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(54) **ORGANIC ELECTROLUMINESCENT MATERIALS AND DEVICES**

(71) Applicant: **Universal Display Corporation,** Ewing, NJ (US)

(72) Inventors: **Jui-Yi Tsai,** Lawrenceville, NJ (US); **Walter Yeager,** Yardley, PA (US); **Jason Brooks,** Philadelphia, PA (US); **Scott Beers,** Flemington, NJ (US); **Gregory S. Kottas,** Yardley, PA (US); **Edward Barron,** Hamilton, NJ (US); **Raymond Kwong,** Plainsboro, NJ (US)

(73) Assignee: **UNIVERSAL DISPLAY CORPORATION**, Ewing, NJ (US)

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(51) **Int. Cl.**
H01L 51/54 (2006.01)
C09K 11/06 (2006.01)
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(52) **U.S. Cl.**
CPC **H01L 51/0085** (2013.01); **C07F 15/0033** (2013.01); **C09K 11/06** (2013.01);
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(58) **Field of Classification Search**
None
See application file for complete search history.

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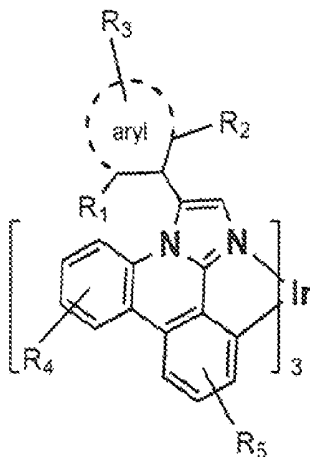(Continued)

Primary Examiner — Marie R. Yamnitzky
(74) *Attorney, Agent, or Firm* — Duane Morris LLP

(57) **ABSTRACT**

Imidazo[1,2-f]phenanthridine compounds are provided. The compounds have a twisted aryl moiety further substituted by alkyl having four or more atoms. The compounds may be used in organic light emitting devices, particularly as emissive dopants, providing devices with improved efficiency, stability, and manufacturing. In particular, the compounds provided herein may be used in blue devices having high efficiency.

17 Claims, 3 Drawing Sheets

Related U.S. Application Data

(60) Provisional application No. 61/122,259, filed on Dec. 12, 2008.

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FIGURE 1

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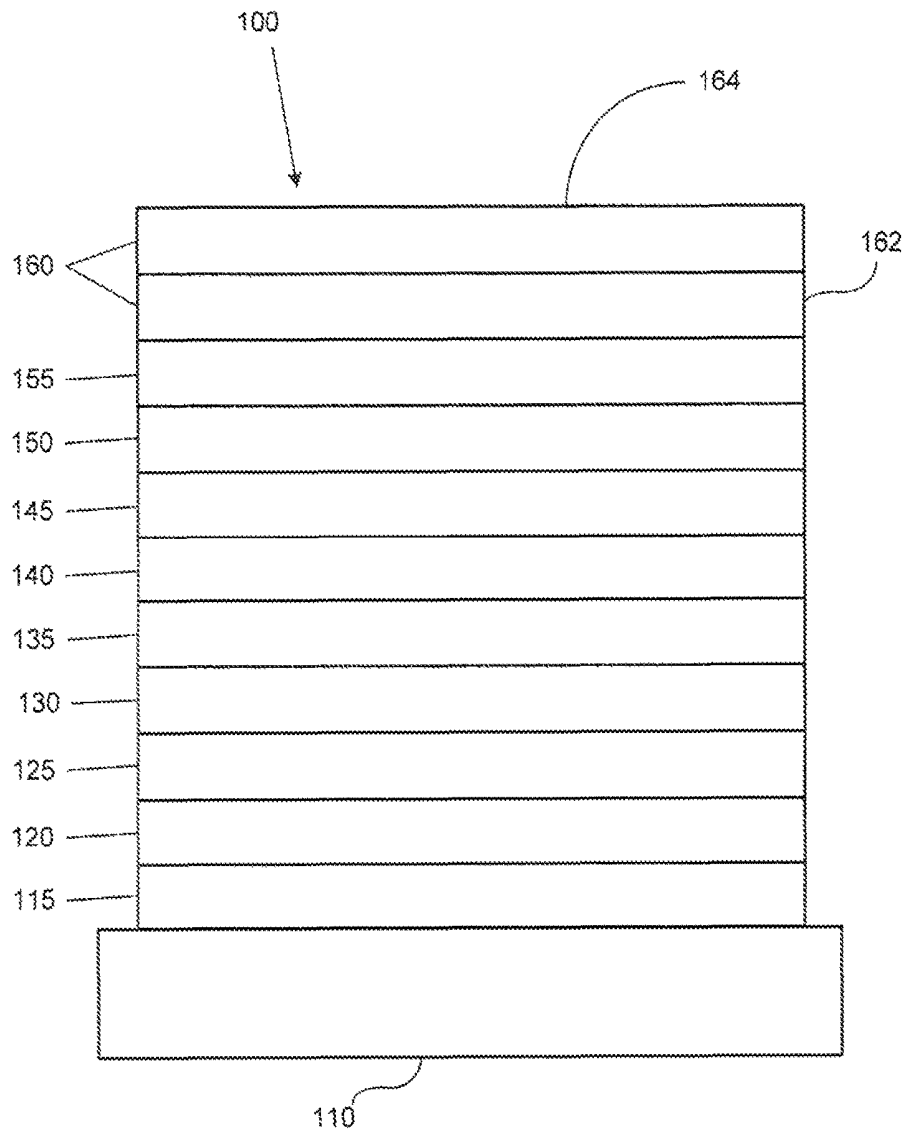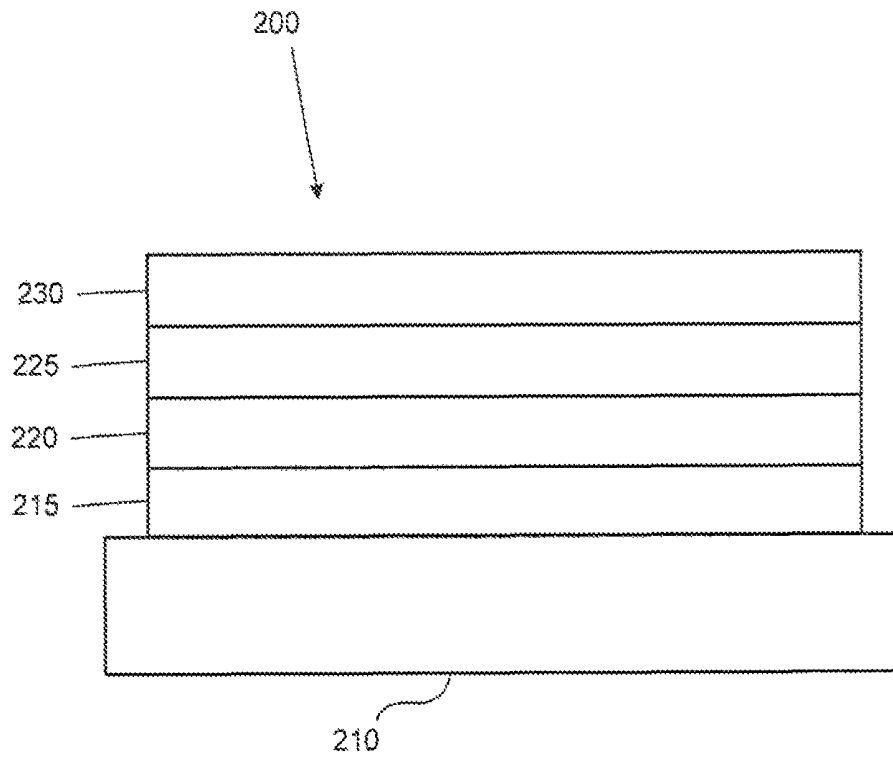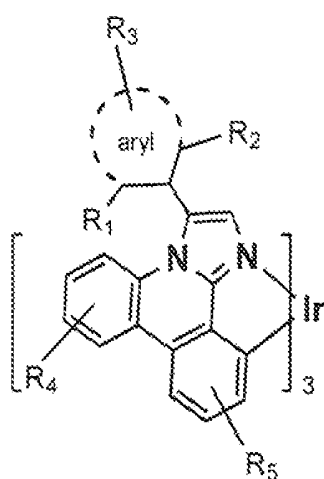
FIGURE 2

FIGURE 3

ORGANIC ELECTROLUMINESCENT MATERIALS AND DEVICES

This application is a continuation of U.S. application Ser. No. 12/632,251, filed Dec. 7, 2009, now U.S. Pat. No. 8,815,415, which claims priority to U.S. Provisional Application No. 61/122,259, filed Dec. 12, 2008, the disclosures of which are expressly incorporated herein by reference in their entirety.

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

FIELD OF THE INVENTION

The present invention relates to organic light emitting devices (OLEDs), and specifically phosphorescent organic materials used in such devices. More specifically, the invention relates to imidazo[1,2-f]phenanthridine compounds and devices containing these compounds.

BACKGROUND

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.

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

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.

One example of a green emissive molecule is tris(2-phenylpyridine) indium, denoted $Ir(ppy)_3$, which has the structure of Formula I:
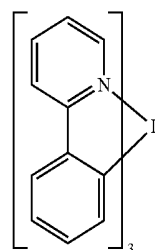
In this, and later figures herein, we depict the dative bond from nitrogen to metal (here, Ir) as a straight line.

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.

As used herein, "top" means furthest away from the substrate, while "bottom" means closest to the substrate. Where a first layer is described as "disposed over" a second layer, the first layer is disposed further away from substrate. There may be other layers between the first and second layer, unless it is specified that the first layer is "in contact with" the second layer. For example, a cathode may be described as "disposed over" an anode, even though there are various organic layers in between.

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.

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

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

As used herein, and as would be generally understood by one skilled in the art, a first work function is "greater than"

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or "higher than" a second work function if the first work function has a higher absolute value. Because work functions are generally measured as negative numbers relative to vacuum level, this means that a "higher" work function is more negative. On a conventional energy level diagram, with the vacuum level at the top, a "higher" work function is illustrated as further away from the vacuum level in the downward direction. Thus, the definitions of HOMO and LUMO energy levels follow a different convention than work functions.

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

SUMMARY OF THE INVENTION

Compounds are provided having the formula:
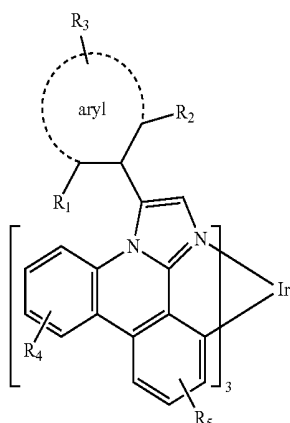
FORMULA I

R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, and aryl. At least one of R_1 and R_2 is an alkyl having four or more atoms. R_3, R_4, and R_5 may represent mono, di, tri, or tetra substitutions. R_3, R_4, and R_5 are independently selected from the group consisting of hydrogen, alkyl, and aryl. In one aspect, R_1 and R_2 are the same. In another aspect, R_1 and R_2 are different. In yet another aspect, one of R_1 and R_2 is an aryl.

The alkyl having four or more atoms may be a branched alkyl, a cyclic alkyl, a bicyclic alkyl, or a multicyclic alkyl.

In one aspect, the alkyl having four or more atoms may contain all carbon atoms. In another aspect, the alkyl having four or more atoms may be a substituted alkyl which may further contain at least one of oxygen atoms, nitrogen atoms, and sulfur atoms.

The compound may have the formula
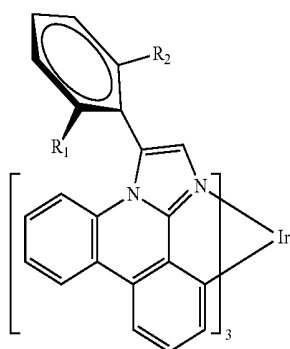
4

Specific examples of the compound are provided including Compounds 1-36. Preferably, the compound is Compound 1 or Compound 2.

Additionally, a compound including a ligand is provided. The ligand has the formula:
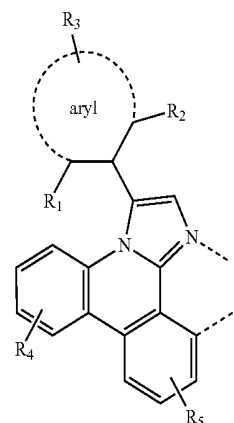
R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, and aryl, and at least one of R_1 and R_2 is an alkyl having four or more atoms. R_3, R_4, and R_5 may represent mono, di, tri, or tetra substitutions. R_3, R_4, and R_5 are independently selected from the group consisting of hydrogen, alkyl, and aryl.

An organic light emitting device is also provided. The device has an anode, a cathode, and an organic layer disposed between the anode and the cathode. The organic layer further comprises a compound having FORMULA I. Preferably the organic layer is an emissive layer having a host and an emissive dopant, and the compound is the emissive dopant.

A consumer product is also provided. The product contains a device that has an anode, a cathode, and an organic layer disposed between the anode and the cathode, wherein the organic layer further comprises a compound having FORMULA I.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows an organic light emitting device.

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

FIG. 3 shows an imidazo[1,2-f]phenanthridine compound.

DETAILED DESCRIPTION

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.

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

More recently, OLEDs having emissive materials that emit light from triplet states ("phosphorescence") have been demonstrated. Baldo et al., "Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices," Nature, vol. 395, 151-154, 1998; ("Baldo-I") and Baldo et al., "Very high-efficiency green organic light-emitting devices based on electrophosphorescence," Appl. Phys. Lett., vol. 75, No. 3, 4-6 (1999) ("Baldo-II"), which are incorporated by reference in their entireties. Phosphorescence is described in more detail in U.S. Pat. No. 7,279,704 at cols. 5-6, which are incorporated by reference.

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. The properties and functions of these various layers, as well as example materials, are described in more detail in U.S. Pat. No. 7,279,704 at cols. 6-10, which are incorporated by reference.

More examples for each of these layers are available. For example, a flexible and transparent substrate-anode combination is disclosed in U.S. Pat. No. 5,844,363, which is incorporated by reference in its entirety. An example of a p-doped hole transport layer is m-MTDATA doped with F.sub.4-TCNQ at a molar ratio of 50:1, as disclosed in U.S. Patent Application Publication No. 2003/0230980, which is incorporated by reference in its entirety. Examples of emissive and host materials are disclosed in U.S. Pat. No. 6,303,238 to Thompson et al., which is incorporated by reference in its entirety. An example of an n-doped electron transport layer is BPhen doped with Li at a molar ratio of 1:1, as disclosed in U.S. Patent Application Publication No. 2003/0230980, which is incorporated by reference in its entirety. U.S. Pat. Nos. 5,703,436 and 5,707,745, which are incorporated by reference in their entireties, disclose examples of cathodes including compound cathodes having a thin layer of metal such as Mg:Ag with an overlying transparent, electrically-conductive, sputter-deposited ITO layer. The theory and use of blocking layers is described in more detail in U.S. Pat. No. 6,097,147 and U.S. Patent Application Publication No. 2003/0230980, which are incorporated by reference in their entireties. Examples of injection layers are provided in U.S. Patent Application Publication No. 2004/0174116, which is incorporated by reference in its entirety. A description of protective layers may be found in U.S. Patent Application Publication No. 2004/0174116, which is incorporated by reference in its entirety.

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

The simple layered structure illustrated in FIGS. 1 and 2 is provided by way of non-limiting example, and it is understood that embodiments of the invention may be used in connection with a wide variety of other structures. The specific materials and structures described are exemplary in nature, and other materials and structures may be used. Functional OLEDs may be achieved by combining the various layers described in different ways, or layers may be omitted entirely, based on design, performance, and cost factors. Other layers not specifically described may also be included. Materials other than those specifically described may be used. Although many of the examples provided herein describe various layers as comprising a single material, it is understood that combinations of materials, such as a mixture of host and dopant, or more generally a mixture, may be used. Also, the layers may have various sublayers. The names given to the various layers herein are not intended to be strictly limiting. For example, in device 200, hole transport layer 225 transports holes and injects holes into emissive layer 220, and may be described as a hole transport layer or a hole injection layer. In one embodiment, an OLED may be described as having an "organic layer" disposed between a cathode and an anode. This organic layer may comprise a single layer, or may further comprise multiple layers of different organic materials as described, for example, with respect to FIGS. 1 and 2.

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

Unless otherwise specified, any of the layers of the various embodiments may be deposited by any suitable method. For the organic layers, preferred methods include thermal evaporation, ink-jet, such as described in U.S. Pat. Nos. 6,013,982 and 6,087,196, which are incorporated by reference in their entireties, organic vapor phase deposition (OVPD), such as described in U.S. Pat. No. 6,337,102 to Forrest et al., which is incorporated by reference in its entirety, and deposition by organic vapor jet printing (OVJP), such as described in U.S. Pat. No. 7,431,968, which is incorporated by reference in its entirety. Other suitable deposition methods include spin coating and other solution based processes. Solution based processes are preferably carried out in nitrogen or an inert atmosphere. For the other layers, preferred methods include thermal evaporation. Preferred patterning methods include deposition through a mask, cold welding such as described in U.S. Pat. Nos. 6,294,398 and 6,468,819, which are incorporated by reference in their entireties, and patterning associated with some of the deposition methods such as ink-jet and OVJD. Other methods may also be used. The materials to be deposited may be modified to make them compatible with a particular deposition method. For example, substituents such as alkyl and aryl groups, branched or unbranched, and preferably

containing at least 3 carbons, may be used in small molecules to enhance their ability to undergo solution processing. Substituents having 20 carbons or more may be used, and 3-20 carbons is a preferred range. Materials with asymmetric structures may have better solution 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.

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.).

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.

The terms halo, halogen, alkyl, cycloalkyl, alkenyl, alkynyl, arylkyl, heterocyclic group, aryl, aromatic group, and heteroaryl are known to the art, and are defined in U.S. Pat. No. 7,279,704 at cols. 31-32, which are incorporated herein by reference.

Imidazo 1,2-f]phenanthridine (herein called "imidazophenanthridine") compounds containing a twisted aryl moiety further substituted with an alkyl having four or more atoms are provided. FIG. **3** shows a structure for such substituted imidazophenanthridine compounds. These compounds can be used in phosphorescent organic light emitting devices to provide high efficiency, high stability, long lifetime, improved manufacturing and improved color. Specifically, phosphorescent organic light emitting devices containing imidazo[1,2-f]phenanthridine iridium complexes containing a twisted aryl moiety further substituted with bulky alkyl groups (i.e., alkyl groups containing four or more atoms) as the emitting materials can have significantly higher efficiency than devices containing emitting materials which lack the bulky alkyl substituted twisted aryl group. The compounds may be used as phosphorescent emissive dopants in color OLEDs and white OLEDs. In particular, the compounds can be used as emissive dopants in high efficiency blue phosphorescent OLEDs. The development of dopant materials, such as the substituted imidazophenanthridine compounds provided herein, suitable for use in blue emissive devices are particularly desirable.

The indium imidazo[1,2-f]phenanthridine complexes contain a twisted aryl moiety that is further substituted at the 2 and/or n position, wherein n is the number of atoms in the aryl moiety, and the atom of the aryl moiety connected to the imiadzole is the 1 position, with an alkyl group having four or more atoms. These compounds containing bulky alkyl groups may have high photoluminescence (PL) and high electroluminescence (EL) efficiencies. Without being bound by theory, it is believed that the bulky alkyl substituents on the twisted aryl provide steric protection of the imidazole which is especially sensitive to self-quenching interactions. Imidazoles are prone to stacking because of their more polar

nature, and the stacking of the imidazole rings may readily deactivates the active state of the complex via self-quenching. It is thought that bulky alkyl substituents present on the twisted aryl moiety of the compound may prevent stacking of the imidazole rings thereby inhibiting self-quenching. In particular, the three dimensional arrangement of the 2, n alkyl groups having four or more atoms is particularly good at protecting the imidazole heterocycle. In addition, the steric protection provided by the 2, n bulky alkyl substituents may then result in an increased quantum yield. Therefore, the addition of bulky alkyl groups to the aryl may improve device efficiency and device lifetime.

While substituted imidazophenanthridine compounds and their use in OLEDs are known, several problems may be associated with devices containing these compounds. For example, as shown in Table 2, substitution with an alkyl group at the 2 position of imidazophenanthridine, such as in Comparative Example 1, high PL and EL efficiencies can be obtained but the device lifetime is poor. Another example is the twisted aryl at the 3 position of imidazophenanthridine with less bulky R_1 and R_2 groups (e.g., alkyl containing one, two, or three atoms), such as in Comparative Example 2, can increase the device lifetime, but PL efficiency is low, thus resulting in low device efficiency. Therefore, it is desirable to develop a dopant that can provide high device efficiency and high device lifetime.

In order to increase efficiency and maintain lifetime, compounds were synthesized in which bulky alkyl groups were added to the 2 and/or n positions of the twisted aryl moiety of the imidazophenanthridine compound. Both the size of the alkyl group (i.e., a bulky alkyl having four or more atoms) and the site of substitution (i.e., the 2 and/or n positions of the twisted aryl moiety) are believed to be important for the beneficial properties of the compounds provided herein. As discussed above, the bulky alkyl groups can improve the quantum yield and provide high efficiency likely due to steric protection of the imidazole. The bulky alkyl substituents may also lead to improved luminescence quantum yield by protecting the imidazole from reacting with oxygen, a pathway which decreases quantum yield. Again, the position of the bulky alkyl is thought to be important in order to obtain increased quantum yield. For example, a compound containing a bulky alkyl substituent at another position on the imidazophenanthridine compound may not demonstrate the same EL and PL (see Comparative example 3 in Table 2). Moreover, the compounds provided herein may provide devices having long lifetimes. For example, device lifetimes for inventive compound, such as Compounds 1 and 2, can be significantly longer then device lifetimes for other imidazophenanthridine compounds lacking the bulky alkyl substituted twisted aryl (see Table 2). In addition, certain bulky alkyl groups at the 2 and n positions may provide cleaner sublimation thus improving device performance and processing.

Asymmetric compounds in which R_1 and R_2 are not the same, but at least one of R_1 and R_2 is an alkyl having four or more atoms, are also provided. These asymmetrical compounds may provide improved lifetime and efficiency as well as offer several additional advantages. For example, asymmetric compounds may offer advantages for sublimation and processing. Asymmetric compounds maintain the advantages of the symmetric compounds discussed above, and may further benefit from having a less bulky (e.g., hydrogen, alkyl having 3 or fewer atoms) substituent at the other of R_1 and R_2. By having one less bulky substituent and one more bulky substituent, these compounds may have a lower molecular weight and thus may be expected to have a lower sublimation temperature while preserving the benefits of high luminescence quantum yield. So then, asymmetric compounds may provide a means to further tune the prop-

erties of the emissive dopant having beneficial properties in device lifetime and device stability.

In addition, synthesis of the imidazophenanthridine compounds containing a twisted aryl further substituted by alkyl having four or more atoms provided herein involves only one intermediate. Therefore, the synthesis of these compounds may be advantageous compared to the synthesis of other compounds which require more steps and more intermediates in order to yield product.

Imidazo[1,2-f]phenanthridine compounds are provided, which may be advantageously used in OLEDs, having the formula:
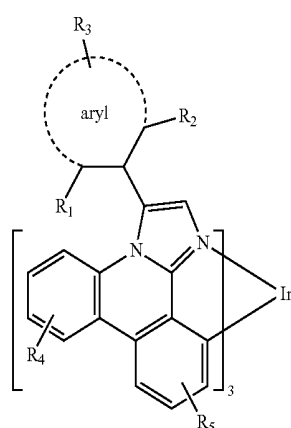
FORMULA I

where R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, and aryl, and at least one of R_1 and R_2 is an alkyl having four or more atoms. R_3, R_4, and R_5 may represent mono, di, tri, or tetra substitutions, and R_3, R_4, and R_5 are independently selected from the group consisting of hydrogen, alkyl, and aryl. In one aspect, R_1 and R_2 are the same. In another aspect, R_1 and R_2 are different. In yet another aspect, one of R_1 and R_2 is an aryl.

In one aspect, the alkyl having four or more atoms is a branched alkyl. A branched alkyl substituent having four or more atoms may further prevent stacking of the imidazole rings by providing additional bulk (i.e., more atoms) thereby increasing the steric protection provided by the bulky alkyl substituent and improving quantum yield. In another aspect, the alkyl having four or more atoms is a cyclic alkyl. In particular, the cyclic alkyl can be a bicyclic alkyl and a multicyclic alkyl. Similarly, the presence of a cyclic, bicyclic and/or multicyclic alkyl at R_1 and R_2 may provide increased bulk and greater steric protection thereby improving quantum yield.

In one aspect, the alkyl having four or more atoms contains only carbon atoms. In another aspect, the alkyl having four or more atoms is a heteroalkyl. As used herein, "heteroalkyl" refers to an alkyl having four or more atoms wherein at least one of the atoms is a commonly used heteroatom. As used herein, "heteroatom" refers to an atom other than carbon or hydrogen including, but not limited to, oxygen, nitrogen, phosphorous, sulfur, selenium, arsenic, chlorine, bromine, silicon, and fluoride. Preferably, the heteroalkyl contains an oxygen atom. The heteroalkyl substituent acts as an electron withdrawing group thereby reducing the LUMO level (i.e., increasing electron stability) and improving the device stability. Moreover, based on standard calculations, the heteroalkyl may result in minimal red-shifting of the compound. Thus, these compounds provide good blue emission as well as improved stability, lifetime and processing.

