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(54) Title: HOLE TRANSPORT MATERIALS HAVING A SULFUR-CONTAINING GROUP

(57) Abstract: Novel materials are provided, having a single phenyl or a chain of phenyls where there is a nitrogen atom on each end of the single phenyl or chain of phenyls. The nitrogen atom may be further substituted with particular thiophene, benzothio-
phene, and triphenylene groups. Organic light-emitting devices are also provided, where the novel materials are used as a hole transport material in the device. Combinations of the hole transport material with specific host materials are also provided.



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HOLE TRANSPORT MATERIALS HAVING A SULFUR-CONTAINING GROUP

[0001] This application claims priority to and benefit under 35 U.S.C. § 119(e) to U.S. Provisional Application Serial No. 61/077,073, filed June 30, 2008, the disclosure of which is herein expressly incorporated by reference in its entirety.

[0002] The claimed invention was made by, on behalf of, and/or in connection with one or more of the following parties to a joint university corporation research agreement: Regents of the University of Michigan, Princeton University, 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

[0003] The present invention relates to novel materials. More specifically, the present invention relates to novel materials useful in organic light emitting devices (OLEDs).

BACKGROUND

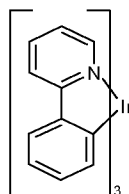
[0004] Opto-electronic devices that make use of organic materials are becoming increasingly desirable for a number of reasons. Many of the materials used to make such devices are relatively inexpensive, so organic opto-electronic devices have the potential for cost advantages over inorganic devices. In addition, the inherent properties of organic materials, such as their flexibility, may make them well suited for particular applications such as fabrication on a flexible substrate. Examples of organic opto-electronic devices include organic light emitting devices (OLEDs), organic phototransistors, organic photovoltaic cells, and organic photodetectors. For OLEDs, the organic materials may have performance advantages over conventional materials. For example, the wavelength at which an organic emissive layer emits light may generally be readily tuned with appropriate dopants.

[0005] OLEDs make use of thin organic films that emit light when voltage is applied across the device. OLEDs are becoming an increasingly interesting technology for use in applications such as flat panel displays, illumination, and backlighting. Several OLED materials and

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

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

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



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

[0009] As used herein, the term "organic" includes polymeric materials as well as small molecule organic materials that may be used to fabricate organic opto-electronic devices. "Small molecule" refers to any organic material that is not a polymer, and "small molecules" may actually be quite large. Small molecules may include repeat units in some circumstances. For example, using a long chain alkyl group as a substituent does not remove a molecule from the "small molecule" class. Small molecules may also be incorporated into polymers, for example as a pendent group on a polymer backbone or as a part of the backbone. Small molecules may also serve as the core moiety of a dendrimer, which consists of a series of chemical shells built on the core moiety. The core moiety of a dendrimer may be a fluorescent or phosphorescent small molecule emitter. A dendrimer may be a "small molecule," and it is believed that all dendrimers currently used in the field of OLEDs are small molecules.

[0010] As used herein, "top" means furthest away from the substrate, while "bottom" means closest to the substrate. Where a first layer is described as "disposed over" a second layer, the first layer is disposed further away from substrate. There may be other layers between the first and second layer, unless it is specified that the first layer is "in contact with" the second layer.

For example, a cathode may be described as "disposed over" an anode, even though there are various organic layers in between.

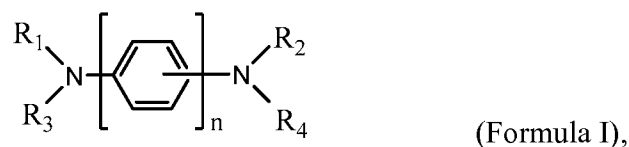
[0011] As used herein, "solution processible" means capable of being dissolved, dispersed, or transported in and/or deposited from a liquid medium, either in solution or suspension form.

[0012] A ligand is referred to as "photoactive" when it is believed that the ligand contributes to the photoactive properties of an emissive material.

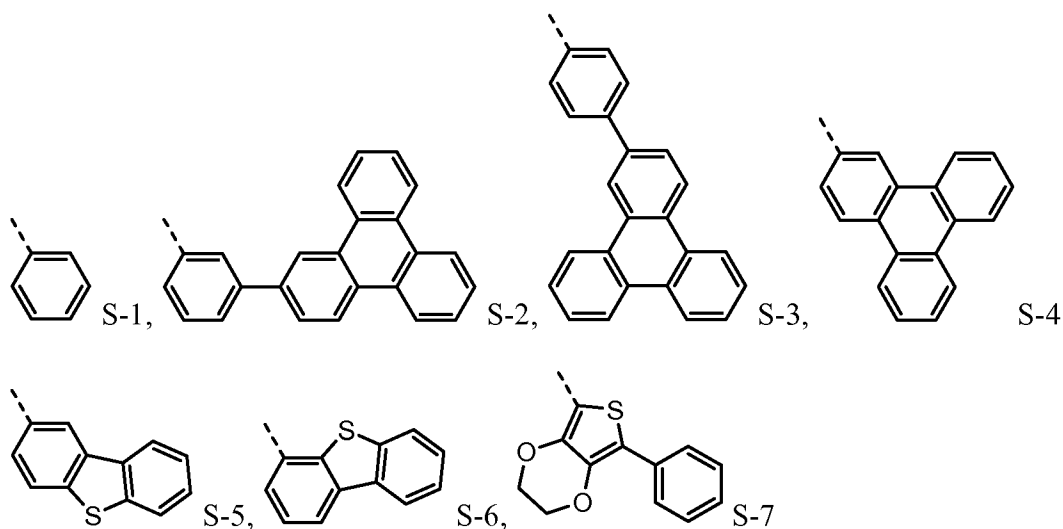
[0013] More details on OLEDs, and the definitions described above, can be found in US Pat. No. 7,279,704, which is incorporated herein by reference in its entirety.

SUMMARY OF THE INVENTION

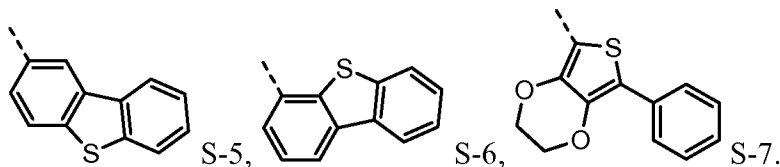
[0014] Novel materials are provided, having the chemical structure:



[0015] n is 1, 2 or 3, and the phenyl rings between the nitrogen atoms may be attached to each other and to the nitrogen atoms in a para or meta configuration independently selected for each attachment. Each of R_1 , R_2 , R_3 and R_4 may be independently selected from the group consisting of:



where the dotted line shows the point of attachment to an N atom of Formula I. At least one of R₁, R₂, R₃ and R₄ is:



Each of R₁, R₂, R₃ and R₄ may be further substituted with substituents that are not fused to R₁, R₂, R₃ and R₄. Preferably, at least one of R₁, R₂, R₃, and R₄ is S-5. Preferably, at least one of R₁, R₂, R₃, and R₄ is S-6. Preferably, at least one of R₁, R₂, R₃, and R₄ is S-7. Preferably, both R₁ and R₂ are S-6.

[0016] In one aspect, the materials provided having the chemical structure Formula I more specifically have the structure Formula II.

[0017] In another aspect, each of R₁, R₂, R₃, and R₄ is independently selected from the group consisting of S-1 and S-5 through S-7.

