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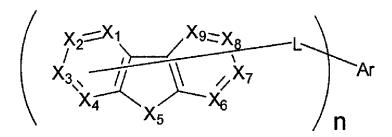
- (71) Applicant (for all designated States except US): UNIVER-SAL DISPLAY CORPORATION [US/US]; 375 Phillips Blvd., Ewing, New Jersey 08618 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): XIA, Chuanjin [CN/US]; 375 Phillips Blvd., Ewing, New Jersey 08618 (US). HARIKRISHNA-MOHAN, Siddharth [IN/US]; 375 Phillips Blvd., Ewing, New Jersey 08618 (US). ADAMOVICH, Vadim [RU/US]; 375 Phillips Blvd., Ewing, New Jersey 08618 (US).
- (74) Agents: MCGROARTY, John et al.; KILPATRICK, TOWNSEND & STOCKTON, LLP, Two Embarcadero Center, 8th Floor, San Francisco, California 94111 (US).

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(54) Title: AZA - DIBENZOTHIOPHENE, AZA - DIBENZOFURAN AND AZA - DIBENZOSELENOPHENE DERIVATIVES FOR USE IN OLED'S



(57) Abstract: Compounds comprising an aza-dibenzo moiety and a condensed aromatic moiety having at least three benzene rings are provided. In particular, the compounds may comprise an azadibenzofuran, azadibenzothiophene, or azadibenzoselenophene joined directly or indirectly to an anthracene. The compounds may be used in the electron transport layer of organic light emitting devices to provide devices with improved properties.





AZA-DIBENZOTHIOPHENE, AZA-DIBENZOFURAN AND AZA-DIBENZOSELENOPHENE DERIVATIVES FOR USE IN OLED'S

[0001] 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

[0002] The present invention relates to organic light emitting devices (OLEDs). More specifically, the present invention relates to phosphorescent materials comprising an aza-dibenzo moiety and a condensed aromatic moiety having at least three benzene rings. These materials may be used in OLEDs to provide devices having improved performance.

BACKGROUND

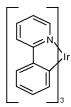
[0003] Opto-electronic devices that make use of organic materials are becoming increasingly desirable for a number of reasons. Many of the materials used to make such devices are relatively inexpensive, so organic opto-electronic devices have the potential for cost advantages over inorganic devices. 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.

[0004] OLEDs make use of thin organic films that emit light when voltage is applied across the device. OLEDs are becoming an increasingly interesting technology for use in applications such as flat panel displays, illumination, and backlighting. Several OLED materials and

configurations are described in U.S. Pat. Nos. 5,844,363, 6,303,238, and 5,707,745, which are incorporated herein by reference in their entirety.

[0005] 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.

[0006] One example of a green emissive molecule is tris(2-phenylpyridine) iridium, denoted Ir(ppy)₃, which has the structure:



[0007] In this, and later figures herein, we depict the dative bond from nitrogen to metal (here, Ir) as a straight line.

[0008] 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.

[0009] 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.

[0010] 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.

[0011] 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.

[0012] 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.

[0013] As used herein, and as would be generally understood by one skilled in the art, a first work function is "greater than" or "higher than" a second work function if the first work function has a higher absolute value. Because work functions are generally measured as negative numbers relative to vacuum level, this means that a "higher" work function is more negative. On a conventional energy level diagram, with the vacuum level at the top, a "higher" work function is illustrated as further away from the vacuum level in the downward direction. Thus, the definitions of HOMO and LUMO energy levels follow a different convention than work functions.

[0014] More details on OLEDs, and the definitions described above, can be found in US Pat. No. 7,279,704, which is incorporated herein by reference in its entirety.

SUMMARY OF THE INVENTION

[0015] Compounds comprising an aza-dibenzo moiety and a condensed aromatic moiety having at least three benzene rings are provided. The compounds have the formula $Ar(L_iD_i)_n$.

[0016] Ar contains a condensed aromatic ring having at least three benzene rings and the condensed aromatic ring has a triplet energy lower than 440 nm. Ar is optionally further substituted. L is a single bond or a bivalent linking group. n is at least 1. i is an indexing variable that identifies n structures for L_i and D_i that may be the same or different for different values of i. Each L_i is independently a single bond or a bivalent linking group. Each D_i independently has the structure:

$$X_{2} = X_{1}$$
 $X_{3} = X_{6}$
 $X_{5} = X_{6}$

[0017] X_5 is O, S or Se. Each of X_1 , X_2 , X_3 , X_4 , X_6 , X_7 , X_8 , and X_9 is independently selected from C(R) or N. At least one of X_1 , X_2 , X_3 , X_4 , X_6 , X_7 , X_8 , and X_9 is N. Each R is independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl. R is optionally bound to L.

[0018] In one aspect, the compound has the formula:

$$\begin{pmatrix} x_2 = X_1 & X_9 = X_8 & \\ X_3 & X_4 & X_5 & X_6 \end{pmatrix}$$
 Ar Formula I.

[0019] In another aspect, the compound has a formula selected from the group consisting of:

4

Formula II

Ar

$$\begin{array}{c}
X_2 = X_1 \\
X_3 \\
X_4 \\
X_5
\end{array}$$
Formula III

$$\begin{array}{c}
X_2 = X_1 \\
X_9 = X_8 \\
X_7
\end{array}$$

$$\begin{array}{c}
X_9 = X_8 \\
X_2 = X_1
\end{array}$$

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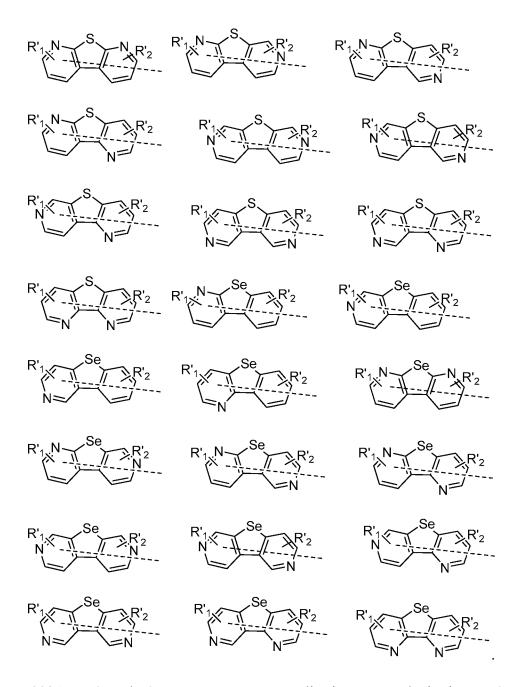
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\end{array}$$

[0020] In one aspect, each D_i is independently selected from the group consisting of:



[0021] R'₁ and R'₂ may represent mono, di, tri, or tetra substitutions. R'₁ and R'₂ are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

[0022] In one aspect, L is a single bond. In another aspect, each L_i is independently selected from the group consisting of:

$$\begin{array}{c} R_1 \\ R_2 \\ R_1 \\ R_1 \\ R_2 \\ R_1 \\ R_1 \\ R_1 \\ R_2 \\ R_1 \\ R_1 \\ R_2 \\ R_3 \\ R_4 \\ R_4 \\ R_5 \\ R_5 \\ R_5 \\ R_6 \\ R_7 \\ R_8 \\$$

[0023] R₁ and R₂ may represent mono, di, tri, or tetra substitutions. R₁ and R₂ are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

[0024] In one aspect, Ar is selected from the group consisting of:

$$R_3$$
 R_5
 R_5
 R_6
 R_7
 R_8
 R_8

[0025] R₃, R₄, R₅ and R₆ may represent mono, di, tri, or tetra substitutions. R₃, R₄, R₅ and R₆ are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

[0026] In one aspect, n is 1. In another aspect, n is greater than 1 and each D_i has the same structure. In yet another aspect, n is greater than 1 and at least two D_i have different structures. In a further aspect, n is 2.

[0027] Preferably, the compound has the formula:

$$\begin{pmatrix} X_2 & X_1 & X_9 = X_8 & L \\ X_3 & X_4 & X_5 & X_6 & N \end{pmatrix} \xrightarrow{R_4} R_5$$
Formula VI.

[0028] R₃, R₄, and R₅ may represent mono, di, tri, or tetra substitutions. R₃, R₄, and R₅ are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

[0029] Specific, non-limiting examples of the compounds comprising an aza-dibenzo moiety and an aromatic moiety having extended conjugation are provided. In one aspect, the compound is selected from the group consisting of:

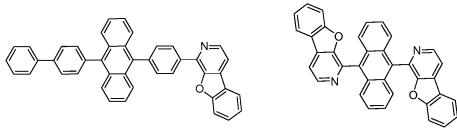
Compound 17

Compound 18

Compound 16

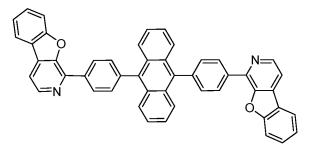
Compound 28

Compound 29

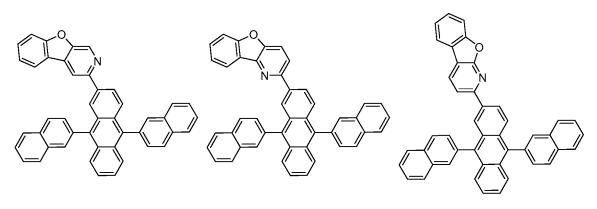


Compound 30

Compound 31



Compound 32



Compound 33

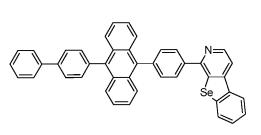
Compound 34

Compound 35

Compound 45

Compound 46

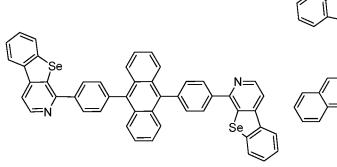
Compound 47



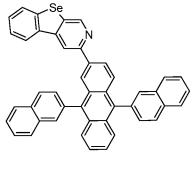
Compound 48

Se N= N= Se Se

Compound 49



Compound 50



Compound 51

Compound 63 Compound 64 Compound 65

[0030] A first device comprising an organic light emitting device is also provided. The organic light emitting device comprises an anode, a cathode, and an organic layer that is disposed between the anode and the cathode. The organic layer comprises a compound having the formula $Ar(L_iD_i)_n$.