In one aspect, the compound has the formula:
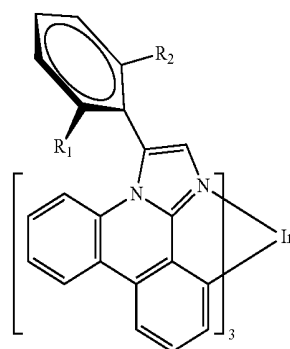
Particular examples of compounds described herein include compounds selected from the group consisting of:
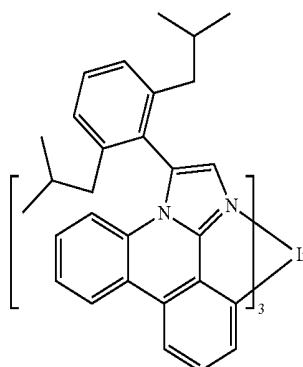
Compound 1
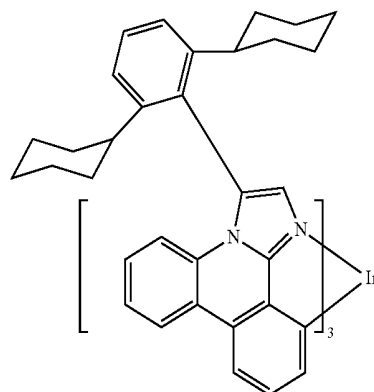
Compound 2

Compound 3

11

-continued

Compound 4

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Compound 5

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Compound 6

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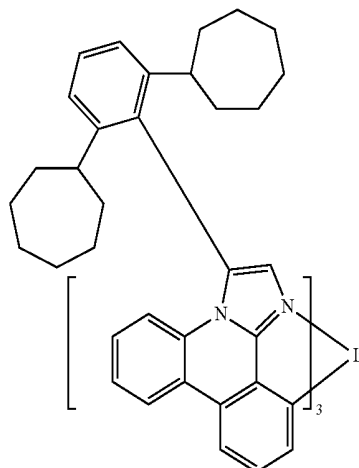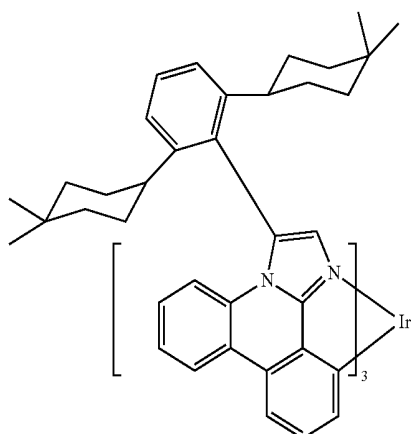
12

-continued

Compound 7

Compound 8

Compound 9

-continued

Compound 10

Compound 11

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Compound 12

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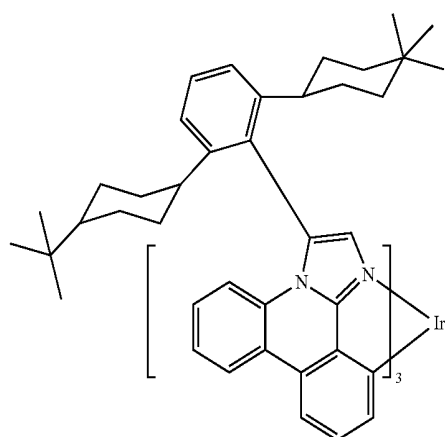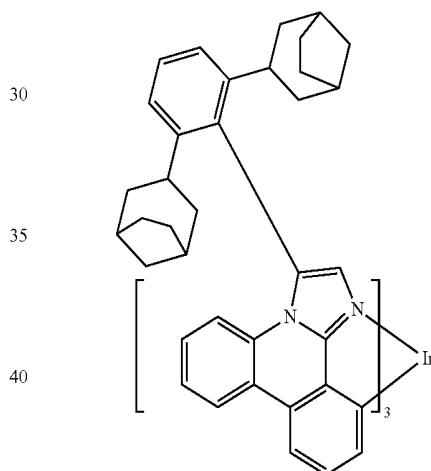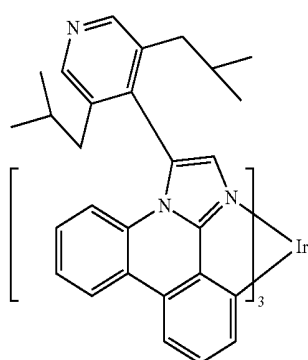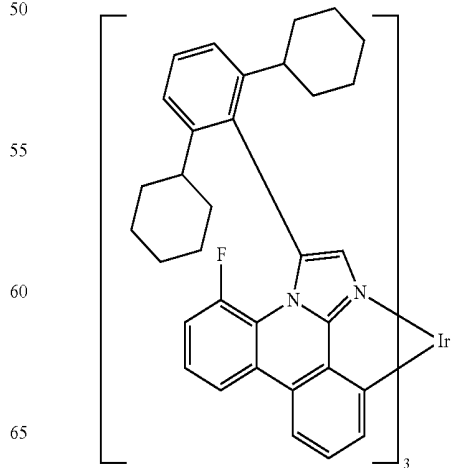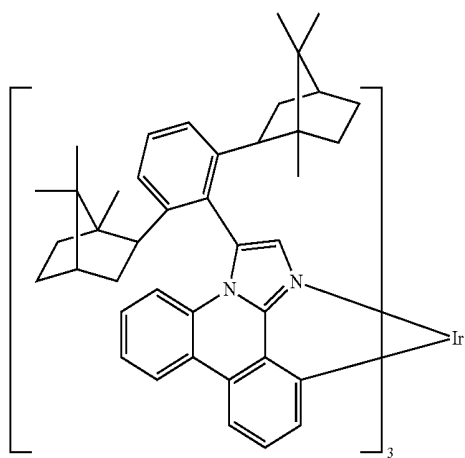
-continued

Compound 13
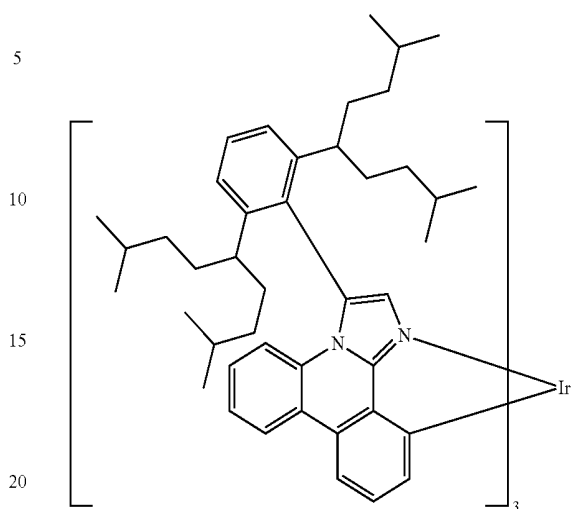
Compound 14
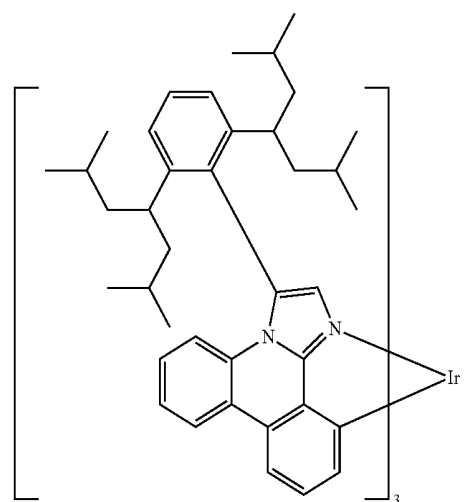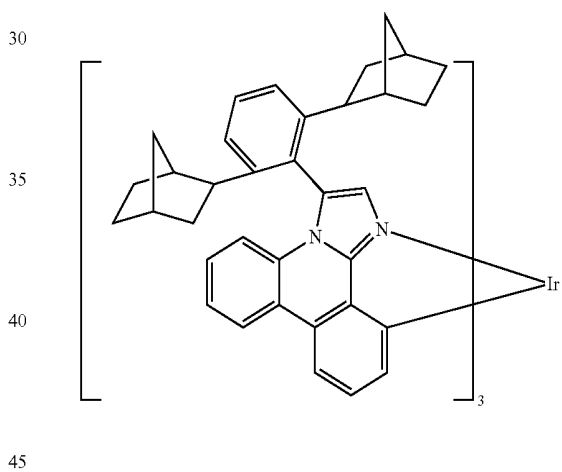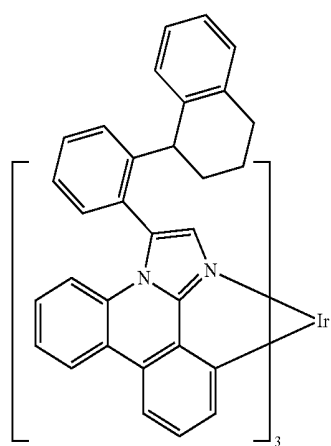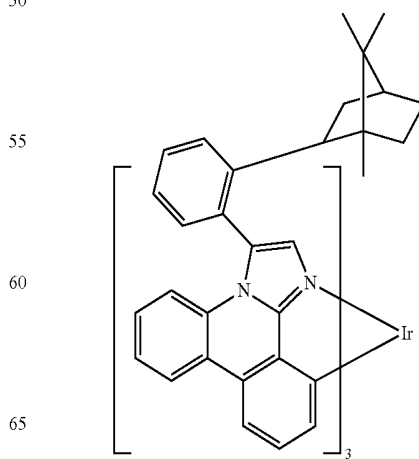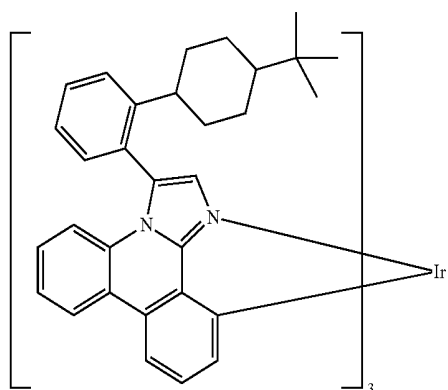
Compound 15

-continued

Compound 16
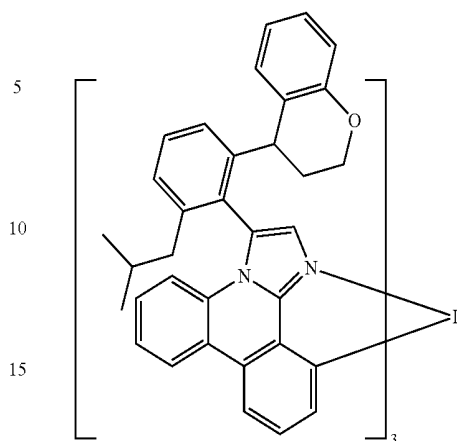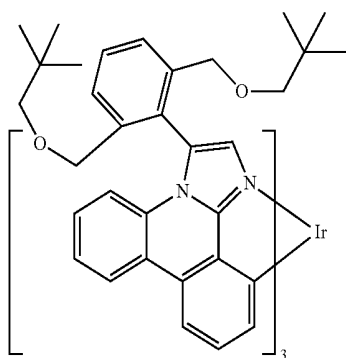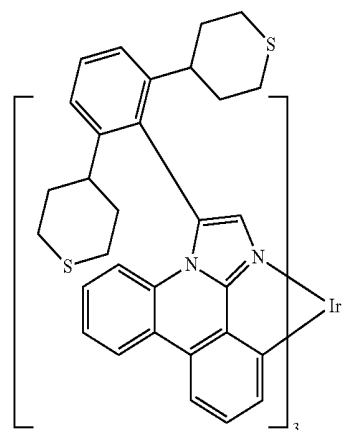
Compound 17

Compound 18

Compound 19

-continued

Compound 20

Compound 21

Compound 22

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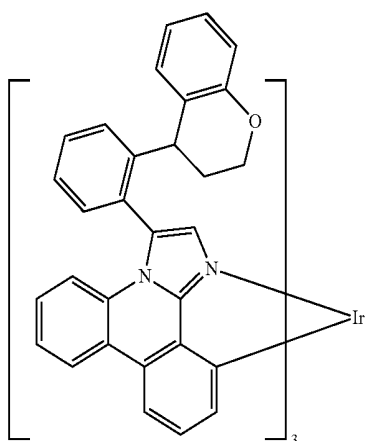
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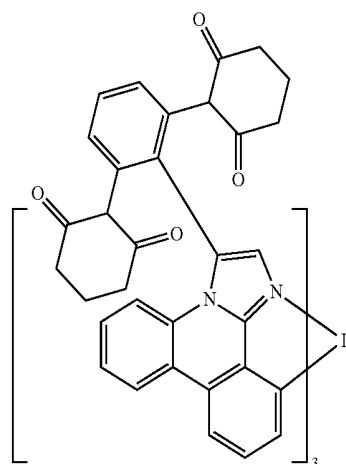
Compound 23
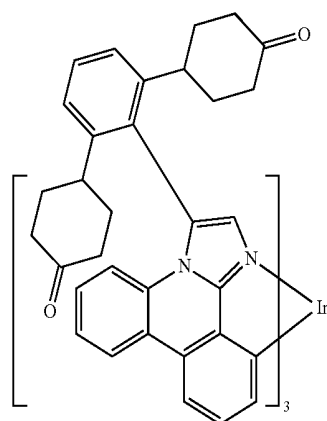
Compound 24
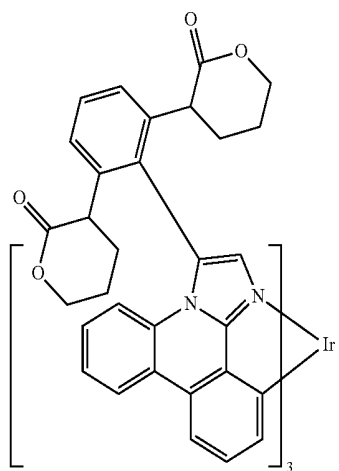
Compound 25

18

-continued

Compound 26

Compound 27

Compound 28

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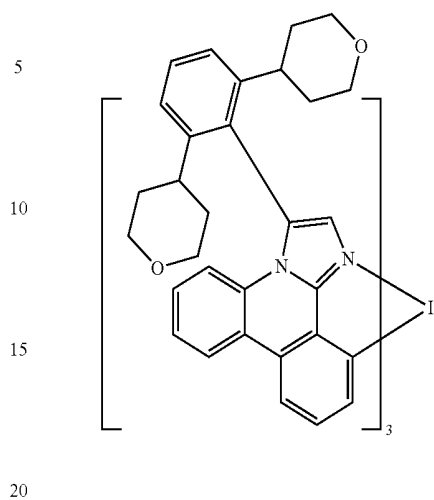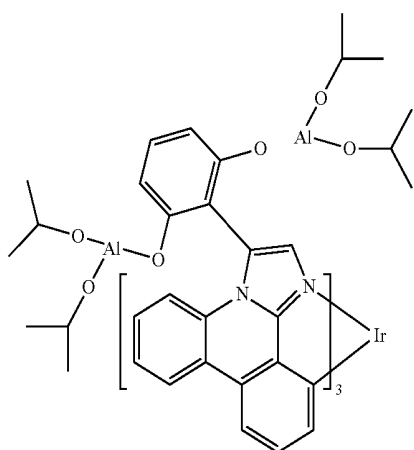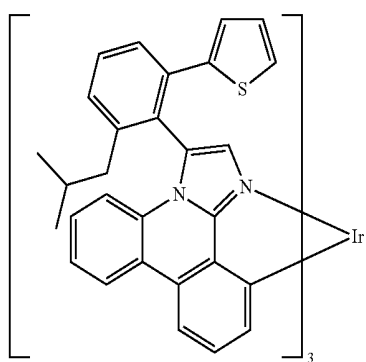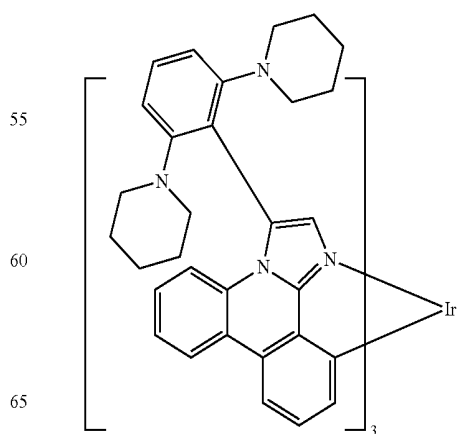
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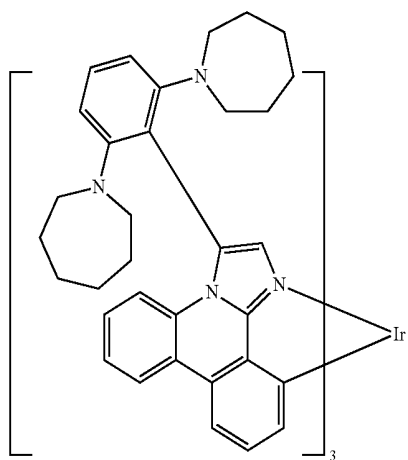
Compound 29

20
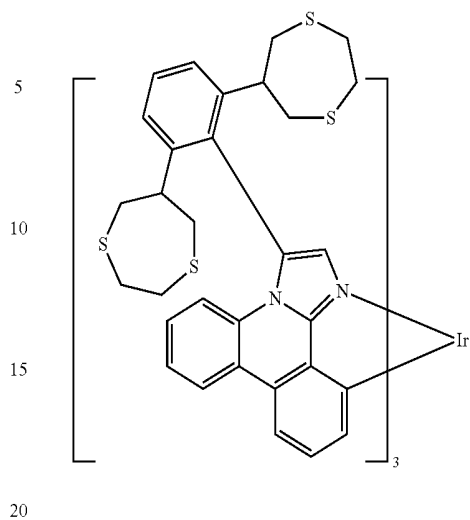
-continued

Compound 32

Compound 30
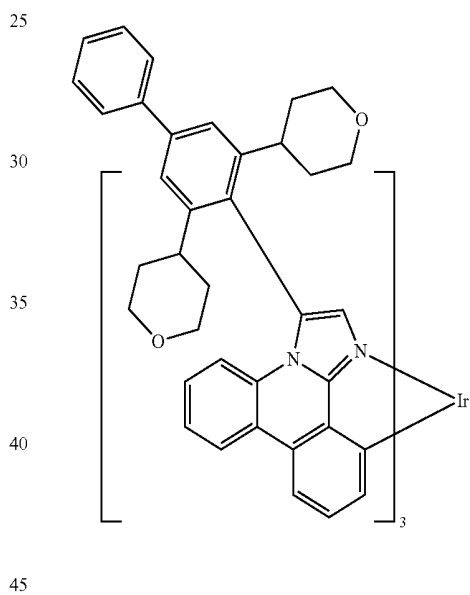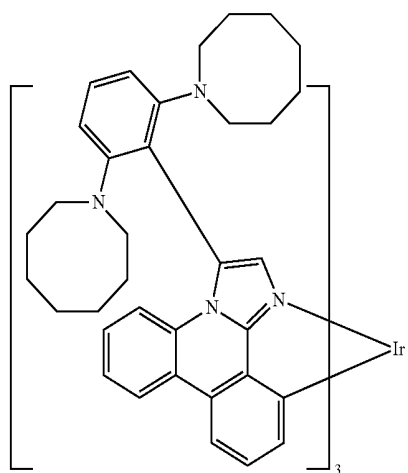
Compound 33

Compound 31
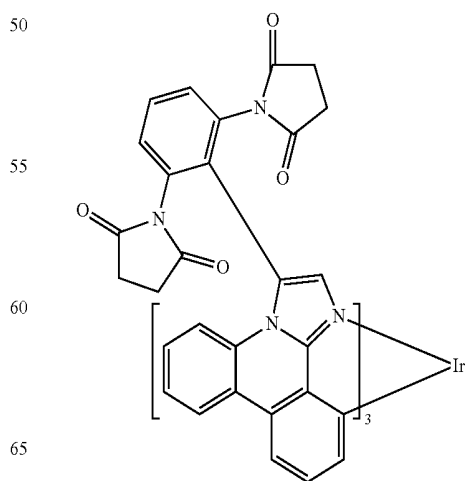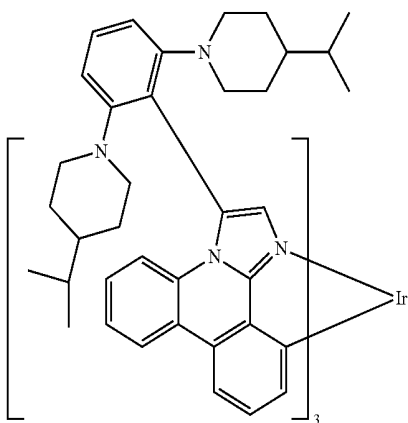
Compound 34

21
-continued

Compound 35
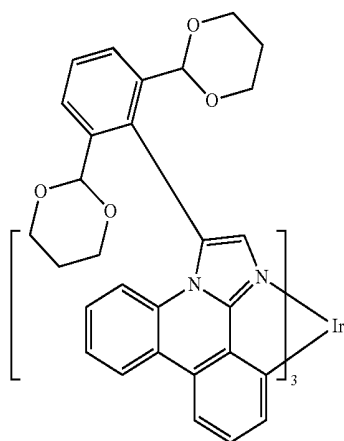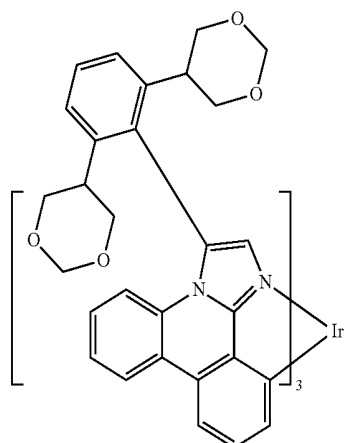
Compound 36

More preferably, the compound is selected from the group consisting of Compound 1 and Compound 2.

A compound including a ligand is also provided, wherein the ligand has the formula:
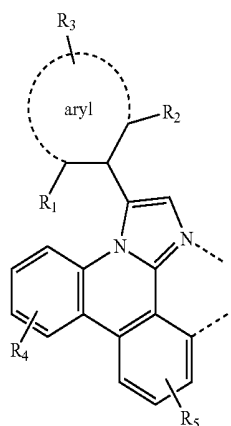
R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, and aryl, and at least one of R_1 and R_2 is an alkyl having four or more atoms. R_3, R_4, and R_5 may represent mono, di, tri, or tetra substitutions. R_3, R_4, and R_5 are independently selected from the group consisting of hydrogen, alkyl, and aryl. The dashed lines represent attachment of the ligand to a metal. Metals consisting of the non-radioactive metals with atomic numbers greater than 40

22

may be suitable for use in the complex. For example, the complex may include a metal selected from the group consisting of Re, Ru, Os, Rh, Ir, Pd, Pt, Cu and Au. Preferably, the metal is Ir. Moreover, the complex including the ligand provided may be a homoleptic complex or a heteroleptic complex. Preferably, the complex containing the ligand provided is a tris Ir complex.

