complex was further purified by zone sublimation method and confirmed by both MS and NMR.

Compound XXII: *fac*-tris [2-(biphenyl-3-yl)-4-tert-butylpyridine] Ir(III)

Step 1: 2-amino-4-*tert*-butylpyridine

[0064] To 100 g (0.73 mol) of 4-*tert*-butyl-pyridine and 31.0 g (0.79 mol) of sodium amide was added 181 mL (1.5 mol) of N,N,-dimethylanirme. The reaction mixture was heated with stirring under nitrogen for 7 hours at 150°C. After cooling, the reaction mixture was added to 400 mL of ice. - 250 mL of ethyl acetate was added to the mixture to extract the organic phase. The organic phase was evaporated and fractional distilled. About -50 g (45% yield) of 2-amino-4-*tert*-butylpyridine was obtained. MS results confirmed the desired products.

Step 2: 2-bromo-4-*tert*-butylpyridine

[0065] 39.0 g (0.26 mol) of 2-amino-4-fert-butyl-pyridme was added with -100 mL of 60% HBr, then stirred at -10°C to -17°C. 124.0 g (0.78 mol) of pre-cooled Br_2 (~0°C) was added dropwise added and the mixture was stirred for 20 mins. Pre-cooled (0°C) $NaNO_2$ solution of 46.0 g (0.67mol) of $NaNO_2$ dissolved in -80 mL of water was added dropwise into the reaction mixture at -10°C to -17°C. After addition, the reaction was stirred for one hour. Ice-cooled -25% NaOH solution was added slowly until the solution became basic. 200 mL of ethyl acetate was added to the mixture to extract the organic phase. The organic phase solvent was evaporated and distilled under vacuum. -47 g (85% yield) of 2-bromo-4-*tert*-butyl-pyridine was obtained. The product was confirmed by MS.

Step 3: 2-(biphenyl-3 -yl)-4-tert-butylpyridine

[0066] 15.0 g (0.7 mol) of 2-bromo-4-*tert*-butyl-pyridine was added to 13.8 g (0.7 mol) of 3-biphenylboronic acid, 2.4 g (0.002mol) of $Pd(Ph_3)_4$, 26 g (0.188 mol) of K_2CO_3, 100 mL of DME and 100 mL of water. The reaction mixture was refluxed for 20 hours and separated on silica gel column with 10% ethyl acetate in hexane. ~ 18.0 g (-90% yield)

2-(biphenyl-3-yl)-4-*tert*-butylpyridine was obtained. M S confirmed the desired product.

Step 4: *fac*-tris(2-(3-biphenyl)-4-*tert*-butylpyridine Ir(III)

[0067] 7.1 g (0.024 mol) of 2-(bi phenyl-3-yl)-4-*tert*-butylpyridine was added to 3.40 g (0.007 mol) of Ir(acac)3 and -10 mL of ethylene glycol. The reaction mixture was heated to reflux for 24 hours and cooled. ~ 5.6 g (~ 80% yield) complex was obtained which was separated by silica column. It was further purified by zone sublimation. MS and NMR both confirmed the desired product.

Compound XXIII: *fac*-tris[2-phenyl-6-methylpyridine] Ir(III)

Step 1: 2-phenyl-6-methylpyridine

[0068] Phenylboronic acid (42.6 g, 0.349 mol) was reacted with 2-bromo-6-methylpyridine (50.0 g, 0.290 mol) under standard Suzuki coupling condition. Vacuum distillation of the product (10 mm Hg, 135-150 °C) afforded 32.0 g (76 %) of 2-(4-methylphenyl)-5-methylpyridine as a colorless liquid.

Step 2: *fac*-tris[2-phenyl-6-methylpyridine] Ir(III)

[0069] 2-phenyl-6-methylpyridine (32 g, 0.189 mol) was heated to 260°C in a 100 mL, 3-necked flask equipped with a stir bar, nitrogen inlet, and a Dean-Stark trap. Ir(acac)$_3$ (7.7 g, 0.016 mol) was then added, and the reaction mixture was kept at 260°C for 48 hours while the resulting acetylacetone was distilled off. Methanol (200 mL) was then added, and the brown precipitate (5.0 g) was collected by vacuum filtration. Purification through a silica gel plug with 70/30 CH_2Cl_2/hexane yielded 2.2 g of a yellow solid that was further purified on a basic alumina column with 40-50/60-50 methylene/chloride as the eluent, affording 950 mg of pure material. Vacuum sublimation yielded 600 mg of the pure product.