[0031] Ar contains a condensed aromatic ring having at least three benzene rings and the condensed aromatic ring has a triplet energy lower than 440 nm. Ar is optionally further substituted. L is a single bond or a bivalent linking group. n is at least 1. i is an indexing variable that identifies n structures for L_i and D_i that may be the same or different for different values of i. Each L_i is independently a single bond or a bivalent linking group. Each D_i independently has the structure:

$$X_{2} = X_{1}$$
 $X_{3} = X_{8}$
 $X_{5} = X_{6}$

[0032] X_5 is O, S or Se. Each of X_1 , X_2 , X_3 , X_4 , X_6 , X_7 , X_8 , and X_9 is independently selected from C(R) or N. At least one of X_1 , X_2 , X_3 , X_4 , X_6 , X_7 , X_8 , and X_9 is N. Each R is independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl. R is optionally bound to L.

[0033] The various specific aspects discussed above for compounds having the formula $Ar(L_iD_i)_n$ are also applicable to the compounds having formula $Ar(L_iD_i)_n$ when used in a first device. In particular, specific aspects of Ar, L, n, i, L_i, D_i, X₁-X₉, R, R'₁, R'₂, R₁-R₆, Formula I, Formula II, Formula IV, Formula V and Formula VI of the compounds having the

formula $Ar(L_iD_i)_n$, as discussed above, are also applicable to a compound having the formula $Ar(L_iD_i)_n$ that is used in the first device.

[0034] Specific, non-limiting examples of devices comprising the compounds disclosed herein are provided. In one aspect, the compound used in the first device is selected from the group consisting of Compound 1 – Compound 65.

[0035] In one aspect, the organic layer is a non-emissive layer and the compound is a non-emissive compound. In another aspect, the organic layer is an electron transport layer and the compound is an electron transport material. In yet another aspect, the electron transport layer is doped with an n-type conductivity dopant. In one aspect, the n-type conductivity dopant is a compound containing Li, Na, K, Rb, or Cs. Preferably, the n-type conductivity dopant is selected from the group consisting of LiF, CsF, NaCl, KBr, and LiQ.

[0036] In another aspect, the organic layer further comprises an emissive compound that is a transition metal complex having at least one ligand selected from the group consisting of:

[0037] Each of R'a, R'b and R'c may represent mono, di, tri, or tetra substituents. Each of R'a, R'b and R'c are independently selected from a group consisting of hydrogen, deuterium, alkyl, heteroalkyl, aryl, or heteroaryl. Two adjacent substituents may form into a ring.

[0038] In one aspect, the first device is a consumer product. In another aspect, the first device is an organic light emitting device.

BRIEF DESCRIPTION OF THE DRAWINGS

[0039] FIG. 1 shows an organic light emitting device.

[0040] FIG. 2 shows an inverted organic light emitting device that does not have a separate electron transport layer.

[0041] FIG. 3 shows an exemplary compound comprising an aza-dibenzo moiety and an aromatic moiety having extended conjugation.

DETAILED DESCRIPTION

[0042] 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.

[0043] 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.

[0044] 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 US Pat. No. 7,279,704 at cols. 5-6, which are incorporated by reference.

[0045] 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 US 7,279,704 at cols. 6-10, which are incorporated by reference.

[0046] 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.

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

[0048] The simple layered structure illustrated in FIGS. 1 and 2 is provided by way of nonlimiting example, and it is understood that embodiments of the invention may be used in connection with a wide variety of other structures. The specific materials and structures described are exemplary in nature, and other materials and structures may be used. Functional OLEDs may be achieved by combining the various layers described in different ways, or layers may be omitted entirely, based on design, performance, and cost factors. Other layers not specifically described may also be included. Materials other than those specifically described may be used. Although many of the examples provided herein describe various layers as comprising a single material, it is understood that combinations of materials, such as a mixture of host and dopant, or more generally a mixture, may be used. Also, the layers may have various sublayers. The names given to the various layers herein are not intended to be strictly limiting. For example, in device 200, hole transport layer 225 transports holes and injects holes into emissive layer 220, and may be described as a hole transport layer or a hole injection layer. In one embodiment, an OLED may be described as having an "organic layer" disposed between a cathode and an anode. This organic layer may comprise a single layer, or may further comprise multiple layers of different organic materials as described, for example, with respect to FIGS. 1 and 2.

[0049] Structures and materials not specifically described may also be used, such as OLEDs comprised of polymeric materials (PLEDs) such as disclosed in U.S. Pat. No. 5,247,190 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 [0050] deposited by any suitable method. For the organic layers, preferred methods include thermal evaporation, ink-jet, such as described in U.S. Pat. Nos. 6,013,982 and 6,087,196, which are incorporated by reference in their entireties, organic vapor phase deposition (OVPD), such as described in U.S. Pat. No. 6,337,102 to Forrest et al., which is incorporated by reference in its entirety, and deposition by organic vapor jet printing (OVJP), such as described in U.S. patent application Ser. No. 10/233,470, which is incorporated by reference in its entirety. Other suitable deposition methods include spin coating and other solution based processes. Solution based processes are preferably carried out in nitrogen or an inert atmosphere. For the other layers, preferred methods include thermal evaporation. Preferred patterning methods include deposition through a mask, cold welding such as described in U.S. Pat. Nos. 6,294,398 and 6,468,819, which are incorporated by reference in their entireties, and patterning associated with some of the deposition methods such as ink-jet and OVJD. Other methods may also be used. The materials to be deposited may be modified to make them compatible with a particular deposition method. For example, substituents such as alkyl and aryl groups, branched or unbranched, and preferably containing at least 3 carbons, may be used in small molecules to enhance their ability to undergo solution processing. Substituents having 20 carbons or more may be used, and 3-20 carbons is a preferred range. Materials with asymmetric structures may have better solution processibility than those having symmetric structures, because asymmetric materials may have a

lower tendency to recrystallize. Dendrimer substituents may be used to enhance the ability of small molecules to undergo solution processing.

[0051] 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.).

[0052] 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.

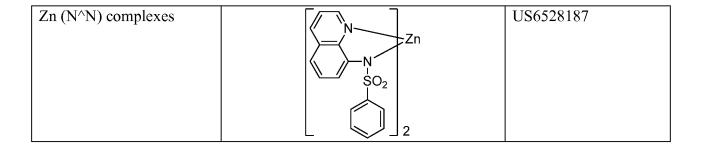
[0053] The terms halo, halogen, alkyl, cycloalkyl, alkenyl, alkynyl, arylkyl, heterocyclic group, aryl, aromatic group, and heteroaryl are known to the art, and are defined in US 7,279,704 at cols. 31-32, which are incorporated herein by reference.

[0054] Various materials have been reported for use in the electron transport layer (ETL) of OLEDs. For example, anthracene-benzimidazole compounds, azatriphenylene derivatives, anthracene-benzothiazole compounds, and metal 8-hydroxyquinolates are all commonly used electron transporting materials. Table 1 summarizes several commonly used electron transporting materials.

Table 1.

Anthracene- benzoimidazole compounds		WO2003060956
		US20090179554
Aza triphenylene derivatives		US20090115316
Anthracene-benzothiazole compounds		Appl. Phys. Lett. 89, 063504 (2006)
Metal 8-hydroxyquinolates (e.g., Alq ₃ , Zrq ₄)	$\begin{bmatrix} \\ \\ \\ \\ \end{bmatrix}$ $\begin{bmatrix} \\ \end{bmatrix}$ $\begin{bmatrix} \\ \\ \end{bmatrix}$ $\begin{bmatrix} $	Appl. Phys. Lett. 51, 913 (1987) US7230107
Metal hydroxybenoquinolates	Be O 2	Chem. Lett. 5, 905 (1993)
Bathocuprine compounds such as BCP, BPhen, etc		Appl. Phys. Lett. 91, 263503 (2007)
		Appl. Phys. Lett. 79, 449 (2001)

5-member ring electron deficient heterocycles (e.g.,triazole, oxadiazole, imidazole, benzoimidazole)		Appl. Phys. Lett. 74, 865 (1999)
	N-N N-N	Appl. Phys. Lett. 55, 1489 (1989)
	N-N N-N	Jpn. J. Apply. Phys. 32, L917 (1993)
Silole compounds	N N Si N N	Org. Electron. 4, 113 (2003)
Arylborane compounds	B—S—B	J. Am. Chem. Soc. 120, 9714 (1998)
Fluorinated aromatic compounds	F F F F F F F F F F F F F F F F F F F	J. Am. Chem. Soc. 122, 1832 (2000)
Fullerene (e.g., C60)		US20090101870
Triazine complexes	F F F F F F F F F F F F F F F F F F F	US20040036077



[0055] Even though many materials have been reported for use as an ETL material, the development a device with low operating voltage and good stability has remained problematic. Alq is a commonly used ETL material, but Alq has limitations for use in OLEDs. While Alq may have good stability, devices comprising Alq may have high operating voltage due to low electron mobility. Anthracene compounds with benzimidazole substituents have also been reported as ETL materials. See, e.g., US6878469 and US20090179554. However, these compounds may also have limitations when used as an ETL material in a device. Introducing electron deficient heterocycles, such as benzimidazole, oxadiazole, triazole, triazine, and pyridine, may increase electron affinity thereby resulting in good electron transporting properties and lowered device voltage, but often these compounds provide reduced device lifetime, too.