[0018] In yet another aspect, at least one of R₁, R₂, R₃, and R₄ is S-8 or S-9. In a further aspect, each of R₁, R₂, R₃, and R₄ is independently selected from the group consisting of S-1 and S-5 through S-9.

[0019] Specific examples of compositions of matter having Formula I are provided, including materials selected from the group consisting of A-1 through A-6. Preferably, the composition of matter is A-1. Also, specific examples of compositions of matter having Formula I are provided, including materials selected from the group consisting of B-1 through B-6. Preferably, the composition of matter is B-1. Additionally, specific examples of compositions of matter having Formula I are provided, including materials selected from the group consisting of C-1 through C-6. Preferably, the composition of matter is C-1. Moreover, specific examples of compositions of matter having Formula I are provided, including materials selected from the group consisting of D-1 through D-6. Preferably, the composition of matter is D-1.

[0020] Organic light-emitting devices and consumer products containing such devices are also provided, where the novel materials are used as a hole transport material in the device.

Selections for the compositions of matter having Formula I described as preferred for use in materials having Formula I are also preferred for use in a device or consumer product that includes materials having Formula I. These selections include those described for the substituents R₁, R₂, R₃, and R₄, Formula II, and the structures A-1 through A-6, B-1 through B-6, C-1 through C-6, and D-1 through D-6.

[0021] Combinations of the hole transport material with specific host materials are also provided. In one aspect, the host is a compound comprising a triphenylene containing benzo-fused thiophene.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] FIG. 1 shows an organic light emitting device.

[0023] FIG. 2 shows an inverted organic light emitting device that does not have a separate electron transport layer.

[0024] FIG. 3 shows chemical formulae for novel compounds.

DETAILED DESCRIPTION

[0025] 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.

[0026] 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.

[0027] 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.

[0028] 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.

[0029] 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.

[0030] 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.

[0031] 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.

[0032] Structures and materials not specifically described may also be used, such as OLEDs comprised of polymeric materials (PLEDs) such as disclosed in U.S. Pat. No. 5,247,190 to Friend et al., which is incorporated by reference in its entirety. By way of further example, OLEDs having a single organic layer may be used. OLEDs may be stacked, for example as described in U.S. Pat. No. 5,707,745 to Forrest et al, which is incorporated by reference in its entirety. The OLED structure may deviate from the simple layered structure illustrated in FIGS. 1 and 2. For example, the substrate may include an angled reflective surface to improve out-coupling, such as a mesa structure as described in U.S. Pat. No. 6,091,195 to Forrest et al., and/or a pit structure as described in U.S. Pat. No. 5,834,893 to Bulovic et al., which are incorporated by reference in their entireties.

[0033] 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. 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

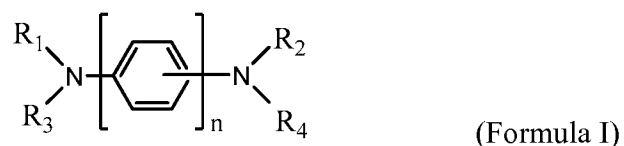
materials may have a lower tendency to recrystallize. Dendrimer substituents may be used to enhance the ability of small molecules to undergo solution processing.

[0034] 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.).

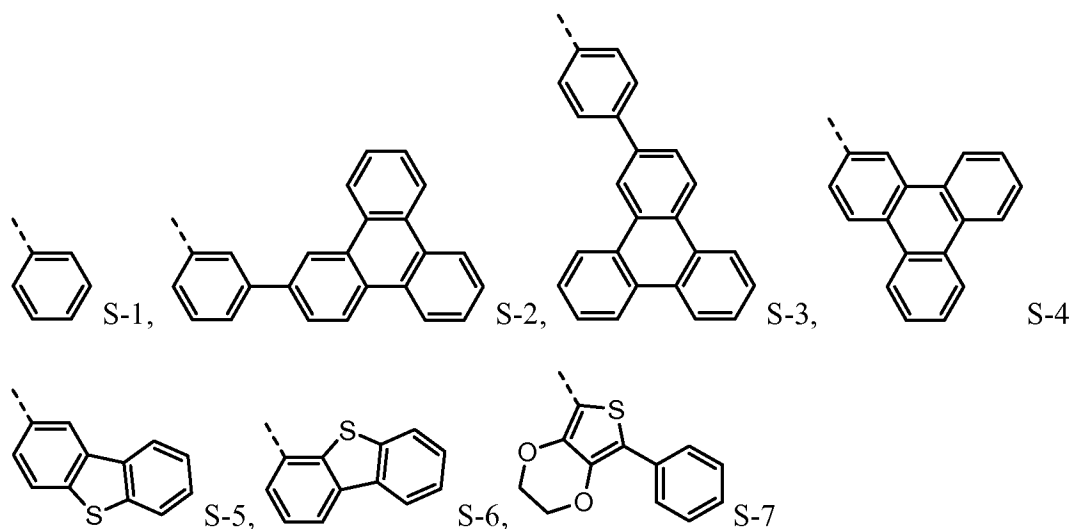
[0035] The materials and structures described herein may have applications in devices other than OLEDs. For example, other optoelectronic devices such as organic solar cells and organic photodetectors may employ the materials and structures. More generally, organic devices, such as organic transistors, may employ the materials and structures.

[0036] 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.

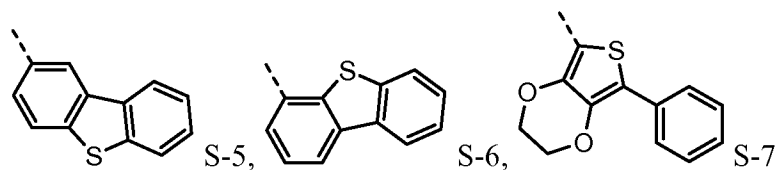
[0037] A novel composition of matter is provided. The novel composition of matter includes a "core" similar to that of naphthylphenylbiphenyl diamine (α -NPD). As used herein, the core of α -NPD has two nitrogen atoms connected to each other by two phenyl rings, all connected in the para position. Novel compositions of matter are provided having more possibilities for the core, including two nitrogen atoms connected by 1, 2 or 3 phenyl rings, where each connection may independently be para or meta. At least one group attached to a nitrogen atom of the core includes a sulfur containing group. Thus, a novel composition of matter is provided having the structure:



where n is 1, 2 or 3, and the phenyl rings between the nitrogen atoms may be attached to each other and to the nitrogen atoms in a para or meta configuration independently selected for each attachment. Each of R₁, R₂, R₃ and R₄ are independently selected from the group consisting of:



where the dotted line shows the point of attachment to an N atom of Formula I. At least one of R₁, R₂, R₃ and R₄ is:



Each of R₁, R₂, R₃ and R₄ may be further substituted with substituents that are not fused to R₁, R₂, R₃ and R₄.

[0038] Without being limited to any theory as to why the novel materials are desirable, it is believed that the benzidine (4,4'-diaminobiphenyl) core, along with the variations described herein, are particularly desirable. Benzidine with one phenyl and one 1-naphthyl attached to each of the nitrogens is α -NPD and is a widely used hole transport layer in OLEDs. However, α -NPD does not work well in certain devices, particularly blue and green devices, which have

higher energy triplets and charge carriers. It is believed that the naphthyl group of α -NPD, in connection with high energy charge carriers and triplets, may be responsible for this instability, and that a sulfur containing group as disclosed herein in Groups A - D, preferably dibenzothiophene (DBT), has superior stability in this context.

