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(54) **Organic light emitting materials and devices**

Organische lichtemittierende Materialien und eine Vorrichtung

Matériaux électroluminescents organiques et dispositifs

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(73) Proprietors:
• **Universal Display Corporation**
Ewing, NJ 08648 (US)
• **University of Southern California**
Los Angeles CA 90007-4344 (US)

(72) Inventors:
• **Ma, Bin**
Plainsboro,
New Jersey 08536 (US)
• **Knowles, David B.**
Apollo, PA 15613 (US)
• **Brown, Cory S.**
Pittsburgh, PA 15219 (US)
• **Murphy, Drew**
Norwalk, California 906502 (US)
• **Thompson, Mark E.**
Anaheim, CA 92807 (US)

(74) Representative: **Kiriczi, Sven Bernhard**
Schneiders & Behrendt
Mühlthaler Strasse 91d
81475 München (DE)

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DescriptionField of the Invention

5 **[0001]** The present invention relates to organic light emitting devices (OLEDs), and more specifically to organic materials used in such devices.

Background

10 **[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.

15 **[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 an fluorescent or phosphorescent small molecule emitter.

25 **[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, which are incorporated herein by reference in their entirety.

30 **[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 devices. For example, a transparent electrode material, such as indium tin oxide (ITO), may be used as the bottom electrode. A transparent top electrode, such as disclosed in U.S. Patent Nos. 5, 307,436 and 5,707,745, which are incorporated by reference in their entireties, may also be used. For a device intended to emit light only through the bottom electrode, the top electrode does not need to be transparent, and may be comprised of a thick and reflective metal layer having a high electrical conductivity. Similarly, for a device intended to emit light only through the top electrode, the bottom electrode may be opaque and / or reflective. Where an electrode does not need to be transparent, using a thicker layer may provide better conductivity, and using a reflective electrode may increase the amount of light emitted through the other electrode, by reflecting light back towards the transparent electrode. Fully transparent devices may also be fabricated, where both electrodes are transparent. Side emitting OLEDs may also be fabricated, and one or both electrodes may be opaque or reflective in such devices.

35 **[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.

40 **[0007]** One application for phosphorescent emissive materials 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. CE coordinates are described in H. Zollinger, "Color Chemistry" VCH Publishers, 1991 and H. J. A. Dartnall, J. K. Bowmaker, and J. D. Mollon, Proc. Roy. Soc. B (London), 1983,220, 115-130.

45 **[0008]** Another application for phosphorescent emissive materials is a display, full color or otherwise, that is intended to be powered by battery, such as the display of a cellular telephone or a digital camera. For such applications, power efficiency is a particularly important parameter, because efficient emission may significantly extend battery life, and/or enable the use of smaller batteries. Lighting is another application where efficiency is of particular importance, because of the sheer volume of power used for lighting applications. Efficiency is also important for many other applications.

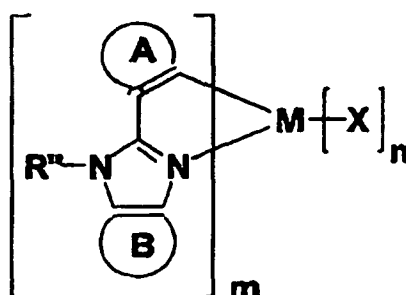
Moreover, a high efficiency may lead to a longer lifetime, because inefficient devices generally lose power to heat instead of emitting light, and heat may adversely affect device lifetime.

[0009] WO 02/15645 A1 discloses emissive phosphorescent organometallic compounds wherein the photoactive ligand may have an imidazole group. Photoactive ligands bearing a benzimidazole group are not disclosed.

[0010] US 2002/0094453 A1 relates to metal coordination compounds suitable as organic materials for luminescent devices, wherein the photoactive ligand comprises a benzimidazole group attached to an olefinic group, which is part of an unsaturated cyclus.

Summary of the Invention

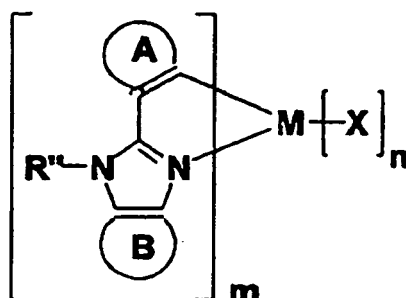
[0011] The present invention is directed to an organic light emitting device according to claim 1, comprising an anode, a cathode and an emissive layer disposed between the anode and the cathode, the emissive layer including a material according to claim 8 having the structure:



wherein M is Pt, A is selected from the group consisting of aryl and heteroaryl rings, and B is an aryl ring, R'' is selected from the group consisting of H and any substituent, wherein X is an ancillary ligand, and wherein m is 1 and n is 1.

[0012] According to a embodiment at least one of A and B includes a substituent. According to a further embodiment the emissive material is incorporated into a polymer. According to a further embodiment the emissive material is incorporated into a dendrimer. According to a further embodiment the emissive layer further comprises a host material. According to a further embodiment the emissive material is a dopant in the host material. According to a further embodiment the emissive material consists essentially of a neat film of the emissive material.

[0013] The present invention is further directed to an emissive material having the structure:



wherein M is Pt, A is selected from the group consisting of aryl and heteroaryl rings, and B is an aryl ring, and R'' is selected from the group consisting of H and any substituent, wherein X is an ancillary ligand, and wherein m is 1 and n is 1.

[0014] According to an embodiment at least one of A and B includes a substituent. According to a further embodiment the emissive material is incorporated into a polymer. According to a further embodiment the emissive material is incorporated into a dendrimer. According to a further embodiment the emissive layer further comprises a host material. According to a further embodiment the emissive material is a dopant in the host material. According to a further embodiment the emissive material consists essentially of a neat film of the emissive material.

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.

[0016] Fig. 2 shows an inverted organic light emitting device that does not have a separate electron transport layer.

[0017] Figure 3 shows plots of luminous efficiency v. luminance for various devices

[0018] Figure 4 shows plots of external quantum efficiency v. luminance for various devices.

Detailed Description

[0019] 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.

[0020] 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.

[0021] 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 exhibit 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.

[0022] 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.

[0023] 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.

[0024] 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).

[0025] Fig. 1 shows an organic light emitting device 100. The figures are not necessarily drawn to scale. Device 100 may include a substrate 110, an anode 115, a hole injection layer 120, a hole transport layer 125, an electron blocking layer 130, an emissive layer 135, a hole blocking layer 140, an electron transport layer 145, an electron injection layer 150, a protective layer 155, and a cathode 160. Cathode 160 is a compound cathode having a first conductive layer 162 and a second conductive layer 164. Device 100 may be fabricated by depositing the layers described, in order.

[0026] 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.

[0027] 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 No. 5,844,363. 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.

[0028] 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 F₄-TCNQ at a molar ratio of 50:1, as disclosed in United States Patent Application No. 10/173,682 to Forrest et al. . Other hole transport layers may be used.