[0056] It is very difficult to predict whether the additional of electron deficient groups will result in improved device properties. For example, devices comprising an anthracene compound with a benzimidazole substituent may have reasonable device lifetime and operating voltage, as compared to devices using Alq as an ETL material; however, devices that use these electron deficient heterocyclic compounds in the ETL often have very short lifetimes. For example, devices using 1,3,5-tris(1-phenyl-1H-benzo[d]imidazol-2-yl)benzene (TPBi) as the ETL material have good efficiency, but very poor lifetime. Therefore, it is very difficult to predict which compounds may provide a low operating voltage and a long device lifetime.

[0057] Azadibenzofurans, azadibenzothiophenes, and azadibenzoselenophenes have been used as building blocks for host materials in phosphorescent OLEDs. See, JP2008074939. These materials have lower LUMOs, i.e., better electron affinity, than the corresponding dibenzofurans, dibenzothiophenes, and dibenzoselenophenes. It is believed that the electron affinity of these aza heterocyclic compounds may be advantageously used in ETL materials.

[0058] The compounds provided herein comprise an aromatic moiety with condensed aromatic rings with a low triplet energy and an aza-dibenzo moiety. By combining the aza-dibenzo moiety, e.g., azadibenzofuran, azadibenzothiophene, and azadibenzoselenophene, and the aromatic moiety, e.g., anthracene, in a compound, the result is ETL materials providing low voltage and good device stability. In particular, the compounds provided herein include anthracene compounds substituted with azadibenzofuran, azadibenzothiophene, or azadibenzoselenophene. These compounds may be used as ETL materials in OLEDs to provide devices with lower operating voltage while maintaining good device stability. Without being bound by theory, it is believed that the aza-dibenzo moiety of the compound improves device voltage by reducing the LUMO and the aromatic moiety having a low triplet energy, i.e., higher conjugation, improves device stability by delocalizing and destabilizing the electron.

[0059] Additionally, the ETL materials provided herein can be doped with n-type conductivity dopants, e.g., LiF, CsF, NaCl, KBr, and LiQ.

[0060] Compounds comprising an aza-dibenzo moiety and a condensed aromatic moiety having at least three benzene rings are provided. The compounds have the formula $Ar(L_iD_i)_n$.

[0061] Ar contains a condensed aromatic ring having at least three benzene rings and the condensed aromatic ring has a triplet energy lower than 440 nm. Ar is optionally further substituted. L is a single bond or a bivalent linking group. n is at least 1. i is an indexing variable that identifies n structures for L_i and D_i that may be the same or different for different values of i. Each L_i is independently a single bond or a bivalent linking group. Each D_i independently has the structure:

$$X_{2} = X_{1}$$
 $X_{3} = X_{6}$
 $X_{5} = X_{6}$

[0062] X_5 is O, S or Se. Each of X_1 , X_2 , X_3 , X_4 , X_6 , X_7 , X_8 , and X_9 is independently selected from C(R) or N. At least one of X_1 , X_2 , X_3 , X_4 , X_6 , X_7 , X_8 , and X_9 is N. Each R is independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl. R is optionally bound to L.

[0063] In one aspect, the compound has the formula:

[0064] In another aspect, the compound has a formula selected from the group consisting of:

Formula II

Ar

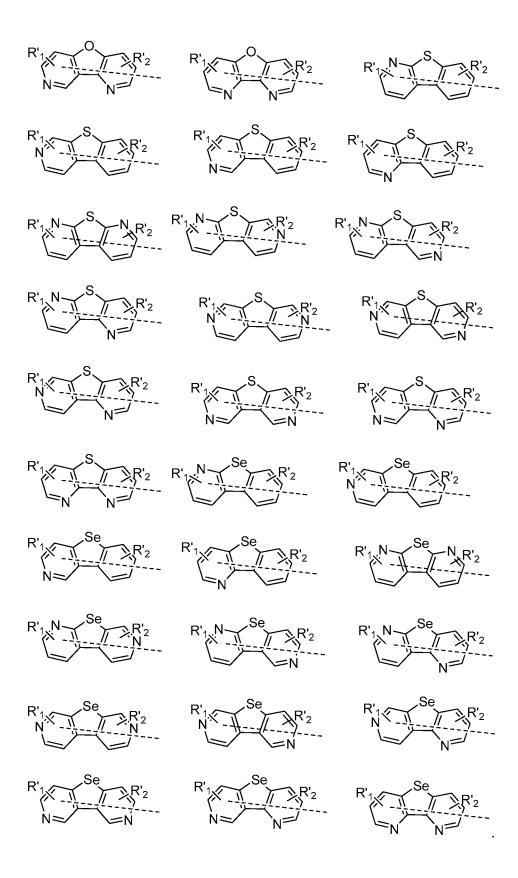
Formula III

Ar

$$X_2 = X_1$$
 $X_3 = X_8$
 $X_4 = X_5$
 $X_5 = X_8$
 $X_7 = X_8$
 $X_8 = X_8$

[0065] In one aspect, each D_i is independently selected from the group consisting of:

$$R'_{1}$$
 $N = 0$ R'_{2} R'_{1} $N = 0$ R'_{2} $N = 0$ R'_{2}



[0066] R'₁ and R'₂ may represent mono, di, tri, or tetra substitutions. R'₁ and R'₂ are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

[0067] In one aspect, L is a single bond. In another aspect, each L_i is independently selected from the group consisting of:

$$\begin{array}{c} R_1 \\ R_2 \\ R_1 \\ R_2 \\ R_1 \\ R_1 \\ R_2 \\ R_1 \\ R_1 \\ R_2 \\ R_3 \\ R_4 \\ R_4 \\ R_5 \\ R_7 \\ R_7 \\ R_8 \\ R_9 \\$$

[0068] R_1 and R_2 may represent mono, di, tri, or tetra substitutions. R_1 and R_2 are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

[0069] In one aspect, Ar is selected from the group consisting of:

[0070] R₃, R₄, R₅ and R₆ may represent mono, di, tri, or tetra substitutions. R₃, R₄, R₅ and R₆ are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

[0071] In one aspect, n is 1. In another aspect, n is greater than 1 and each D_i has the same structure. In yet another aspect, n is greater than 1 and at least two D_i have different structures. In a further aspect, n is 2.

[0072] Preferably, the compound has the formula:

[0073] R₃, R₄, and R₅ may represent mono, di, tri, or tetra substitutions. R₃, R₄, and R₅ are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

[0074] Specific, non-limiting examples of the compounds comprising an aza-dibenzo moiety and an aromatic moiety having extended conjugation are provided. In one aspect, the compound is selected from the group consisting of:

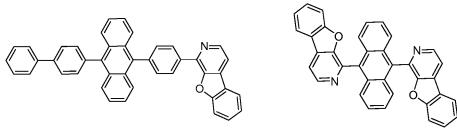
Compound 17

Compound 18

Compound 16

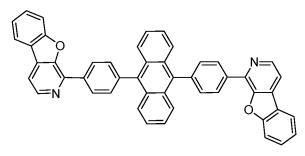
Compound 28

Compound 29

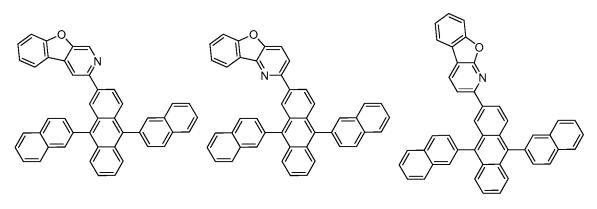


Compound 30

Compound 31



Compound 32



Compound 33

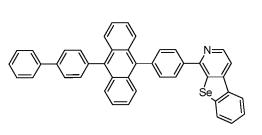
Compound 34

Compound 35

Compound 45

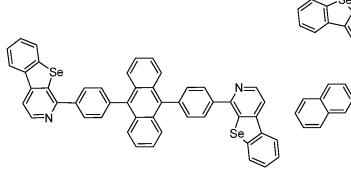
Compound 46

Compound 47



Compound 48

Compound 49



Compound 50

Compound 51

Compound 63 Compound 64 Compound 65

[0075] A first device comprising an organic light emitting device is also provided. The organic light emitting device comprises an anode, a cathode, and an organic layer that is disposed between the anode and the cathode. The organic layer comprises a compound having the formula $Ar(L_iD_i)_n$.

[0076] Ar contains a condensed aromatic ring having at least three benzene rings and the condensed aromatic ring has a triplet energy lower than 440 nm. Ar is optionally further substituted. L is a single bond or a bivalent linking group. n is at least 1. i is an indexing variable that identifies n structures for L_i and D_i that may be the same or different for different values of i. Each L_i is independently a single bond or a bivalent linking group. Each D_i independently has the structure:

$$X_{2} = X_{1}$$
 $X_{3} = X_{8}$
 $X_{5} = X_{6}$

[0077] X_5 is O, S or Se. Each of X_1 , X_2 , X_3 , X_4 , X_6 , X_7 , X_8 , and X_9 is independently selected from C(R) or N. At least one of X_1 , X_2 , X_3 , X_4 , X_6 , X_7 , X_8 , and X_9 is N. Each R is independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl. R is optionally bound to L.

[0078] The various specific aspects discussed above for compounds having the formula $Ar(L_iD_i)_n$ are also applicable to the compounds having formula $Ar(L_iD_i)_n$ when used in a first device. In particular, specific aspects of Ar, L, n, i, L_i, D_i, X₁-X₉, R, R'₁, R'₂, R₁-R₆, Formula I, Formula II, Formula IV, Formula V and Formula VI of the compounds having the

formula $Ar(L_iD_i)_n$, as discussed above, are also applicable to a compound having the formula $Ar(L_iD_i)_n$ that is used in the first device.