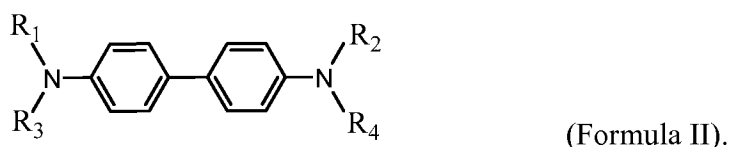
[0039] Hole transport materials incorporating dibenzothiophene group may have more efficiency and/or longer lived than devices incorporating other groups, such as biphenyl, naphthalene. It is believed that the following two points are important factors for HTL in phosphorescent device stability: 1) HTL should not only have good hole (oxidation) stability while transporting holes, but also should have good electron (reduction) stability; 2) HTL should have higher triplet energy than dopants in its adjacent emissive layer to prevent it from quenching caused by the exciton migration. Dibenzothiophene is a conjugated compound with reversible reduction (by solution electrochemistry), indicating that it may be a stable electron carrier. In addition, dibenzothiophene itself has much higher triplet energy (414 nm) than many other organic molecules, such as biphenyl, naphthalene. The enhanced stability and efficiency of dibenzothiophene-containing HTL may be attributed to a combination of the above effects. This may lead to the devices using the HTL materials described herein have higher stability and efficiency than devices using conventional HTL such as α -NPD.

[0040] Hole transport materials incorporating 3,4-ethylenedioxythiophene (EDOT) group may also be desirable such as higher hole conductivity hence low device voltage. Poly(3,4-ethylenedioxythiophene) (PEDOT) is a very important conducting polymer. Its complex with poly(styrene sulfonic acid) has been widely used for antistatic coatings and hole injection layer for polymer OLEDs. The oxyethane bridge across the 3,4 positions of the monomer makes the thiophene very electron rich, therefore sufficient HOMO raising is effected and polymerization is forced to occur through the open 2,5-positions yielding a linear, highly conjugated polymer. The oxidized form of the polymer is highly stable under ambient conditions. The redox property of the film does not change over a long period of time. It is desired to incorporate the EDOT building block into a triarylamine HTL (e.g., benzidine) scaffold to improve the redox properties of the hole injection/transporting materials. The direct linkage of EDOT to nitrogen will raise the HOMO of the molecule and therefore make it better aligned with the ITO interface.

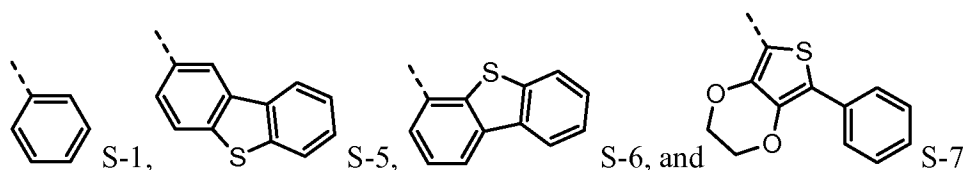
[0041] It is preferred that the sulfur containing group of Group A-D is directly attached to a nitrogen of the core. It is believed that such direct attachment maintains a higher triplet energy for the molecule, which is desirable in many situations.

[0042] Preferably, at least one of R_1 and R_3 , and at least one of R_2 and R_4 , is a group that includes a sulfur-containing group from one of the groups A - D. While molecules having a sulfur-containing group attached to only one nitrogen of the core are useable, it is believed that molecules having at least one sulfur containing group attached to each nitrogen of the core results in a more stable molecule. It is also believed that adding additional sulfur containing groups after there is at least one attached to each nitrogen may not result in much further improvement. While it is generally easier to use only one type of sulfur-containing group in a molecule, possible multiple times, different sulfur-containing groups may also be used in the same molecule.

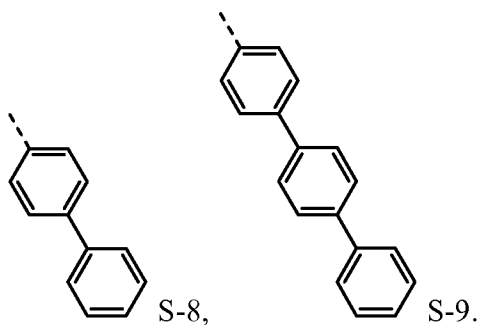
[0043] The core of α -NPD is preferred, where the part of the composition represented by Formula I is more specifically:



[0044] Molecules where each of R_1 , R_2 , R_3 and R_4 are independently selected from the group consisting of:

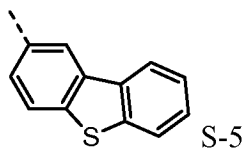


may be preferred. Such molecules include at least one sulfur-containing group per one of Groups A-D, and any substituents that are not such groups are a phenyl, which should not strongly affect the electronic properties imparted to the molecule by the sulfur-containing group. The following substituents may be used for reasons similar to phenyl:

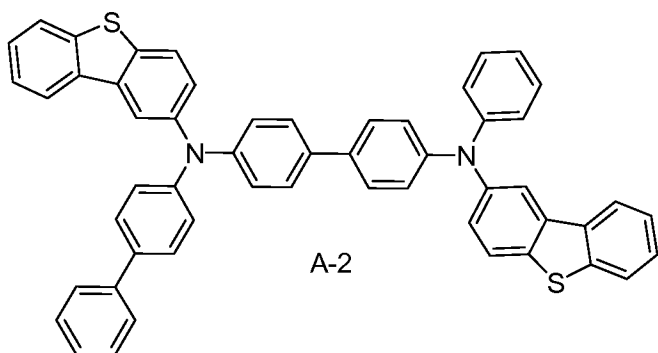
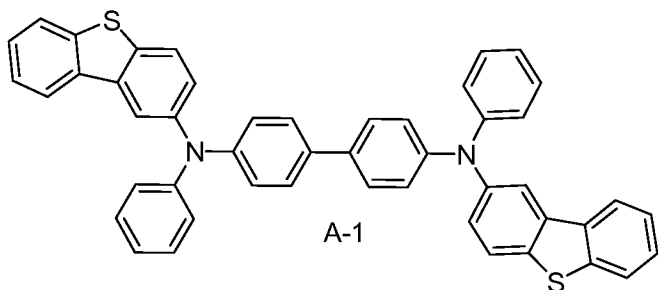