[0029] 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 Alq₃, 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 or dendrimer molecule. Other emissive layer materials and structures may be used.

[0030] Electron transport layer 140 may include a material capable of transporting electrons. Electron transport layer 140 may be intrinsic (undoped), or doped. Doping may be used to enhance conductivity. Alq₃ 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 No. 10/173,682 to Forrest et al. . Other electron transport layers may be used.

[0031] 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 and 5,707,745 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.

[0032] Blocking layers may be used to reduce the number of charge carriers (electrons or holes) and / or excitons that leave the emissive layer. An electron blocking layer 130 may be disposed between emissive layer 135 and the hole transport layer 125, to block electrons from leaving emissive layer 135 in the direction of hole transport layer 125. Similarly, a hole blocking layer 140 may be disposed between emissive layer 135 and electron transport layer 145, to block holes from leaving emissive layer 135 in the direction of electron transport layer 140. Blocking layers may also be used to block excitons from diffusing out of the emissive layer. The theory and use of blocking layers is described in more detail in United States Patent No. 6,097,147 and United States Patent Application No. 10/173,682 to Forrest et al.

[0033] 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.

[0034] 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.

[0035] 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 an example of how some layers may be omitted from the structure of device 100.

[0036] 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.

[0037] 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. .

[0038] 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 organic vapor jet deposition (OVJD), such as described in U.S. Patent Application No. 10/233,470 . Other suitable deposition methods include spin coating and other solution based processes. 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.

[0039] 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

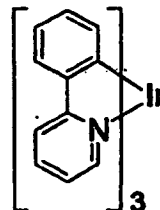
the devices are intended for use in a temperature range comfortable to humans, such as 18 degrees C to 30 degrees C, and more preferably at room temperature (20 - 25 degrees C).

[0040] 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.

[0041] Industry standards for full color displays call for a saturated red, green and blue emissive materials. It is desirable to have a material that may be "tuned" over a broad range of color-coordinates, such that particular colors for example highly saturated colors may be obtained.

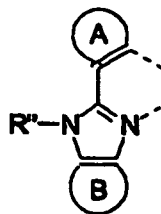
[0042] Phosphorescent light emitting materials are of interest due, in part, to the high efficiencies that may be achieved with such materials. An example of such a material is Ir(ppy)₃:

Formula 1:



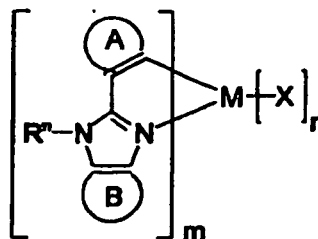
[0043] In an embodiment of the invention, a highly tunable phosphorescent light emitting material is provided. The material may include a ligand having the following structure:

Formula 2:



[0044] In formula 2, rings A and B may be any aryl or heteroaryl ring. Preferably, ring B is an aryl ring, because a heteroaryl B ring may be difficult to synthesize. Preferably, rings A and B are 5 or 6-membered aryl ring systems. Aryl rings are also preferred over heteroaryl rings because it is believed that device stability is better when A and B are aryl rings. Rings A and B may incorporate a single or multiple heteroatoms. Nitrogen is an example of a suitable heteroatom. Rings A and B may be benzannulated and may contain substituents. H or any substituent may be used on rings A and B, as well as R''. Preferred substituents include alkyl, alkoxy, amino, halogen, carboxy, aryl, heteroaryl, alkenyl, and alkynyl. Rings A and B may be selected from the same ring system, or may be different. Rings A and B may include the same or different substituents. R'' may be H or any substituent.

[0045] The ligand of formula 2 may be attached to a metal M having an atomic weight greater than 40. Preferred metals include Ir, Pt, Pd, Rh, Re, Ru, Os, Tl, Pb, Bi, In, Sn, Sb, Te, Au, and Ag. More preferably, the metal is Pt. Most preferably, the metal is Ir. Multiple ligands may be attached to the metal. In one embodiment, ligands are attached to the metal M as follows:

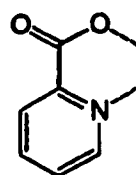
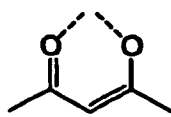
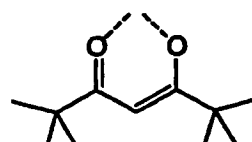
Formula 3:

[0046] Rings A and B, as well as R'', are as described with respect to formula 2.

[0047] "X" may be referred to as an "ancillary ligand." Preferred ligands include any mono-anionic ligand. X may coordinate to the metal in a single or multiple locations. For example, X may be a bidentate ligand. The X ligand is referred to as "ancillary" because it is believed that it may modify the photoactive properties of the material, as opposed to directly contributing to the photoactive properties. By way of contrast, the ligand to the left is referred to as "photoactive" because it is believed that it contributes to the photoactive properties of the material. The definitions of photoactive and ancillary are intended as non-limiting theories.

[0048] "m" is the number of photoactive ligands of a particular type, and "n" is the number of ancillary ligands of a particular type. Depending upon the metal M, a certain number of ligands may be attached to the metal. Generally, the ligands are bidentate, which means that they form two bonds with the metal, but bidentate ligands are not required. For example, two chlorines could be attached to the metal in place of a bidentate ancillary ligand. "m" is at least one, and may be any integer greater than zero up to the maximum number of ligands that may be attached to the metal. "n" may be zero, and may be any integer greater than zero, subject to the requirement that "m" is at least one. "m" + "n" may be less than the total number of ligands that may be attached to M, such that ligands other than those specifically illustrated in Formula 2 may also be attached to M. These additional ligands may be photoactive or ancillary. For iridium, to which 3 bidentate ligands may be attached, "m" may be 1, 2 or 3, and "n" may be 0, 1 or 2.

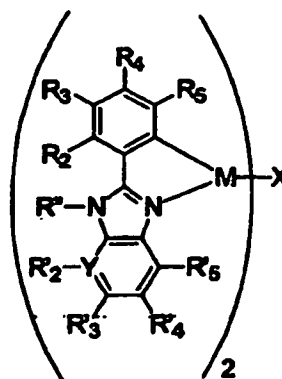
[0049] Preferred ancillary ligands include acetylacetonate (acac), picolinate (pic) and dipivaloylmetanate (t-butyl acac). Some preferred ancillary ligands have the following structure according to Formula 4(pic), Formula 5 (acac), and Formula 6 (t-butyl acac). Other ancillary ligands may be used. Further non-limiting examples of ancillary ligands may be found in PCT Application Publication WO 02/15645 A1 to Lamansky et al. at pages 89-90: :

**Picolinate****Acetylacetonate****dipivaloylmetanate**

[0050] In an embodiment not within the ambit of the claims, n is zero, and m is the maximum number of ligands that may be attached to the metal. For example, for Ir, m is three in this preferred embodiment, and the structure may be referred to as a "tris" structure. The tris structure is preferred because it is believed to be particularly stable. The stability of the tris structure, combined with the stability and color tuning provided by the R₃ group, may result in a particularly stable blue emitting phosphorescent material.