Additionally, an organic light emitting device is also provided. The device may include an anode, a cathode, and an organic emissive layer disposed between the anode and the cathode. The organic emissive layer further comprises a compound having FORMULA I. Preferably, the organic layer further comprises a compound selected from the group consisting of:
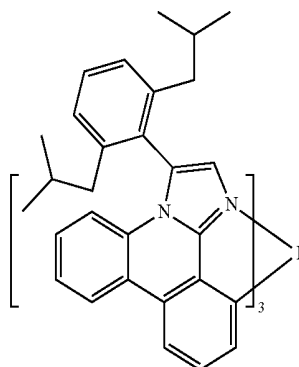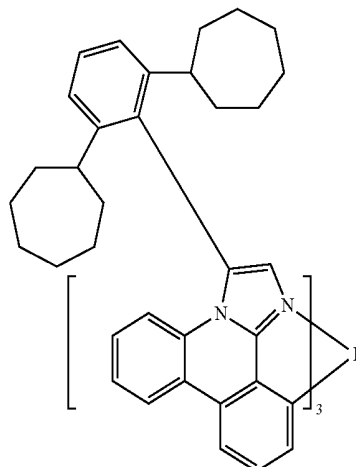
Compound 1

Compound 2

Compound 3

23
-continued
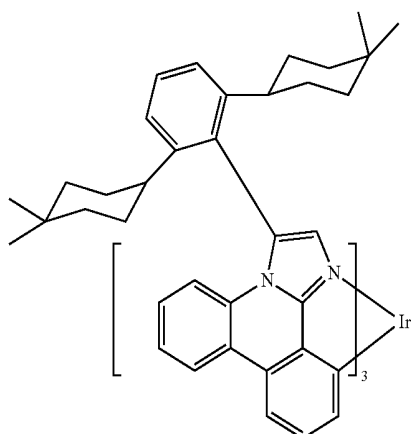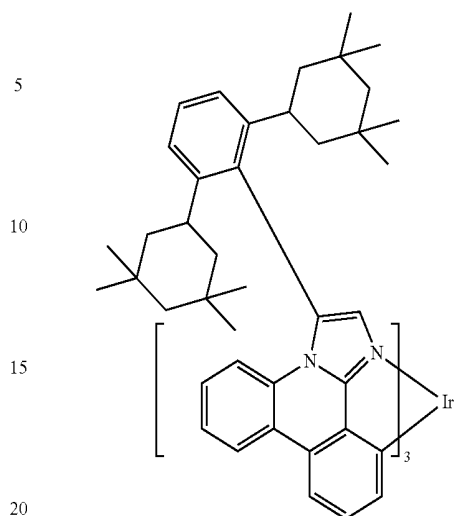
24
-continued

Compound 4
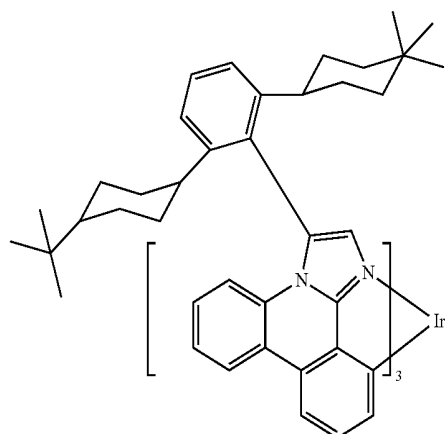
5

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15

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Compound 7

Compound 8

Compound 5

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35

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Compound 9

Compound 6

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60

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-continued

-continued

Compound 10

Compound 13

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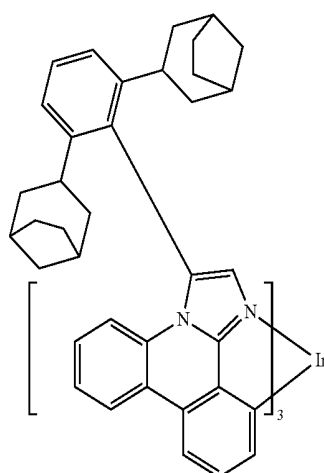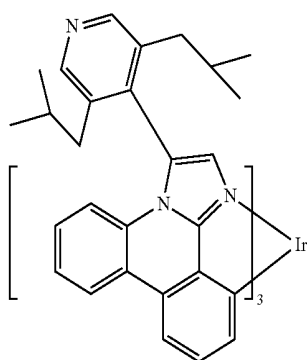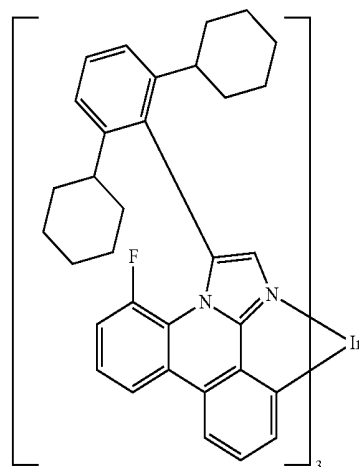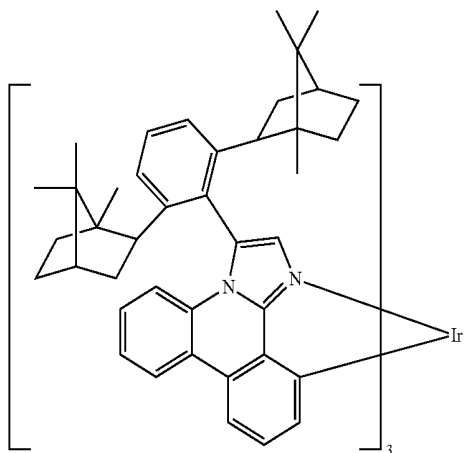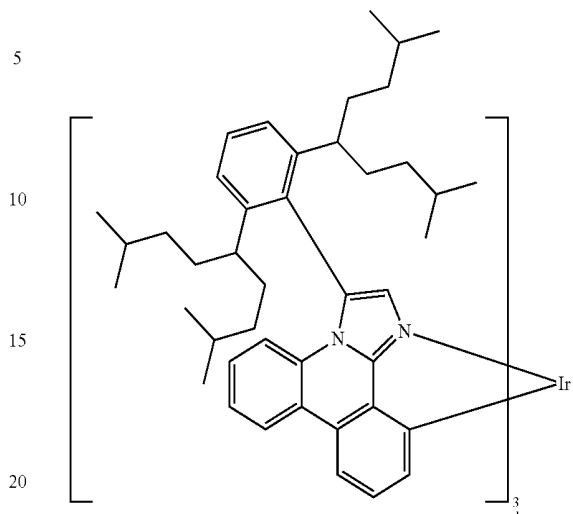
Compound 11 25

Compound 14

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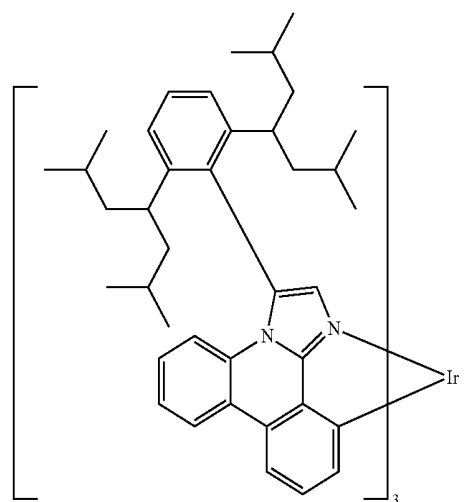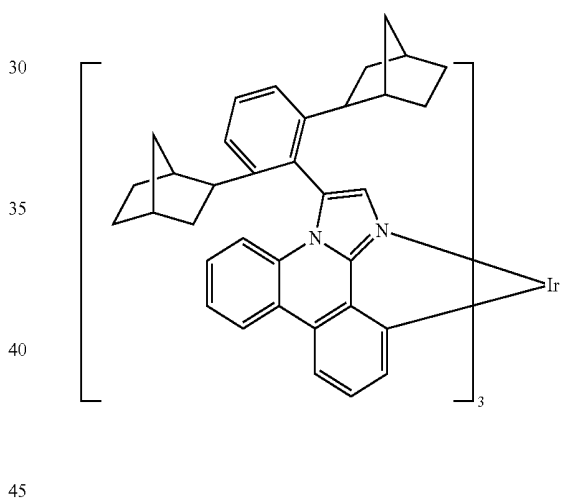
Compound 12 50

Compound 15

55

60
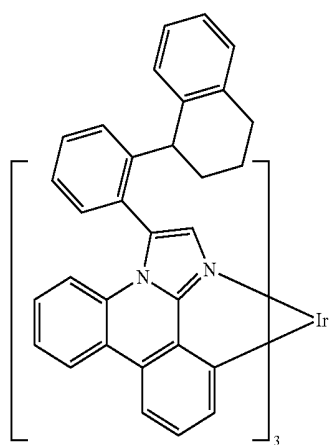
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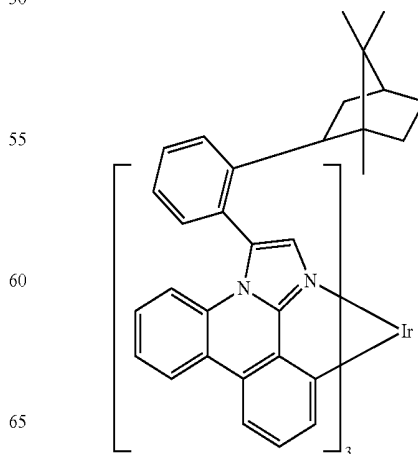
27

-continued

Compound 16

Compound 17

Compound 18
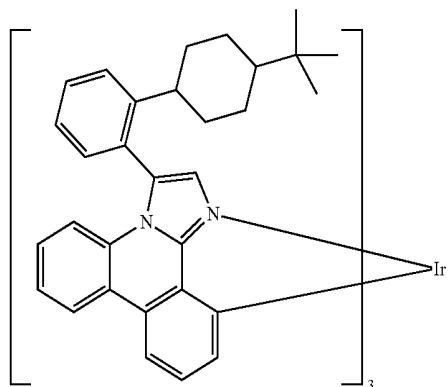
Compound 19

28
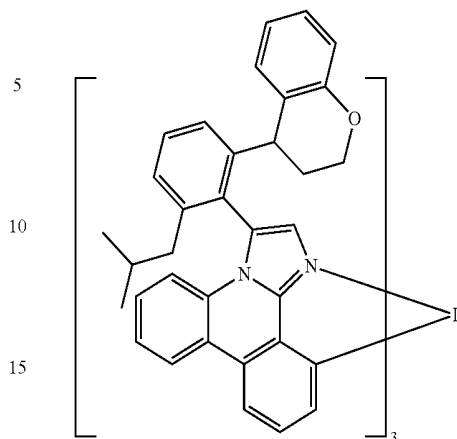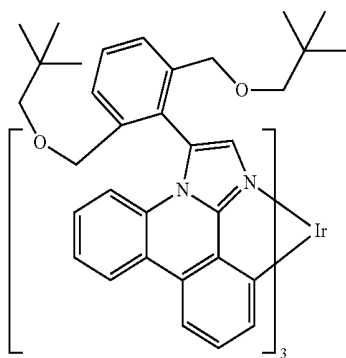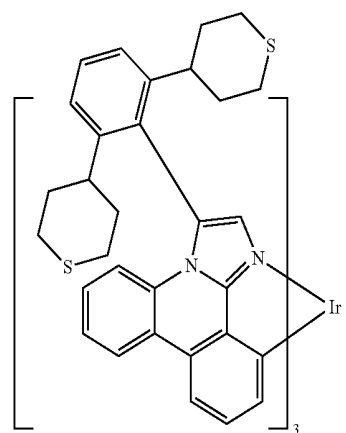
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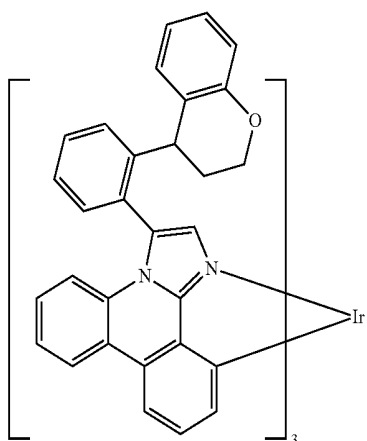
Compound 20
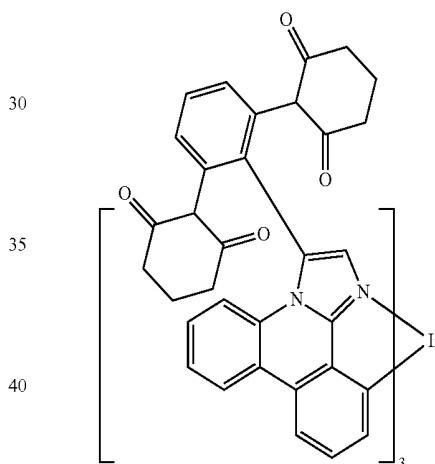
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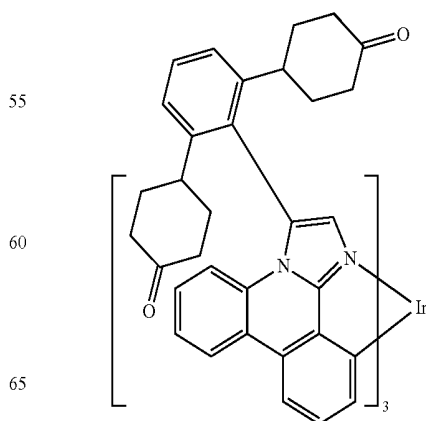
Compound 22

29

-continued

Compound 23
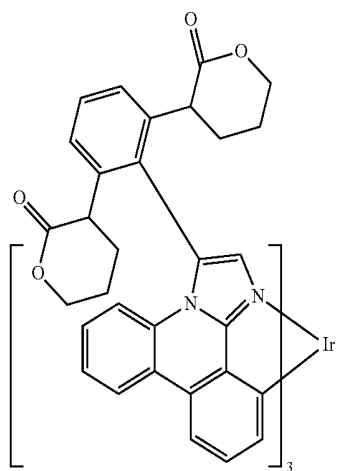
Compound 24

Compound 25

30
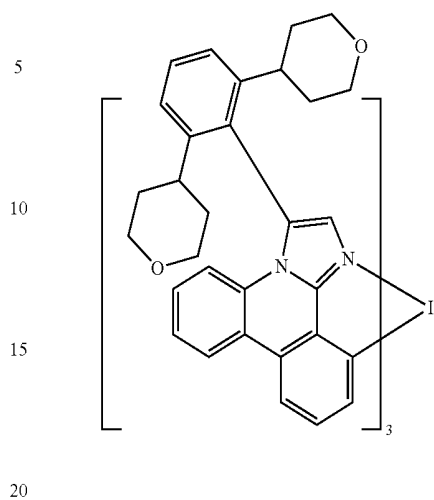
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Compound 26
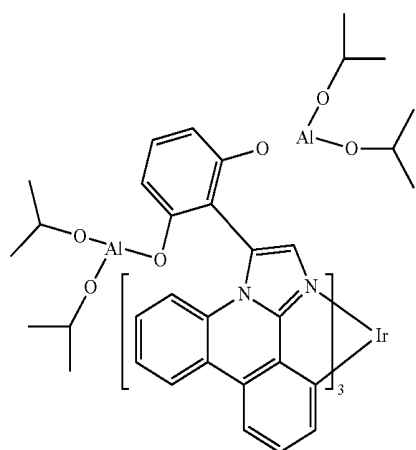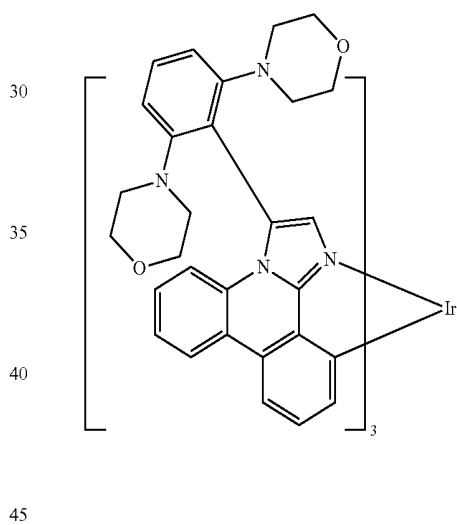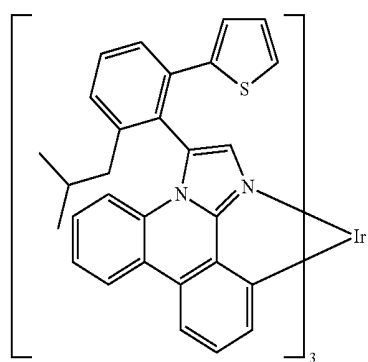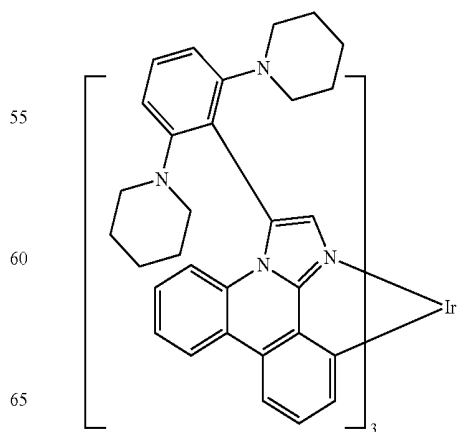
Compound 27

Compound 28

31

-continued
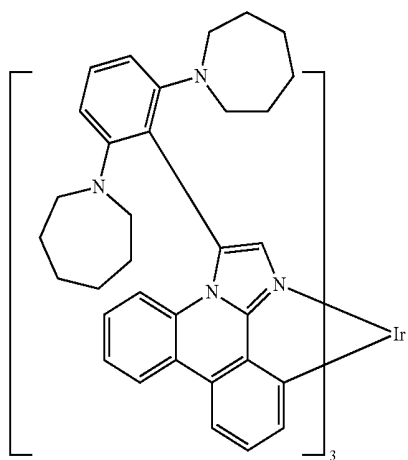
Compound 29

32

-continued
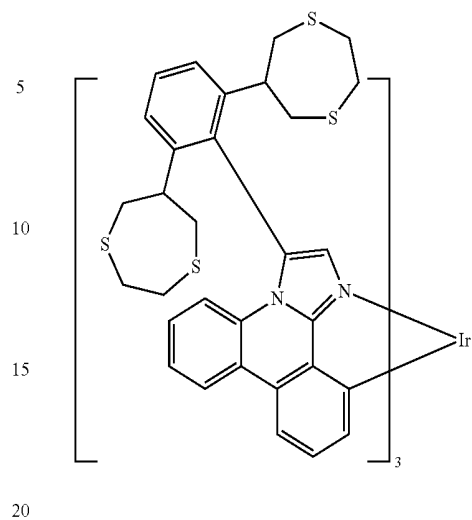
Compound 32

Compound 33
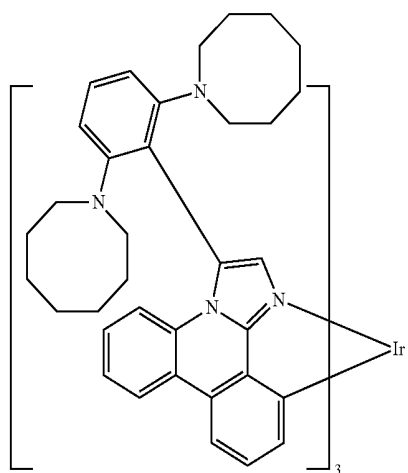
Compound 30
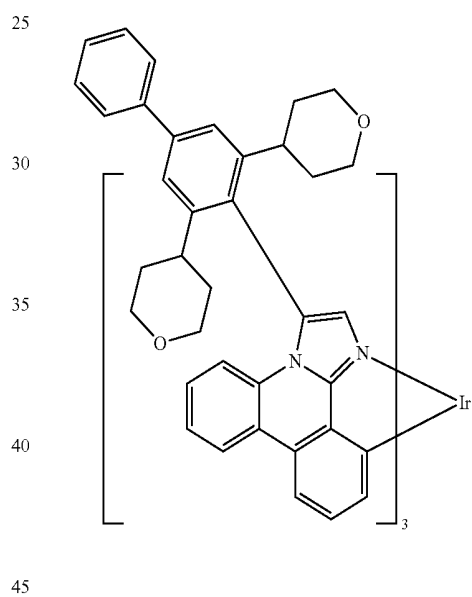
Compound 34
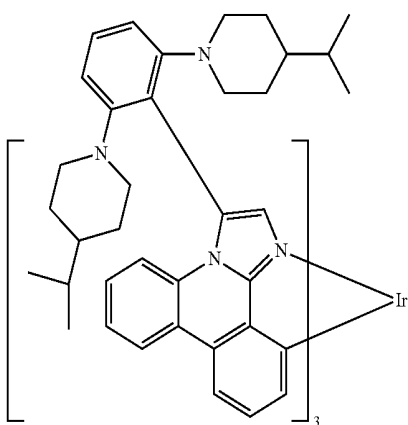
Compound 31
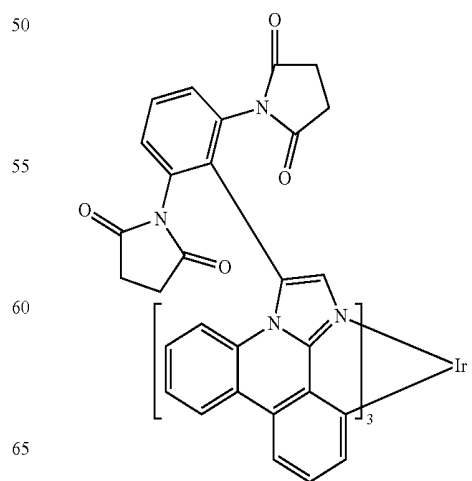
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Compound 35
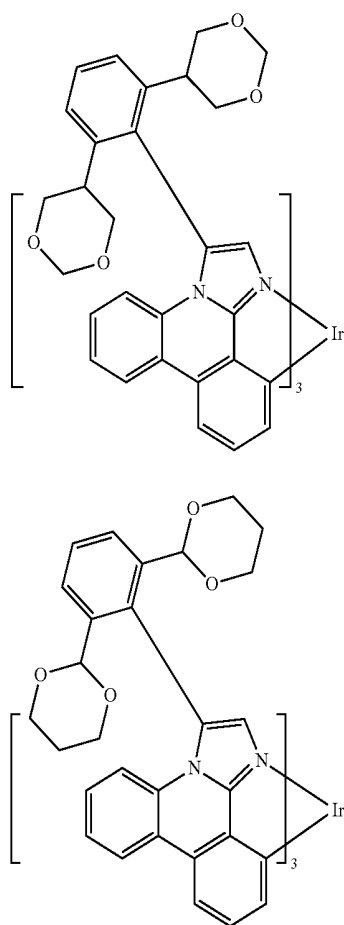
Compound 36

More preferably, the organic layer contains a compound selected from the group consisting of Compound 1 and Compound 2. Devices containing these compounds have been shown to have particularly good properties, such as high efficiency and long lifetime.

The organic layer may be an emissive layer in which the compound having FORMULA I is an emissive compound. The organic emissive layer may further comprise a host. Preferably, the host has the formula:
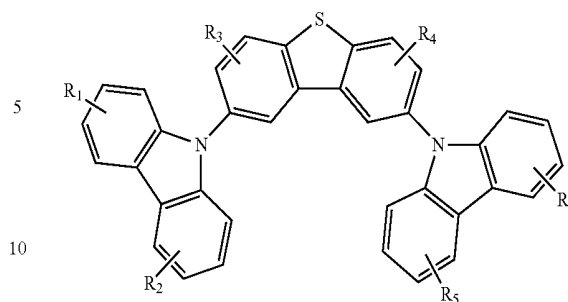
wherein each of R_1 through R_6 are independently selected from the group consisting of any alkyl, alkoxy, amino, alkenyl, alkynyl, arylkyl, aryl, heteroaryl and hydrogen, and where each of R_1 through R_6 may represent multiple substitutions.

A consumer product comprising a device is also provided, wherein the device further comprises an anode, a cathode and an organic layer. The organic layer further comprises a compounds having FORMULA I.