Compound XXIV: *fac*-tris[2-(biphenyl-3-yl)-5-tert-butylpyridine] Ir(III)

Step 1: 2-(biphenyl-3-yl)-5-bromopyridinee

[0070] To a 1000 mL, 3-necked flask equipped with a stir bar, nitrogen inlet, and a reflux condenser were added 2,5-dibromopyridine (39.9 g, 84.2 mmol), 3-biphenylboronic acid (20.0 g, 101 mmol), palladium(II) acetate (0.47 g, 2.1 mmol), triphenylphosphine (2.2 g, 8.4 mmol), sodium carbonate (24.1 g, 227 mmol), dimethoxyethane (170 mL), and water (114 mL). The reaction mixture was heated at reflux for 16 h, after which ethyl acetate (200 mL) was added. The organic layer was then dried over magnesium sulfate and evaporated to dryness. Purification of the resulting solid on a silica gel column with ethyl acetate/hexane as the eluent yielded 19.0 g (73 %) of 2-(biphenyl-3-yl)-5-bromopyridine as a white solid.

Step 2: 2-(biphenyl-3-yl)-5-tert-butylpyridine

[0071] To a suspension of copper(I) cyanide (17.3 g, 194 mmol) in 1730 mL of anhydrous THF in an oven-dried, five liter, three-necked flask equipped with a mechanical stirrer and a nitrogen inlet was added *tert*-butylmagnesium chloride (200 mL, 2.0 M, 400 mmol) via an addition funnel, and the mixture was stirred at -78°C for 30 min. A solution of 2-(biphenyl-3-yl)-5-bromopyridine (15.0 g, 48 mmol) in 100 mL of dry THF was then added dropwise, and the mixture was stirred for 3 hours at -78°C and then overnight at room temperature. Saturated aqueous ammonium hydroxide was then added to quench the reaction mixture, the pH was adjusted to 10 with aqueous sodium hydroxide, and the mixture was extracted with methylene chloride. The organic layer was dried over magnesium sulfate and evaporated to dryness to give 9.0 g of light yellow liquid that was purified by flash silica gel chromatography with a 2.5/97.5 to 7.5/92.5 ethyl acetate/hexane gradient as the eluent, affording 2.6 g (19 %) of 2-(biphenyl-3-yl)-5-*tert*-butylpyridine as a colorless liquid.

Step 3: *fac*-tris[2-(biphenyl-3-yl)-5-tert-butylpyridine] Ir(III)

[0072] Ethylene glycol (20 mL) and 2-(biphenyl-3-yl)-5-*tert*-butylpyridine (2.6 g, 9.1 mmol) were combinded in a 100 mL, three-necked flask equipped with a stir bar, reflux condenser, and a nitrogen inlet and heated to reflux. Ir(acac)$_3$ (1.1 g, 2.3 mmol) was then added and the reaction mixture was maintained at reflux for 24 hours and cooled to room temperature. Methanol (50 mL) was added, and the yellow product (2.1 g) was collected by vacuum filtration and passed through a silica gel column with 70/30 dichloromethane/hexane as the eluent, affording 1.8 g of pure material. Vacuum sublimation yielded 1.0 g of the product.

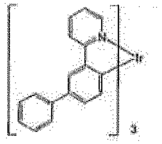
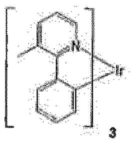
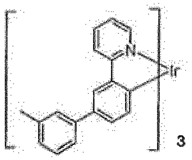
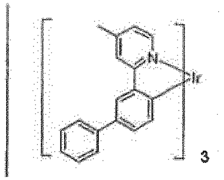
DEVICE FABRICATION AND MEASUREMENT

[0073] All devices were fabricated by high vacuum (<10^{-7} Torr) thermal evaporation. The anode electrode is ~1200 Å of indium tin oxide (ITO). The cathode consists of 10 Å of LiF followed by 1,000 Å of Al. All devices are encapsulated with a glass lid sealed with an epoxy resin in a nitrogen glove box (<1 ppm of H_2O and O_2) immediately after fabrication, and a moisture getter was incorporated inside the package.

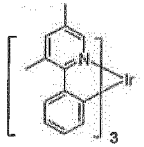
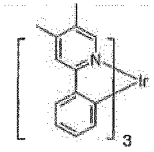
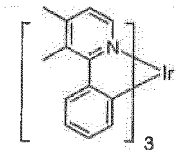
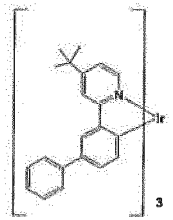
Device Examples 43-51 and Comparative Examples 5-6

[0074] The organic stack consisted of sequentially, from the ITO surface, 100 Å thick of copper phthalocyanine (CuPc) as the hole injection layer (HIL), 300 Å of 4,4'-bis[N-(1-naphthyl)-N-phenylaminobiphenyl (α-NPD), as the hole transporting layer (HTL), 300 Å of 4,4'-bis(N-carbazolyl)biphenyl (CBP) doped with 6-12 wt% of the dopant emitter (invention compounds and comparative compounds) as the emissive layer (EML), 50 A of HPT as the ETL2, and 400 A of tris(8-hydroxyquinolinato)aluminum (Alq_3) as the ETL1. The current-voltage-luminance (FVL) characteristics and operational lifetimes are measured and summarized in the Table 5. A typical display brightness level of 1000 cd/m^2 for green emitting devices is chosen for the comparison between different devices.