[0051] In one embodiment, m + n is equal to the total number of bidentate ligands that may be attached to the metal in question - for example, 3 for Ir. In another embodiment not within the ambit of the claims; m + n may be less than the maximum number of bidentate ligands that may be attached to the metal, in which case other ligands - ancillary, photoactive, or otherwise - may also be attached to the metal. Preferably, if there are different photoactive ligands attached to the metal, each photoactive ligand has the structure in Formula 2.

[0052] In one embodiment not within the ambit of the claims; the material of Formula 3 has the structure of Formula 7:

Formula 7:

[0053] Y may be selected from the group consisting of C and N. Preferably, Y is C, because it is believed that using compounds in accordance with Formula 3 lead to more stable devices when the top and bottom rings are aryl rings as opposed to heteroaryl rings. R₂, R₃, R₄, R₅, R'₂, R'₃, R'₄, R'₅, and R' may each independently selected from the group consisting of H and any substituent. Where there are multiple substituents, R'', R₂, R₃, R₄, R₅, R'₂, R'₃, R'₄ and R'₅ may be linked to another of the groups R'', R₂, R₃, R₄, R₅, R'₂, R'₃, R'₄ and R'₅ to form a ring.

[0054] It is understood that the various embodiments described herein are by way of example only. For example, many of the materials and structures described herein may be substituted with other materials and structures without deviating from the spirit of the invention. It is understood that various theories as to why the invention works are not intended to be limiting. For example, theories relating to charge transfer are not intended to be limiting.

Material Definitions:

[0055] As used herein, abbreviations refer to materials as follows:

CBP:	4,4'-N,N-dicarbazole-biphenyl
m-MTDATA	4,4',4''-tris(3-methylphenylphenylamino)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:	naphthyl-phenyl-diamine
TPD:	N,N'-bis(3-methylphenyl)-N,N'-bis-(phenyl)-benzidine
BAIq:	aluminum(III)bis(2-methyl-8-quinolinato)4-phenylphenolate
mCP:	1,3-dicarbazole-benzene
DCM:	4-(dicyanomethylene)-6-(4-dimethylaminostyryl-2-methyl)-4H-pyran
DMQA:	N,N'-dimethylquinacridone

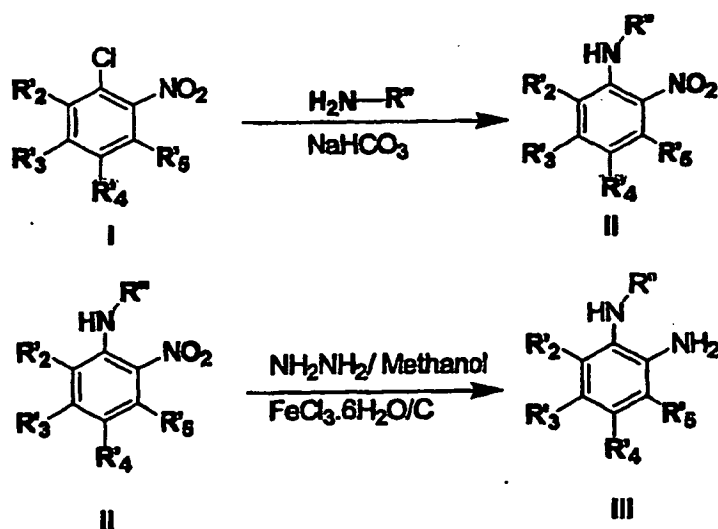
Experimental:

[0056] 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.

[0057] In general, synthesis of the benzimidazole ligands can be prepared as shown in the following two steps depicted in Reaction A and B. Substituted or unsubstituted aromatic diamines can be found commercially or synthesized via Reaction A. In reaction A, the substituted or unsubstituted 2-chloronitrobenzenes represented by graphic formula I,

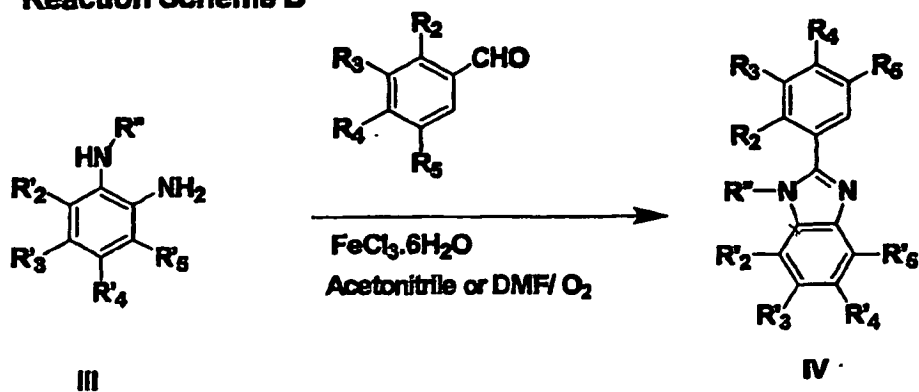
reacts neat with a substituted aniline and a base such as NaHCO_3 by refluxing under nitrogen atmosphere to give compounds represented by graphic formula II. The product after purification can be reduced to the corresponding aromatic diamines by using any number of reducing agents i.e. hydrazine and the addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to give III

Reaction Scheme A

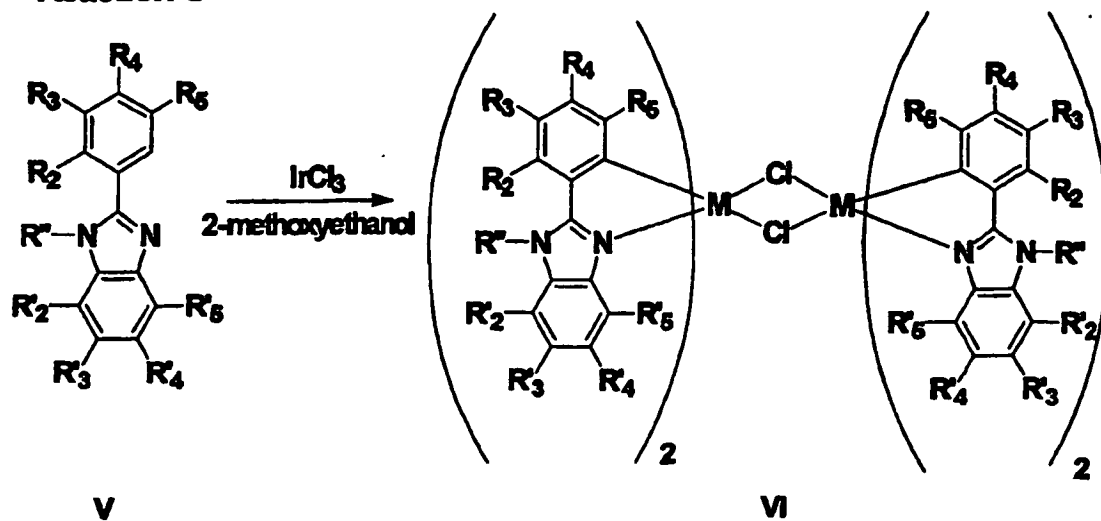


[0058] The synthesis of substituted or unsubstituted benzimidazole ligands can be prepared using diamines represented by graphic formula III as described in Reaction B. Diamines III can then be reacted with a substituted or unsubstituted benzaldehyde as depicted in Reaction Scheme B as described in Synthesis 2000,10,1380-90 to give the substituted benzimidazole ligands represented by graphic formula IV.