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

In addition to and/or in combination with the materials disclosed herein, many hole injection materials, hole transporting materials, host materials, dopant materials, exiton/hole blocking layer materials, electron transporting and electron injecting materials may be used in an OLED. Non-limiting examples of the materials that may be used in an OLED in combination with materials disclosed herein are listed in Table 1 below. Table 1 lists non-limiting classes of materials, non-limiting examples of compounds for each class, and references that disclose the materials.
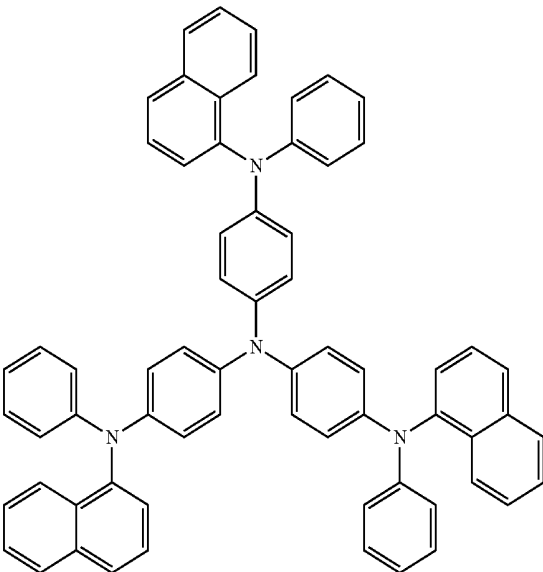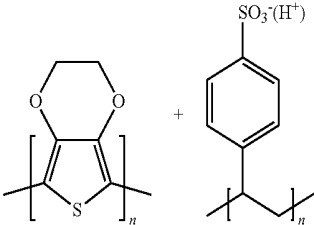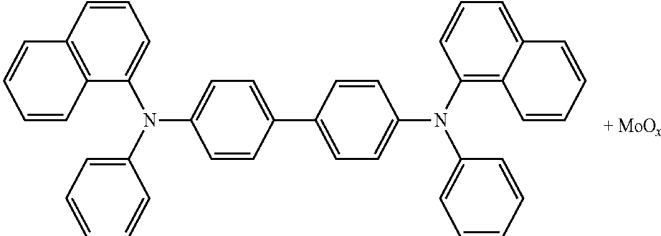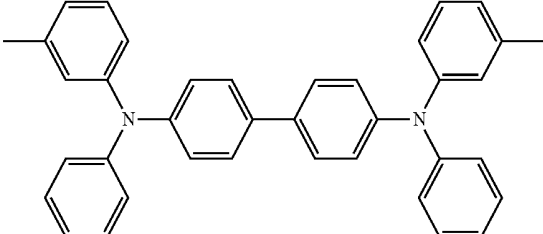
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
	Hole injection materials	
Phthalocyanine and porphryin compounds		Appl. Phys. Lett. 69, 2160 (1996)
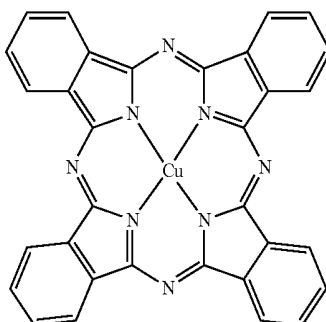
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MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Starburst triarylamines		J. Lumin. 72-74, 985 (1997)
CF$_x$ Fluorohydrocarbon polymer	$-\left[CH_xF_y\right]_n-$	Appl. Phys. Lett. 78, 673 (2001)
Conducting polymers (e.g., PEDOT:PSS, polyaniline, polypthiophene)		Synth. Met. 87, 171 (1997)
Arylamines complexed with metal oxides such as molybdenum and tungsten oxides	$+ MoO_x$	SID Symposium Digest, 37, 923 (2006)

Hole transporting materials

| Triarylamines (e.g., TPD, α-NPD) | | Appl. Phys. Lett. 51, 913 (1987) |

-continued
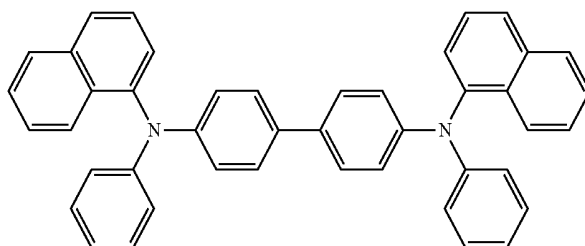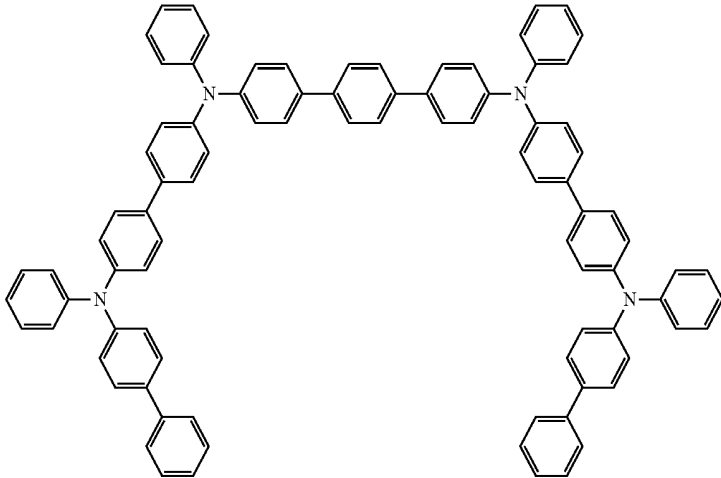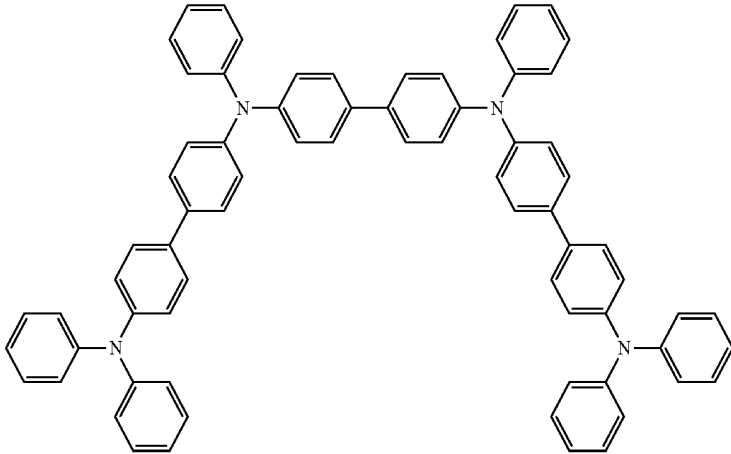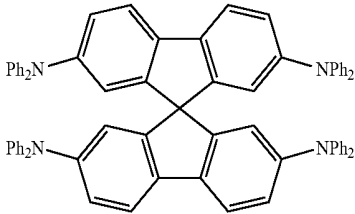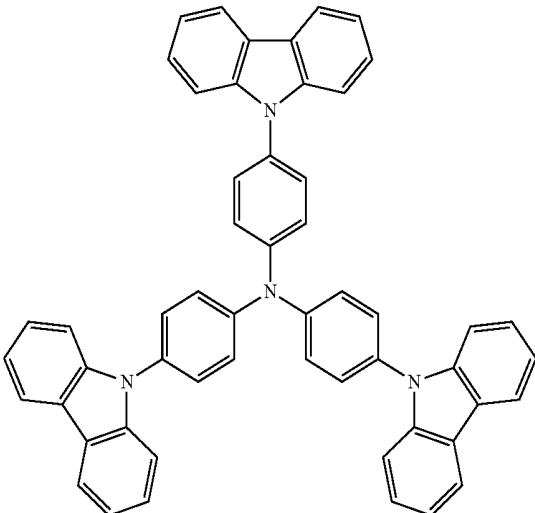
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		U.S. Pat. No. 5,061,569
		EP650955
		J. Mater. Chem. 3, 319 (1993)
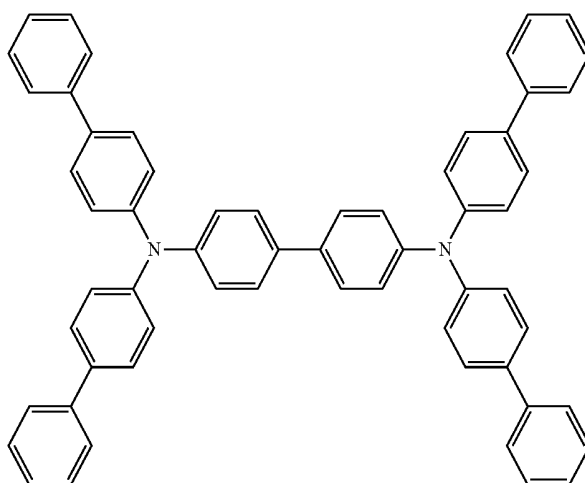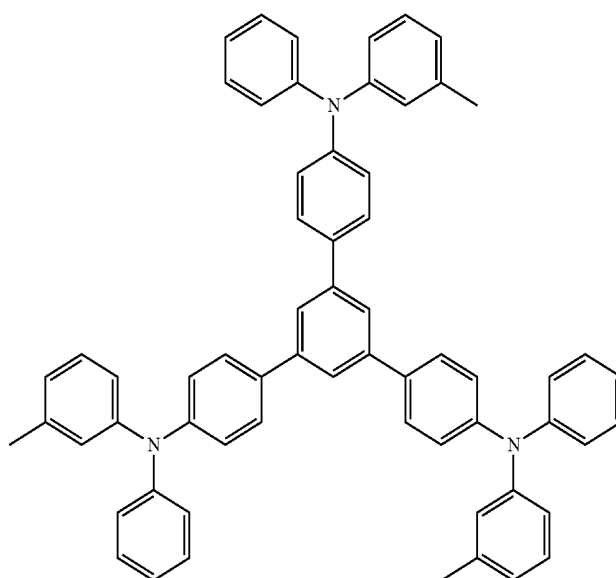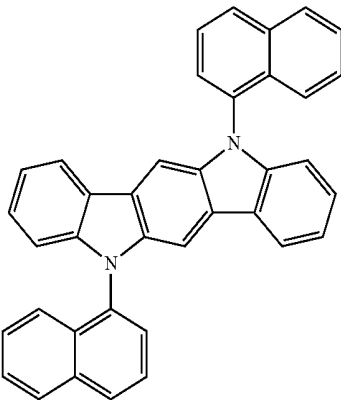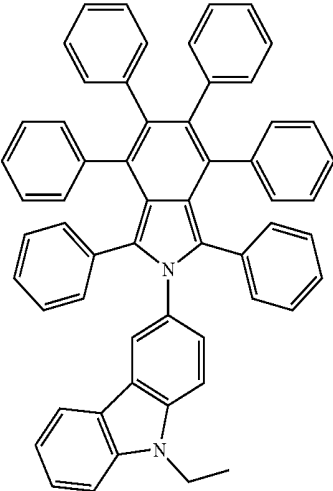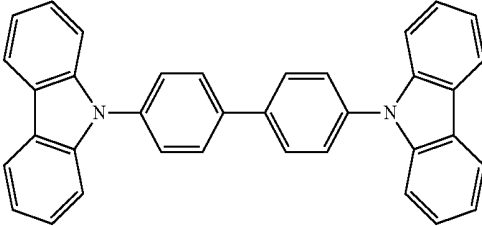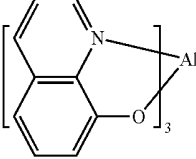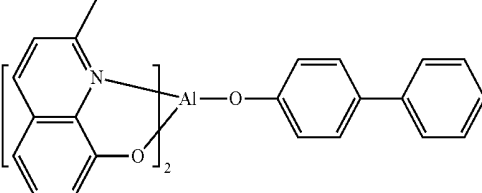
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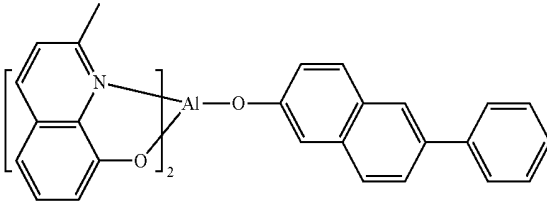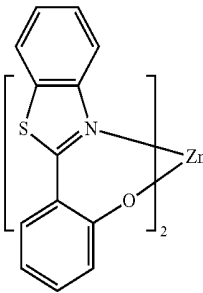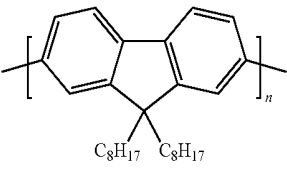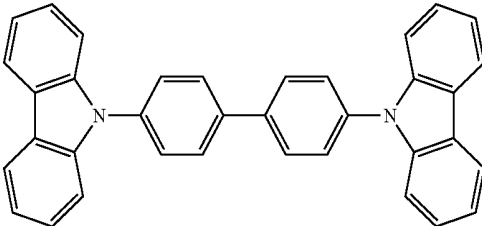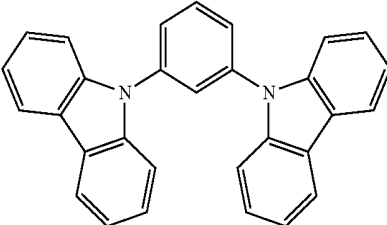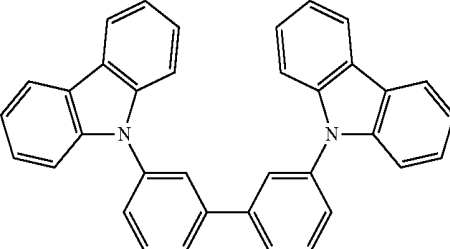
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		Appl. Phys. Lett. 90, 183503 (2007)
		Appl. Phys. Lett. 90, 183503 (2007)
Triaylamine on spirofluorene core		Synth. Met. 91, 209 (1997)
Arylamine carbazole compounds		Adv. Mater. 6, 677 (1994)
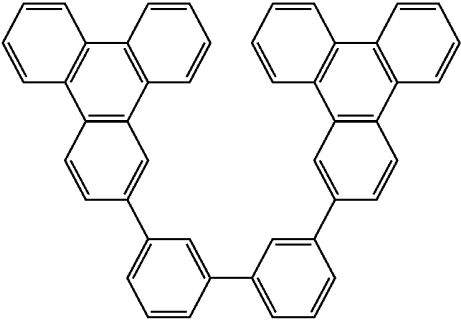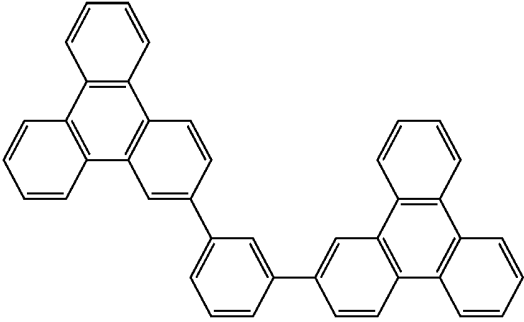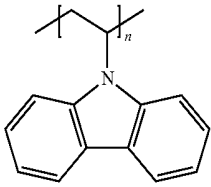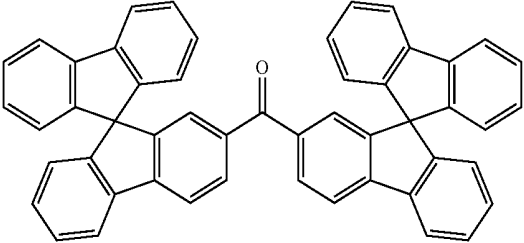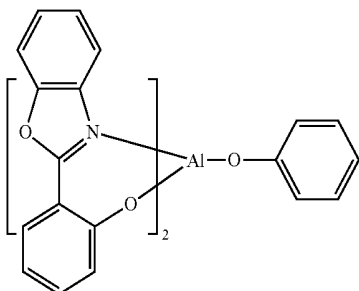
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MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Indolocarbazoles		Synth. Met. 111, 421 (2000)
Isoindole compounds		Chem. Mater. 15, 3148 (2003)

Phosphorescent OLED host materials

Red hosts

Arylcarbazoles		Appl. Phys. Lett. 78, 1622 (2001)
Metal 8-hydroxyquinolates (e.g., Alq₃, BAlq)		Nature 395, 151 (1998)
		US20060202194

-continued

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		WO200501455
Metal phenoxybenzothiazole compounds		Appl. Phys. Lett. 90, 123509 (2007)
Conjugated oligomers and polymers (e.g., polyfluorene)		Org. Electron. 1, 15 (2000)

Green hosts

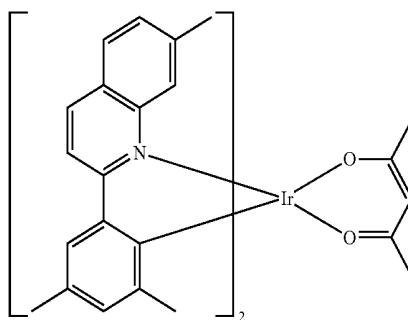|		
Arylcarbazoles		Appl. Phys. Lett. 78, 1622 (2001)
		US2003175553
		WO2001039234

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MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Aryltriphenylene compounds		US20060280965
		US20060280965
Polymers (e.g., PVK)		Appl. Phys. Lett. 77, 2280 (2000)
Spirofluorene compounds		WO2004093207
Metal phenoxybenzooxazole compounds		WO05089025

-continued
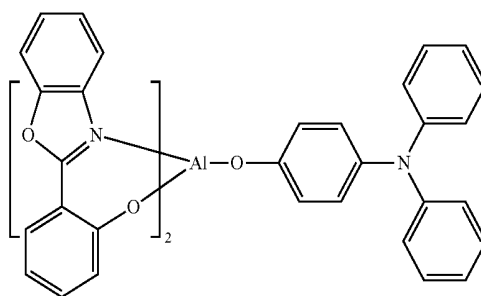
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		WO06132173
		JP200511610
Spirofluorene-carbazole compounds		JP2007254297
		JP2007254297
Indolocabazoles		WO07063796
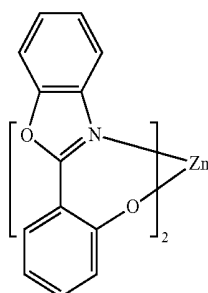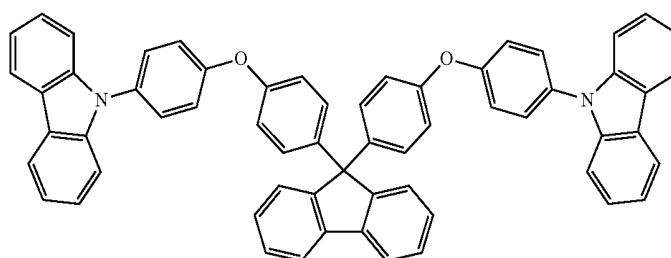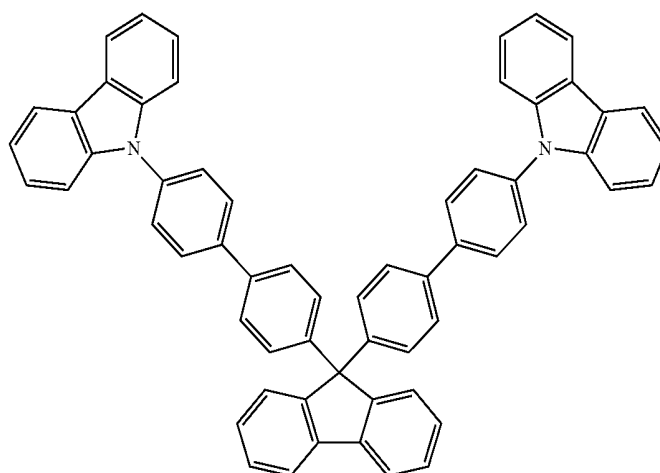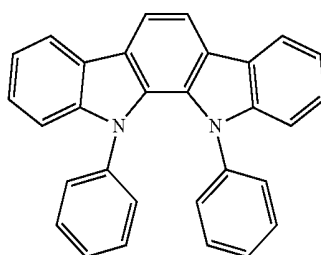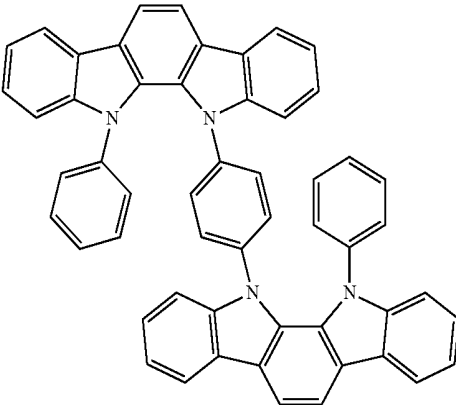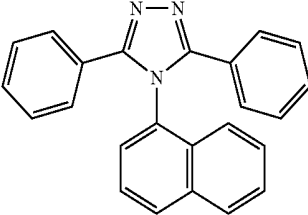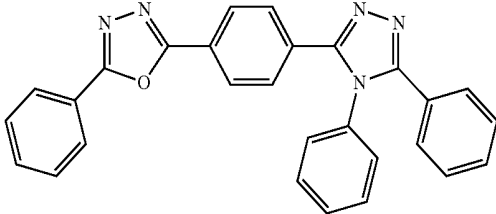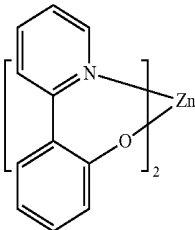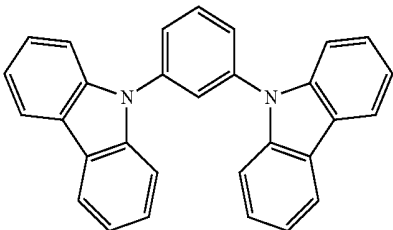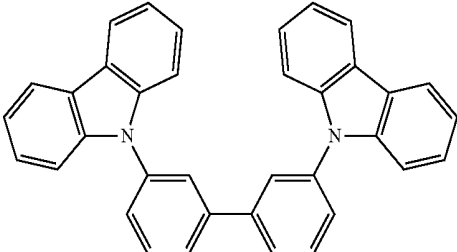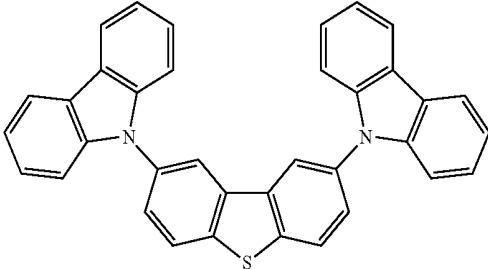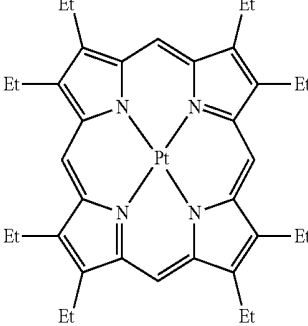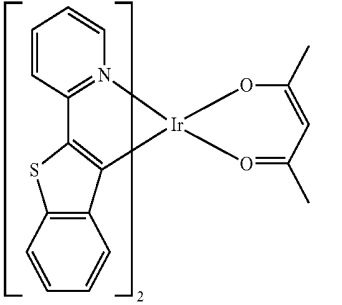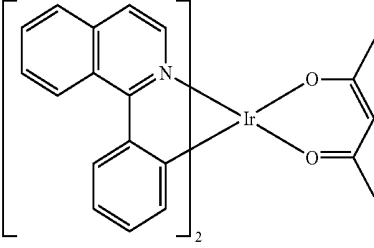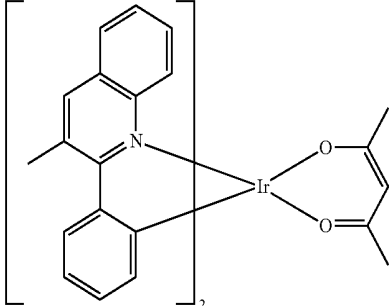
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MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		WO07063754
5-member ring electron deficient heterocycles (e.g., triazole, oxadiazole)		J. Appl. Phys. 90, 5048 (2001)
		WO04107822
Metal phenoxypyridine compounds		WO05030900

Blue hosts

Arylcarbazoles		Appl. Phys. Lett, 82, 2422 (2003)
		US20070190359

-continued

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Dibenzothiopbene-carbazole compounds		WO2006114966

Phosphorescent dopants
Red dopants

Heavy metal porphyrins (e.g., PtOEP)		Nature 395, 151 (1998)
Iridium(III) organometallic complexes		Appl. Phys. Lett. 78, 1622 (2001)
		U.S. Pat. No. 06,835,469
		U.S. Pat. No. 06,835,469

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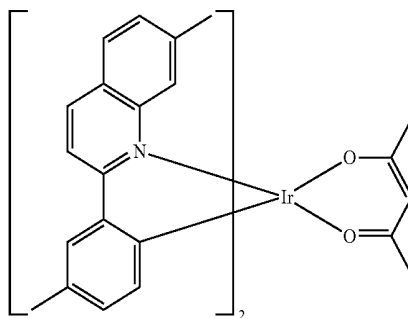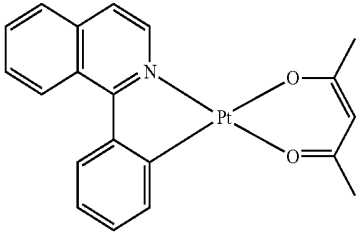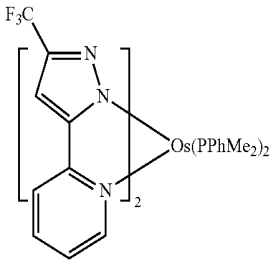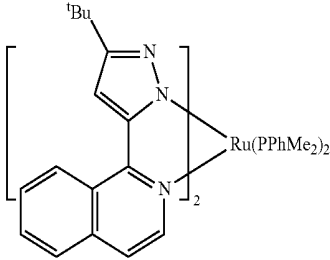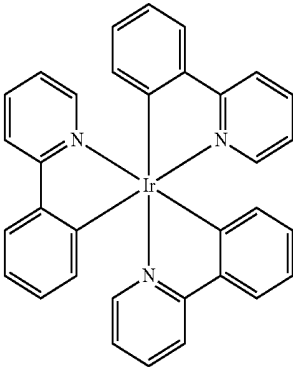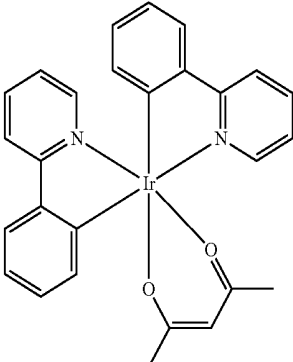
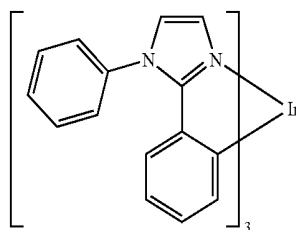| MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		US20060202194
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		U.S. Pat. No. 07,087,321
		Adv. Mater. 19, 739 (2007)
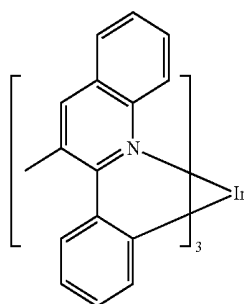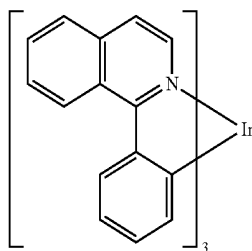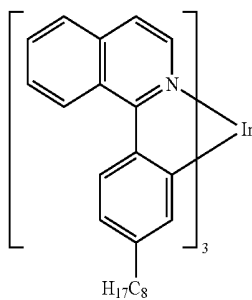
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MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Platinum(II) organotmetallic complexes		WO2003040257
Osminum(III) complexes		Chem. Mater. 17, 3532 (2005)
Ruthenium(II) complexes		Adv. Mater. 17, 1059 (2005)