[0079] In one aspect, the compound has the formula:

$$\begin{pmatrix} X_2 = X_1 & X_9 = X_8 & \\ X_3 = X_6 & X_7 & Ar \\ X_4 = X_5 & X_6 & Ar \end{pmatrix}$$
n Formula I

[0080] In another aspect, the compound has a formula selected from the group consisting of:

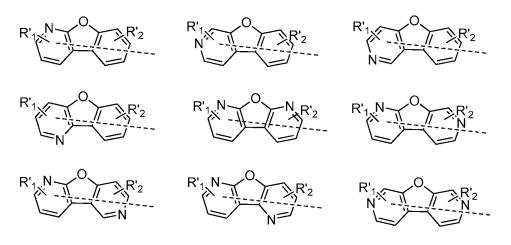
Formula II

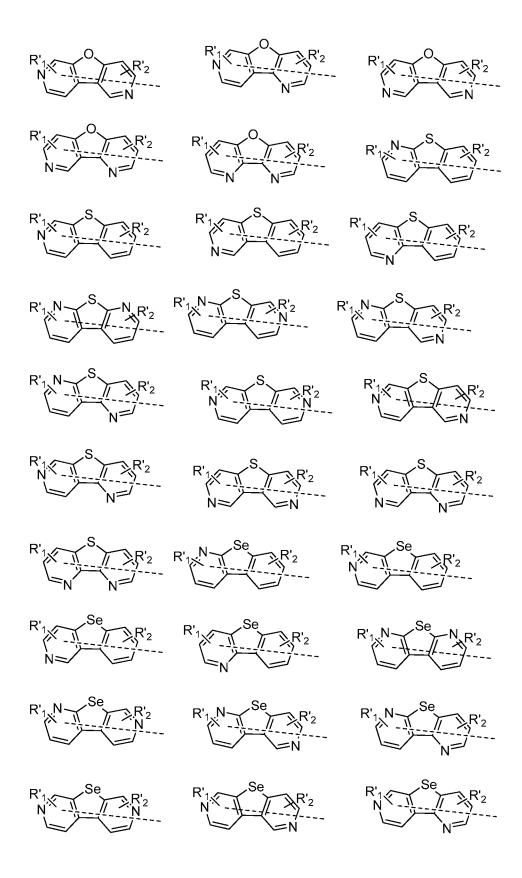
Ar

Formula III

$$X_2 = X_1$$
 $X_3 = X_8$
 $X_4 = X_5$
 $X_5 = X_8$
 $X_7 = X_8$
 $X_8 = X_8$
 $X_8 = X_8$
 $X_9 = X_8$

[0081] In one aspect, each D_i is independently selected from the group consisting of:





[0082] R'₁ and R'₂ may represent mono, di, tri, or tetra substitutions. R'₁ and R'₂ are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

[0083] In one aspect, L is a single bond. In another aspect, each L_i is independently selected from the group consisting of:

$$\begin{array}{c} R_1 \\ R_2 \\ \\ R_3 \\ R_4 \\ R_4 \\ R_4 \\ R_5 \\ R_5 \\ R_6 \\$$

[0084] R_1 and R_2 may represent mono, di, tri, or tetra substitutions. R_1 and R_2 are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

[0085] In one aspect, Ar is selected from the group consisting of:

$$R_{3} = R_{5}$$

$$R_{3} = R_{5}$$

$$R_{3} = R_{5}$$

$$R_{4} = R_{5}$$

$$R_{5} = R_{6}$$

$$R_{5} = R_{6}$$

$$R_{6} = R_{7} = R_{7}$$

$$R_{4} = R_{7} = R_{7}$$

$$R_{5} = R_{7} = R_{7}$$

$$R_{7} = R_{7} = R_{7}$$

$$R_{8} = R_{7} = R_{7} = R_{7}$$

$$R_{1} = R_{1} = R_{2}$$

$$R_{2} = R_{2} = R_{3}$$

$$R_{3} = R_{4} = R_{5}$$

$$R_{4} = R_{5}$$

$$R_{5} = R_{6}$$

$$R_{6} = R_{4} = R_{6}$$

[0086] R₃, R₄, R₅ and R₆ may represent mono, di, tri, or tetra substitutions. R₃, R₄, R₅ and R₆ are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

[0087] In one aspect, n is 1. In another aspect, n is greater than 1 and each D_i has the same structure. In yet another aspect, n is greater than 1 and at least two D_i have different structures. In a further aspect, n is 2.

[0088] Preferably, the compound has the formula:

[0089] R₃, R₄, and R₅ may represent mono, di, tri, or tetra substitutions. R₃, R₄, and R₅ are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

[0090] Specific examples of devices comprising the compounds disclosed herein are provided. In one aspect, the compound used in the first device is selected from the group consisting of Compound 1 – Compound 65.

[0091] In one aspect, the organic layer is a non-emissive layer and the compound is a non-emissive compound. In another aspect, the organic layer is an electron transport layer and the compound is an electron transport material. In yet another aspect, the electron transporting layer is doped with an n-type conductivity dopant. In one aspect, the n-type conductivity dopant is a compound containing Li, Na, K, Rb, or Cs. Preferably, the n-type conductivity dopant is selected from the group consisting of LiF, CsF, NaCl, KBr, and LiQ.

[0092] In another aspect, the organic layer further comprises an emissive compound that is a transition metal complex having at least one ligand selected from the group consisting of:

[0093] Each of R'a, R'b and R'c may represent mono, di, tri, or tetra substituents. Each of R'a, R'b and R'c are independently selected from a group consisting of hydrogen, deuterium, alkyl, heteroalkyl, aryl, or heteroaryl. Two adjacent substituents may form into a ring.

[0094] In one aspect, the first device is a consumer product. In another aspect, the first device is an organic light emitting device.

COMBINATION WITH OTHER MATERIALS

[0095] The materials described herein as useful for a particular layer in an organic light emitting device may be used in combination with a wide variety of other materials present in the device. For example, emissive dopants disclosed herein may be used in conjunction with a wide variety of hosts, transport layers, blocking layers, injection layers, electrodes and other layers that may be present. The materials described or referred to below are non-limiting examples of materials that may be useful in combination with the compounds disclosed herein, and one of skill in the art can readily consult the literature to identify other materials that may be useful in combination.

HIL/HTL:

[0096] A hole injecting/transporting material to be used in embodiments of the present invention is not particularly limited, and any compound may be used as long as the compound is typically used as a hole injecting/transporting material. Examples of the material include, but are not limited to: a phthalocyanine or porphryin derivative; an aromatic amine derivative; an indolocarbazole derivative; a polymer containing fluorohydrocarbon; a polymer with conductivity dopants; a conducting polymer, such as PEDOT/PSS; a self-assembly monomer derived from compounds such as phosphonic acid and sliane derivatives; a metal oxide

derivative, such as MoO_x; a p-type semiconducting organic compound, such as 1,4,5,8,9,12-Hexaazatriphenylenehexacarbonitrile; a metal complex, and a cross-linkable compounds.

[0097] Examples of aromatic amine derivatives used in HIL or HTL include, but are not limited to the following general structures:

$$Ar^{2}$$
 Ar^{3}
 Ar^{4}
 Ar^{4}
 Ar^{4}
 Ar^{5}
 Ar^{5}
 Ar^{5}
 Ar^{6}
 Ar^{6}
 Ar^{7}
 Ar^{7}
 Ar^{8}
 Ar^{7}
 Ar^{8}
 Ar^{8}
 Ar^{7}
 Ar^{8}
 Ar^{8}

[0098] Each of Ar¹ to Ar⁹ is selected from the group consisting aromatic hydrocarbon cyclic compounds such as benzene, biphenyl, triphenyl, triphenylene, naphthalene, anthracene, phenalene, phenanthrene, fluorene, pyrene, chrysene, perylene, azulene; group consisting aromatic heterocyclic compounds such as dibenzothiophene, dibenzofuran, dibenzoselenophene, furan, thiophene, benzofuran, benzothiophene, benzoselenophene, carbazole, indolocarbazole, pyridylindole, pyrrolodipyridine, pyrazole, imidazole, triazole, oxazole, thiazole, oxadiazole, oxatriazole, dioxazole, thiadiazole, pyridine, pyridazine, pyrimidine, pyrazine, triazine, oxazine, oxathiazine, oxadiazine, indole, benzimidazole, indazole, indoxazine, benzoxazole, benzisoxazole, benzothiazole, quinoline, isoquinoline, cinnoline, quinazoline, quinoxaline, naphthyridine, phthalazine, pteridine, xanthene, acridine, phenazine, phenothiazine, phenoxazine, benzofuropyridine, furodipyridine, benzothienopyridine, thienodipyridine, benzoselenophenopyridine, and selenophenodipyridine; and group consisting 2 to 10 cyclic structural units which are groups of the same type or different types selected from the aromatic hydrocarbon cyclic group and the aromatic heterocyclic group and are bonded to each other directly or via at least one of oxygen atom, nitrogen atom, sulfur atom, silicon atom, phosphorus atom, boron atom, chain structural unit and the aliphatic cyclic group. Wherein each Ar is

further substituted by a substituent selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, alkenyl, alkynyl, arylalkyl, heteroalkyl, aryl and heteroaryl.

[0099] In one aspect, Ar¹ to Ar⁹ is independently selected from the group consisting of:

[0100] k is an integer from 1 to 20; X^1 to X^8 is CH or N; Ar^1 has the same group defined above.

[0101] Examples of metal complexes used in HIL or HTL include, but are not limited to the following general formula:

$$\begin{bmatrix} \begin{pmatrix} Y^1 \\ Y^2 \end{pmatrix}_{m}^{M-Ln}$$

[0102] M is a metal, having an atomic weight greater than 40; (Y¹-Y²) is a bidentate ligand, Y1 and Y² are independently selected from C, N, O, P, and S; L is an ancillary ligand; m is an integer value from 1 to the maximum number of ligands that may be attached to the metal; and m+n is the maximum number of ligands that may be attached to the metal.

[0103] In one aspect, (Y^1-Y^2) is a 2-phenylpyridine derivative.

[0104] In another aspect, (Y^1-Y^2) is a carbene ligand.

[0105] In another aspect, M is selected from Ir, Pt, Os, and Zn.