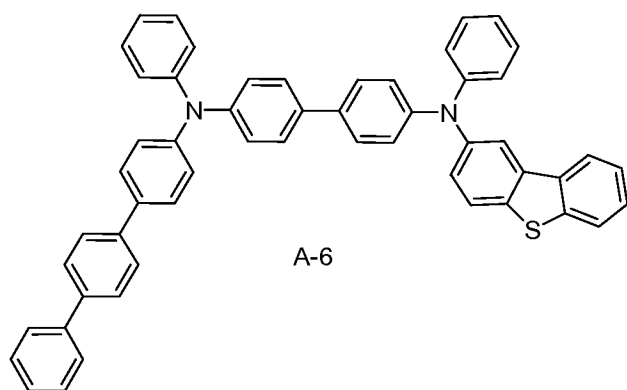
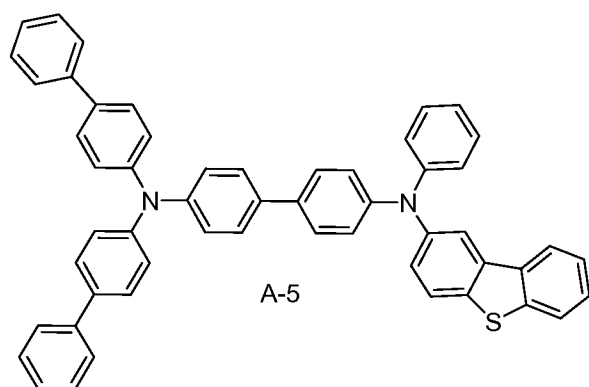
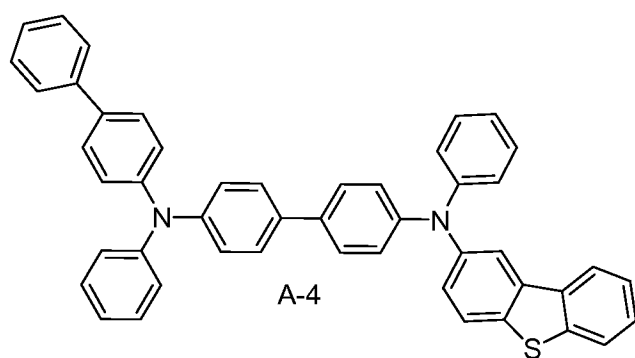
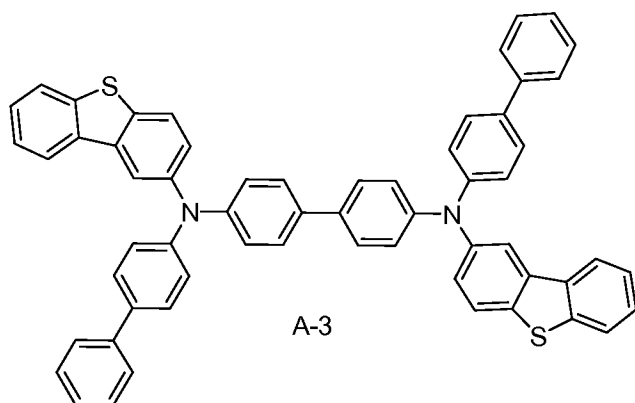
[0045] Molecules including each of the sulfur-containing groups of Groups A-D disclosed herein may be preferred, depending upon the context.

[0046] A composition of matter where at least one of R_1 , R_2 , R_3 and R_4 is

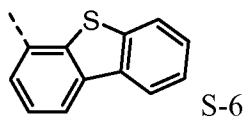


may be preferred. These compounds may be referred to as being in the A-group of compounds. Non-limiting examples of specific preferred molecules including this substituent include:

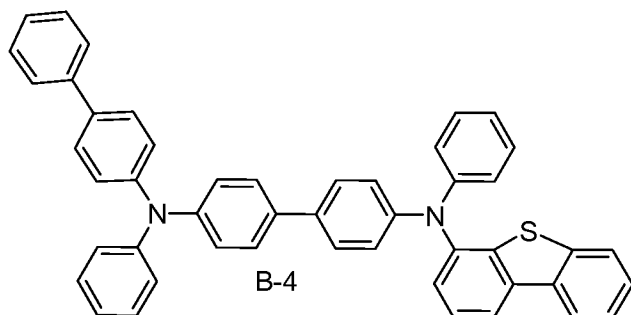
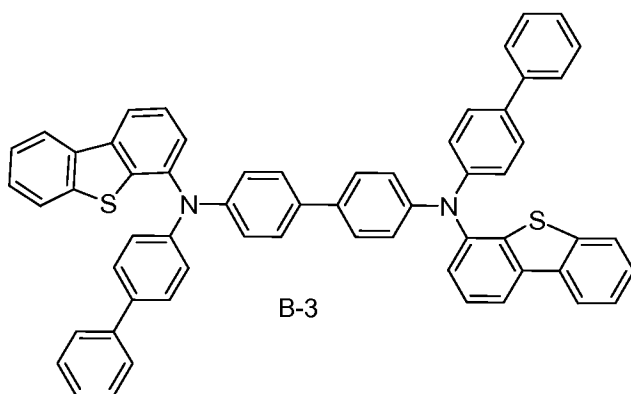
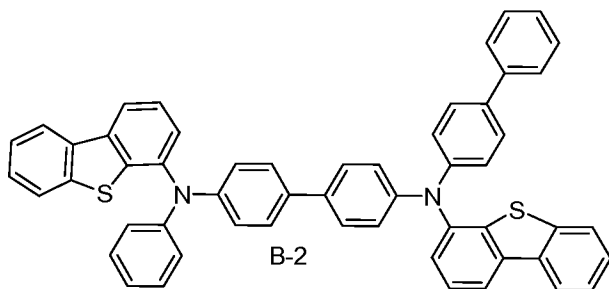
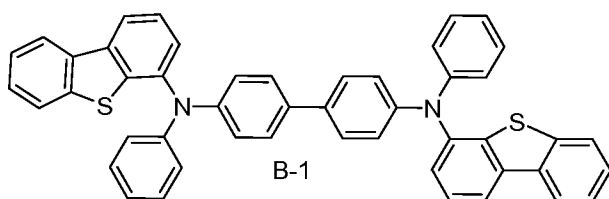


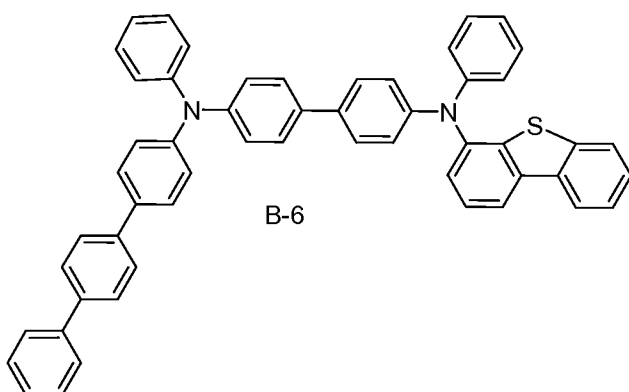
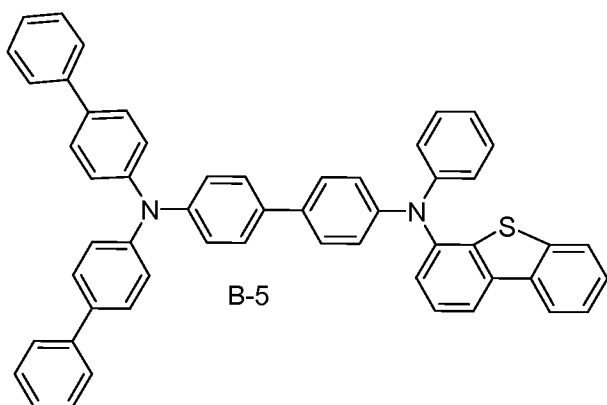


[0047] A composition of matter where at least one of R₁, R₂, R₃ and R₄ is

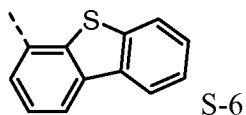


may be preferred. These compounds may be referred to as being in the B-group of compounds. Non-limiting examples of specific preferred molecules including this substituent include:

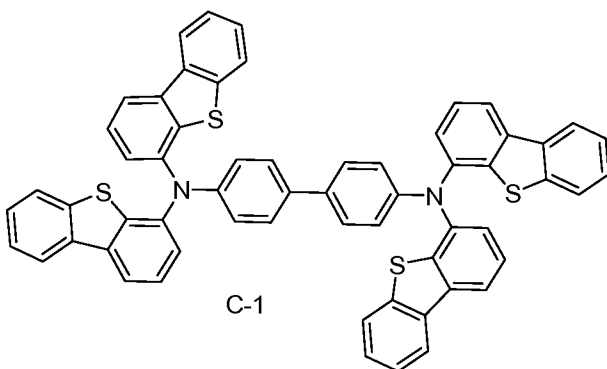


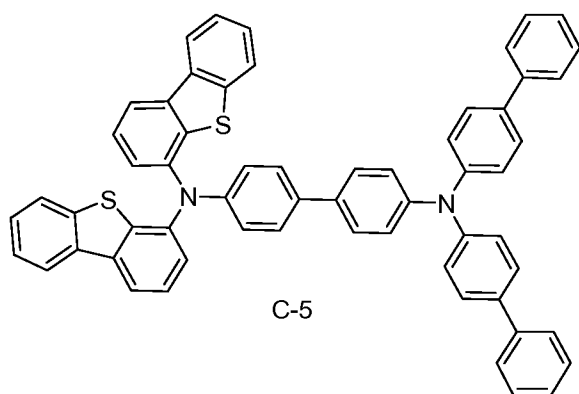
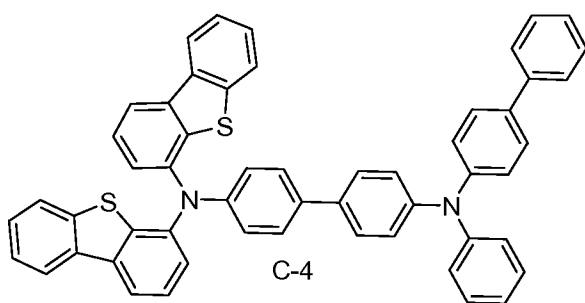
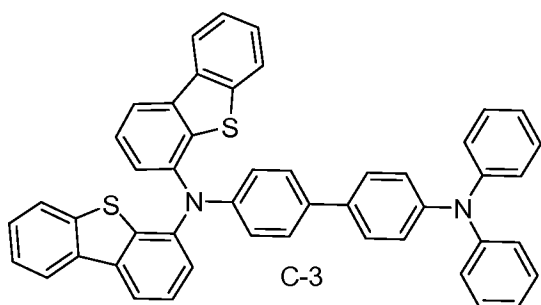
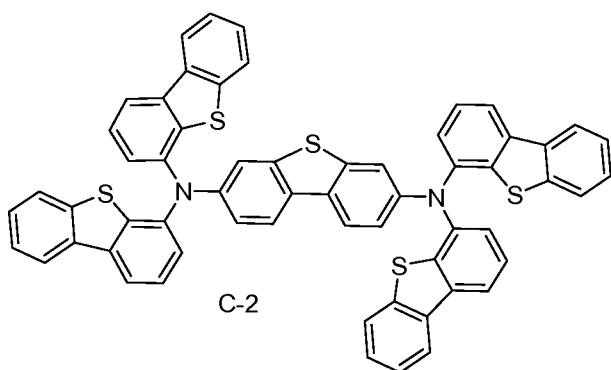


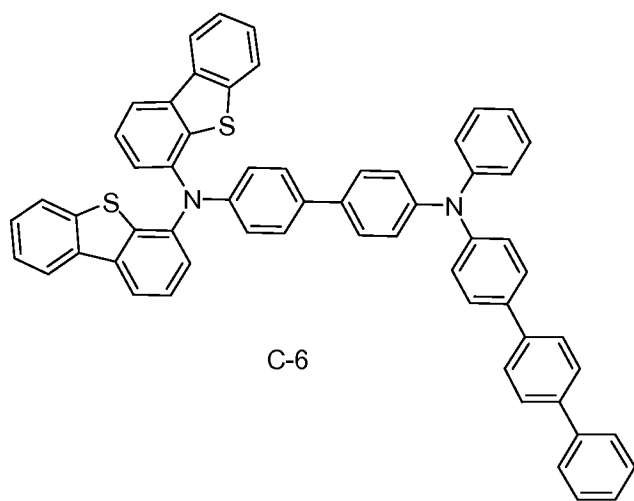
[0048] A composition of matter where both R_1 and R_2 are



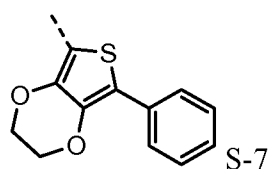
may be preferred. These compounds may be referred to as being in the C-group of compounds. The C-group of compounds is a subset of the B-group of compounds. Non-limiting examples of specific preferred molecules including this substituent include:



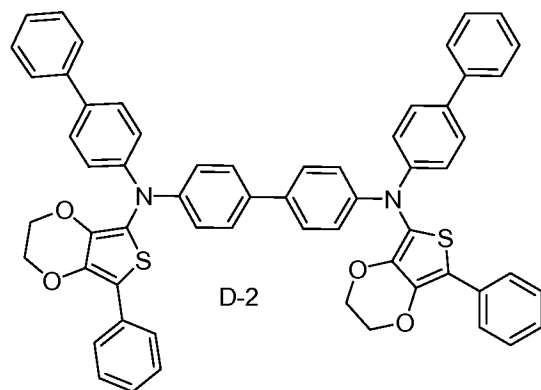
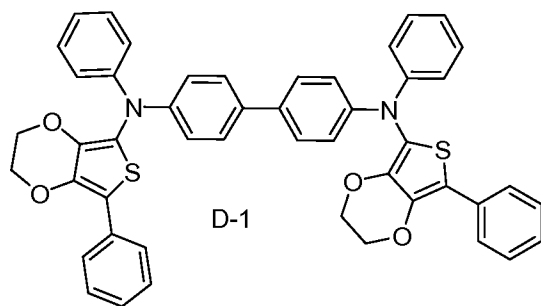


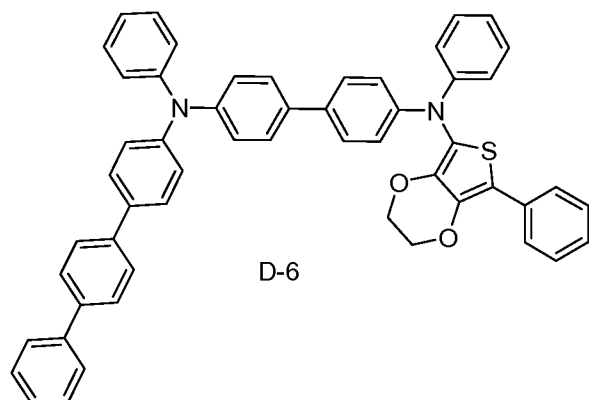
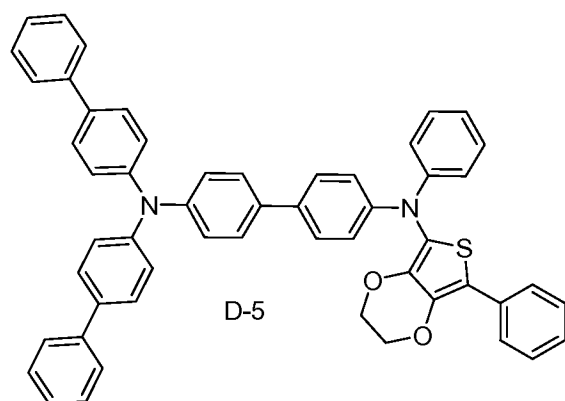
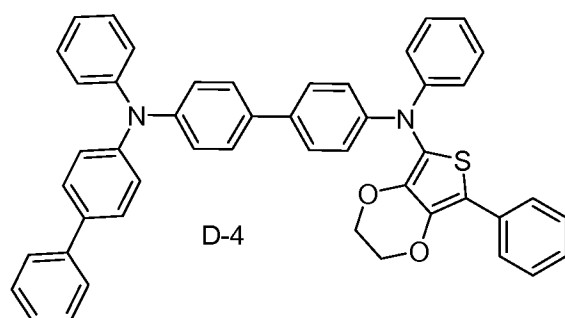
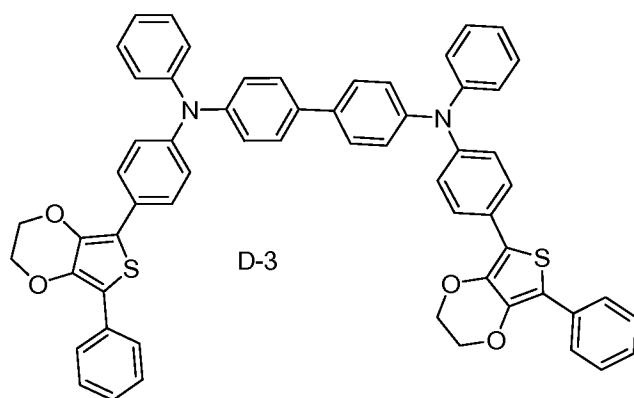