Green dopants

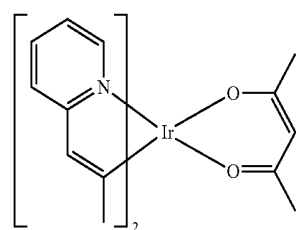| Iridium(III) organometallic complexes		Inorg. Chem. 40, 1704 (2001)
	and its derivatives	
		US2002034656

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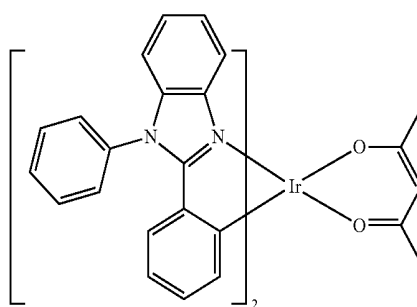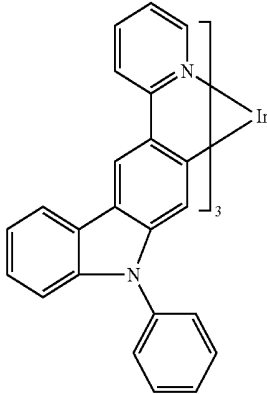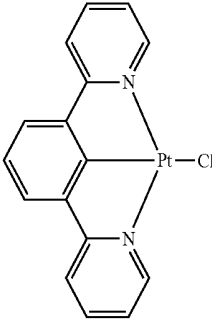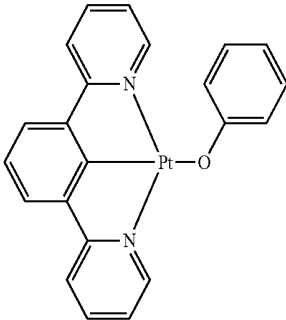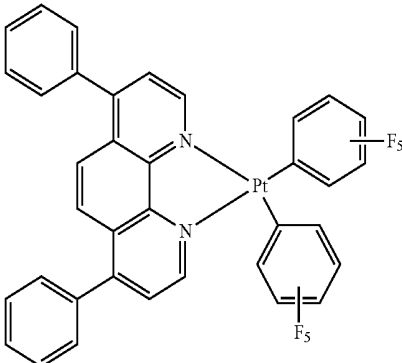
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		US2007190359
		US 2006008670 JP2007123392
		Adv. Mater. 16, 2003 (2004)
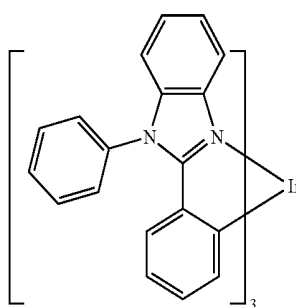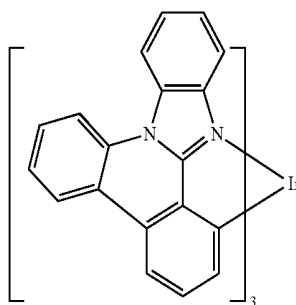
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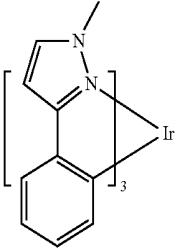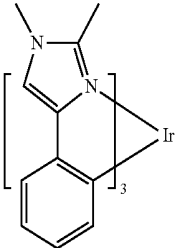| MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		Angew. Chem. Int. Ed. 2006, 45, 7800
Pt(ll) organometallic complexes		Appl. Phys. Lett. 86, 153505 (2005)
		Appl. Phys. Lett. 86, 153505 (2005)
		Chem. Lett. 34, 592 (2005)
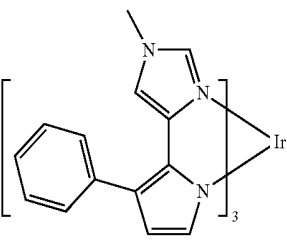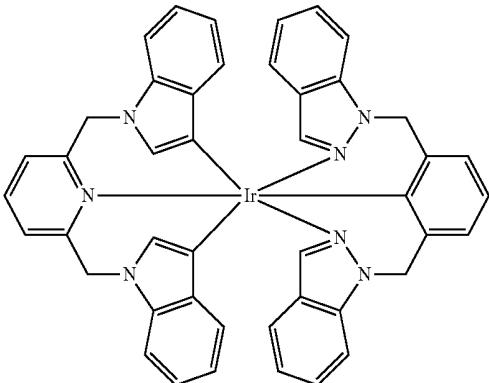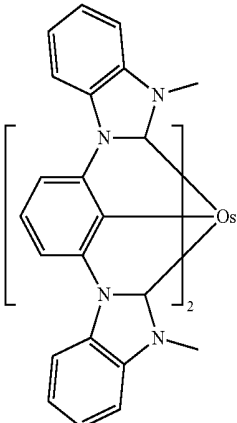
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MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Gold complexes		Chem. Commun. 2906 (2005)
Rhenium(III) complexes		Inorg. Chem. 42, 1248 (2003)

Blue dopants

Iridium(III) organometallic complexes		WO2002002714
		WO2006009024
		US2006251923

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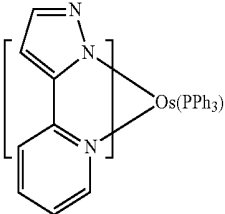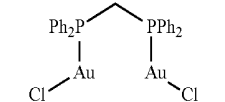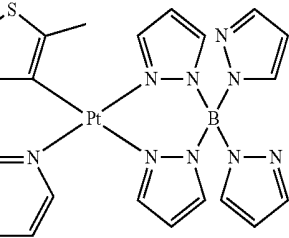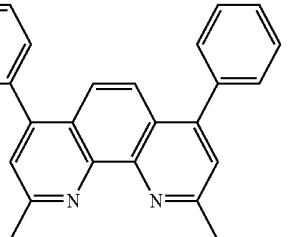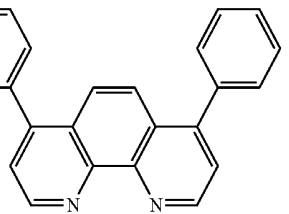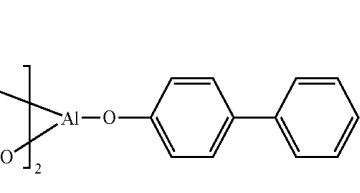
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MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		WO2006056418, US2005260441
		US2007190359
		US2002134984
		Angew. Chem. Int. Ed. 47, 1 (2008)
		Chem. Mater. 18, 5119 (2006)
		Inorg. Chem. 46, 4308 (2007)

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		WO05123873
		WO05123873
		WO07004380
		WO06082742
Osmium(II) complexes		US2005260449

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MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		Organometallics 23, 3745 (2004)
Gold complexes		Appl. Phys. Lett. 74, 1361 (1999)
Platinum(II) complexes		WO06098120, WO06103874

Exciton/hole blocking layer materials

Bathocuprine compounds (e.g., BCP, BPhen)		Appl. Phys, Lett. 75, 4 (1999)
		Appl. Phys. Lett. 79, 449 (2001)
Metal 8-hydroxyquinolates (e.g., BAlq)		Appl. Phys. Lett. 81, 162 (2002)

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MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
5-member ring electron deficient heterocycles such as triazole, oxadiazole, imidazole, benzoimidaxole		Appl. Phys. Lett. 81, 162 (2002)
Triphenylene compounds		U320050025993
Fluorinated aromatic compounds		Appl. Phys. Lett. 79, 156 (2001)
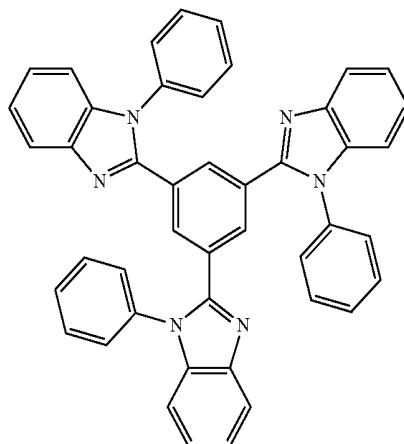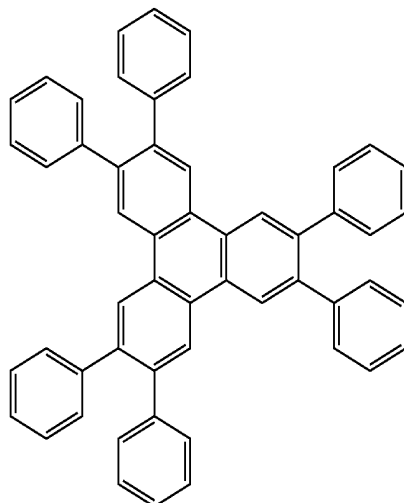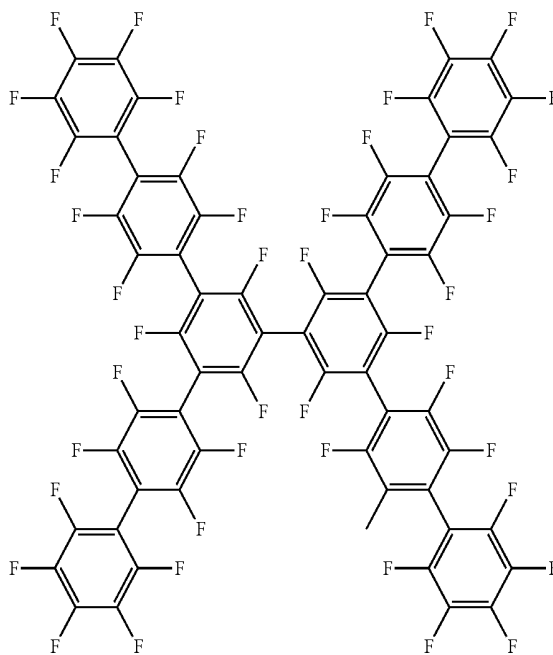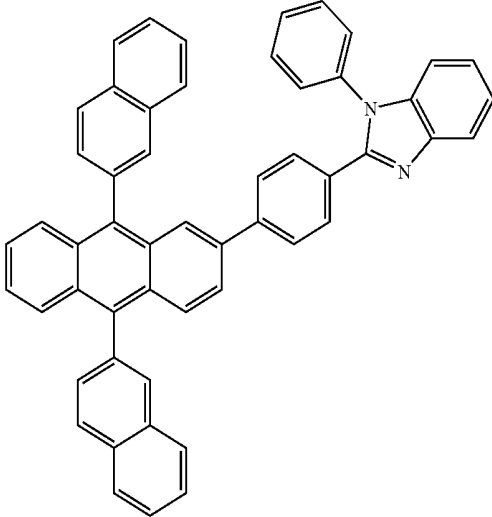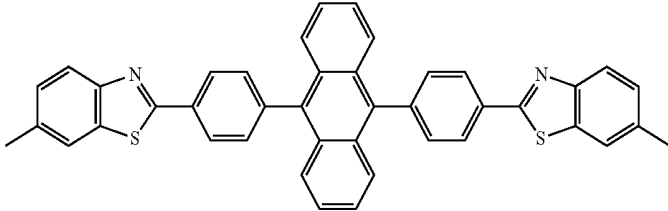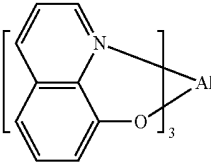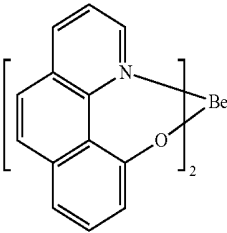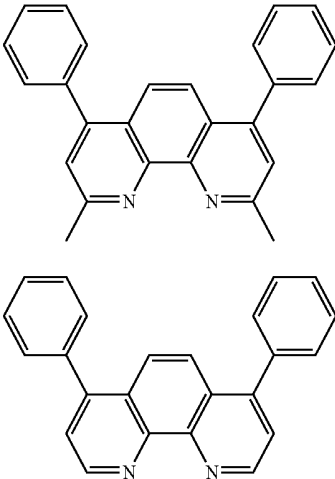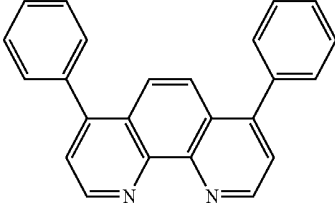
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MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS

Electron transporting materials

Anthracene-benzoimidazole compounds		WO03060956
Anthracene-benzothiazole compounds		Appl. Phys. Lett. 89, 063504 (2006)
Metal 8-hydroxyquinolates (e.g., Alq₃)		Appl. Phys, Lett. 51, 913 (1987)
Metal hydroxy-benoquinolates		Chem. Lett. 5, 905 (1993)
Bathocuprine compounds such as BCP, BPhen, etc		Appl. Phys. Lett. 91, 263503 (2007)
		Appl. Phys. Lett. 79, 449 (2001)

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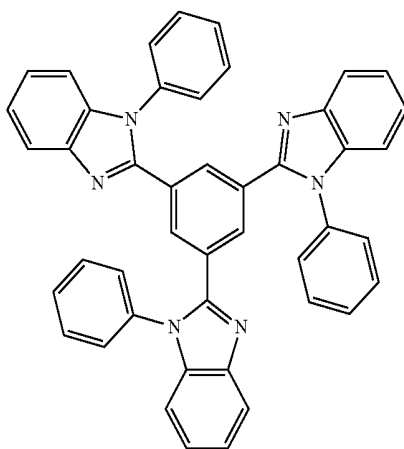
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
5-member ring electron deficient heterocycles (e.g., triazole, oxadiazole, imidazole, benzoimidazole)		Appl. Phys. Lett. 74, 865 (1999)
		Appl. Phys. Lett. 55, 1489 (1989)
		Jpn. J. Apply. Phys. 32, L917 (1993)
Silole compounds		Org. Electron. 4, 113 (2003)
Arylborane compounds		J. Am. Chem. Soc. 120, 9714 (1998)
Fluorinated aromatic compounds		J. Am. Chem. Soc. 122, 1832 (2000)
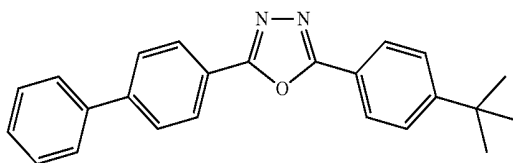
EXPERIMENTAL

Compound Examples

Synthesis of Comparative Example 2

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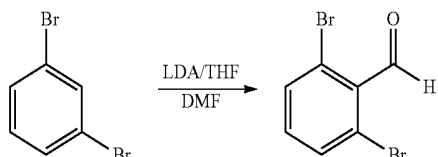
Into a 1000 mL 3-neck flask equipped with magnetic stirring, a condenser and a thermocouple was charged with 100 mL of 2.0 M Lithium diisopropylamide (LDA) in THF. This solution was cooled to −75° C. Next, 1,3-Dibromoben-zene (39.3 g, 0.167 mol) dissolved in 200 mL of anhydrous THF was added dropwise over a ½ h period to the cooled solution of LDA. The internal temperature was maintained at −75° C. (+/−5° C.) for 2 h. Next, dimethylformamide (30.8 g, 0.4 mol) dissolved in 50 mL of anhydrous THF and was added dropwise to the cooled reaction mixture over a ½ h period. The internal temperature was maintained at −75° C. (+/−5° C.) for 2 h. The reaction mixture was quenched by dropwise addition of 100 mL of 5% sulfuric acid. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature. The organic layer was separated and the aqueous was extracted with 1×100 mL of diethyl ether and 1×50 mL of ethyl acetate. The organics were combined and washed 1×100 mL of brine. The organic extracts were then dried over sodium su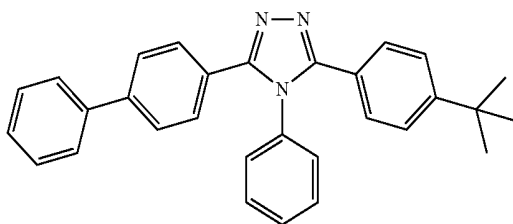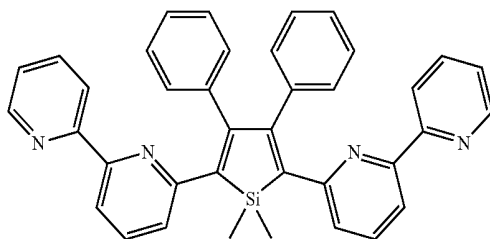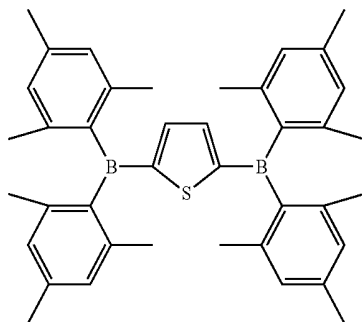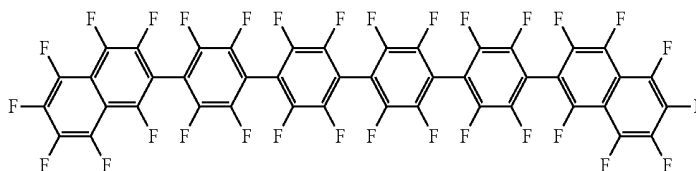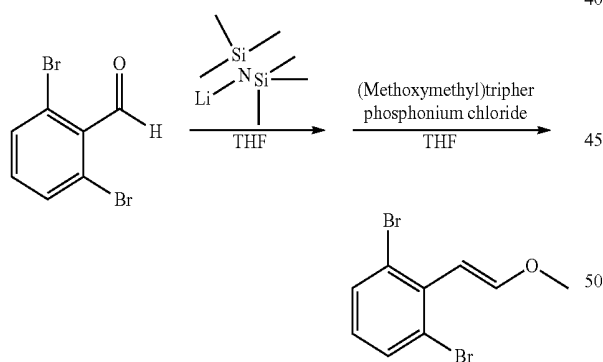lfate, filtered and concentrated under vacuum. The crude product was recrystallized from hexanes to yield 21.6 g (49% yield) of product. Step 2


(Methoxymethyl)triphenylphosphonium chloride (34.3 g, 0.10 mol) was charged into a 500 mL 3-neck flask with 75 mL of THF. This solution was cooled to −78° C. followed by dropwise addition of 100 mL (0.1 mol) of 1.0 M of lithium bis(trimethylsilyl)amide in THF. Addition time was approximately 20 minutes and the internal temperature was maintained at −78° C. to −70° C. The cooling bath was then removed and the reaction mixture was allowed to warm to 0 to 3° C. The reaction mixture was then cooled back down to −78° C. Next, 2,6-dibromobenzaldehyde (22.8 g, 0.086 mol) dissolved in 75 mL of THF was added dropwise to the cooled reaction mixture over a 20 min period. The internal temperature was maintained between at −78° C. to −70° C.

The reaction mixture was then allowed to gradually warm to room temperature. The reaction mixture was quenched with aqueous ammonium chloride and then extracted with 3×300 mL of ethyl acetate. The organic extracts were combined, washed once with 200 mL of 10% LiCl solution and were dried over magnesium sulfate. The extracts were then filtered and the solvent removed under vacuum. The crude product was purified by vacuum distillation to yield 22.5 g (90%) of product as a light-orange oil.

Step 3
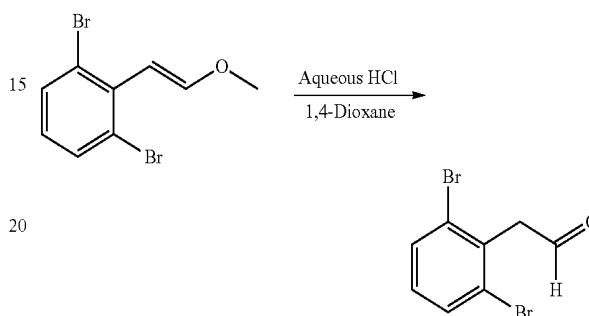
70 mL of conc. HCl was slowly added to a 500 mL round bottom flask containing 110 mL of water. o-Methyl 2,6-dibromophenylacetaldehyde (22.5 g, 0.077 mol) was dissolved in 70 mL of 1,4-dioxane and this solution was added all at once to the 500 mL round bottom flask. The reaction mixture was stirred and heated at a gentle reflux for 18 h. The reaction mixture was cooled to room temperature and was extracted with 2×400 mL ethyl acetate. These extracts were combined and were washed with 1×100 mL aq. 10% LiCl. The extracts were then dried over sodium sulfate, filtered and the solvent removed under vacuum. The 2,6-dibromophenyl acetaldehyde was purified using silica gel chromatography with 15%/75% methylene chloride/hexanes as the eluent. 17.1 g (80% yield) of white solids was obtained as the product.

Step 4
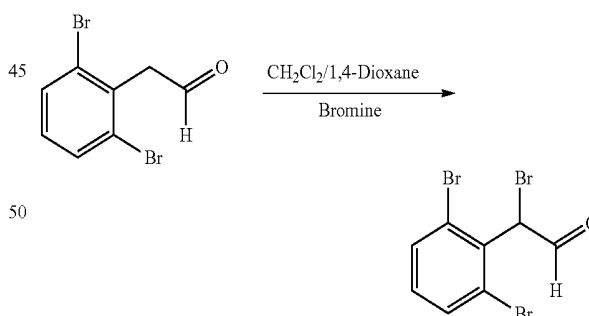
To a 200 mL round bottom flask was added 3.75 g (0.013 mol) of the 2,6-dibromophenylacetaldehyde, 30 mL of methylene chloride and 60 mL of 1,4-dioxane. Next, 2.32 g, (0.014 mol) of bromine was dissolved in 30 mL of methylene chloride and was added dropwise to the reaction mixture at room temperature over a 10 min period. Stirring was continued at room temperature for 2 h. An additional (0.23 g, 0.001 mol) of bromine was added to the reaction mixture. This mixture was stirred for one hour at room temperature. The reaction mixture was concentrated under vacuum. The crude product was then dissolved in 50 mL of diethyl ether and was washed 1×50 mL aqueous sodium bisulfite and

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1×50 mL aqueous 10% lithium chloride. The ethereal extract was dried over sodium sulfate then was filtered and the solvent removed under vacuum to yield 4.2 g (90% yield) of a yellow viscous oil as the product which was immediately used for the next step.

Step 5
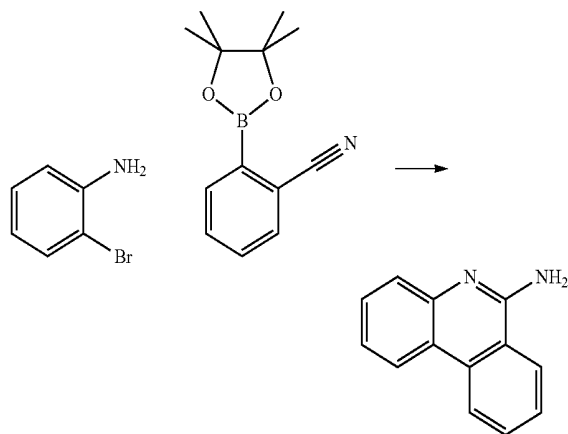
To a 1 L 3-neck flask was added 19 g (0.11 mol) of 2-bromoaniline, 27.7 g (0.12 mol) of 2-cyanophenylboronic acid pinacol ester, 74.5 g (0.32 mol) of potassium phosphate tribasic monohydrate and 1.8 g (0.002 mol) of [1,1'-bis[(diphenylphosphino)ferrocene]dichoro-palladium(II) complex with dichloromethane(1:1). This mixture was degassed and backfilled with nitrogen. Next, water (13 mL) and 350 mL of 1,4-dioxane were added to the reaction mixture and the degassing procedure was repeated. The reaction mixture was stirred and heated under nitrogen at reflux for 18 h. After cooling, the reaction mixture was diluted with 350 mL of water. The reaction mixture was extracted with 3×250 mL of ethyl acetate. These extracts were combined and dried over magnesium sulfate. The extracts were filtered and the solvent removed under vacuum. The crude product was triturated with a hexane/ethyl acetate mixture. A light gray solid was isolated via filtration.
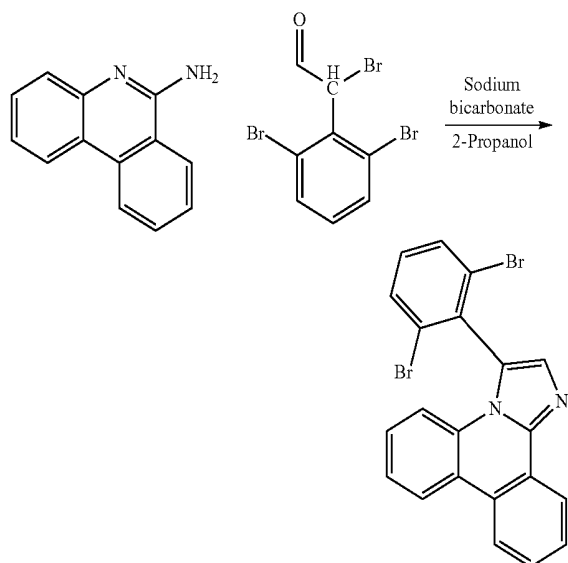
A 200 mL round bottom flask was charged with 0.77 g (0.004 mol) of 6-aminophenanthridine and 50 mL of anhy-

78

drous 2-propanol. To this mixture was added 1.42 g (0.004 mol) of α-bromo-2,6-dibromophenylacetaldehyde all at once. This mixture was then heated at reflux for 24 h. Next, the reaction mixture was cooled to 60° C. and 0.67 g (0.008 mol) of sodium bicarbonate was added all at once. This mixture was then heated at reflux for 24 h. The reaction mixture was cooled to room temperature, diluted with 300 mL of water and then was extracted with 3×200 mL of ethyl acetate. These organic extracts were combined, were washed 1×100 mL of aqueous 10% LiCl, were dried over sodium sulfate, then were filtered and concentrated under vacuum. The crude product was purified by silica gel column chromatography (1-7% ethyl acetate/methylene) to yield 1 g (55% yield) of off-white solids as the product.