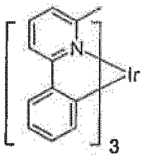
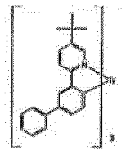
TABLE 5

						At 1000 cd/m^2			At 40 mA/cm^2	
Device	Structure	Device Structure	T_{sub} (°C)	λ_{max} (nm)	CIE	Luminous efficiency (cd/A)	Voltage (V)	Power efficiency (lm/W)	$T_{1/2}$(hr)	cd·hr/m 2 (x million)
Comparative Example Device 5	 Ir(5-Phppy)$_3$	6%	310	518	0.31 0.64	38.3	8.2	14.7	500	5.34
Comparative Example Device 6	 Ir(3'-Meppy)$_3$	8%	218	522	0.32 0.62	35.1	7.9	14.0	560	5.45
43	 **Compound XVI**	10%	294-306	522	0.30 0.65	42	7.9	16.8	318	3.91
44	 **Compound XVII**	10%	302	516	0.29 0.65	60	6.6	28.5	190	3.04

(continued)

						At 1000 cd/m^2			At 40 mA/cm^2	
Device	Structure	Device Structure	T_{sub} (°C)	λ_{max} (nm)	CIE	Luminous efficiency (cd/A)	Voltage (V)	Power efficiency (lm/W)	$T_{1/2}$(hr)	cd·hr/m 2 (x million)
45	 **Compound XVIII**	8%	231	526	0.35 0.61	38.5	8.6	17.1	220	2.24
47	 **Compound XX**	9%	240	506	0.28 0.62	40	6.4	19.6	130	1.79
48	 **Compound XXI**	9%	255	520	0.32 0.63	36.4	7.4	15.4	650	6.43
49	 **Compound XXII**	12%	330	518	0.31 0.64	53	5.7	29.2	100	1.79

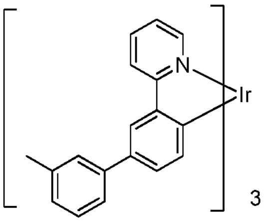
(continued)

						At 1000 cd/m^2			At 40 mA/cm^2	
Device	Structure	Device Structure	T_{sub} (°C)	λ_{max} (nm)	CIE	Luminous efficiency (cd/A)	Voltage (V)	Power efficiency (lm/W)	$T_{1/2}$(hr)	cd·hr/m 2 (x million)
50	 **Compound XXIII**	9%	226-237	508	0.27 0.63	32.8	7.4	13.9	120	1.2
51	 **Compound XXIV**	9%	278-284	518	0.31 0.64	45.9	6.6	21.9	100	1.2

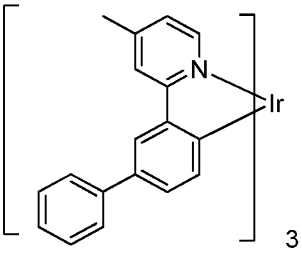
[0075] It can be seen from Table 5 that some invention compounds show similar or higher efficiency and lifetime versus the comparative examples Ir(5-Phppy)$_3$ and Ir(3'Meppy)$_3$. Device Example 48 shows an efficiency of 36.4 cd/A at 1000 cd/m^2 and a device stability of 6.43x10^7 cd-hr/m^2 [defined as T$_{1/2}$(hr)xL$_0$(cd/m^2) where $T_{1/2}$ is the time for the initial luminance L$_0$ to drop to 50%] under a constant current drive of 40 mA/cm2 at room temperature. Under the same condition, Ir(5-Phppy)$_3$ (Comparative Example 5) is 38.3 cd/A and 5.34x10^7 cd·hr/m^2, and Ir(3'Meppy)$_3$ (Comparative Example 6) is 35.1 cd/A and 5.45x10^7 cd·hr/m^2.