[0049] A composition of matter where at least one of R_1 , R_2 , R_3 and R_4 is

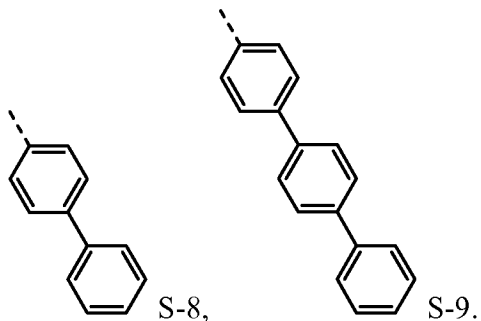


may be preferred. These compounds may be referred to as being in the D-group of compounds. Non-limiting examples of specific preferred molecules including this substituent include:

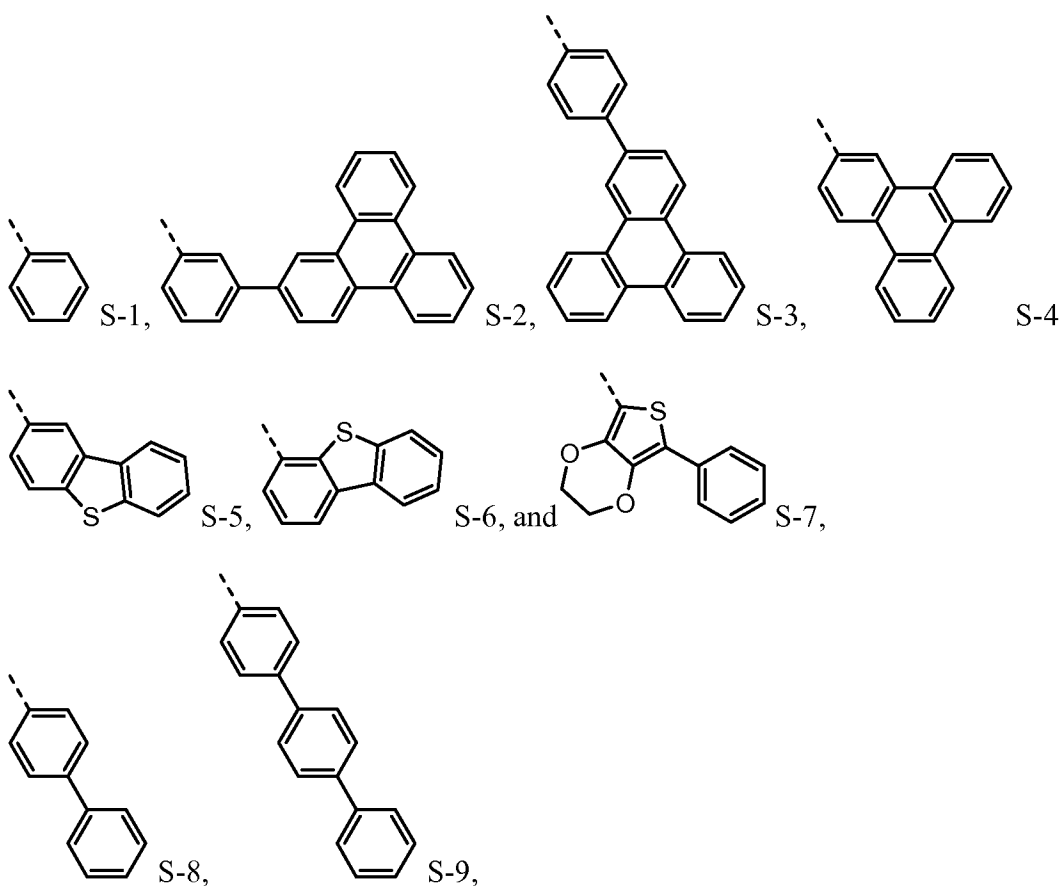




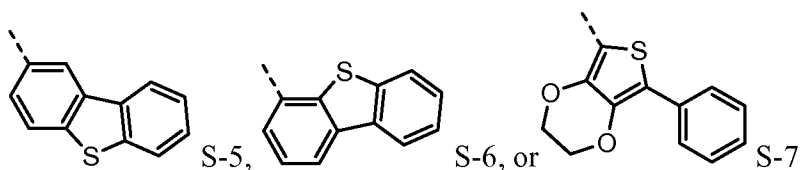
[0050] For the R groups that do not include a sulfur containing group from one of groups A-D, the following structures are preferred:



[0051] A composition of matter of Formula I is preferred where each of R_1 , R_2 , R_3 and R_4 is independently selected from the group consisting of:

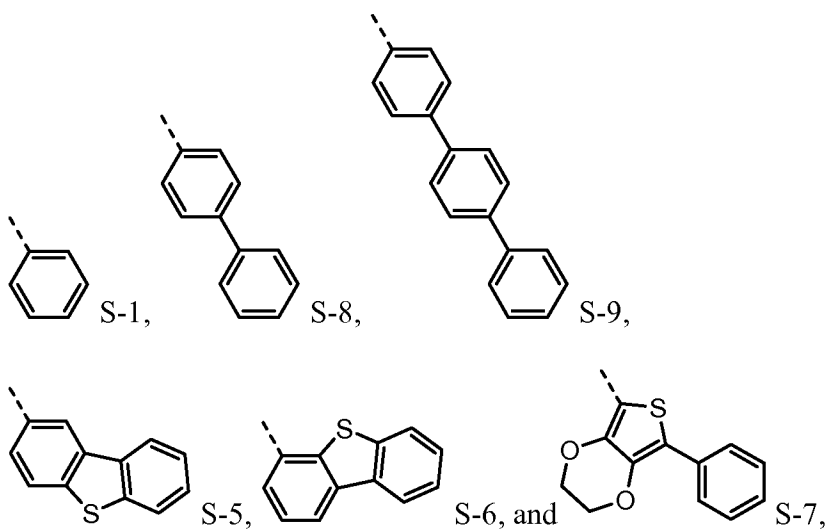


at least one of R_1 , R_2 , R_3 and R_4 is selected from the group consisting of:

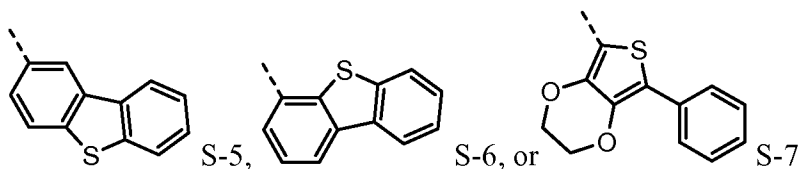


and there are no further substitutions to R_1 , R_2 , R_3 and R_4 .