Step 7

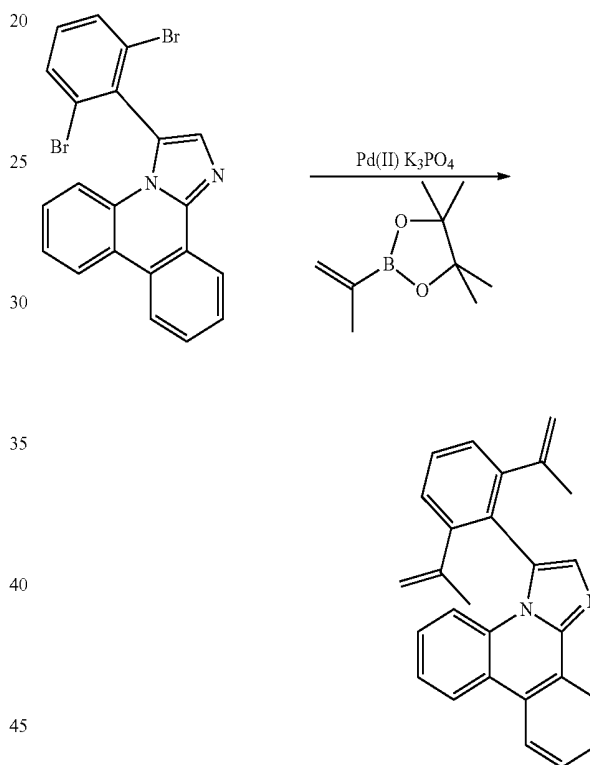To a 200 mL flask was added dibromide from Step 6 (2.34 g, 5.175 mmol), isopropenyl boronic acid pinacol ester (10.44 g, 62.1 mmol), palladium(II) acetate (0.17 g, 0.76 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (0.62 g, 1.52 mmol), potassium phosphate tribasic monohydrate (5.96 g, 25.88 mmol), 122 mL of toluene and 122 mL of water. The reaction mixture was fully degassed by freezing-pump-thaw technique. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 16 h. The reaction mixture was filtered through a pad of Celite. The toluene layer was separated and the aqueous was extracted once with 75 mL of toluene. The toluene extracts were combined, dried over sodium sulfate, then were filtered and concentrated under vacuum. The product was purified using silica gel chromatography with 1-8% ethyl acetate/methylene chloride as the eluent to give 1.7 g (87% yield) of product.

Step 8

Chlorotris(triphenylphosphine)
Rhodium-(1)
———————————→
toluene
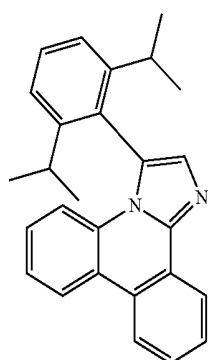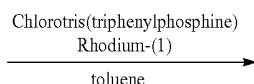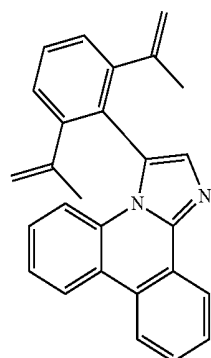
2,6-diisopropenylimidazophenanthridine (1.7 g, 4.6 mmol) was dissolved in 75 mL of toluene. This solution was added to a Parr hydrogenator vessel that was purged with N_2 and contained 1.5 g of chlorotris(triphenylphosphine) rhodium(I). This vessel was placed on the Parr hydrogenator and the vessel was filled with hydrogen and evacuated (repeated a total of three times). The vessel was then filled with hydrogen to 45 psi. This mixture was reacted with shaking for 21 h. The solvent from the reaction mixture was removed under vacuum. The crude product was chromatographed using a silica gel column with 1-8% ethyl acetate/methylene chloride as the eluent to yield 1.65 g of product.

Step 9
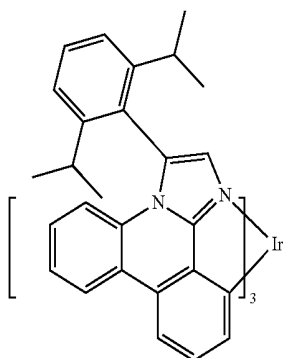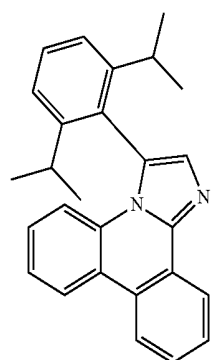
Ir(acac)₃
———————————→

Comparative Example 2

To a 50 mL Schlenk tube was added the ligand from Step 8 (1.47 g, 3.88 mmol), Ir(acac)₃ (0.38 g, 0.78 mmol) and tridecane (50 drops). The mixture was degassed and heated in a sand bath at 240° C.-250° C. with stirring under a nitrogen for 66 h. After cooling, the reaction mixture was dissolved with a mixture of solvent (CH_2Cl_2:hexanes=1:1) and subject to flash column chromatography with 1:1 CH_2Cl_2:hexanes as the eluent. The solid after column chromatography was recrystallized from a mixture of CH_2Cl_2 and methanol to yield 0.65 g (65%) of product.

Synthesis of Compound 1

Pd(II)
———————————→
B(OH)₂
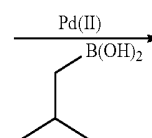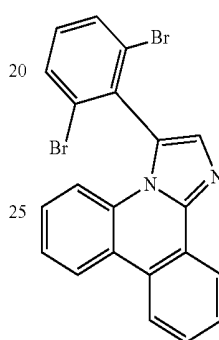
Step 1:

To a 200 mL flask was added dibromide (1.0 g, 2.2 mmol), isobutyl boronic acid (2.7 g, 26.5 mmol), Pd₂(dba)₃ (0.15 g, 0.16 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (0.27 g, 0.65 mmol), potassium phosphate tribasic monohydrate (8.7 g, 37.58 mmol) and 100 mL of toluene. The reaction mixture was fully degassed by freezing-pump-thaw technique. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 16 h. The reaction mixture was filtered through a pad of Celite. The toluene layer was separated and the aqueous was extracted once with 75 mL of toluene. The toluene extracts were combined, dried over sodium sulfate, then were filtered and concentrated under vacuum. The product was purified using silica gel chromatography with 1-8% ethyl acetate/methylene chloride as the eluent to give 0.76 g of product (84% yield).

-continued

Ir(acac)₃
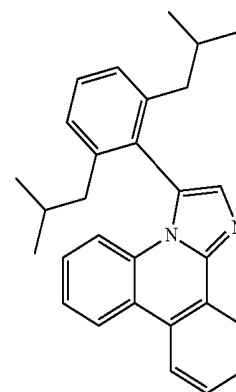
Step 1:

To a 200 mL flask was added the dibromide (4 g, 8.84 mmol), 1-cyclohexene boronic acid pinacol ester (18.37 g, 88.27 mmol), Pd(OAc)₂ (1.98 g, 2.9 mmol), 2-dicyclohex-ylphosphino-2',6'-dimethoxybiphenyl (2.4 g, 5.83 mmol), potassium phosphate tribasic monohydrate (10.18 g, 44.23 mmol), 100 mL of toluene and 100 mL of water. The reaction mixture was fully degassed by freezing-pump-thaw technique. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 16 h. The reaction mixture was filtered through a pad of Celite. The toluene layer was separated from the filtrate. The aqueous layer was extracted with 75 mL of toluene. The toluene extracts were combined, dried over sodium sulfate, then were filtered and concentrated under vacuum. The crude product was purified by column chromatography with 1-4% ethyl acetate/methylene chloride as the eluent to yield 3.2 g of product.

Compound 1

Step 2:

To a 50 mL Schlenk tube was added the ligand (2.8 g, 6.89 mmol), Ir(acac)₃ (0.68 g, 1.38 mmol) and tridecane (50 drops). The mixture was degassed and heated in a sand bath at 240-250° C. with stirring under a nitrogen for 73 h. After cooling, the reaction mixture was dissolved with a mixture of solvent (CH₂Cl₂:hexanes=1:1) and subject to flash column chromatography with 1:1 CH₂Cl₂:hexanes as the eluent. The solid after column chromatography was recrystallized from a mixture of CH₂Cl₂ and methanol to yield 1.69 g (87%) of product.
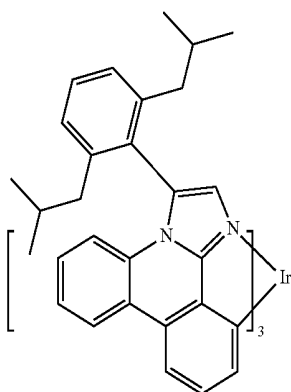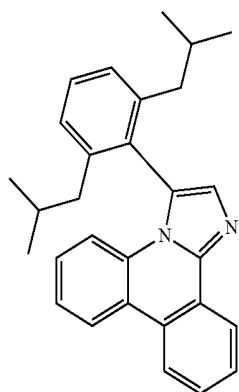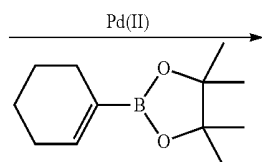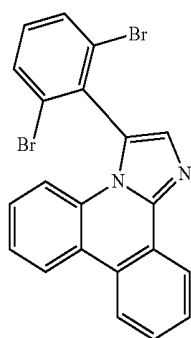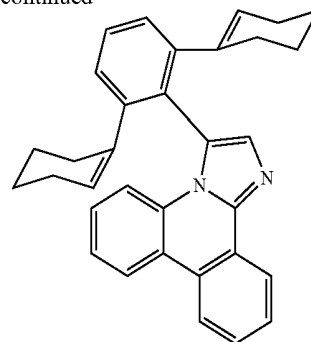
Synthesis of Compound 2

Pl/C, Pd/C, H₂

Pd(II)

Step 2:

3.2 g (0.007 mol) of the cyclohexenyl compound was dissolved in 150 mL of toluene. This solution was added to a Parr hydrogenation vessel that was purged with nitrogen and was charged with 2.8 g of 10% palladium on activated carbon and 1.4 g of platinum, 5 wt % (dry basis) on activated carbon wet, Degussa type F101. This heterogeneous mixture was shaken on the Parr hydrogenator for 72 h. The reaction mixture was filtered through a pad of Celite. The toluene

filtrate was concentrated under vacuum. The crude product was purified by column chromatography with 1-5% ethyl acetate/methylene chloride as the eluent to yield 3.1 g of product.

Compound 2

Step 3:

To a 50 mL Schlenk tube were added ligand (2.3 g, 5.08 mmol), Ir(acac)₃ (0.5 g, 1.01 mmol and tridecane (50 drops). The mixture was degassed and heated in a sand bath with stirring under a nitrogen for 73 h. After cooling, the reaction mixture was dissolved with a mixture of solvent (CH₂Cl₂: hexanes=1:1) and subject to flash column chromatography with 1:1 CH₂Cl₂:hexanes as the eluent. The solid after column chromatography was recrystallized from a mixture of CH₂Cl₂ and methanol to yield 0.93 g (58%) of product.
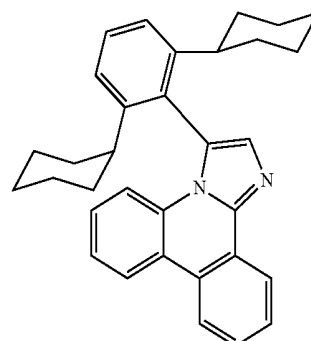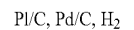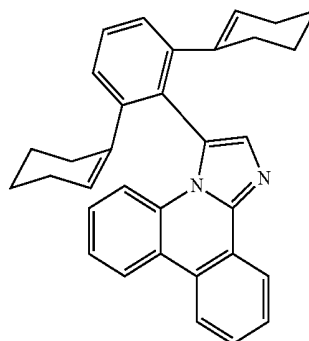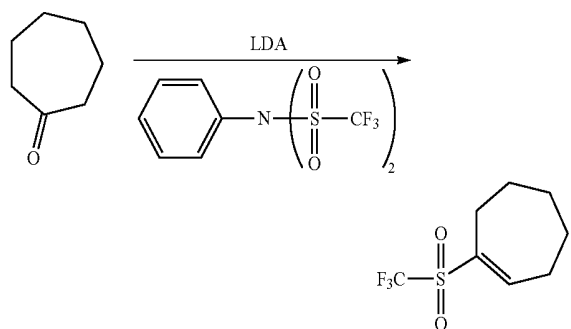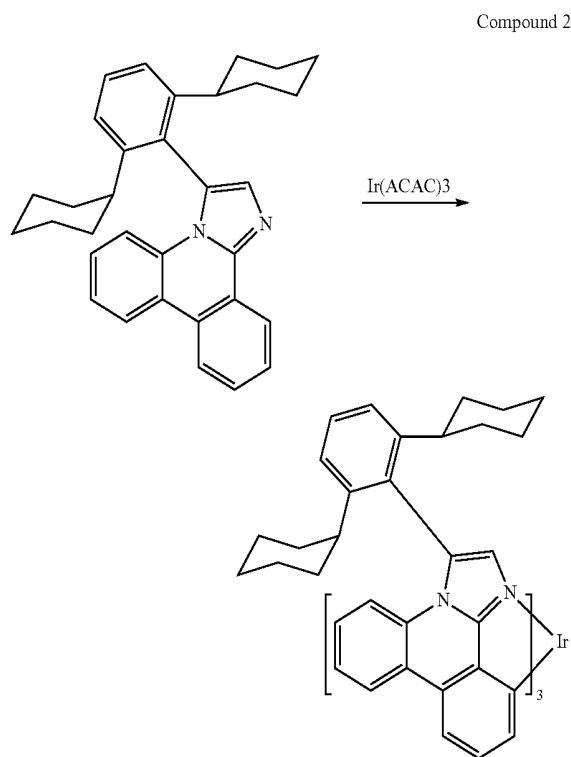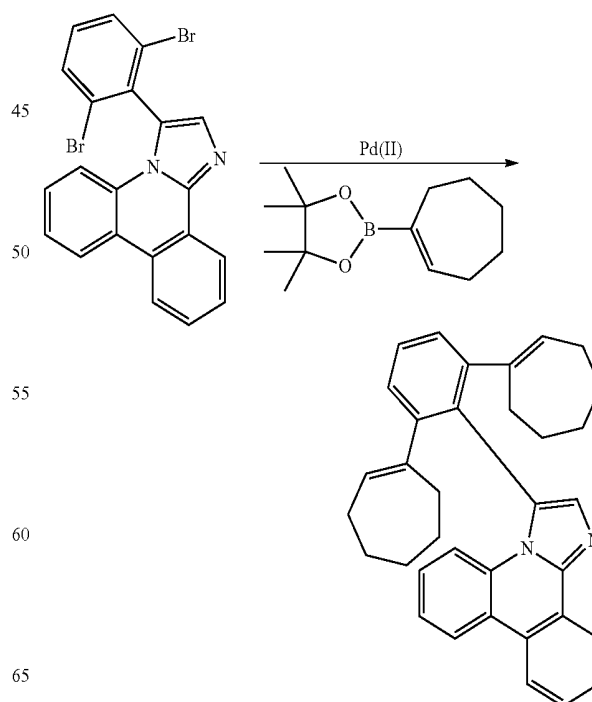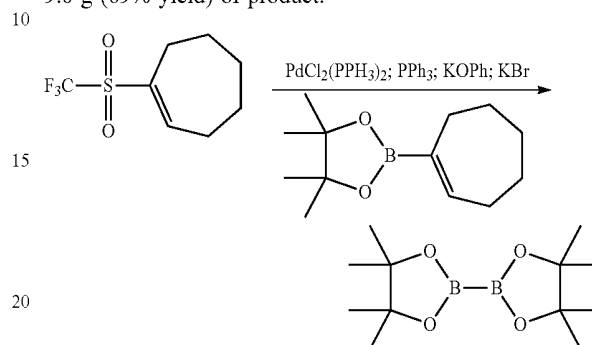
Synthesis of Compound 3

Step 1.

To a 500 mL 3-neck flask was charged diisopropylamine (9.9 g, 0.098 mol) and 100 mL of THF. This solution was cooled to −78° C. and 45.6 mL, 0.073 mol of n-BuLi 1.6 M in hexanes were added to the cooled reaction mixture via syringe. This mixture was stirred for ½ h at −78° C., then cycloheptanone (6.0 g, 0.054 mol) in 30 mL of THF was added dropwise to the cooled reaction mixture. This solution was stirred at −78° C. for 2 h. A THF solution of N-phenyl-bis-trifluoromethane sulfoimide (21.2 g, 0.059 mol) was

added dropwise to the cooled mixture. The mixture was then allowed to gradually warm to room temperature and was stirred overnight. The reaction mixture was quenched with aqueous ammonium chloride then was extracted 2×300 mL of ethyl acetate. The extracts were then dried over magnesium sulfate and were filtered and concentrated under vacuum. The crude product was chromatographed with 30-40% methylene chloride/hexanes as the eluent to yield 9.0 g (69% yield) of product.

Step 2.

PdCl₂(PPh₃)₂ (1.722 g, 2.45 mmol), PPh₃ (1.28 g, 4.9 mmol), bis(pinacolato)diboron (90.76 g, 357 mmol) and KOPh (16.2 g, 122.7 mmol) were added to a flask. The flask was flushed with nitrogen and then charged with toluene (300 mL) and the triflate (20 g, 81.8 mmol). The mixture was then stirred at 50° C. for 16 h. The reaction mixture was diluted with 200 mL of water. The toluene layer was separated. The aqueous layer was extracted 200 mL of toluene. The toluene extracts were combined, washed 100 mL of aqueous 10% lithium chloride, dried over magnesium sulfate, filtered and concentrated under vacuum. The crude product was distilled using a Kugelrohr distillation setup. The pot temperature was started at 85° C. and was increased to 115° C. This distilled mixture was chromatographed with 20-25% methylene chloride/hexanes as the eluent to yield 9.85 g (55% yield) of product.

85

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Step 3.

To a 500 mL round bottom flask was added the dibromide (4.7 g, 0.01 mol), the boronic acid pinacol ester (9.81 g, 0.0442 mol), Pd(OAc)$_2$ (0.75 g, 0.0033 mol), dicyclohexyl-phosphino-2',6'-dimethoxybiphenyl (2.73 g, 0.007 mol), potassium phosphate tribasic monohydrate (12.0 g, 0.052 mol), 200 mL of toluene and 75 mL of water. The reaction mixture was evacuated and back-filled with nitrogen. The reaction was then heated to reflux and stirred under a nitrogen atmosphere for 16 h. The mixture was filtered through a pad of Celite. The toluene layer was separated and the aqueous was extracted with 100 mL of toluene. The toluene portions were combined and dried over magnesium sulfate. This dried organic mixture was then filtered and concentrated under vacuum. The crude product was purified by silica gel chromatography. The first purification involved eluting the column with 1-4% ethyl acetate/methylene chloride. The second purification involved eluting the column with 2-12% ethyl acetate/hexanes. The yield was 4.1 g (82%).
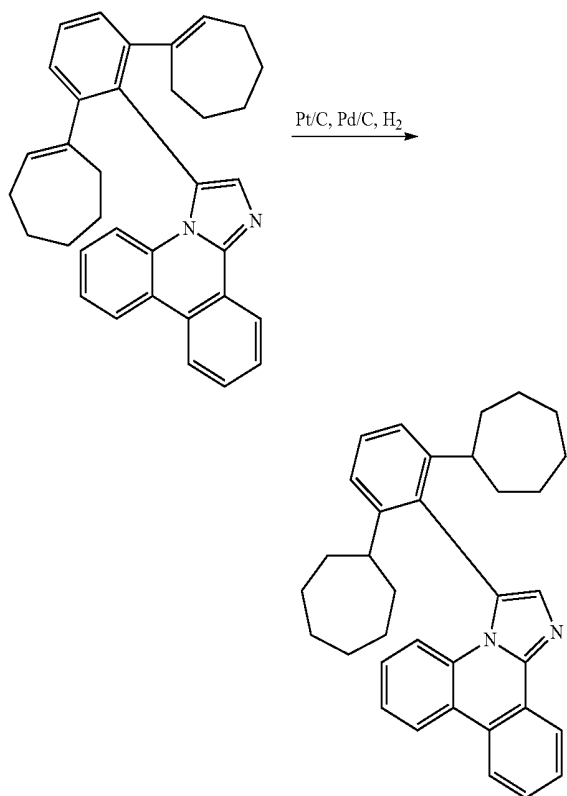

Step 4.

The alkenyl product from Step 3 was dissolved in 200 mL of toluene and was charged into a Parr hydrogenation bottle containing 2.8 g of 10% Pd/C and 1.4 g of 5% Pt/C Degussa Type F101 RA/W. This mixture was placed on the Parr hydrogenator for 18 h. The reaction mixture was filtered through a pad of Celite and the pad was rinsed with 200 mL of toluene. The toluene filtrate was concentrated under vacuum. The crude product was purified by silica gel chromatography with 5-15% ethyl acetate/hexanes as the eluent. The product obtained (3.6 g, 0.0074 mol) was dissolved in THF and was cooled to −78° C. To this cooled solution was added 6.3 mL of 1.6M n-BuLi in hexanes via syringe over a 5 min period. The reaction mixture was stirred for an additional 5 min then was quenched by adding 50 mL of water dropwise. This mixture was warmed to room temperature then was extracted 2×150 mL ethyl acetate.

These extracts were dried over magnesium sulfate then were filtered and concentrated under vacuum. These extracts were then passed through a neutral alumina (deactivated by the addition of 6% (w/w) water) column that was eluted with 20-70% methylene chloride/hexanes. The material was dissolved in 50 mL of methylene chloride and was stirred at room temperature for 18 h with 0.8 g of Si-TAAcoH and 0.8 g of Si-Thiourea. This mixture was then filtered, concentrated under vacuum and the resulting material was recrystallized from hexanes to yield 2.93 g (71% yield) of product.

Compound 3
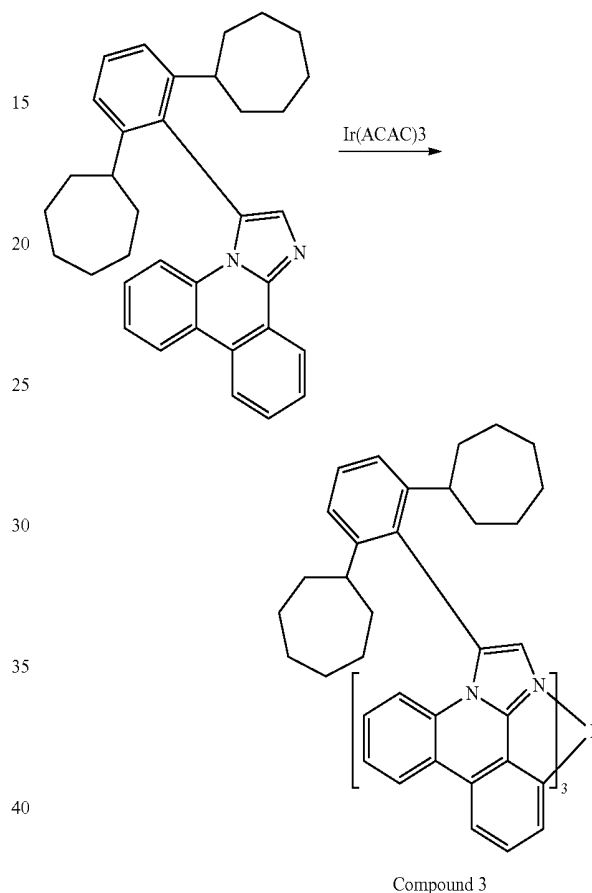
Step 5.

To a 50 mL Schlenk tube were added the ligand (2.93 g, 6.03 mmol), Ir(acac)$_3$ (0.59 g, 1.205 mmol) and tridecane (50 drops). The mixture was degassed and heated in a sand bath with stirring under a nitrogen for 73 h. After cooling, the reaction mixture was dissolved with a mixture of solvent (CH$_2$Cl$_2$:hexanes=1:1) and subject to flash column chromatography with 1:1 CH$_2$Cl$_2$:hexanes as the eluent. The solid after column chromatography was recrystallized from a mixture of CH$_2$Cl$_2$ and methanol to yield 1.18 g of product.