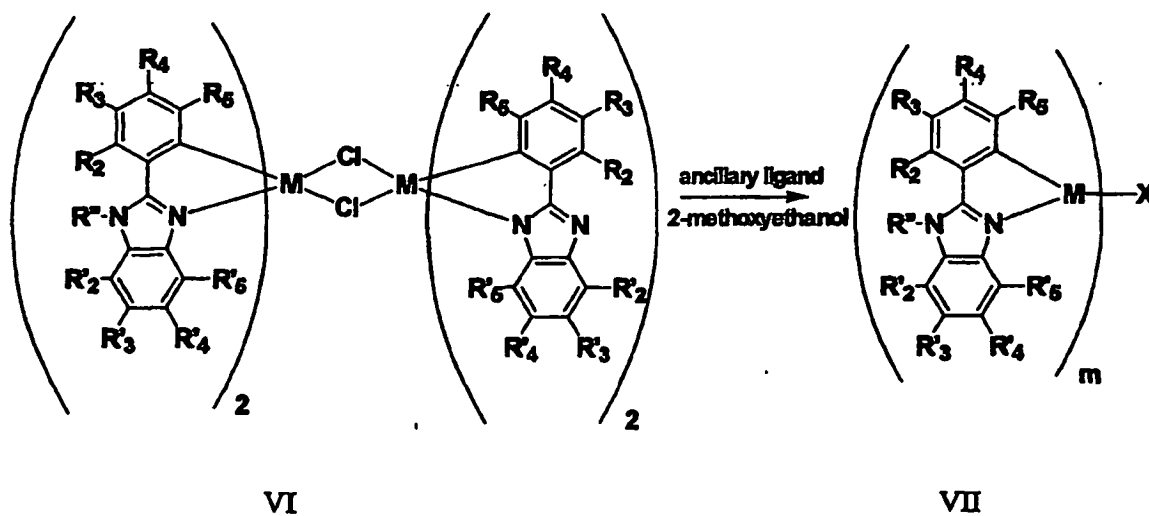
Reaction Scheme B



[0059] In Reaction C, the benzimidazole ligands prepared Reaction B and represented by graphic formula IV, can be reacted with a variety of metals, e.g., iridium, platinum, in the presence of a solvent, e.g., 2-methoxyethanol or 2-ethoxyethanol and water under refluxing conditions to produce the dichloro-bridge dimer represented by graphic formula V. A solid precipitate that is formed upon completion of the reaction is collected by vacuum filtration techniques and further purified if necessary.

Reaction C

[0060] In Reaction D the dichlorobridge dimers represented by graphic formula **VI** can be reacted with a variety of mono-anionic coordinating ligands, e.g. acetonacetyl (acac), picolinic acid, 4-dimethylaminopicolinic acid (DMAPic) and mono-anionic metal-carbon coordination ligands e.g., substituted 2-phenylpyridines, etc and is denoted by **X**. The final isolated products represented by graphic **VII** are purified by standard techniques.

Reaction D

[0061] The materials listed in Table 1 were fabricated according to Formula 7 using the synthetic routes described above or similar routes:

Table 1* Examples 1-25 and 28 are reference examples.

Cmp	M	R ₂	R ₃	R ₄	R ₅	R''	Y	R' ₂	R' ₄	X	C.I.E (MeCl ₂)	PL (nm)
1	Ir	H	H	H	H	CH ₃	C	H	H	acac	0.32, 0.60	509
2	Ir	F	H	F	H	CH ₃	C	H	H	pic	0.25, 0.48	476
3	Ir	H	H	OCH ₃	H	CH ₃	C	H	H	acac	0.23, 0.53	488
4	Ir	H	H	CF ₃	H	CH ₃	C	H	H	pic	0.34, 0.59	510
5	Ir	H	CF ₃	H	H	H	C	H	H	pic	0.28, 0.55	490
6	Ir	H	H	H	H	C ₆ H ₅	C	H	CF ₃	acac	0.37, 0.60	522
7	Ir	H	H	OCH ₃	H	CH ₃	C	H	H	tris	0.25, 0.54	488
8	Ir	H	H	N(CH ₃) ₂	H	C ₆ H ₅	C	H	H	acac	0.35, 0.60	519
9	Ir	H	H	CF ₃	H	C ₆ H ₅	N	H	H	acac	0.54, 0.45	584
10	Ir	H	H	H	H	<i>p</i> OCH ₃ Ph	C	H	H	acac	0.36, 0.60	515
11	Ir	Cl	Cl	H	Cl	C ₆ H ₁₀	C	H	OCH ₃	acac	0.50, 0.49	580
12	Ir	OCH ₃	H	OCH ₃	H	-CH ₃	C	H	H	acac	0.33, 0.53	494
13	Ir	F	F	F	H	CH ₃	C	H	H	acac	0.28, 0.55	490
14	Ir	F	F	F	H	CH ₃	C	H	H	pic	0.28, 0.55	488
15	Ir	Cl	Cl	H	Cl	CH ₃	C	H	H	acac	0.26, 0.47	470
16	Ir	H	CF ₃	F	H	CH ₃	C	H	H	acac	0.27, 0.53	485
17	Ir	H	CF ₃	F	H	CH ₃	C	H	H	pic	0.24, 0.46	474
18	Ir	H	F	OCH ₃	H	CH ₃	C	H	H	acac	0.29, 0.52	488
19	Ir	H	Dioxolene ring		H	CH ₃	C	H	H	acac	0.35, 0.54	522
20	Ir	H	CF ₃	H	CF ₃	CH ₃	C	H	H	acac	0.30, 0.56	490
21	Ir	H	CF ₃	H	CF ₃	CH ₃	C	H	H	pic	0.30, 0.56	488
22	Ir	H	H	OCF ₃	H	CH ₃	C	H	H	acac	0.32, 0.58	500
23	Ir	H	H	OCF ₃	H	CH ₃	C	H	H	pic	0.27, 0.54	486
24	Ir	CF ₃	H	CF ₃	H	CH ₃	C	H	H	acac	0.55, 0.45	580