[0052] A composition of matter of Formula I is preferred where each of R_1 , R_2 , R_3 and R_4 is independently selected from the group consisting of:



at least one of R_1 , R_2 , R_3 and R_4 is selected from the group consisting of:



and there are no further substitutions to R_1 , R_2 , R_3 and R_4 .

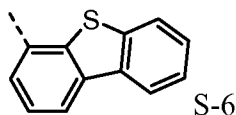
[0053] Molecules A-1, B-1, C-1 and D-1 have been synthesized, and a description of the synthesis is provided. The other molecules in the A, B, C and D groups of molecules, and the variations to those molecules described herein, can be readily fabricated using similar chemical synthesis.

[0054] 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 may include a host and a phosphorescent dopant. The device may also include an organic hole transport layer comprising a hole transport material, disposed between the organic emissive layer and the anode, and in direct contact with the organic emissive layer. The hole transport layer may have the structure of the novel compositions of matter disclosed herein, i.e., the structure of the novel materials having a core consistent with Formula I. The phosphorescent dopant is preferably an organo-metallic iridium material.

[0055] In addition, consumer products wherein the consumer product includes an organic light emitting device including a composition of matter having the structure of Formula I, as described, are provided. Selections for the substituents and structures described as preferred for the compositions of matter having the structure Formula I are also preferred for the devices and the consumer products including devices that comprise a composition of matter having the structure of Formula I. These selections include those described for substituents R₁, R₂, R₃, and R₄, Formula II, and structures A-1 through A-6, B-1 through B-6, C-1 through C-6, and D-1 through D-6.

[0056] Organic light emitting devices having at least one of R₁, R₂, R₃ and R₄ being:



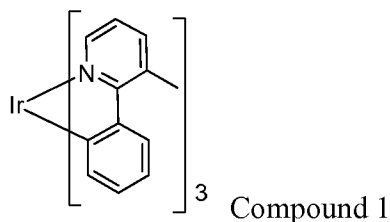
were fabricated. Specifically, molecule B-1 was used to fabricate devices, and it is believed that other molecules as disclosed herein having the same sulfur containing group would have similar performance. The devices had particularly good performance.

[0057] It is believed that the compounds having a sulfur containing group disclosed herein, when used as a hole transport layer, work particularly well in devices where the host is a compound comprising a triphenylene containing benzo-fused thiophene. Such hosts are disclosed in U.S. Patent Application 61/013,391, filed December 28, 2007, inventor Ma, Bin, which is incorporated herein by reference in its entirety and particularly for claimed subject matter. Compound 2 is an example of such a host. The B group of materials are preferred hole transport materials for this combination.

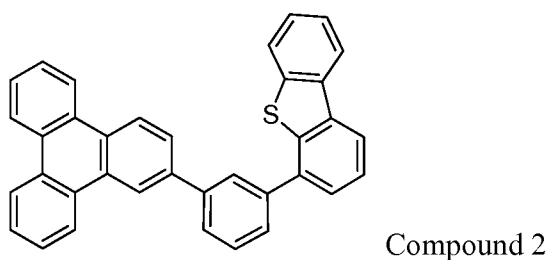
[0058] It is believed that sulfur containing hole transport materials described herein are desirable for use in fluorescent OLEDs in addition to phosphorescent OLEDs.

[0059] As used herein, the following compounds have the following structures:

Compound 1 - disclosed in JP 2000-299497:



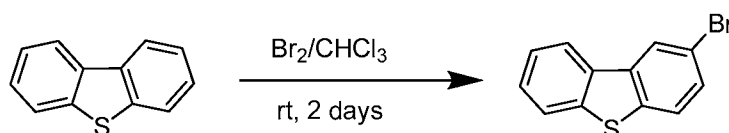
Compound 2 - disclosed in U.S. Patent Application 61/013,391, filed December 28, 2007, inventor Ma, Bin.



[0060] Bis(2-methyl-8-hydroxyquinolinolato)(4-phenylphenolato) aluminum (BALq) and tris-(8-hydroxyquinolato) aluminum (Alq₃) are well known materials. LG-101 and LG-201 are proprietary materials available for purchase from LG Chem, Inc. of Korea.