Claims

1. A compound having a chemical structure selected from the group consisting of:



XVI



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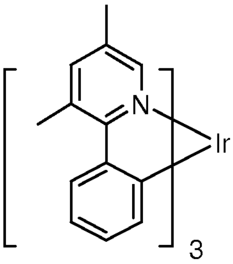

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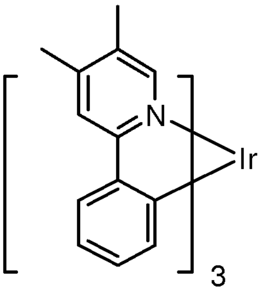

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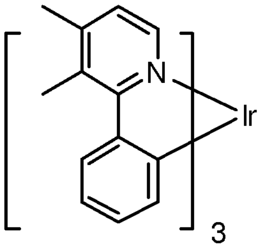
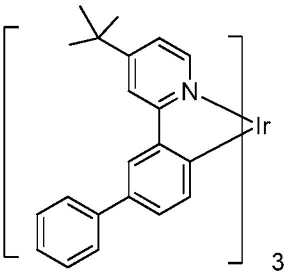


XXI



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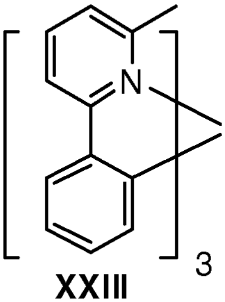

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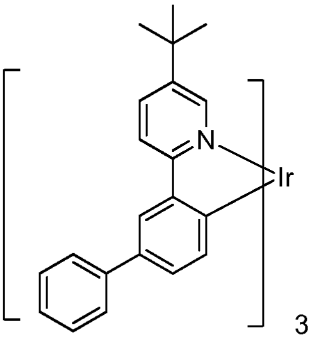
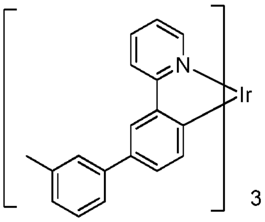


XXIV

2. An organic light emitting device comprising
an anode
a cathode, and
an emissive layer disposed between the anode and the cathode wherein the emissive layer comprises an emissive material having the formula:



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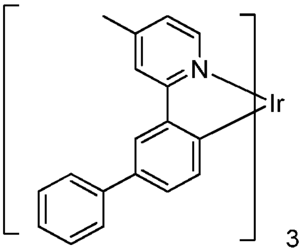

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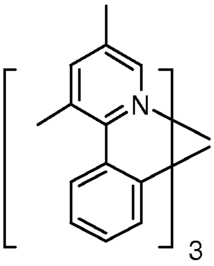

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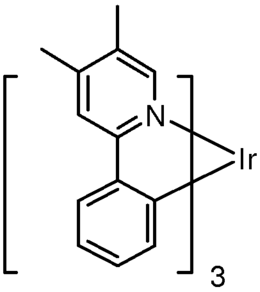

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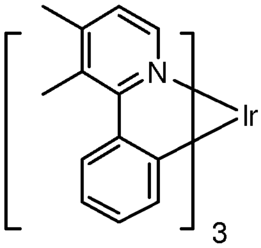

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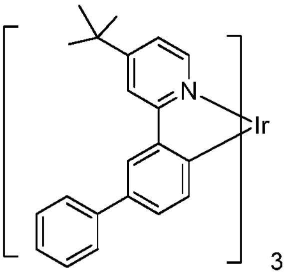

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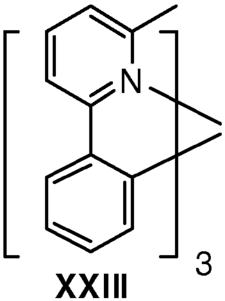

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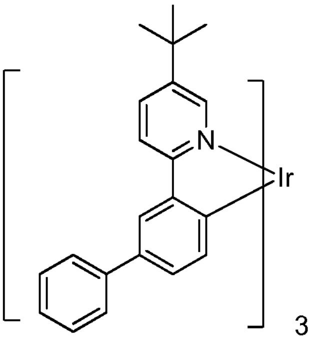
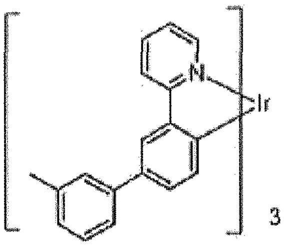


XXIV

Patentansprüche

1. Eine Verbindung mit einer chemischen Struktur ausgewählt aus der Gruppe bestehend aus:



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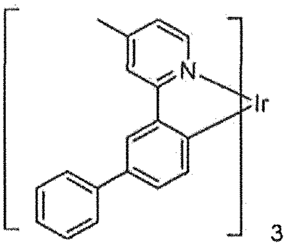

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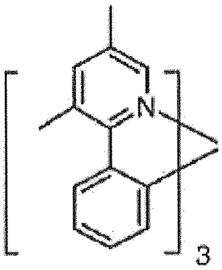

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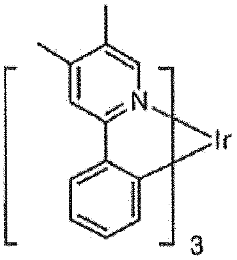