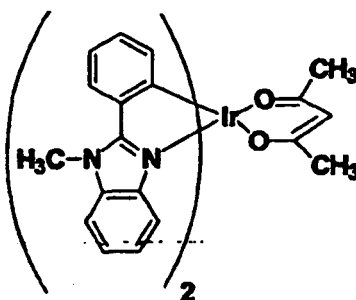
(continued)

Cmp	M	R ₂	R ₃	R ₄	R ₅	R''	Y	R' ₂	R' ₄	X	C.I.E (MeCl ₂)	PL (nm)
25	Ir	F	F	F	F	CH ₃	C	H	H	acac	0.32, 0.58	496
26	Pt	H	H	H	H	CH ₃	C	H	H	acac	0.31, 0.56	486
27	Pt	F	H	F	H	CH ₃	C	H	H	acac	0.28, 0.52	479
28	Ir	H	H	H	H	CH ₂ CH ₂ -R' ₂	C	CH ₂ CH ₂ -R''	H	acac	0.33, 0.60	508

[0062] For each of the materials fabricated, $R'_3 = R'_5 = H$. An entry of "tris" for the ancillary ligand X indicates a deviation from Formula 7, in that there was no ancillary ligand X, and three photoactive ligands ($m = 3, n = 0$). In compound 28, the R'' and R'_2 substituent are linked, i.e., the two substituent positions are linked by an ethylene group. PL is the peak photoluminescent wavelength, measured in nm. The Pt compounds according to the invention also deviate from Formula 7, because Pt may coordinate to only two bidentate ligands, such that the Pt compounds listed in Table 1 have one ancillary and only one photoactive ligand ($m = 1, n = 1$), not two photoactive ligands as indicated in Formula 7.

[0063] For each compound 1 through 28, a small amount of the compound was dissolved in dichloromethane. Each solution was optically pumped, and the resultant photoluminescent spectra were measured. The resultant peak wavelengths and CIE coordinates are tabulated in Table 1.

[0064] An embodiment not within the ambit of the claims, compound 1, has the structure of Formula 8:



[0065] Devices incorporating compounds 1, 3 and 5, as well as $\text{Ir}(\text{ppy})_3$, were fabricated and characterized. All samples were fabricated on glass substrates coated with an ITO anode about 130-150nm thick, obtained from Applied Films Corp. of Longmont, Colorado. Thin films were deposited by thermal evaporation at a pressure of $<1 \times 10^{-6}$ Torr. First CuPc was deposited as a hole injection layer on the anode to a thickness of 10nm at a rate of 0.3 \AA/s . Next NPD was deposited as a hole transport layer to a thickness of 30nm at a rate of 1.5 \AA/s . Next, the emissive layer was deposited by co-evaporation from different sources. Each device had an emissive layer having CBP as a host material, doped with 6% by weight of the compound being characterized. Devices were fabricated having compounds 1, 3 and 5, as well as $\text{Ir}(\text{ppy})_3$, as dopants. The CBP of the emissive layer was deposited at a rate of 1.6 \AA/s (with 6% doping) to a thickness of 30nm. Next, on the emissive layer, BA1q was deposited as a hole blocking layer to a thickness of 10nm at a rate of 1.0 \AA/s . Next, on the hole blocking layer, Alq_3 was deposited as an electron transport layer to a thickness of 40nm at a rate of 1.0 \AA/s . Next, on the electron transport layer, lithium fluoride (LiF) was deposited as an electron injecting layer at a thickness of 0.5nm at a rate of 0.5 \AA/s . Lastly, a cathode of aluminum (Al) was deposited on the electron injecting layer at a thickness of 100nm at a rate of 2 \AA/s to complete the organic light emitting device.

[0066] The devices incorporating compounds 1, 3 and 5, as well as $\text{Ir}(\text{ppy})_3$, were characterized at various luminances. Figure 3 shows plots of luminous efficiency v. luminance. Plots 310, 320, 330 and 340 are for devices doped with compound 1, compound 3, compound 5, and $\text{Ir}(\text{ppy})_3$, respectively. Figure 4 shows plots of external quantum efficiency v. luminance. Plots 410, 420, 430 and 440 are for devices doped with compound 1, compound 3, compound 5, and $\text{Ir}(\text{ppy})_3$, respectively.

[0067] Figures 3 and 4 show that devices fabricated with compound 1 are more efficient than similar devices fabricated with $\text{Ir}(\text{ppy})_3$. While compound 3 appears to be about as efficient as $\text{Ir}(\text{ppy})_3$, and compound 5 appears less efficient, the device structure has been optimized for $\text{Ir}(\text{ppy})_3$. Using a different structure may improve the efficiency of compounds 1, 3 and 5 compared to $\text{Ir}(\text{ppy})_3$. The greater efficiency of compound 1 compared to $\text{Ir}(\text{ppy})_3$ in a device structure optimized for $\text{Ir}(\text{ppy})_3$ shows that compound 1 represents a significant improvement in efficiency. Figure 3 further shows that a device using compound 1 is able to achieve a luminous efficiency of at least 20 cd/A, and more preferably 22.5 cd/A, at a luminance of 500 cd/m^2 , which is superior to the $\text{Ir}(\text{ppy})_3$ device tested.

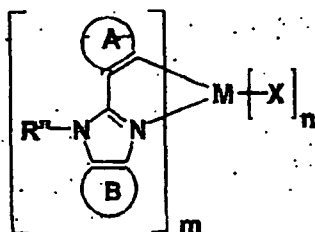
[0068] A device was fabricated as described above, except compound 5 was doped into the emissive layer at a concentration of 12% instead of 6%. The device with 12% doping exhibited a slightly better efficiency than the device with compound 5 at 6% doping, indicating that some improvement in efficiency may be obtained by optimizing the device.

[0069] While the present invention is described with respect to particular examples and embodiments, it is understood that the present invention is not limited to these examples and embodiments. The present invention as claimed therefore includes variations from the particular examples and preferred embodiments described herein, as will be apparent to one of skill in the art.

Claims

1. An organic light emitting device, comprising:

- (a) an anode;
 (b) a cathode; and
 (c) an emissive layer disposed between the anode and the cathode, the emissive layer including a material having the structure:



wherein M is Pt, A is selected from the group consisting of aryl and heteroaryl rings, and B is an aryl ring, R" is selected from the group consisting of H and any substituent, wherein X is an ancillary ligand, and wherein m is 1 and n is 1.

2. The device of claim 1, wherein at least one of A and B includes a substituent.

3. The device of claim 1, wherein the emissive material is incorporated into a polymer.

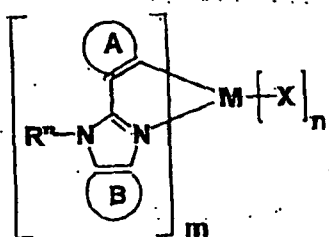
4. The device of claim 1, wherein the emissive material is incorporated into a dendrimer.