[0106] In a further aspect, the metal complex has a smallest oxidation potential in solution vs. Fc^{+}/Fc couple less than about 0.6 V.

Host:

[0107] The light emitting layer of the organic EL device in some embodiments of the present invention preferably contains at least a metal complex as light emitting material, and may contain a host material using the metal complex as a dopant material. Examples of the host material are not particularly limited, and any metal complexes or organic compounds may be used as long as the triplet energy of the host is larger than that of the dopant.

[0108] Examples of metal complexes used as hosts are preferred to have the following general formula:

$$\begin{bmatrix} \begin{pmatrix} Y^3 \\ Y^4 \end{pmatrix}_m M - Ln \end{bmatrix}$$

[0109] M is a metal; (Y^3-Y^4) is a bidentate ligand, Y^3 and Y^4 are independently selected from C, N, O, P, and S; L is an ancillary ligand; m is an integer value from 1 to the maximum number of ligands that may be attached to the metal; and m+n is the maximum number of ligands that may be attached to the metal.

[0110] In one aspect, the metal complexes are:

$$\begin{bmatrix} \begin{pmatrix} O \\ N \end{pmatrix}_{m} Al-L_{3-m} & \begin{bmatrix} O \\ N \end{bmatrix}_{m} Zn-L_{2-m} \end{bmatrix}$$

[0111] (O-N) is a bidentate ligand, having metal coordinated to atoms O and N.

[0112] In another aspect, M is selected from Ir and Pt.

[0113] In a further aspect, (Y^3-Y^4) is a carbene ligand.

[0114] Examples of organic compounds used as hosts are selected from the group consisting of aromatic hydrocarbon cyclic compounds such as benzene, biphenyl, triphenyl, triphenylene, naphthalene, anthracene, phenalene, phenanthrene, fluorene, pyrene, chrysene, perylene, azulene; group consisting aromatic heterocyclic compounds such as dibenzothiophene, dibenzofuran, dibenzoselenophene, furan, thiophene, benzofuran, benzothiophene, benzoselenophene, carbazole, indolocarbazole, pyridylindole, pyrrolodipyridine, pyrazole, imidazole, triazole, oxazole, thiazole, oxadiazole, oxatriazole, dioxazole, thiadiazole, pyridine, pyridazine,

pyrimidine, pyrazine, triazine, oxazine, oxathiazine, oxadiazine, indole, benzimidazole, indazole, indoxazine, benzoxazole, benzisoxazole, benzothiazole, quinoline, isoquinoline, cinnoline, quinazoline, quinoxaline, naphthyridine, phthalazine, pteridine, xanthene, acridine, phenazine, phenothiazine, phenoxazine, benzofuropyridine, furodipyridine, benzothienopyridine, thienodipyridine, benzoselenophenopyridine, and selenophenodipyridine; and group consisting 2 to 10 cyclic structural units which are groups of the same type or different types selected from the aromatic hydrocarbon cyclic group and the aromatic heterocyclic group and are bonded to each other directly or via at least one of oxygen atom, nitrogen atom, sulfur atom, silicon atom, phosphorus atom, boron atom, chain structural unit and the aliphatic cyclic group. Wherein each group is further substituted by a substituent selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, alkenyl, alkynyl, arylalkyl, heteroalkyl, aryl and heteroaryl.

[0115] In one aspect, the host compound contains at least one of the following groups in the molecule:

[0116] R¹ to R⁷ is independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, alkenyl, alkynyl, arylalkyl, heteroalkyl, aryl and heteroaryl, when it is aryl or heteroaryl, it has the similar definition as Ar's mentioned above.

[**0117**] k is an integer from 0 to 20.

[0118] X^1 to X^8 is selected from CH or N.

HBL:

[0119] A hole blocking layer (HBL) may be used to reduce the number of holes and/or excitons that leave the emissive layer. The presence of such a blocking layer in a device may result in substantially higher efficiencies as compared to a similar device lacking a blocking layer. Also, a blocking layer may be used to confine emission to a desired region of an OLED.

[0120] In one aspect, the compound used in the HBL contains the same molecule used as host described above.

[0121] In another aspect, the compound used in the HBL contains at least one of the following groups in the molecule:

[0122] k is an integer from 0 to 20; L is an ancillary ligand, m is an integer from 1 to 3.

ETL:

[0123] Electron transport layer (ETL) may include a material capable of transporting electrons. Electron transport layer may be intrinsic (undoped), or doped. Doping may be used to enhance conductivity. Examples of the ETL material are not particularly limited, and any metal complexes or organic compounds may be used as long as they are typically used to transport electrons.

[0124] In one aspect, the compound used in the ETL contains at least one of the following groups in the molecule:

[0125] R¹ is selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, alkenyl, alkynyl, arylalkyl, heteroalkyl, aryl and heteroaryl, when it is aryl or heteroaryl, it has the similar definition as Ar's mentioned above.

- [0126] Ar¹ to Ar³ has the similar definition as Ar's mentioned above.
- [0127] k is an integer from 0 to 20.
- [0128] X^1 to X^8 is selected from CH or N.

[0129] In another aspect, the metal complexes used in the ETL contain, but are not limited to, the following general formula:

[0130] (O-N) or (N-N) is a bidentate ligand, having metal coordinated to atoms O, N or N, N; L is an ancillary ligand; m is an integer value from 1 to the maximum number of ligands that may be attached to the metal.

[0131] In any of the above-mentioned compounds used in each layer of the OLED device, the hydrogen atoms can be partially or fully deuterated.

[0132] 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 2 below. Table 2 lists non-limiting classes of materials, non-limiting examples of compounds for each class, and references that disclose the materials.

TABLE 2

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Hole injection materials		
Phthalocyanine and porphryin compounds	N Cu N	Appl. Phys. Lett. 69, 2160 (1996)
Starburst triarylamines		J. Lumin. 72-74, 985 (1997)
CF _x Fluorohydrocarbon polymer	-{-CH _x F _y -} _n	Appl. Phys. Lett. 78, 673 (2001)
Conducting polymers (e.g., PEDOT:PSS, polyaniline, polypthiophene)	SO ₃ -(H ⁺)	Synth. Met. 87, 171 (1997) WO2007002683
Phosphonic acid and sliane SAMs	s—(\	US20030162053
Triarylamine or polythiophene polymers with conductivity dopants	N-C)-N and	EA01725079A1

	Br. St.	
Arylamines complexed with metal oxides such as molybdenum and tungsten oxides	+ MoO _x	SID Symposium Digest, 37, 923 (2006) WO2009018009
Semiconducting organic complexes	NC CN N N NC N NC CN NC CN	US20020158242
Metal organometallic complexes	N Six	US20060240279
Cross-linkable compounds		US20080220265
Hole transporting material	s	
Triarylamines (e.g., TPD, α-NPD)		Appl. Phys. Lett. 51, 913 (1987)

		US5061569
		EP650955
		J. Mater. Chem. 3, 319 (1993)
		Appl. Phys. Lett. 90, 183503 (2007)
		Appl. Phys. Lett. 90, 183503 (2007)
Triaylamine on spirofluorene core	Ph ₂ N NPh ₂	Synth. Met. 91, 209 (1997)

Arylamine carbazole compounds		Adv. Mater. 6, 677 (1994), US20080124572
	N N N N N N N N N N N N N N N N N N N	
Triarylamine with (di)benzothiophene/(di)benzofuran		US20070278938, US20080106190
Indolocarbazoles		Synth. Met. 111, 421 (2000)
Isoindole compounds		Chem. Mater. 15, 3148 (2003)
Metal carbene complexes		US20080018221
Phosphorescent OLED hos	st materials	
Red hosts Arylcarbazoles		Appl. Phys. Lett. 78, 1622 (2001)
Metal 8-hydroxyquinolates (e.g., Alq ₃ , BAlq)	$\begin{bmatrix} \\ \\ \\ \end{bmatrix}_{-0}^{AI}$	Nature 395, 151 (1998)

		US20060202194
		WO2005014551
	$\left[\begin{array}{c} \\ \\ \\ \\ \\ \end{array}\right]_{2}^{AI-O} - \left[\begin{array}{c} \\ \\ \\ \\ \end{array}\right]$	WO2006072002
Metal phenoxybenzothiazole compounds	$\begin{bmatrix} S & N & Zn \\ & & & \end{bmatrix}_2$	Appl. Phys. Lett. 90, 123509 (2007)
Conjugated oligomers and polymers (e.g., polyfluorene)	C ₈ H ₁₇ C ₈ H ₁₇	Org. Electron. 1, 15 (2000)
Aromatic fused rings		WO2009066779, WO2009066778, WO2009063833, US20090045731, US20090045730, WO2009008311, US20090008605, US20090009065
Zinc complexes	H N Zn N H	WO2009062578
Green hosts		
Arylcarbazoles		Appl. Phys. Lett. 78, 1622 (2001)
		US20030175553

		WO2001039234
Aryltriphenylene compounds		US20060280965
		US20060280965
	S	WO2009021126
Donor acceptor type molecules		WO2008056746
Aza-carbazole/DBT/DBF		JP2008074939
Polymers (e.g., PVK)		Appl. Phys. Lett. 77, 2280 (2000)
Spirofluorene compounds		WO2004093207

Metal phenoxybenzooxazole		WO2005089025
compounds	AI-O—A	
		WO2006132173
		JP200511610
Spirofluorene-carbazole compounds		JP2007254297
		JP2007254297
Indolocabazoles		WO2007063796
		WO2007063754
5-member ring electron deficient heterocycles (e.g., triazole, oxadiazole)	N-N N	J. Appl. Phys. 90, 5048 (2001)
	N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-	WO2004107822