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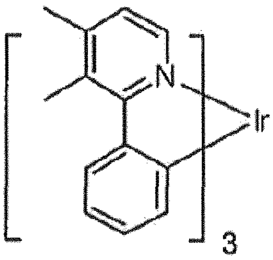

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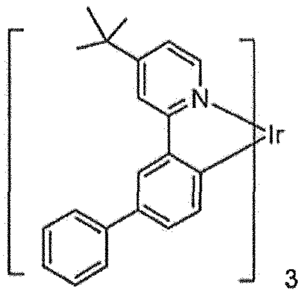

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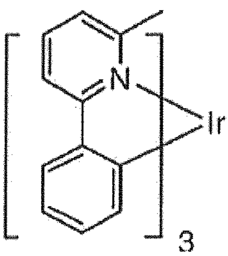

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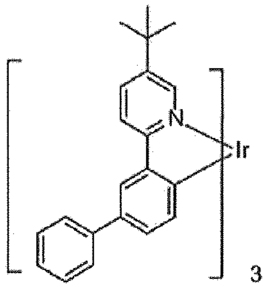
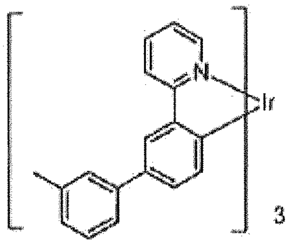


XXIV

2. Eine organische lichtemittierende Vorrichtung umfassend
eine Anode,
eine Kathode, und
eine emittierende Schicht angeordnet zwischen der Anode und der Kathode, wobei die emittierende Schicht ein emittierendes Material mit der folgenden Formel aufweist:



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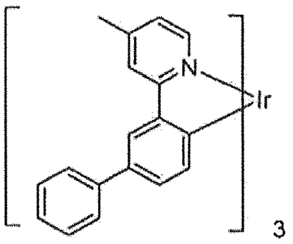

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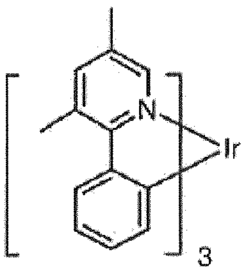

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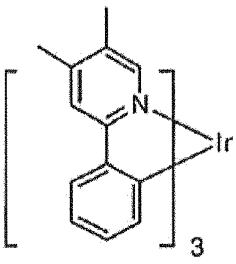

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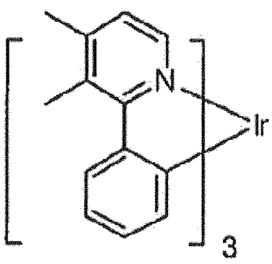

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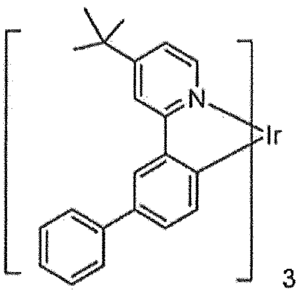

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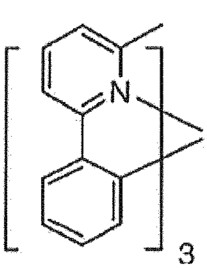

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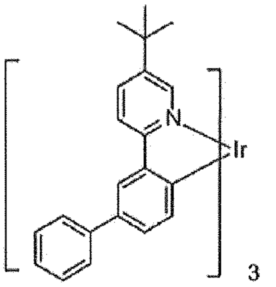
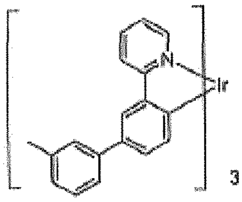


XXIV

Revendications

1. Composé ayant une structure chimique choisie parmi le groupe constitué de :



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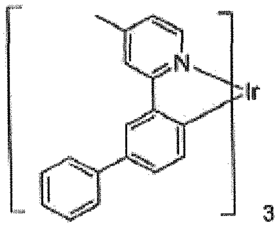

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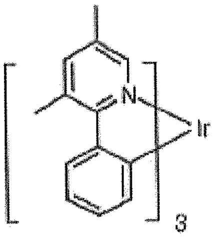

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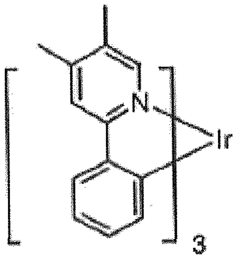

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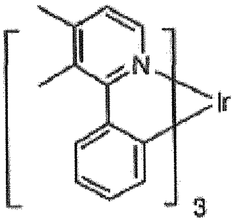

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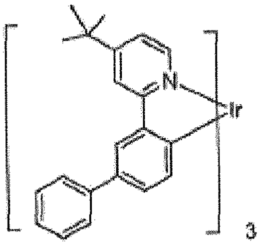