Synthesis of Compound 4
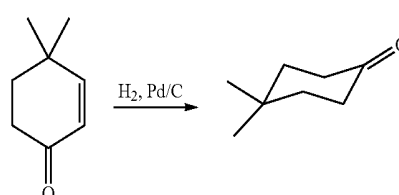
Step 1.

10.0 g (0.08 mol) of 4,4-dimethylcyclohex-2-enone was dissolved in 150 mL of ethanol. This solution was added to

a Parr hydrogenation vessel that was purged with nitrogen and was charged with 0.5 g of 10% palladium on activated carbon. This heterogeneous mixture was shaken on the Parr hydrogenator for 8 h. The reaction mixture was filtered through Celite and evaporated to dryness to yield 7.9 g of product.
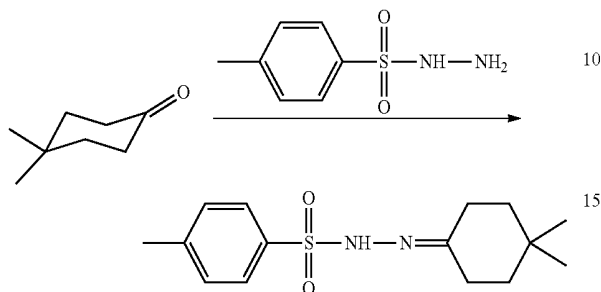
Step 2.

A mixture of p-tolylsulfonylhydrazine (6.8 g, 36.7 mmol), 60 mL of absolute ethanol and the ketone (4.64 g, 36.76 mmol) was heated to reflux at 100° C. After heating for 2 h, the reaction mixture was cooled using an ice-water bath to precipitate the majority of the hydrazone. The resulting solid was collected by filtration and was washed thoroughly with ice-cold ethanol. Air drying for 1 h afforded 7.67 g of the required hydrazone.
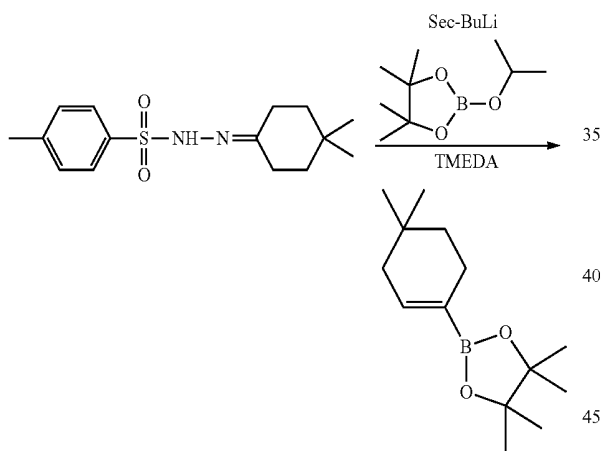
Step 3.

To a dried 500 mL round-bottom flask equipped with a magnetic stirbar and rubber septum, hydrazone (5 g, 17 mmol) was added followed by 100 mL of anhydrous hexanes. To this mixture 100 mL of anhydrous TMEDA were added, and the reaction mixture was cooled to −78° C. and maintained at this temperature for 15 min, after which 60.6 mL (84.9 mmol) of 2.5M sec-BuLi was added over 15 min. The reaction mixture was then stirred for 1 h at −78° C. and then brought to room temperature and stirred for 1.5 h. The mixture was cooled down to −78° C. again and 15.8 g (84.9 mmol) of pinacol isopropyl borate was then added. The reaction was stirred for another hour at −78° C. and then brought to room temperature and stirred for 3 h. The reaction was quenched with the addition of saturated NH₄Cl and then extracted three times with ether. The combined organic extracts were dried over anhydrous MgSO₄, filtered, and concentrated in vacuo. The residue was subject to flash chromatography (40% CH₂Cl₂ in hexanes) to afford 1.53 g (38%) of desired product.
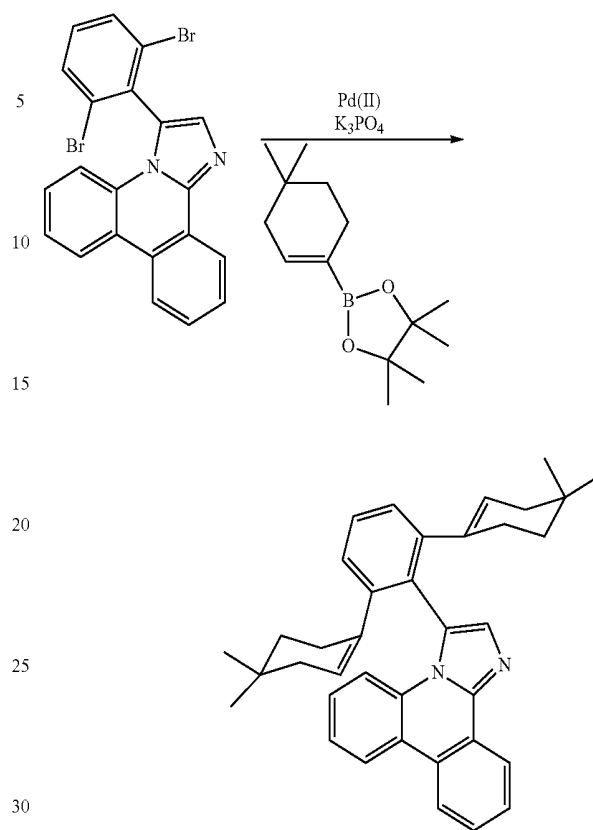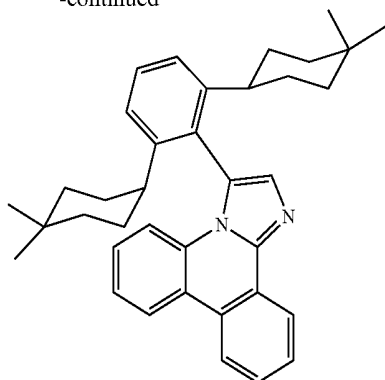
Step 4.

To a 200 mL flask was added dibromide (5 g, 11.06 mmol), bornic acid pinacol ester from step 3 (11.26 g, 47.67 mmol), Pd(OAc)₂ (819 mg, 3.64 mmol), dicyclohexylphosphino-2',6'-dimethoxybiphenyl (2.9 g, 7.3 mmol), potassium phosphate tribasic monohydrate (12.73 g, 55.29 mmol), 150 mL of toluene and 150 mL of water. The reaction mixture was fully degassed by freezing-pump-thaw technique. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 16 h. The reaction mixture was filtered through a pad of Celite. The toluene layer was separated from the filtrate. The aqueous layer was extracted 75 mL of toluene. The toluene extracts were combined, dried over sodium sulfate, then were filtered and concentrated under vacuum. The crude product was passed through a silica gel column. The column was eluted with 10% ethyl acetate in hexanes to yield 4.5 g of desired product.
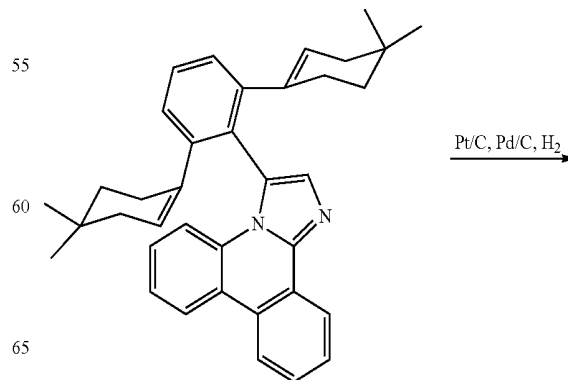
-continued

Step 5.

4.5 (8.81 mol) of the cyclohexenyl product from step 4 was dissolved in 150 mL of toluene. This solution was added to a Parr hydrogenation vessel that was purged with nitrogen and was charged with 3.2 g of 10% palladium on activated carbon and 2.8 g of Platinum, 5 wt % (dry basis) on activated carbon wet, Degussa type F101. This heterogeneous mixture was shaken on the Parr hydrogenator for 16 h. The reaction mixture was filtered through a pad of Celite. The toluene filtrate was concentrated under vacuum. The crude product was passed through a silica gel column. The column was eluted with 10% ethyl acetate in hexanes to yield 4.24 g of product.

Ir(acac)₃

Compound 4
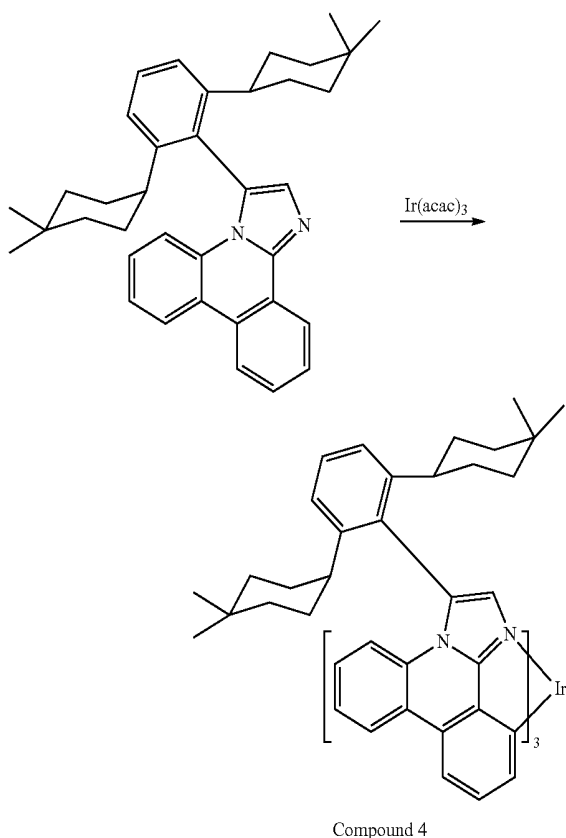
Step 6.

To a 50 mL Schlenk tube were added ligand (2.57 g, 5.03 mmol), Ir(acac)₃ (0.495 g, 1.006 mmol) and tridecane (50 drops). The mixture was degassed and heated in a sand bath with stirring under a nitrogen atmosphere for 73 h. After cooling, the reaction mixture was dissolved with a mixture

of solvent (CH₂Cl₂:dexanes=1:1) and subject to flash column chromatography (CH₂Cl₂:dexanes=1:1). The solid after column chromatography was recrystallized from a mixture of CH₂Cl₂ and methanol to yield 0.8 g of product.

Synthesis of Compound 5
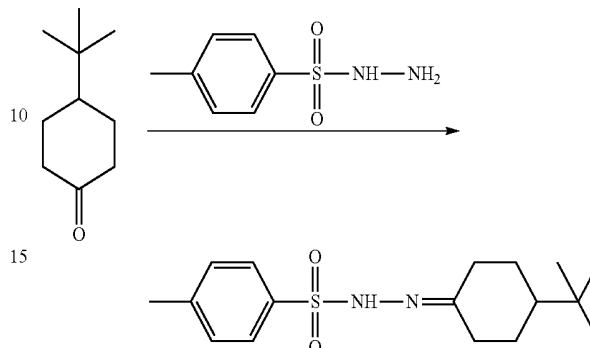
Step 1.

A mixture of 4-tert-butylcyclohexanone (26.5 g, 0.172 mol), p-toluenesulfonylhydrazide (31.74 g, 0.171 mol) and 450 mL of anhydrous ethanol was heated to reflux for 4 h then cooled to room temperature. The reaction mixture was filtered and dried under vacuum to yield 35 g of product.
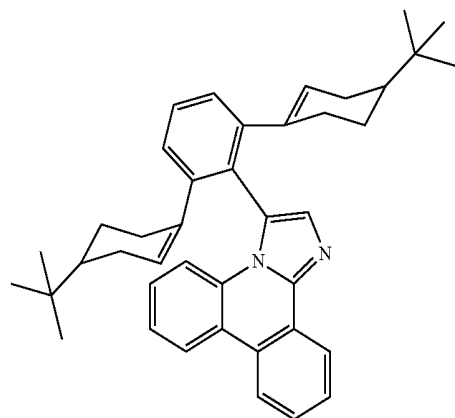
n-BuLi
TMEDA
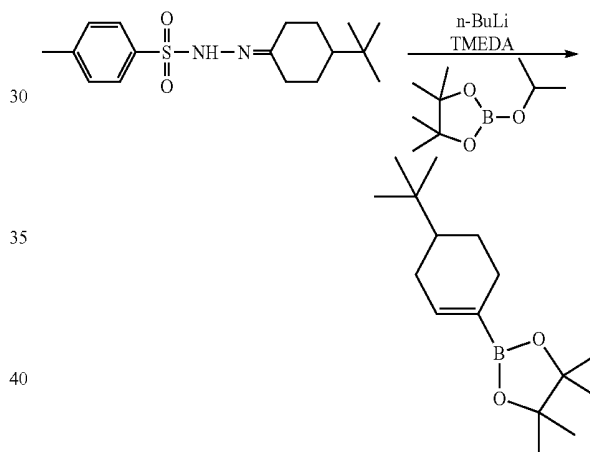
Step 2.

To a dried 500 mL round-bottom flask equipped with a magnetic stirbar and rubber septum, hydrazone (7.5 g, 0.023 mol) was added followed by 70 mL of anhydrous hexanes. To this mixture 70 mL of anhydrous TMEDA was added and the reaction mixture was cooled to −78° C. and maintained at this temperature for 15 min, after which 37 mL (0.092 mol) of 2.5M n-BuLi in hexanes were added over 15 min. The reaction mixture was then stirred for 1 h at −78° C. and then brought to room temperature and stirred for 3.5 h. The mixture was brought to −78° C. again and 17 g (0.092 mol) of pinacol isopropyl borate were added. The reaction was stirred for another hour at −78° C. and then brought to room temperature and stirred for overnight. The reaction was quenched with the addition of saturated NH₄Cl and then was partitioned with 200 mL of ether. This heterogeneous mixture was passed through a Celite pad. The ether layer was separated and the aqueous was extracted 300 mL of ether. The combined organic extracts were dried over anhydrous MgSO₄, filtered, and concentrated under vacuum. The crude product was passed through a silica gel column (20-40% methylene chloride/hexanes). 4.4 g (72% yield) of product was obtained.
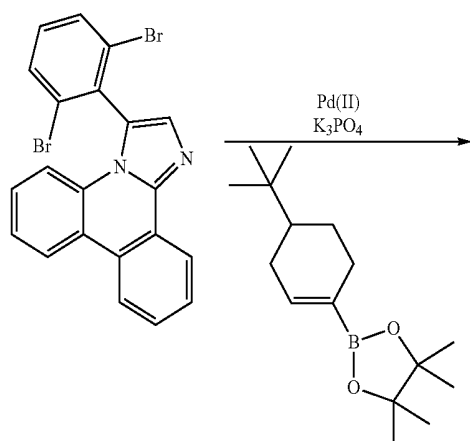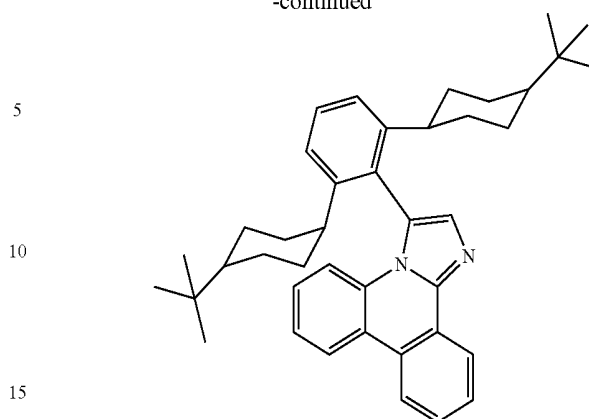
Step 3.

To a 1 L round bottom flask was added dibromide (5 g, 0.011 mol), boronic acid pinacol ester from step 2 (7.3 g, 0.0276 mol), tris(dibenzylideneacetone)dipalladium(O) (0.2 g, 0.22 mmol), dicyclohexylphosphino-2',6'-dimethoxybiphenyl (0.36 g, 0.88 mmol), potassium phosphate tribasic monohydrate (14.0 g, 0.066 mol), 300 mL of toluene and 80 mL of water. The reaction mixture was evacuated and back-filled with nitrogen. The reaction was then heated to reflux and stirred under a nitrogen atmosphere for 16 h. The heterogeneous reaction mixture was filtered through a pad of Celite. The toluene layer was separated and the aqueous was extracted 100 mL of toluene. The toluene portions were combined and dried over magnesium sulfate. This dried organic mixture was then filtered and concentrated under vacuum. The crude product was purified by silica gel chromatography. The column was eluted with 1-4% ethyl acetate/methylene chloride. 5 g (80% yield) of product was obtained.

Step 4.

The alkenyl product (5.0 g, 0.0088 mol) from Step3 was dissolved in 200 mL of toluene and was charged into a Parr hydrogenation bottle that already contained 3.8 g of 10% Pd/C and 3.0 g of 5% Pt/C Degussa Type F101 RA/W. This mixture was placed on the Parr hydrogenator for 58 h. The reaction mixture was filtered through a pad of Celite and the pad was rinsed with 200 mL of toluene. The toluene filtrate was concentrated under vacuum to yield 4.3 g of crude product. The crude product was purified by silica gel chromatography. The column was eluted with 1-5% ethyl acetate/methylene chloride. Next, the product obtained from the column was dissolved in 50 mL of methylene chloride and was stirred at room temperature for 18 h with 1.1 g of Si-TAAcoH and 1.1 g of Si-Thiourea. This is to remove any residual palladium. The product obtained (3.9 g, 0.0068 mol) was dissolved in THF and was cooled to –78° C. To this cooled solution was added 5.8 mL of 1.6 M n-BuLi in hexanes via syringe over a 5 min period. The reaction mixture was stirred for an additional 5 minutes then was quenched by adding 50 mL of water drop wise. This mixture was warmed to room temperature then was extracted 2×150 mL ethyl acetate. These extracts were dried over magnesium sulfate then were filtered and concentrated under vacuum. These extracts were then passed through a neutral alumina (deactivated by the addition of 6% (w/w) water) column that was eluted with 30-60% methylene chloride/hexanes. 3.6 g of product was obtained. The product obtained from the neutral alumina column was recrystallized from hexanes/ethyl acetate. 2.90 g of product was obtained.

93   94
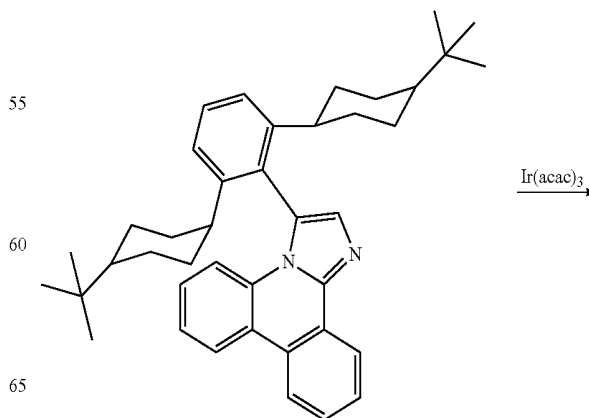
-continued   -continued

Compound 5

H2

H3
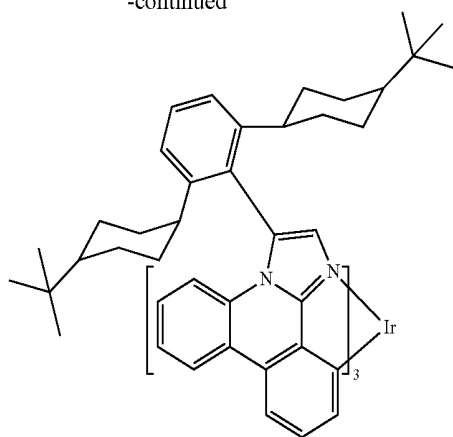
Step 5.

To a 50 mL Schlenk tube were added ligand (2.78 g, 4.86 mmol), Ir(acac)₃ (0.478 g, 0.97 mmol) and tridecane (50 drops). The mixture was degassed and heated in a sand bath with stirring under a nitrogen for 70 h. After cooling, the reaction mixture was dissolved with a mixture of solvent (CH₂Cl₂:dexanes=1:1) and subject to flash column chromatography CH₂Cl₂:hexanes=1:1). The solid after column chromatography was recrystallized from a mixture Of CH₂Cl₂ and methanol to yield 1.0 g of product.

Device Examples

All device examples were fabricated by high vacuum (<10⁻⁷ Torr) thermal evaporation. The anode electrode is 1200 Å of indium tin oxide (ITO). The cathode consisted of IOA of LiF followed by 1000 Å of Al. All devices were encapsulated with a glass lid sealed with an epoxy resin in a nitrogen glove box (<1 ppm of H₂O and O₂) immediately after fabrication, and a moisture getter was incorporated inside the package.

The organic stack of the Device Examples 1 and 2 in Table 2, consisted of sequentially, from the ITO surface, 10 nm of H3 or H4 as the hole injection layer (HIL), 30 nm of 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (α-NPD) as the hole transporting later (HTL), 30 nm of the H2 doped with 9% of the dopant emitter (e.g., invention Compounds 1-2) as the emissive layer (EML), 5 nm of H2 as the ETL2 and 40 nm of Alq as ETL1.

Comparative Examples 1-3 were fabricated similarly to the Device Examples except E1, E2, or E3 was used as the emissive dopant and H1 was used as the host in the EML and as the ETL2 material.
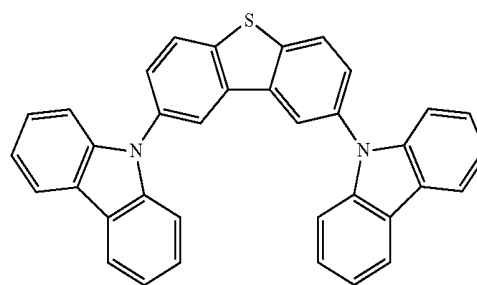
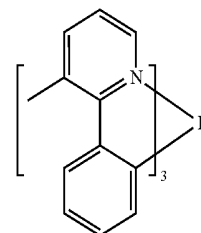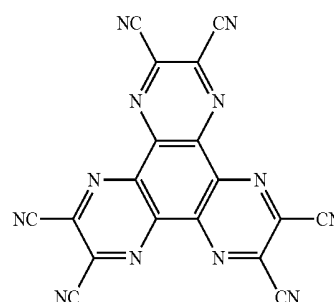As used herein, the following compounds have the following structures:
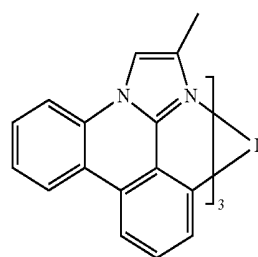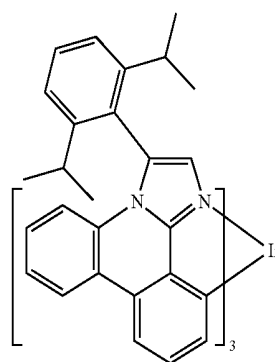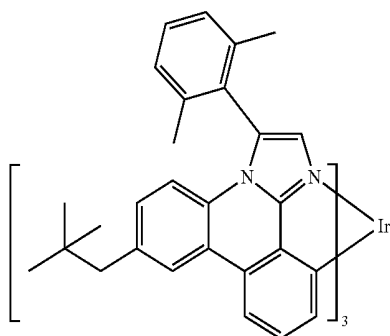
H4

E1

H1

E2

-continued

E3
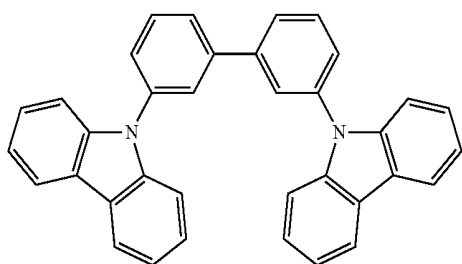
Particular emissive dopants for the emissive layer of an OLED are provided which may lead to devices having particularly good properties. The device structure and the results from device testing are provided in Table 2. Devices having an emissive layer using Compounds 1 and 2 as the emissive dopant show improved device efficiency and stability as well as improved color indicating that these substituted imidazophenanthridine compounds may be beneficial.

Solid state photoluminescent quantum yields (PL %) were determined from 1 weight % of the dopant in polymethylmethacrylate (PMMA), an optically inert polymer matrix. The samples are prepared by dissolving the dopant and PMMA in 1 mL of toluene per 100 mg solids (90 mg of PMMA and 10 mg of the dopant). The samples were filtered and drop-casted onto a pre-cleaned quartz substrate. After the solvent has evaporated, PL quantum yields were measured using a Hamamatsu Absolute PL Quantum Yield Measurement System. The system is comprised of an integrating sphere, xenon light source, monochromater, and multi-channel CCD spectrometer, and is housed in an inert atmosphere glove box to prevent quenching by oxygen. The excitation wavelength was 342 nm.

thermore, Comparative example 3 uses E3 which has a bulky neopentyl group substituted on the other ring of the ligand, yet this does not lead to a large improvement in PL quantum yield. Compounds 1 and 2 with bulky alkyl groups substituted to the twisted aryl are found to have higher PL quantum yield and therefore improved device efficiency. Alkyl groups particularly beneficial as these lead to minimal red-shifting. The use of bulky alkyl substituents (i.e., alkyl groups containing four or more atoms) is believed to be a novel way to modify the compound to inhibit self quenching. These bulky substituted compounds do not suffer the lifetime limitation of compounds having alkyl groups substituted to the 4-imidazole position, as seen for E1 used in Comparative Example 1.