5. The device of claim 1, wherein the emissive layer further comprises a host material.

6. The device of claim 5, wherein the emissive material is a dopant in the host material.

7. The device of claim 1, wherein the emissive material consists essentially of a neat film of the emissive material.

8. An emissive material having the structure:



wherein M is Pt, A is selected from the group consisting of aryl and heteroaryl rings, and B is an aryl ring, and, R" is selected from the group consisting of H and any substituent, wherein X is an ancillary ligand, and wherein m is 1 and n is 1.

9. The emissive material of claim 8, wherein at least one of A and B includes a substituent.

10. The emissive material of claim 8, wherein the emissive material is incorporated into a polymer.

11. The emissive material of claim 8, wherein the emissive material is incorporated into a dendrimer.

12. The emissive material of claim 8, wherein the emissive layer further comprises a host material.

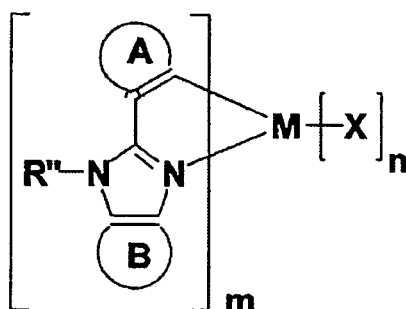
13. The emissive material of claim 12, wherein the emissive material is a dopant in the host material.

14. The emissive material of claim 8, wherein the emissive material consists essentially of a neat film of the emissive material.

Patentansprüche

1. Eine organische Licht-emittierende Einrichtung umfassend:

- (a) eine Anode;
- (b) eine Kathode, und
- (c) eine emittierende Schicht, die zwischen der Anode und der Kathode angeordnet ist, wobei die emittierende Schicht ein Material umfasst, das die folgende Formel aufweist:



worin M Pt ist, A aus der Gruppe bestehend aus Aryl- und Heteroarylringen ausgewählt ist und B ein Arylring ist, R'' aus der Gruppe bestehend aus H und einem beliebigen Substituenten ausgewählt ist, worin X ein Hilfs-
ligand ist und worin m 1 und n 1 ist.

2. Die Einrichtung nach Anspruch 1, in der wenigstens A oder B einen Substituenten umfasst.

3. Die Einrichtung nach Anspruch 1, in der das emittierende Material in ein Polymer eingefügt ist.

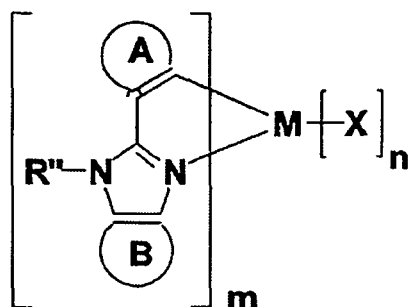
4. Die Einrichtung nach Anspruch 1, in der das emittierende Material in ein Dendrimer eingefügt ist.

5. Die Einrichtung nach Anspruch 1, in der die emittierende Schicht weiterhin ein Wirtmaterial umfasst.

6. Die Einrichtung nach Anspruch 5, in der das emittierende Material ein Dotierungsmittel in dem Wirtmaterial ist.

7. Die Einrichtung nach Anspruch 1, in der das emittierende Material im Wesentlichen aus einem reinen Film des emittierenden Materials besteht.

8. Ein emittierendes Material, das die folgende Formel aufweist:

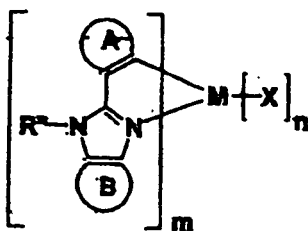


worin M Pt ist, A aus der Gruppe bestehend aus Aryl- und Heteroarylringen ausgewählt ist und B ein Arylring ist und R'' aus der Gruppe bestehend aus H und einem beliebigen Substituenten ausgewählt ist, worin X ein Hilfsligand ist und worin m 1 und n 1 ist.

9. Das emittierende Material nach Anspruch 8, in dem wenigstens A oder B einen Substituenten umfasst.
10. Das emittierende Material nach Anspruch 8, in dem das emittierende Material in ein Polymer eingefügt ist.
11. Das emittierende Material nach Anspruch 8, in dem das emittierende Material in ein Dendrimer eingefügt ist.
12. Das emittierende Material nach Anspruch 8, in dem die emittierende Schicht weiterhin ein Wirtmaterial umfasst.
13. Das emittierende Material nach Anspruch 12, in dem das emittierende Material ein Dotierungsmittel in dem Wirtmaterial ist.
14. Das emittierende Material nach Anspruch 8, in dem das emittierende Material im Wesentlichen aus einem reinen Film des emittierenden Materials besteht.

Revendications

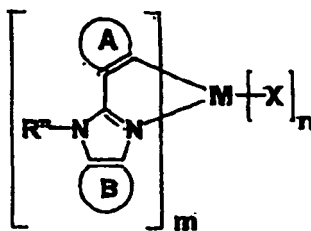
1. Dispositif organique électroluminescent, comprenant
 - (a) une anode ;
 - (b) une cathode ; et
 - (c) une couche émissive placée entre l'anode et la cathode, la couche émissive comprenant un matériau ayant la structure :



où M est Pt, A est choisi parmi le groupe constitué d'anneaux aryle et hétéroaryle, et B est un anneau aryle, R'' est choisi parmi le groupe constitué de H et de tout substituant, où X est un ligand auxiliaire, et où m vaut 1 et n vaut 1.

2. Dispositif selon la revendication 1, dans lequel au moins l'un de A et B comprend un substituant.
3. Dispositif selon la revendication 1, dans lequel le matériau émissif est incorporé dans un polymère.

4. Dispositif selon la revendication 1, dans lequel le matériau émissif est incorporé dans un dendrimère.
5. Dispositif selon la revendication 1, dans lequel la couche émissive comprend de plus un matériau hôte.
- 5 6. Dispositif selon la revendication 5, dans lequel le matériau émissif est un dopant dans le matériau hôte.
7. Dispositif selon la revendication 1, dans lequel le matériau émissif est constitué pour l'essentiel d'un film pur du matériau émissif.
- 10 8. Matériau émissif ayant la structure :



où M est Pt, A est choisi parmi le groupe constitué d'anneaux aryle et hétéroaryle, et B est un anneau aryle, et Rⁿ est choisi parmi le groupe constitué de H et de tout substituant, où X est un ligand auxiliaire, et où m vaut 1 et n vaut 1.