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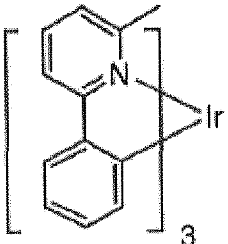

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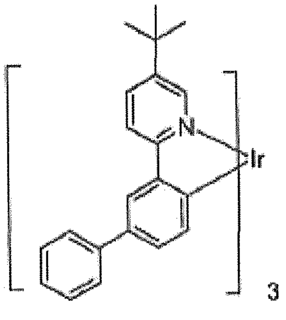
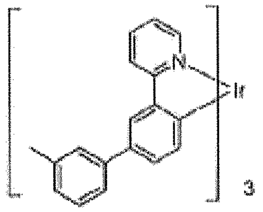


XXIV

2. Dispositif émetteur de lumière organique comportant :

une anode,
une cathode, et
une couche émissive disposée entre l'anode et la cathode, dans lequel la couche émissive comporte un matériau émissif ayant pour formule :



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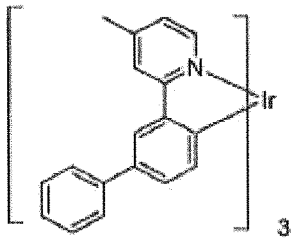

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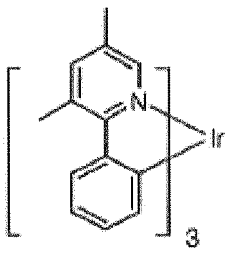
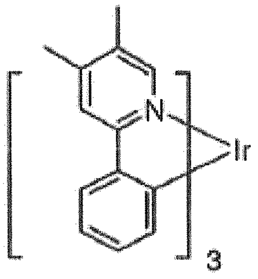
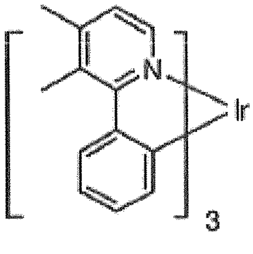


XVIII



XX



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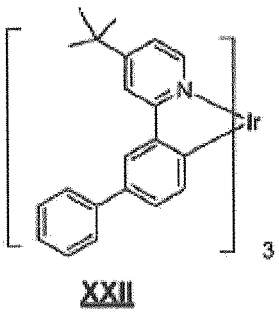

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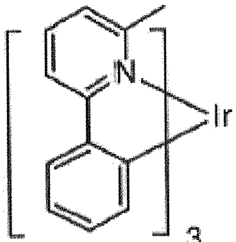

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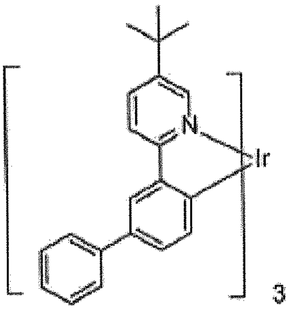