Attaching a methyl group to the 2 position of the imidazophenanthridine, as shown for E1 in Comparative example 1, increased solid state quantum yield of the dopant and lead to higher device efficiency. However, several examples demonstrated that the addition of alkyl substituents at this position can lead to devices having short lifetimes (i.e., less than 100 hours at 2000 nits). Alternatively, it was found that attaching bulky alkyl groups (i.e., alkyls having four or more atoms) increased photoluminescent efficiency and device efficiency. For example, Compounds 1 and 2 have high efficiency, similar to Comparative example 1, and greater efficiency than Comparative examples 2 and 3. Both the selection of bulky alkyl substituents and the site of substitution (i.e., 2 and/or n position of the twisted aryl) may be important to obtain the increased efficiency. For example, E3 used in Comparative example 3 has a bulky neopentyl group substituted away from the imidazole, yet this compound has a relatively low PL yield of 40%. Notably, the compounds provided herein demonstrate significantly long device lifetimes. For example, the device lifetime of invention Compounds 1 and 2 are 3-4 times longer when compared to

TABLE 2

Device Example	Emitter (doping %)	EQE (%) at 1000 cd/m²	V (V) at 1000 cd/m²	T₁/₂ (h) at 2000 cd/m²	CIE	Sublimation temp. (° C.)	HIL	HOST	ETL2	PL %
Comparative 1	E1 (9)	12	8	70	0.15, 0.23	330	H3	H1	H1	52
Comparative 2	E2 (9)	7	8	200	0.15, 0.24	300	H4	H1	H1	26
Comparative 3	E3 (9)	8	8	180	0.15, 0.26	320	H4	H1	H1	40
1	1 (9)	12	7	200	0.15, 0.24	265	H3	H2	H2	56
2	2 (9)	12	8	300	0.15, 0.23	310	H4	H2	H2	60

From Device Examples 1 and 2, it can be seen that the device efficiencies correlate with the solid state PL quantum yields. Comparative Example 1 gives a higher PL efficiency compared to Comparative Example 2. It is believed that the alkyl substitution present in E1 used in Comparative Example 1 inhibits self quenching leading to higher PL and EL efficiencies. Comparative Example 2 uses E2 which has 2,6-dimethyl twisted aryl groups and relatively low PL quantum efficiencies. In these cases the 2,6 alkyl substitutions are not bulky enough to inhibit self quenching. Fur-

Comparative example 1. Bulky alkyl substitution on the twisted aryl may also improve device processing. For example, Compound 1 has an isobutyl substitution and has a sublimation temperature of 265° C., which is the lowest sublimation temperature to be observed to date in this family of imidazo[1,2-f] phenanthridine iridium complexes.

It is understood that the various embodiments described herein are by way of example only, and are not intended to limit the scope of the invention. For example, many of the materials and structures described herein may be substituted

with other materials and structures without deviating from the spirit of the invention. The present invention as claimed may therefore includes variations from the particular examples and preferred embodiments described herein, as will be apparent to one of skill in the art. It is understood that various theories as to why the invention works are not intended to be limiting.

The invention claimed is:

1. A compound having the formula:
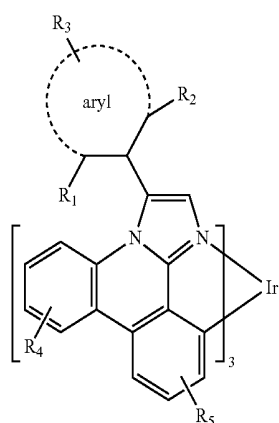
wherein R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, and aryl;

wherein at least one of R_1 and R_2 is an alkyl that is (i) cyclic, (ii) has four or more carbon atoms, and (iii)(a) is a branched alkyl, (b) is a bicyclic alkyl, or (c) is a multicyclic alkyl;

wherein R_3 and R_4 may represent up to tetra-substitutions;

wherein R_5 may represent up to tri-substitutions; and

wherein R_3, R_4, and R_5 are independently selected from the group consisting of hydrogen, alkyl, and aryl.

2. The compound of claim 1, wherein the alkyl that is cyclic and has four or more carbon atoms is a branched alkyl.

3. The compound of claim 1, wherein the alkyl that is cyclic and has four or more carbon atoms is a bicyclic alkyl.

4. The compound of claim 1, wherein the alkyl that is cyclic and has four or more carbon atoms is a multicyclic alkyl.

5. The compound of claim 1, wherein the alkyl that is cyclic and has four or more carbon atoms does not include any heteroatoms.

6. The compound of claim 1, wherein the alkyl that is cyclic and has four or more carbon atoms is a heteroalkyl that contains at least one of an oxygen atom, a nitrogen atom, or a sulfur atom.

7. The compound of claim 1, wherein R_1 and R_2 are the same.

8. The compound of claim 1, wherein R_1 and R_2 are different.

9. The compound of claim 1, wherein one of R_1 and R_2 is an aryl.

10. The compound of claim 1, wherein the compound has the formula:
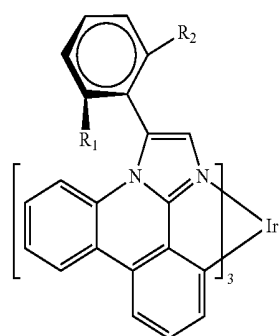
11. The compound of claim 1, wherein the compound is selected from the group consisting of:
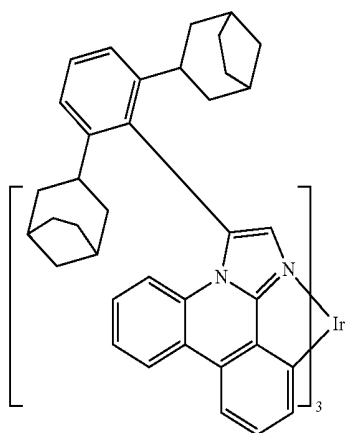

Compound 4
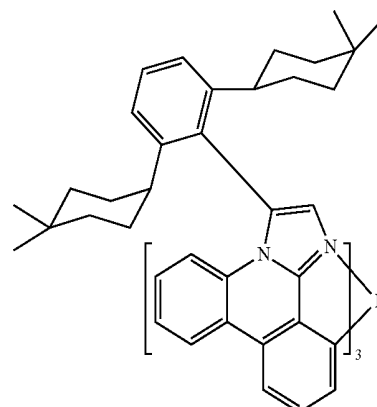
Compound 5
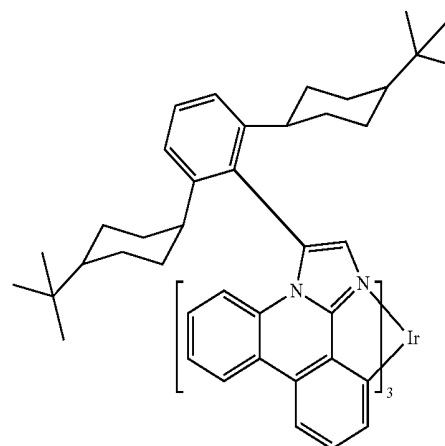
Compound 7
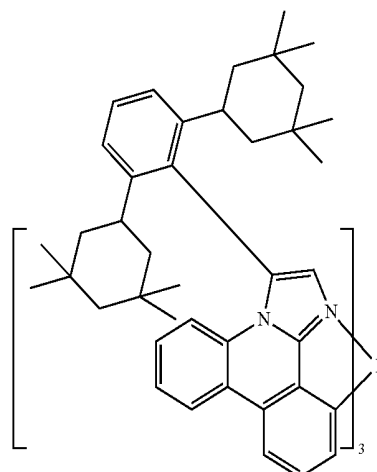
99

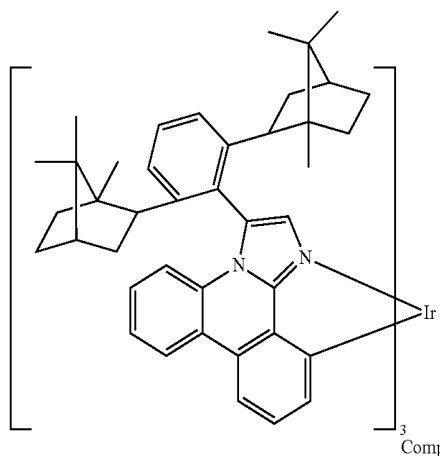-continued

Compound 8

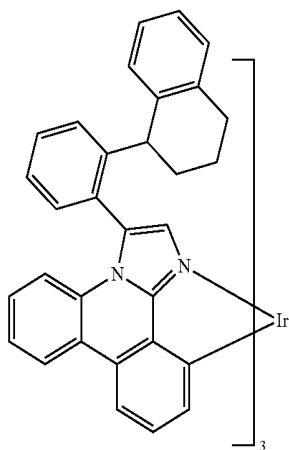Compound 10

Compound 12
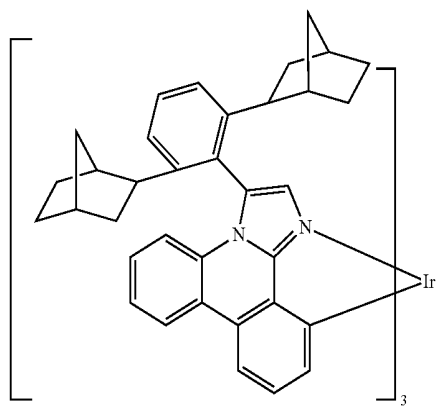
Compound 14
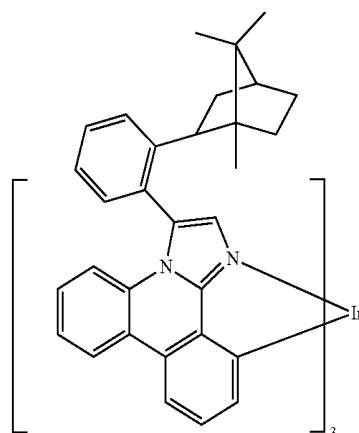
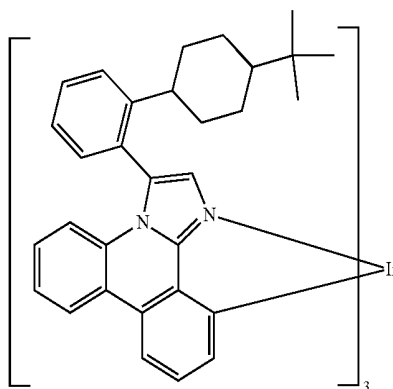**100**

-continued

Compound 15

Compound 16
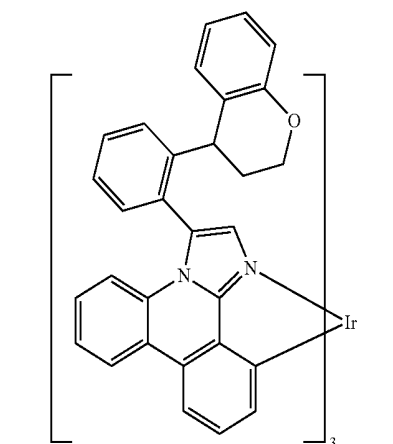
Compound 19

Compound 20

and

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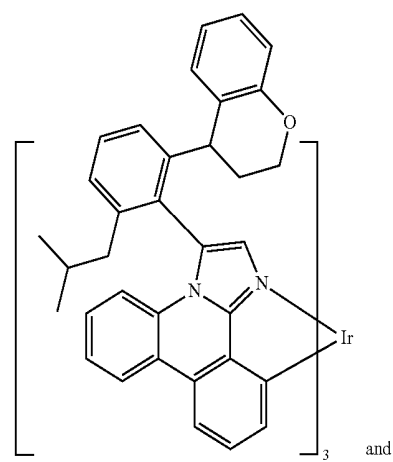
101

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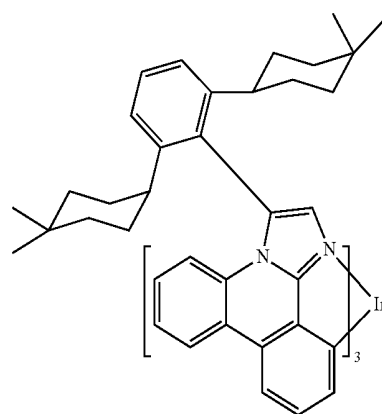
Compound 31

102

Compound 4

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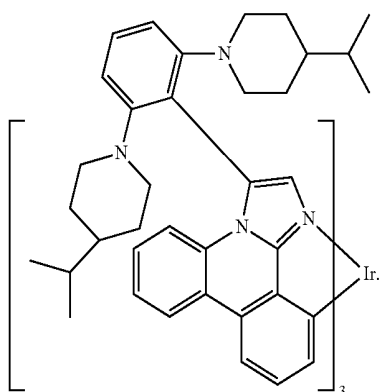
12. A first device comprising an organic light emitting device, further comprising:

an anode;

a cathode; and

an organic layer, disposed between the anode and the cathode, the organic layer comprising a compound having the formula:
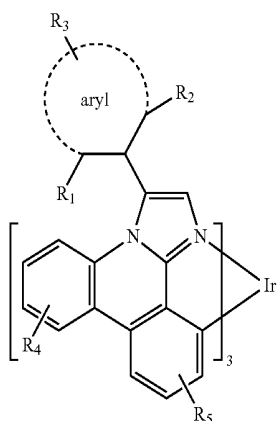
wherein R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, and aryl;

wherein at least one of R_1 and R_2 is an alkyl that is (i) cyclic, (ii) has four or more carbon atoms, and (iii)(a) is a branched alkyl, (b) is a bicyclic alkyl, or (c) is a multicyclic alkyl;

wherein R_3 and R_4 may represent up to tetra-substitutions;

wherein R_5 may represent up to tri-substitutions; and

wherein R_3, R_4, and R_5 are independently selected from the group consisting of hydrogen, alkyl, and aryl.

13. The first device of claim 12, wherein the first device is a consumer product.

14. The first device of claim 12, wherein the compound is selected from the group consisting of:
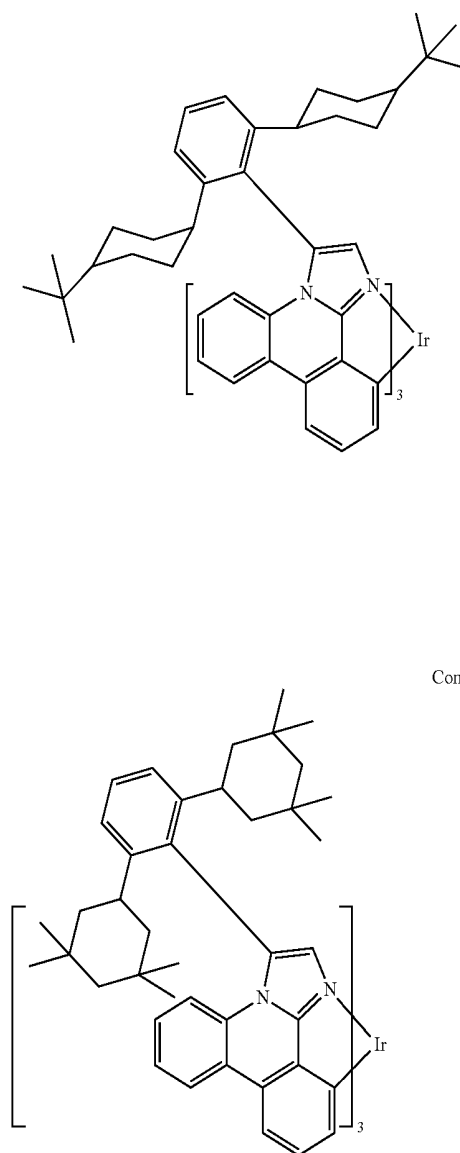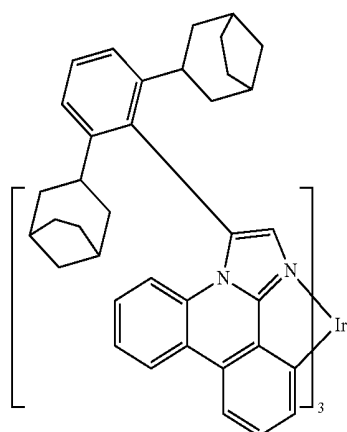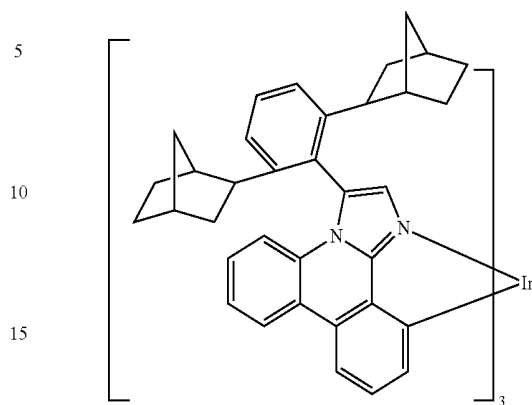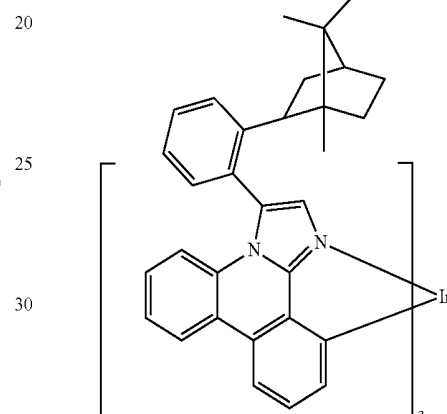
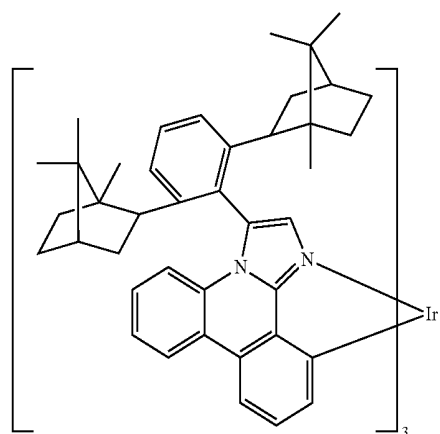Compound 5

Compound 7

103

-continued

Compound 8

5

10

15

20

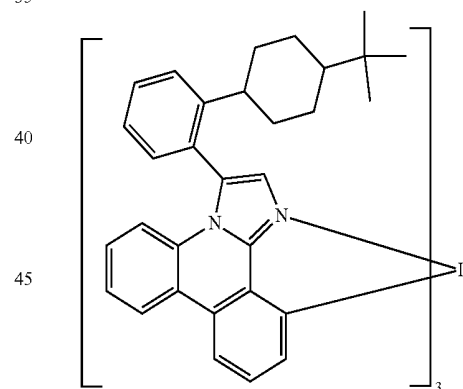Compound 10 25

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Compound 12 50

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104

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Compound 14

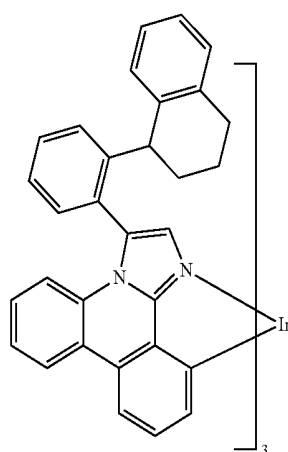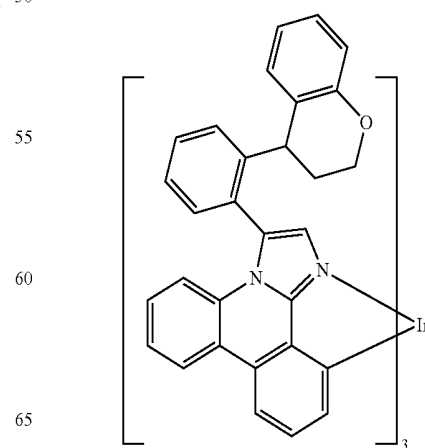Compound 15

Compound 16

Compound 19

-continued
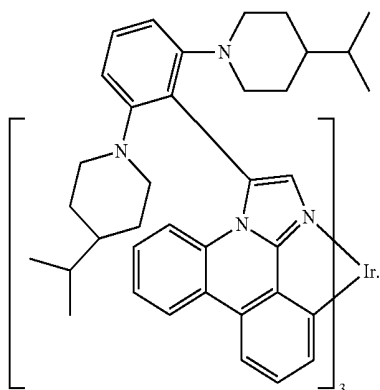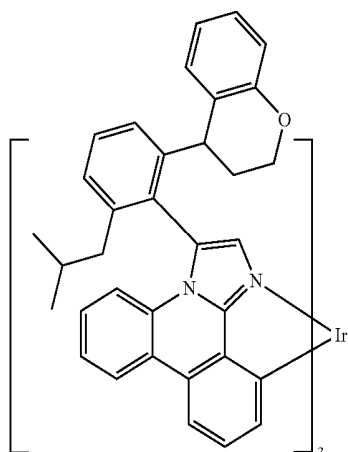
Compound 20
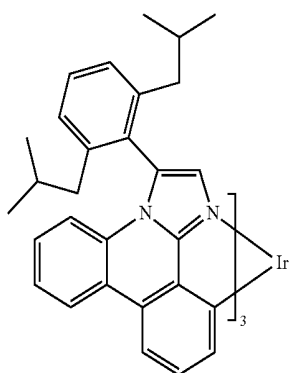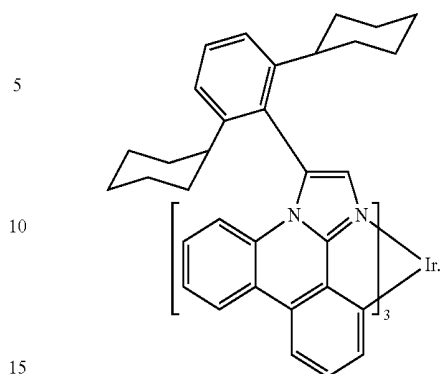

Compound 31

15. The first device of claim **12**, wherein the organic layer further comprises a second compound selected from the group consisting of:

Compound 1

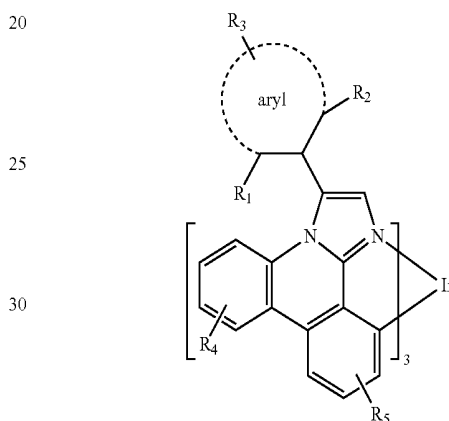-continued

Compound 2

16. The first device of claim **12**, wherein the organic layer is an emissive layer and the compound having the formula
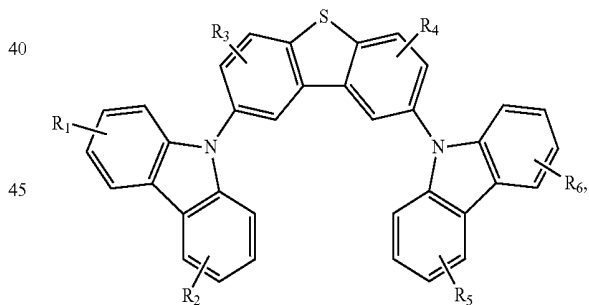

is an emissive compound.

17. The first device of claim **12**, wherein the organic layer further comprises a host having the formula:

wherein each of R_1 through R_6 are independently selected from the group consisting of any alkyl, alkoxy, amino, alkenyl, alkynyl, arylalkyl, aryl, heteroaryl and hydrogen, and where each of R_1 through R_6 may represent multiple substitutions.

* * * * *

专利名称(译)	有机电致发光材料和器件		
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[标]申请(专利权)人(译)	环球展览公司		
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	TSAI JUI YI YEAGER WALTER BROOKS JASON BEERS SCOTT KOTTAS GREGORY S BARRON EDWARD KWONG RAYMOND		
发明人	TSAI, JUI-YI YEAGER, WALTER BROOKS, JASON BEERS, SCOTT KOTTAS, GREGORY S. BARRON, EDWARD KWONG, RAYMOND		
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CPC分类号	H01L51/0085 C07F15/0033 C09K11/06 H05B33/14 C09K2211/1044 H01L51/5016 C09K2211/1051 C09K2211/185 H01L51/0072 H01L51/0074 C09K2211/1048		
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摘要(译)

提供了咪唑并[1,2-f]菲啶化合物。该化合物具有进一步被具有四个或更多个原子的烷基取代的加捻芳基部分。这些化合物可用于有机发光器件，特别是作为发射掺杂剂，为器件提供改进的效率，稳定性和制造。特别地，本文提供的化合物可以用于具有高效率的蓝色器件中。