9. Matériau émissif selon la revendication 8, dans lequel au moins l'un de A et B comprend un substituant.
10. Matériau émissif selon la revendication 8, dans lequel le matériau émissif est incorporé dans un polymère.
11. Matériau émissif selon la revendication 8, dans lequel le matériau émissif est incorporé dans un dendrimère.
12. Matériau émissif selon la revendication 8, dans lequel la couche émissive comprend de plus un matériau hôte.
13. Matériau émissif selon la revendication 12, dans lequel le matériau émissif est un dopant dans le matériau hôte.
14. Matériau émissif selon la revendication 8, dans lequel le matériau émissif est constitué pour l'essentiel d'un film pur du matériau émissif.

Figure 1

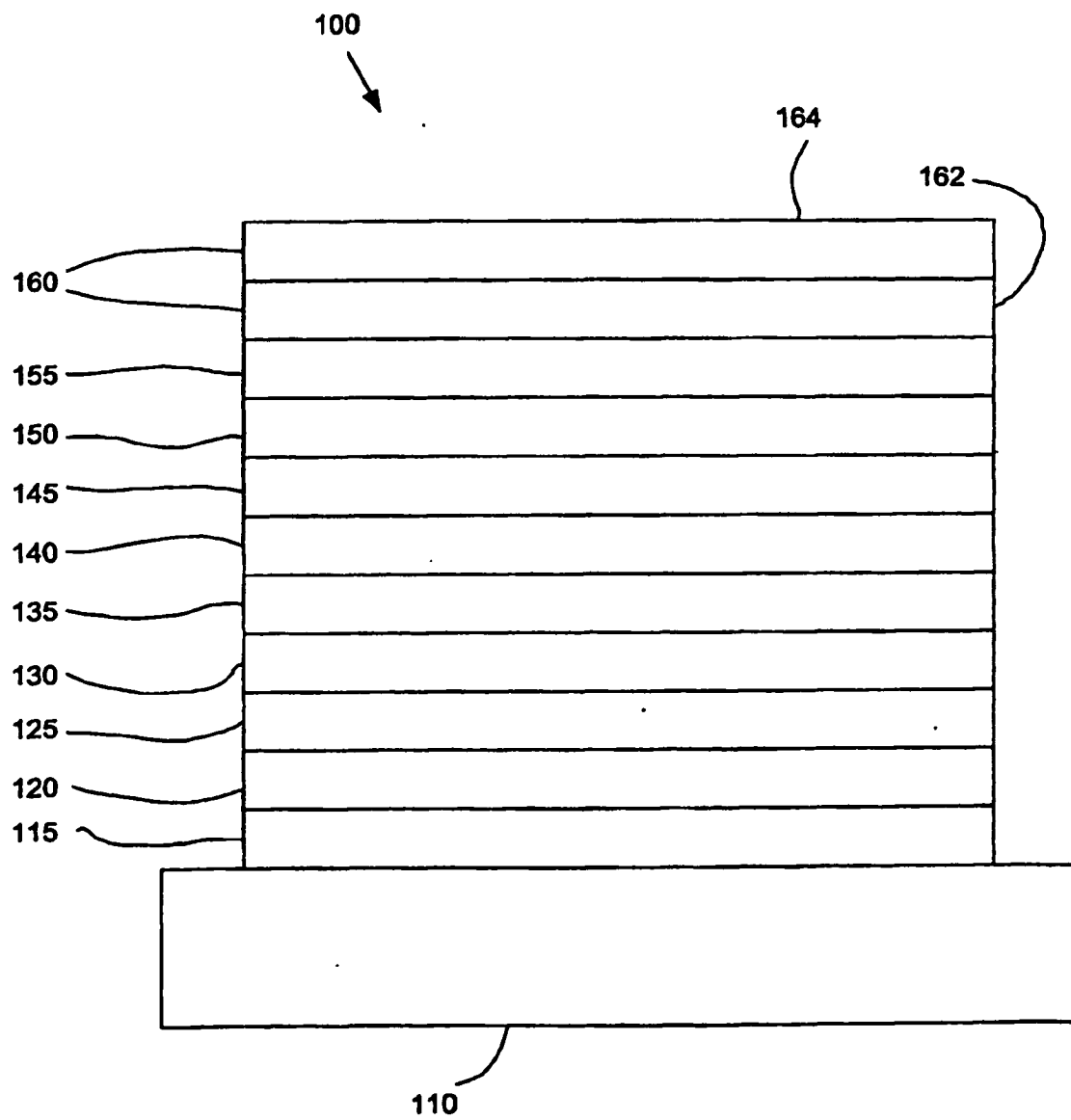
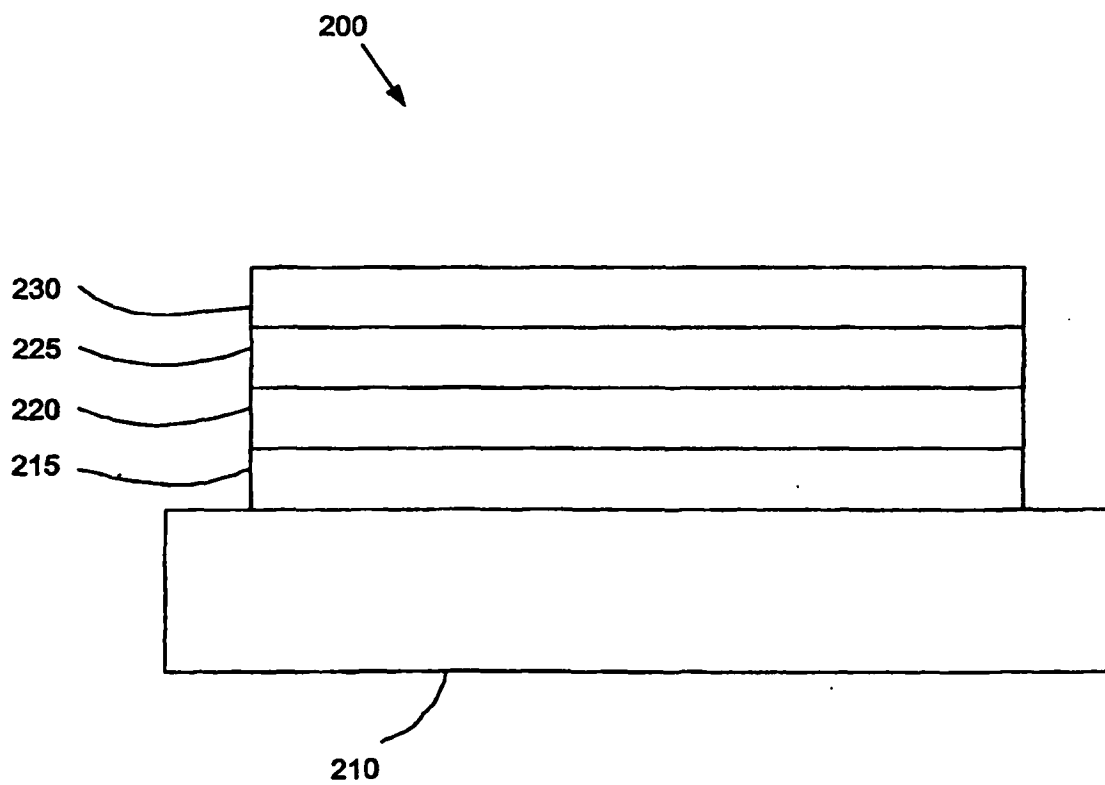