Tetraphenylene complexes		US20050112407
Metal phenoxypyridine compounds	$\begin{bmatrix} \\ \\ \\ \\ \end{bmatrix}_{0}^{Zn}$	WO2005030900
Metal coordination complexes (e.g., Zn, Al with N^N ligands)	Zn 2	US20040137268, US20040137267
Blue hosts		
Arylcarbazoles		Appl. Phys. Lett, 82, 2422 (2003)
		US20070190359
Dibenzothiophene/Dibenz ofuran-carbazole compounds		WO2006114966, US20090167162
		US20090167162

	JN-JN-N	WO2009086028
	S S	US20090030202, US20090017330
Silicon aryl compounds	Si-Si-Si-Si	US20050238919
	Si S	WO2009003898
Silicon/Germanium aryl compounds	Si-Visi-Visi-Visi-Visi-Visi-Visi-Visi-Vi	EP2034538A
Aryl benzoyl ester		WO2006100298
High triplet metal organometallic complex		US7154114
Phosphorescent dopants Red dopants		
ixeu uopanis		

Heavy metal porphyrins (e.g., PtOEP)	Et Et Et	Nature 395, 151 (1998)
	Pt N N Et	
	Et Et	
Iridium(III) organometallic complexes		Appl. Phys. Lett. 78, 1622 (2001)
		US2006835469
		US2006835469
		US20060202194
		US20060202194
		US20070087321
	Ir 3	US20070087321

	$\begin{bmatrix} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & $	Adv. Mater. 19, 739 (2007)
	Ir(acac)	WO2009100991
		WO2008101842
Platinum(II) organometallic complexes	N Pt O	WO2003040257
Osminum(III) complexes		Chem. Mater. 17, 3532 (2005)
Ruthenium(II) complexes	tBu N Ru(PPhMe ₂) ₂	Adv. Mater. 17, 1059 (2005)
Rhenium (I), (II), and (III) complexes	N Re-(CO) ₄	US20050244673
Green dopants		
Iridium(III) organometallic complexes		Inorg. Chem. 40, 1704 (2001)

and its derivatives	
and its derivatives	US20020034656
	US7332232
	US20090108737
	US20090039776
S Ir	US6921915
	US6687266
	Chem. Mater. 16, 2480 (2004)

	N N Ir	US20070190359
		US 20060008670 JP2007123392
		Adv. Mater. 16, 2003 (2004)
		Angew. Chem. Int. Ed. 2006, 45, 7800
	N-S II	WO2009050290
	S N Ir	US20090165846
		US20080015355
Monomer for polymeric metal organometallic compounds		US7250226, US7396598

Pt(II) organometallic complexes, including polydentated ligands	Pt-CI	Appl. Phys. Lett. 86, 153505 (2005)
	Pt-o	Appl. Phys. Lett. 86, 153505 (2005)
	N Pt F ₅	Chem. Lett. 34, 592 (2005)
	N O O	WO2002015645
	Ph Ph	US20060263635
Cu complexes	P Cu N N N	WO2009000673
Gold complexes	N-Au————————————————————————————————————	Chem. Commun. 2906 (2005)

Rhenium(III) complexes	F ₃ C N OC. Re OC. Re	Inorg. Chem. 42, 1248 (2003)
	co co	
Deuterated organometallic complexes		US20030138657
Organometallic complexes with two or more metal centers		US20030152802
	F F F S S S S S S S S S S S S S S S S S	US7090928
Blue dopants		
Iridium(III) organometallic complexes		WO2002002714
		WO2006009024
		US20060251923

	US7393599, WO2006056418, US20050260441, WO2005019373
	US7534505
N N 1 P	US7445855
	US20070190359, US20080297033
	US7338722
	US20020134984
	Angew. Chem. Int. Ed. 47, 1 (2008)
	Chem. Mater. 18, 5119 (2006)

		Inorg. Chem. 46, 4308 (2007)
	F N N Ir	WO2005123873
		WO2005123873
		WO2007004380
		WO2006082742
Osmium(II) complexes		US7279704
	Os(PPh ₃)	Organometallics 23, 3745 (2004)
Gold complexes	Ph ₂ P PPh ₂	Appl. Phys. Lett.74,1361 (1999)
Platinum(II) complexes	Pt N-N B N-N	WO2006098120, WO2006103874
Exciton/hole blocking laye	r 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)
5-member ring electron deficient heterocycles such as triazole, oxadiazole, imidazole, benzoimidazole		Appl. Phys. Lett. 81, 162 (2002)
Triphenylene compounds		US20050025993
Fluorinated aromatic compounds		Appl. Phys. Lett. 79, 156 (2001)
Phenothiazine-S-oxide Electron transporting mate	o, Si-Si-Si-Si-Si-Si-Si-Si-Si-Si-Si-Si-Si-S	WO2008132085
Electron transporting mate	eriais	

Anthracene- benzoimidazole compounds		WO2003060956
		US20090179554
Aza triphenylene derivatives		US20090115316
Anthracene-benzothiazole compounds		Appl. Phys. Lett. 89, 063504 (2006)
Metal 8-hydroxyquinolates (e.g., Alq ₃ , Zrq ₄)	$\begin{bmatrix} \\ \\ \\ \\ \end{bmatrix}$ $\begin{bmatrix} \\ \end{bmatrix}$ $\begin{bmatrix} \\ \\ \end{bmatrix}$ $\begin{bmatrix} $	Appl. Phys. Lett. 51, 913 (1987) US7230107
Metal hydroxybenoquinolates	Be O 2	Chem. Lett. 5, 905 (1993)
Bathocuprine compounds such as BCP, BPhen, etc		Appl. Phys. Lett. 91, 263503 (2007)
		Appl. Phys. Lett. 79, 449 (2001)

5-member ring electron deficient heterocycles (e.g.,triazole, oxadiazole, imidazole, benzoimidazole)		Appl. Phys. Lett. 74, 865 (1999)
	N-N	Appl. Phys. Lett. 55, 1489 (1989)
	N-N N	Jpn. J. Apply. Phys. 32, L917 (1993)
Silole compounds	N N Si N N	Org. Electron. 4, 113 (2003)
Arylborane compounds	B—S—B	J. Am. Chem. Soc. 120, 9714 (1998)
Fluorinated aromatic compounds		J. Am. Chem. Soc. 122, 1832 (2000)
Fullerene (e.g., C60)		US20090101870
Triazine complexes	F F F F F F F F F F F F F F F F F F F	US20040036077

Zn (N^N) complexes	Zn N N SO ₂	US6528187

EXPERIMENTAL

Compound Examples

[0133] Example 1. Synthesis of Compound 1.

[0134] Synthesis of 2-(9,10-di(naphthalen-2-yl)anthracen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. 2-bromo-9,10-di(naphthalen-2-yl)anthracene (4.75 g, 9.32 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (3.08 g, 12.12 mmol), potassium acetate (1.830 g, 18.65 mmol) and dicyclohexyl(2',6'-dimethoxy-[1,1'-biphenyl]-2-yl)phosphine (0.153 g, 0.373 mmol) were mixed in 400 mL of dioxane. The mixture was bubbled with nitrogen for 20 minutes. Pd₂(dba)₃ (0.085 g, 0.093 mmol) was added. The reaction was heated up to 90 °C overnight. The reaction was stopped and filtered through Celite. Solvent was evaporated, coated on Celite and a column was run with 10% ethyl acetate and hexanes. The solid was then recrystallized from 100 mL of ethanol. Yellowish solid 2-(9,10-di(naphthalen-2-yl)anthracen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.8 g, 6.83 mmol, 73.2 % yield) was collected by filtration.

[0135] Synthesis of Compound 1. A mixture of 1-chlorobenzo[4,5]thieno[2,3-c]pyridine (2.4 g, 10.93 mmol), 2-(9,10-di(naphthalen-2-yl)anthracen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.8 g, 6.83 mmol), and potassium phosphate (3.62 g, 17.07 mmol) in 200 mL of toluene and 20 mL of H₂O was bubbled with N₂ for 20 minutes. Pd₂(dba)₃ (0.125 g, 0.137 mmol) and dicyclohexyl(2',6'-dimethoxy-[1,1'-biphenyl]-2-yl)phosphine (0.224 g, 0.546 mmol) were then added, and the mixture was heated to reflux under N₂ for 6 h. The mixture was cooled and the solid was collected by filtration. The solid was washed with water, methanol and acetone and then dried. 3 g of solid was obtained. The solid was refluxed with 300 mL of toluene overnight under nitrogen. After it cooled to room temperature, the solid was collected by filtration. The process was repeated with another 300 mL of toluene. The solid was collected and dried under vacuum. 1-(9,10-di(naphthalen-2-yl)anthracen-2-yl)benzo[4,5]thieno[2,3-c]pyridine (3 g, 4.89 mmol, 71.6 % yield) was obtained.

Device Examples

[0136] All device examples were fabricated by high vacuum (<10⁻⁷ Torr) thermal evaporation. The anode electrode is 800Å of indium tin oxide (ITO). The cathode consisted of 10 Å 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.

[0137] The organic stack of the Device Examples consisted of sequentially, from the ITO surface, 100 Å of Compound A as the hole injection layer (HIL), 300 Å of 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (α-NPD) as the hole transporting layer (HTL), 300 Å of Host

1 doped with Compound A as the emissive layer (EML), 50 Å of Host 1 as the blocking layer (BL), and 450 Å of Compound 1 or Compound 1 doped with LiQ as the electron transport layer (ETL).

[0138] The Comparative Device Example was fabricated similarly to the Device Examples, except Alq was used as the ETL.

[0139] As used herein, the following compounds have the following structures:

[0140] Particular compounds for the ETL of an OLED are provided. These compounds may lead to devices having particularly good properties. The device structures are provided in Table 3, and the corresponding device data is provided in Table 4. Cmpd. is an abbreviation of compound. Comp. is an abbreviation of comparative. Ex. is an abbreviation of example.