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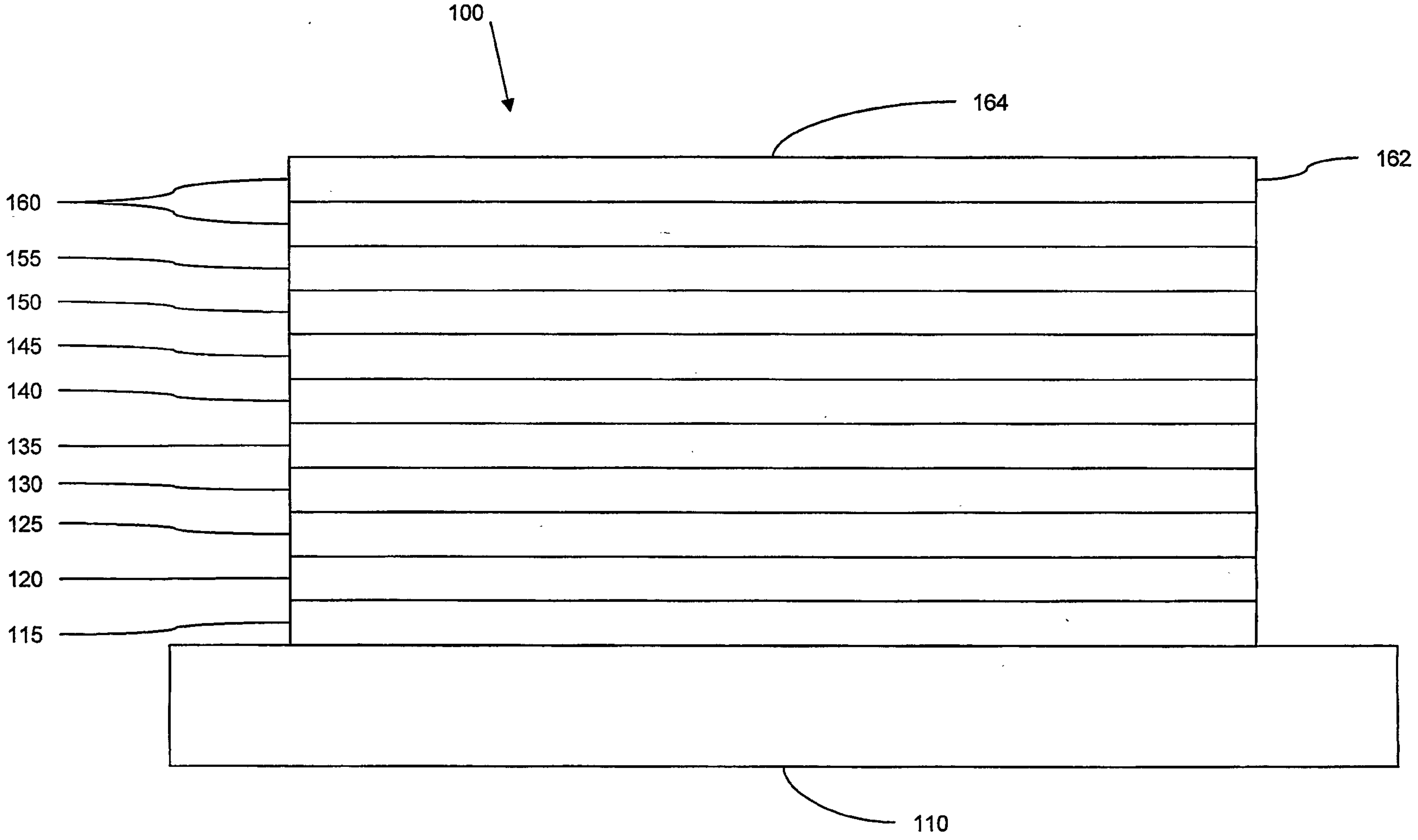