Figure 2



Compounds 1, 3 and 5 vs Ir(ppy)₃, 6% doping

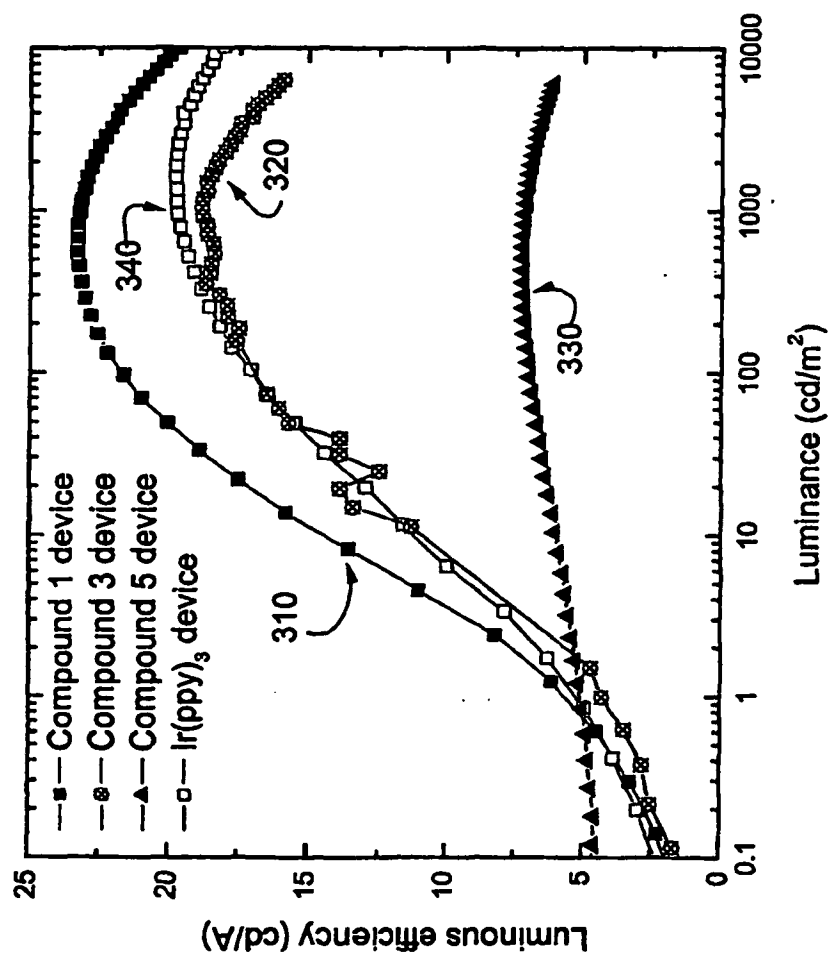


Figure 3

Compounds 1, 3 and 5 vs Ir(ppy)₃, 6% doping

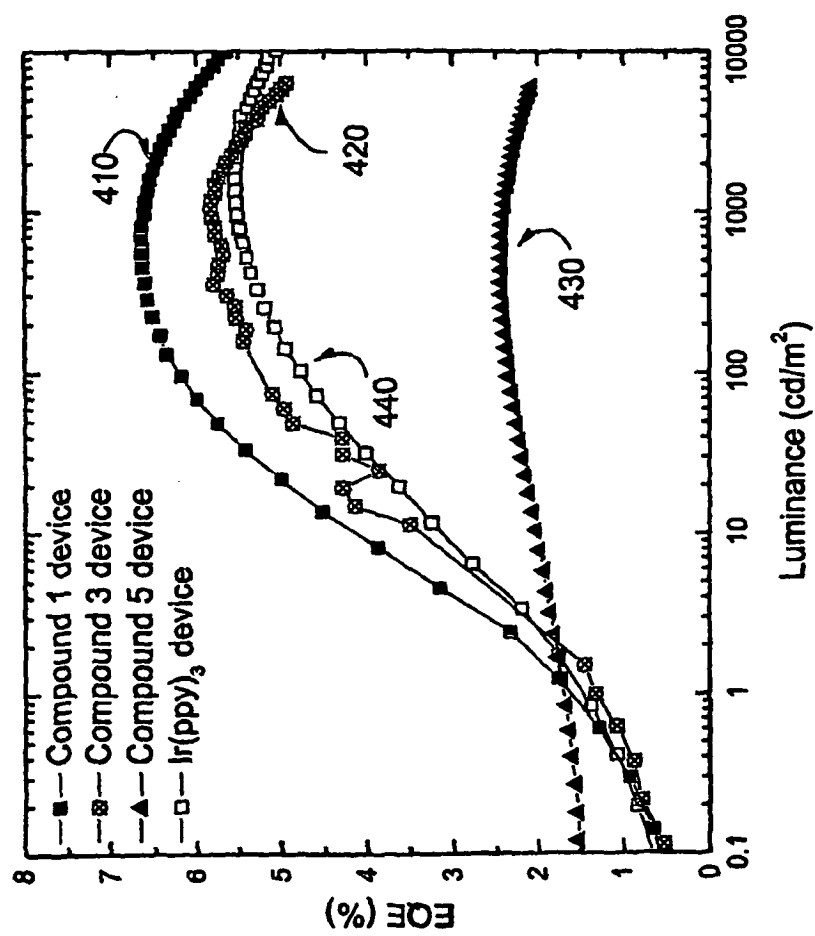


Figure 4

REFERENCES CITED IN THE DESCRIPTION

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专利名称(译)	有机发光材料和器件		
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[标]申请(专利权)人(译)	环球展览公司 南加利福尼亚大学		
申请(专利权)人(译)	通用显示器公司 南加州大学		
当前申请(专利权)人(译)	通用显示器公司 南加州大学		
[标]发明人	MA BIN KNOWLES DAVID B BROWN CORY S MURPHY DREW THOMPSON MARK E		
发明人	MA, BIN KNOWLES, DAVID B. BROWN, CORY S. MURPHY, DREW THOMPSON, MARK E.		
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摘要(译)

本发明涉及一种有机发光器件，包括阳极，阴极和设置在阳极和阴极之间的发光层，发光层包括具有以下结构的材料：其中M是Pt，A选自自由芳基和杂芳基环组成的基团，和B是芳基环，Rⁿ选自H和任何取代基，并且其中m是1且n是1。