Table 3. VTE PHOLEDs

Example	HIL	HTL	EML	(doping %)	BL	ETL
Ex. 1	Cmpd. A	NPD	Host 1	Cmpd. A 10%	Host 1	Cmpd. 1
Ex. 2	Cmpd. A	NPD	Host 1	Cmpd. A 10%	Host 1	Cmpd. 1:LiQ (1:1)
Comp. Ex. 1	Cmpd. A	NPD	Host 1	Cmpd. A 10%	Host 1	Alq

Table 4. VTE device data

	1931	CIE	At 1000 nits					At 40 mA/cm ²	
					LE	EQE	PE	$\mathbf{L_0}$	
Example	X	y	λ_{max}	V (V)	(Cd/A)	(%)	(lm/W)	(nits)	$LT_{80\%}$ (h)
Ex. 1	0.35	0.60	528	7.8	41.5	11.4	16.6	13,566	217
Ex. 2	0.34	0.61	528	6.2	45.2	12.4	22.8	15,853	224
Comp. Ex. 1	0.35	0.60	528	8.1	45.6	12.5	17.7	15,780	221

[0141] Device Examples 1 and 2 showed green PHOLEDs with Compound 1 or Compound 1 doped with LiQ as the ETL. Comparative Example 1 used Alq as the ETL. As can be seen from the tables, Device Examples 1 and 2 with Compound 1 or Compound 1 doped with LiQ as the ETL, respectively, had similar efficiency and device lifetime as compared with Comparative Device Example 1 with Alq as the ETL. However, the device operating voltage of Device Example 1 was lower than the operating voltage of Comparative Example 1, i.e., 7.8 V compared to 8.1 V. The operating voltage of Device Example 2 was even further decreased to 6.2 V. Therefore, devices comprising an inventive compound as the ETL may maintain good lifetime and efficiency and have lowered device voltage.

[0142] 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.

CLAIMS:

1. A compound having the formula $Ar(L_iD_i)_n$,

wherein Ar contains a condensed aromatic ring having at least three benzene rings and the condensed aromatic ring has a triplet energy lower than 440 nm;

wherein Ar is optionally further substituted;

wherein L is a single bond or a bivalent linking group;

wherein n is at least 1;

wherein i is an indexing variable that identifies n structures for L_i and D_i that may be the same or different for different values of i;

wherein each L_i is independently a single bond or a bivalent linking group; wherein each D_i independently has the structure:

$$X_{2} = X_{1}$$
 $X_{3} = X_{6}$
 $X_{4} = X_{5}$
 $X_{5} = X_{6}$

wherein X_5 is O, S or Se;

wherein each of X_1 , X_2 , X_3 , X_4 , X_6 , X_7 , X_8 , and X_9 is independently selected from C(R) or N;

wherein at least one of X_1 , X_2 , X_3 , X_4 , X_6 , X_7 , X_8 , and X_9 is N;

wherein each R is independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl; and

wherein R is optionally bound to L.

2. The compound of claim 1, wherein the compound has the formula:

$$\begin{pmatrix} X_2 & X_1 & X_9 = X_8 & \\ X_3 & X_4 & X_5 & X_6 & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$$

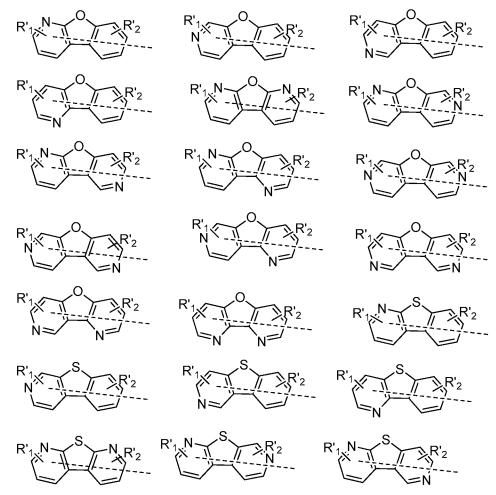
3. The compound of claim 1, wherein the compound has a formula selected from the group consisting of:

Formula II

Ar

$$X_9 = X_8$$
 X_4
 X_5
 $X_9 = X_8$
 X_7
 $X_9 = X_8$
 X_8
 X_8
 X_8
 X_8
 $X_9 = X_8$
 X_9

 $\label{eq:compound} 4. \qquad \text{The compound of claim 1, wherein each D_i is independently selected from the group consisting of:}$



wherein R'₁ and R'₂ may represent mono, di, tri, or tetra substitutions; and wherein R'₁ and R'₂ are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

- 5. The compound of claim 1, wherein L is a single bond.
- $\label{eq:compound} 6. \qquad \text{The compound of claim 1, wherein each L_i is independently selected from the group consisting of:}$

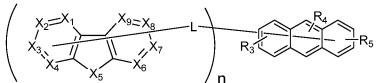
$$\begin{array}{c|c} R_1 & R_2 \\ \hline \\ R_1 & R_2 \\ \hline \end{array}$$

wherein R_1 and R_2 may represent mono, di, tri, or tetra substitutions; and wherein R_1 and R_2 are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

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

wherein R₃, R₄, R₅ and R₆ may represent mono, di, tri, or tetra substitutions; and wherein R₃, R₄, R₅ and R₆ are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

- 8. The compound of claim 1, wherein n is 1.
- 9. The compound of claim 1, wherein n is greater than 1 and each D_i has the same structure.
- $10. \hspace{0.5cm} \text{The compound of claim 1, wherein n is greater than 1 and at least two } D_i$ have different structures.
 - 11. The compound of claim 1, wherein n is 2.
 - 12. The compound of claim 1, wherein the compound has the formula:



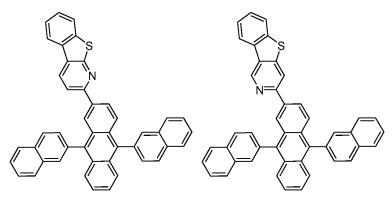
Formula VI,

wherein R₃, R₄, and R₅ may represent mono, di, tri, or tetra substitutions; and wherein R₃, R₄, and R₅ are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

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

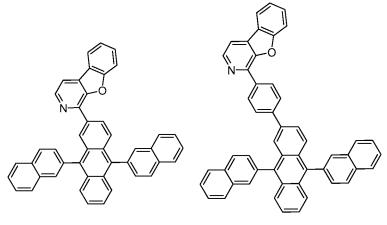
Compound 14

Compound 16



Compound 17

Compound 18



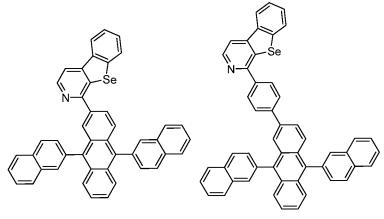
Compound 19

Compound 20

85

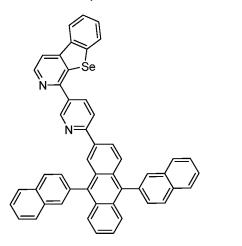
Compound 34

Compound 36

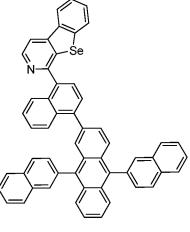


Compound 37

Compound 38



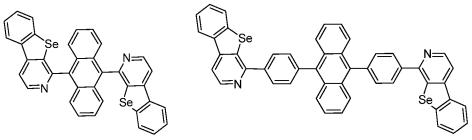
Compound 39



Compound 40

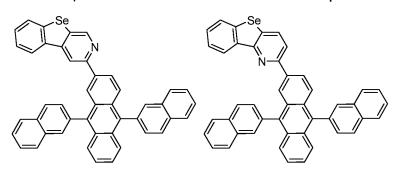
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Compound 47



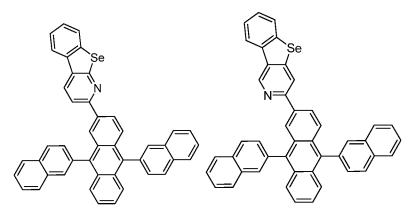
Compound 49

Compound 50



Compound 51

Compound 52



Compound 53

Compound 54

Compound 65

14. A first device comprising an organic light emitting device, comprising: an anode;

a cathode; and

an organic layer, disposed between the anode and the cathode, further comprising a compound having the formula ${\rm Ar}(L_iD_i)_n$,

wherein Ar contains a condensed aromatic ring having at least three benzene rings and the condensed aromatic ring has a triplet energy lower than 440 nm;

wherein Ar is optionally further substituted;

wherein L is a single bond or a bivalent linking group;

wherein n is at least 1;

wherein i is an indexing variable that identifies n structures for L_i and D_i that may be the same or different for different values of i;

wherein each L_i is independently a single bond or a bivalent linking group; wherein each D_i independently has the structure:

$$X_{2} = X_{1}$$
 $X_{3} = X_{6}$
 $X_{5} = X_{6}$

wherein X_5 is O, S or Se;

wherein each of X_1 , X_2 , X_3 , X_4 , X_6 , X_7 , X_8 , and X_9 is independently selected from C(R) or N;

wherein at least one of X_1 , X_2 , X_3 , X_4 , X_6 , X_7 , X_8 , and X_9 is N;

wherein each R is independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl; and wherein R is optionally bound to L.