Figure 1

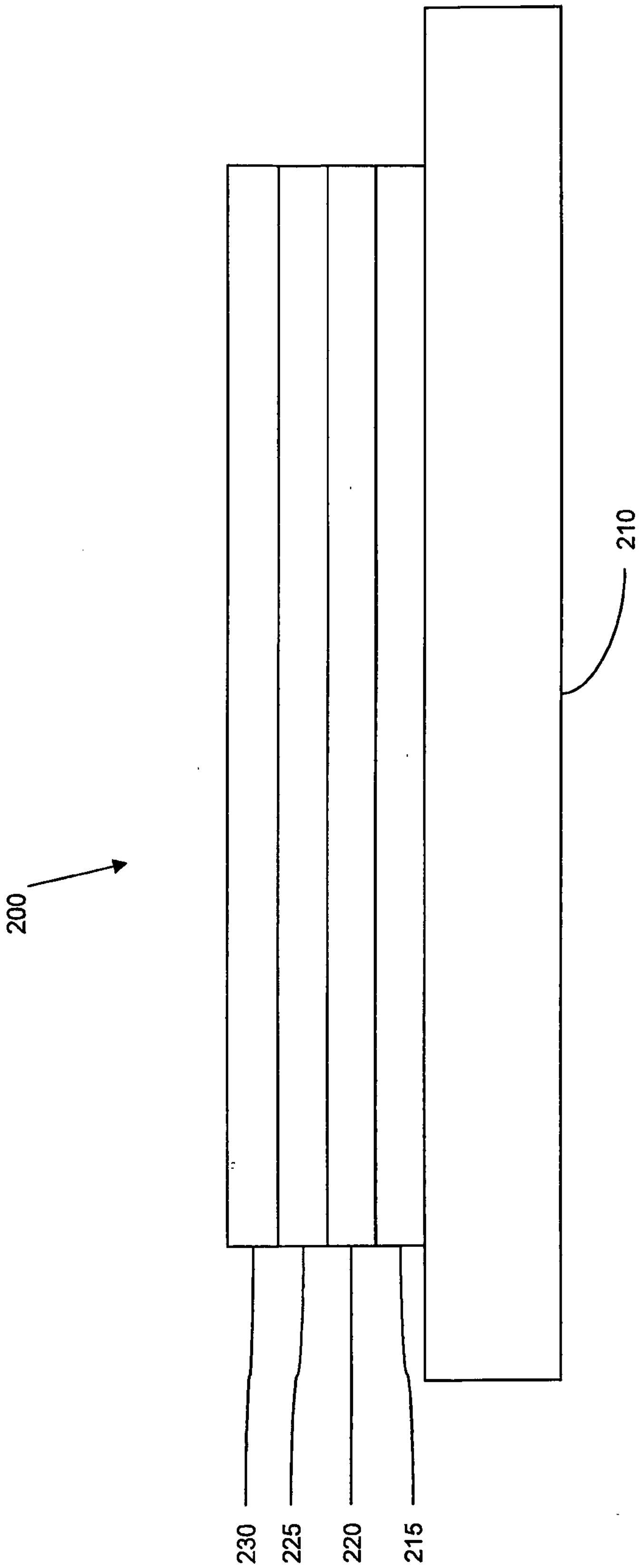

Figure 2

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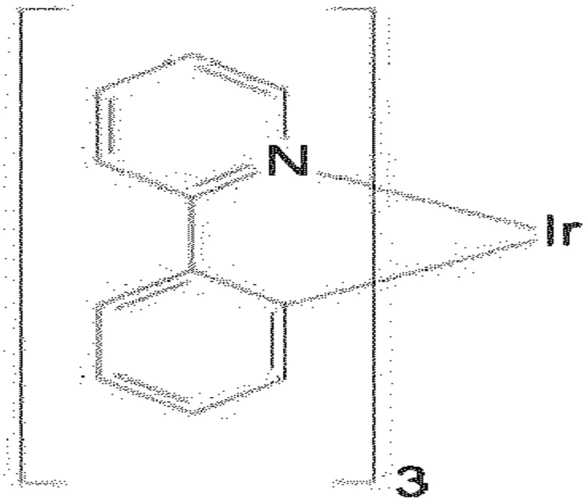
专利名称(译)	稳定高效的电致发光材料		
公开(公告)号	EP2378582B1	公开(公告)日	2016-08-17
申请号	EP2011001394	申请日	2005-07-07
[标]申请(专利权)人(译)	环球展览公司		
申请(专利权)人(译)	通用显示器公司		
当前申请(专利权)人(译)	通用显示器公司		
[标]发明人	KWONG RAYMOND KNOWLES DAVID MA BIN LI CHARLES CEYROLLES WILLIAM J WEAVER MICHAEL S		
发明人	KWONG, RAYMOND KNOWLES, DAVID MA, BIN LI, CHARLES CEYROLLES, WILLIAM, J. WEAVER, MICHAEL, S.		
IPC分类号	H01L51/00 H05B33/14 C09K11/06 C07F15/00 H01L51/50		
CPC分类号	C09K11/06 C07F15/0033 C07F15/006 C07F15/0073 C07F15/0086 C09K2211/1011 C09K2211/1029 C09K2211/1088 C09K2211/1092 C09K2211/185 H01L51/0085 H01L51/5016 H05B33/14 Y10S428/917		
代理机构(译)	MAIWALD专利ADVOCATE GMBH		
优先权	10/886367 2004-07-07 US 11/018453 2004-12-21 US 60/682690 2005-05-19 US		
其他公开文献	EP2378582A1		
外部链接	Espacenet		

摘要(译)

一种有机发光器件，包括阳极，阴极和设置在阳极和阴极之间的发光层，其中发光层包含下式的发光材料：其中M是选自Ir，Pt，Rh或Pd的金属;（X-Y）是辅助配体;m是1至可以与金属连接的配体的最大数量的值;m + n是可以与金属连接的配体的最大数量;R'3，R'4，R'5和R'6各自独立地为H，烷基，链烯基，炔基，杂烷基，链烯基，炔基，杂烷基，芳基，杂芳基，芳烷基;其中R'3，R'4和R'6任选被一个或多个取代基Z取代;另外或可替代地，环A上的R'3和RS4取代位置一起独立地形成稠合环，其中稠合环可以是任选的取代; R 3，R 4，R 5和R 6各自独立地选自H，烷基，链烯基，炔基，烷芳基，CN，CO 2 R，C（O）R，NR 2，NO 2，OR，卤素，芳基，杂芳基，取代的芳基，取代的杂芳基或杂环基;或者，R'3和R6可以通过选自-CR2-CR2 - ， - CR = CR- ， - CR2 - ， - O - ， - NR - ， - O-CR2，-NR-CR2-的基团桥接，和-N = CR-;每个R独立地为H，烷基，烯基，炔基，杂烷基，芳基，杂芳基或芳烷基;其中R任选被一个或



多个取代基Z取代;每个Z独立地为卤素，R1，OR1，N（R1）2，SR1，C（O）R1，C（O）OR1，C（O）N（R1）2，CN，SO2，SOR1，SO2R1或SO3R1;每个R 1独立地为H，烷基，烯基，炔基，杂烷基，芳基或杂芳基;其中R3，R4，R5，R6，R'3，R'4，R'5和R'6中的至少一个是烷基或芳基取代。