15. The first device of claim 14, wherein the compound has the formula:

$$\begin{pmatrix} X_2 = X_1 & X_9 = X_8 & L \\ X_3 & X_4 & X_5 & X_6 & \end{pmatrix}$$
Ar
Formula I

16. The first device of claim 14, wherein the compound has a formula selected from the group consisting of:

Formula II

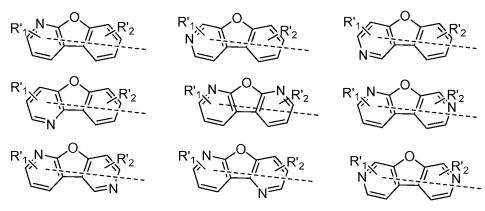
Ar

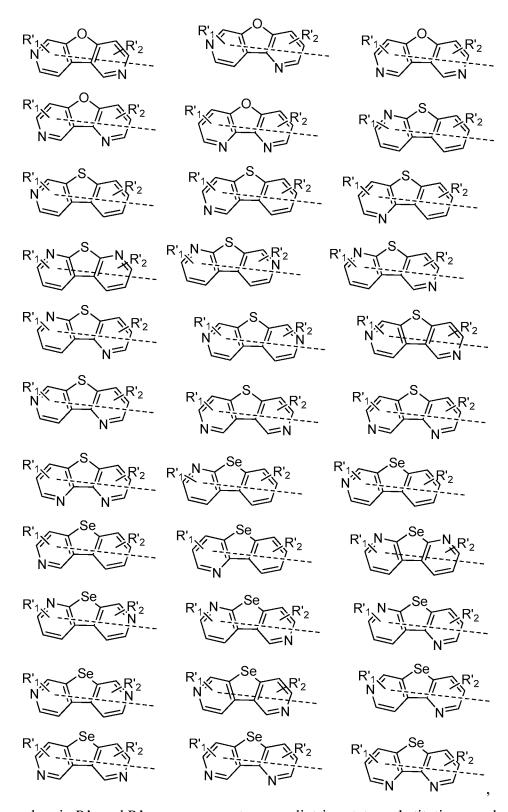
$$X_{9}=X_{8}$$
 X_{7}

Formula III

 $X_{9}=X_{8}$
 X_{7}
 $X_{9}=X_{8}$
 $X_{9}=X_{8}$

17. The first device of claim 14, wherein each D_i is independently selected from the group consisting of:





wherein R'1 and R'2 may represent mono, di, tri, or tetra substitutions; and

wherein R'₁ and R'₂ are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

18. The first device of claim 14, wherein each L_i is selected from the group consisting of:

wherein R_1 and R_2 may represent mono, di, tri, or tetra substitutions; and wherein R_1 and R_2 are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

19. The first device of claim 14, wherein Ar is selected from the group consisting of:

$$R_3$$
 R_5
 R_5
 R_6
 R_7
 R_8
 R_8
 R_8

$$R_3$$
 R_4
 R_5
 R_6
 R_6
 R_7
 R_8
 R_8

wherein R₃, R₄, R₅ and R₆ may represent mono, di, tri, or tetra substitutions; and wherein R₃, R₄, R₅ and R₆ are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

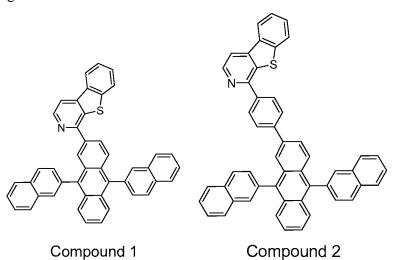
20. The device of claim 14, wherein the compound has the formula:

$$\begin{pmatrix} X_2 = X_1 & X_9 = X_8 & \\ X_3 & X_4 & X_5 & X_6 & \\ & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ &$$

Formula VI,

wherein R₃, R₄, and R₅ may represent mono, di, tri, or tetra substitutions; and wherein R₃, R₄, and R₅ are independently selected from the group consisting of hydrogen, deuterium, alkyl, alkoxy, amino, silyl, cyano, halogen, aryl, and heteroaryl.

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



95

Compound 15

Compound 21

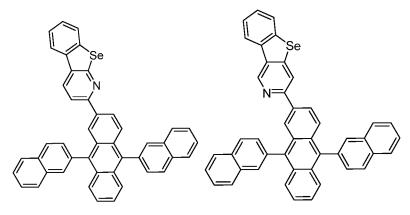
Compound 22

Compound 28

Compound 35

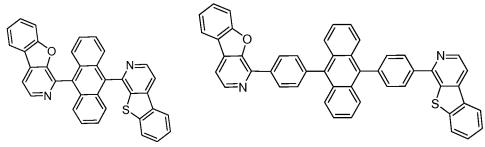
Compound 36

Compound 52



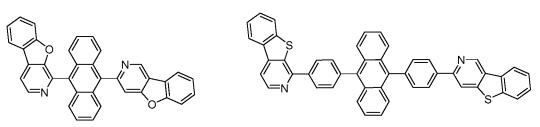
Compound 53

Compound 54



Compound 55

Compound 56



Compound 57

Compound 58

22. The first device of claim 14, wherein the organic layer is a non-emissive layer and the compound is a non-emissive compound.

Compound 65

23. The first device of claim 22, wherein the organic layer is an electron transport layer and the compound is an electron transport material.

24. The first device of claim 23, wherein the electron transport layer is doped with an n-type conductivity dopant.

- 25. The first device of claim 24, wherein the n-type conductivity dopant is a compound containing Li, Na, K, Rb, or Cs.
- 26. The first device of claim 25, wherein the n-type conductivity dopant is selected from the group consisting of LiF, CsF, NaCl, KBr, and LiQ.
- 27. The first device of claim 14, wherein the organic layer further comprises an emissive compound that is a transition metal complex having at least one ligand selected from the group consisting of:

wherein each of R'a, R'b and R'c may represent mono, di, tri, or tetra substituents; wherein each of R'a, R'b and R'c are independently selected from a group consisting of hydrogen, deuterium, alkyl, heteroalkyl, aryl, or heteroaryl; and wherein two adjacent substituents may form into a ring.

28. The first device of claim 14, wherein the first device is a consumer product.

29. The first device of claim 14, wherein the first device is an organic light emitting device.



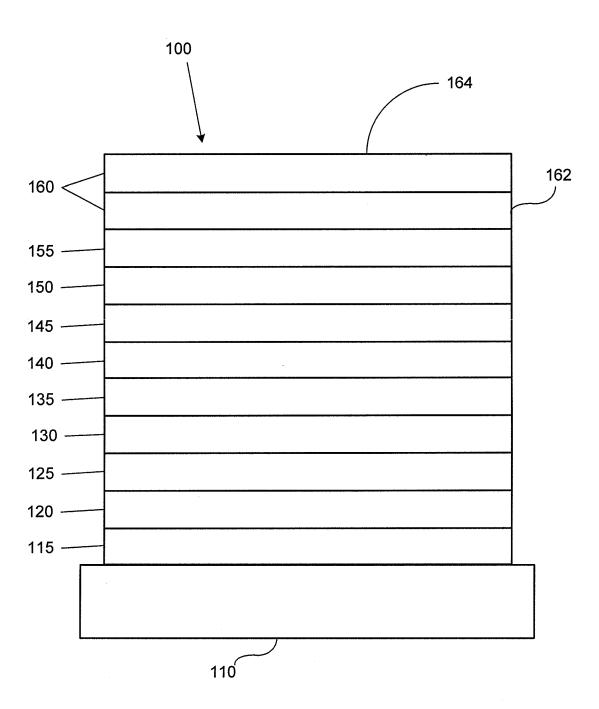


FIGURE 1

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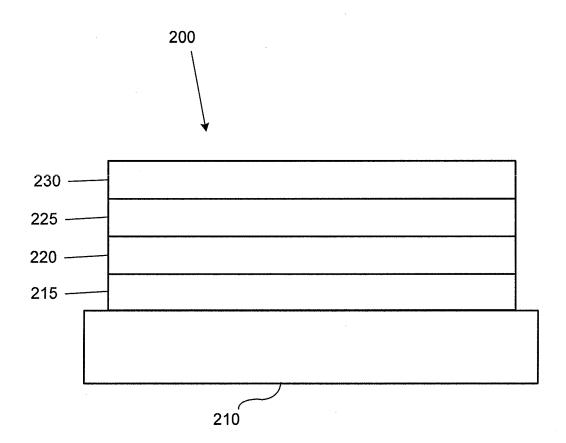


FIGURE 2

3/3

$$\begin{pmatrix} X_2 & X_1 & X_9 = X_8 \\ X_3 & X_4 & X_5 & X_6 \end{pmatrix}$$
 Ar

FIGURE 3

INTERNATIONAL SEARCH REPORT

International application No PCT/US2012/022067

A. CLASSIFICATION OF SUBJECT MATTER INV. C07D491/04 C07D495/04 C07D517/04 H01J1/63 ADD. According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) C07D Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, CHEM ABS Data, WPI Data C. DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to claim No. Category* Citation of document, with indication, where appropriate, of the relevant passages WO 2010/083359 A2 (UNIVERSAL DISPLAY CORP Χ 1-6,8, [US]; LIN CHUN [US]; MA BIN [US]; KWONG 14-18, RAYMOND) 22 July 2010 (2010-07-22) 22-29 examples 6-11 X,P ANTONIO FERNANDEZ-MATO ET AL: 1-3,5,7,"Preparation and study of pyridothienopyrazines and their Ruthenium(II) complexes: a new family of bidentate ligands". TETRAHEDRON, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 67, no. 11, 28 January 2011 (2011-01-28), pages 2035-2043, XP028148968, ISSN: 0040-4020, DOI: 10.1016/J.TET.2011.01.066 [retrieved on 2011-01-28] compounds 3c, 3d Х Further documents are listed in the continuation of Box C. See patent family annex. Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but "A" document defining the general state of the art which is not cited to understand the principle or theory underlying the considered to be of particular relevance invention "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention filing date cannot be considered novel or cannot be considered to "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention citation or other special reason (as specified) cannot be considered to involve an inventive step when the document is combined with one or more other such docu-"O" document referring to an oral disclosure, use, exhibition or ments, such combination being obvious to a person skilled in the art. "P" document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 16 April 2012 03/05/2012 Name and mailing address of the ISA/ Authorized officer European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016 Bakboord, Joan

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2012/022067

Patent document cited in search report				Patent family member(s)	Publication date	
WO 2010083359	A2	22-07-2010	CN EP KR TW US WO	102341401 A 2387576 A2 20110116177 A 201031671 A 2010187984 A1 2010083359 A2	01-02-2012 23-11-2011 25-10-2011 01-09-2010 29-07-2010 22-07-2010	