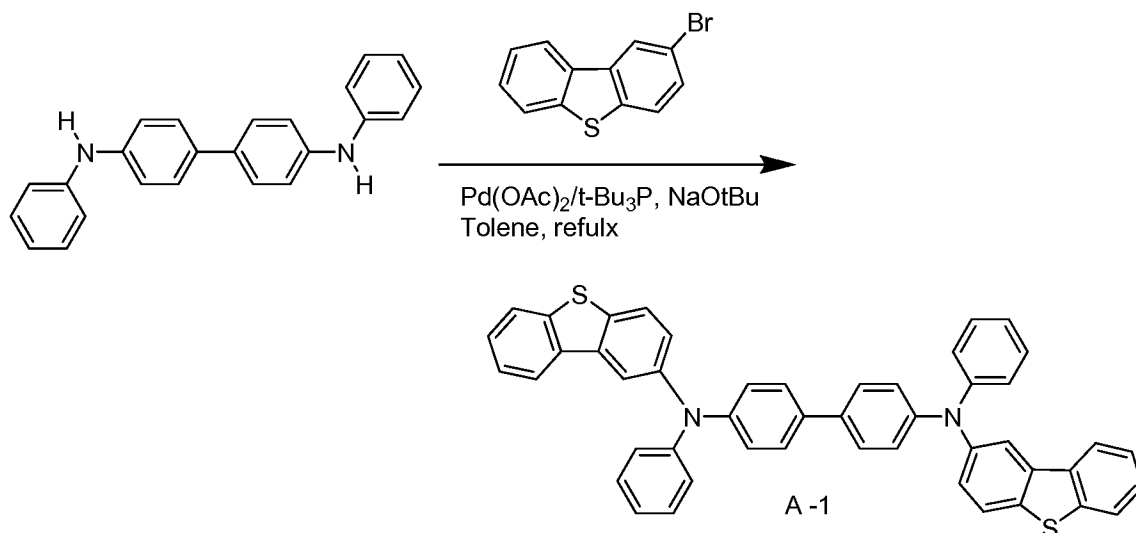
EXPERIMENTAL

Synthesis of A-1



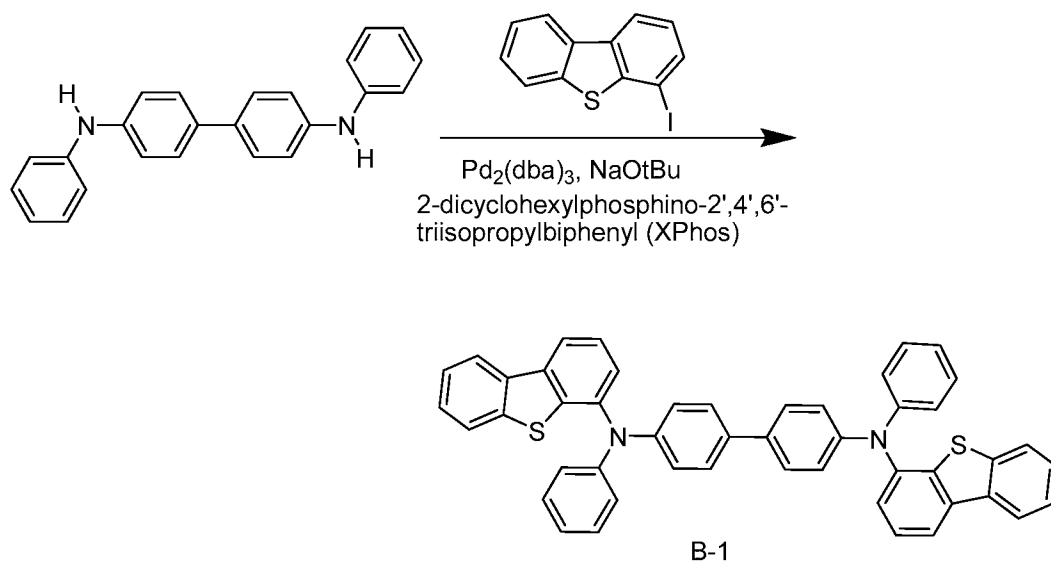
[0061] **Synthesis of 2-bromodibenzothiophene:** Dibenzothiophene (15 g, 79.9 mmol) was dissolved in 1.5 L chloroform. To the solution, bromine (12.76 g, 79.9 mmol) was added dropwise. The reaction mixture was vigorously stirring for 2 days at room temperature and then treated with sodium sulfite water solution. The organic phase was evaporated to give a white solid which has 48% unreacted dibenzothiophene, 50% 2-bromodibenbzothiophene and ~

less 2% 2,8-dibromodibenzothiophene based on GC-MS and HPLC results. The mixture was repeatedly recrystallized with ethyl acetate to get pure 2-bromodibenzothiophene.



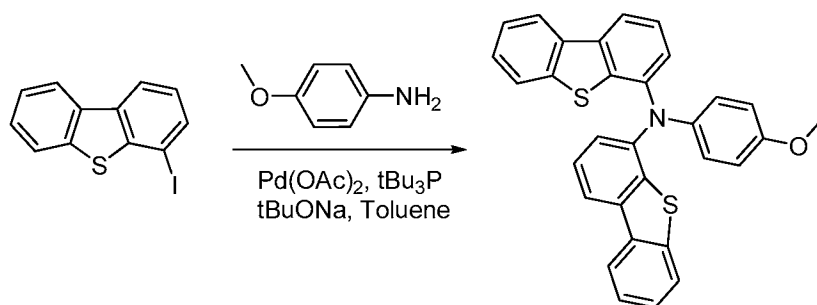
[0062] Synthesis of A-1: 2-bromodibenzothiophene (9.19 mmol), diamine (1.45 g, 4.18 mmol), $\text{Pd}(\text{OAc})_2$ (30 mg, 0.125 mmol), 1 M *t*-Butylphosphine in toluene (0.25 mL, 0.25 mmol), *t*-BuONa (1.3 g, 12.8 mmol) and 150 mL toluene were charged in a 250 mL round bottle flask. The reaction mixture was heated up to reflux for overnight under nitrogen. Reaction mixture was cooled down and was separated with silica gel column to get ~ 2.6 g (89%) product which was confirmed by proton NMR.

Synthesis of B-1



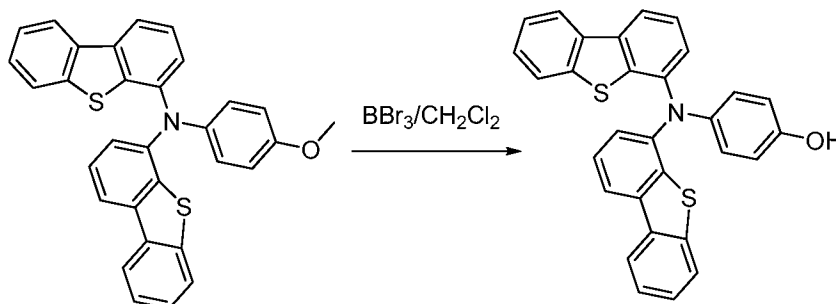
[0063] To a 500 mL round flask was added *N,N'*-Diphenylbenzidine (2.4 g, 7 mmol), 4-iododibenzothiophene (5.6 g, 18 mmol), $\text{Pd}_2(\text{dba})_3$ (0.2 g, 0.2 mmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos, 0.4 g, 0.8 mmol), sodium *t*-butoxide (2.9 g, 30 mmol), and 150 mL of toluene. The reaction was heated to reflux and stirred under a nitrogen atmosphere for 24 h. After cooling, the mixture was purified by a silica gel column. Yield was 2 g.

Synthesis of C-1

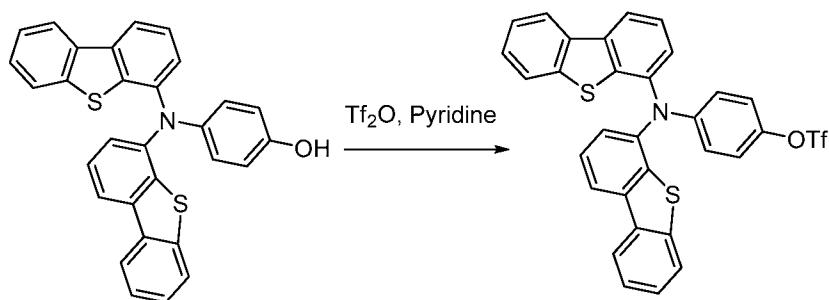


[0064] **Synthesis of N-(dibenzo[b,d]thiophen-4-yl)-N-(4-methoxyphenyl)dibenzo[b,d]thiophen-4-amine:** palladium acetate (0.07 g, 0.33 mmol) and 1.0 M tri(*t*-butyl)phosphine solution in toluene (0.67 mL, 0.67 mmol) were added to a three-neck flask under nitrogen. 150 mL of toluene was then added. The solution was stirred under nitrogen until the color disappeared. To the solution was added 4-iododibenzothiophene (7.4 g, 24 mmol), sodium *tert*-butoxide (3.3 g, 33 mmol), and 4-methoxyaniline (1.4 g, 11 mmol) in sequence. The mixture was then heated

up to reflux for 4 h. After cooled to room temperature, the mixture was filtered through a silica gel plug. The product was purified by column chromatography using 30% of dichloromethane in hexanes as eluent. 4.6 g of desired product was obtained after purification. (85% yield)



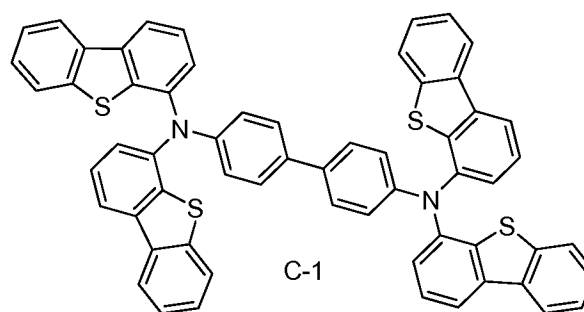
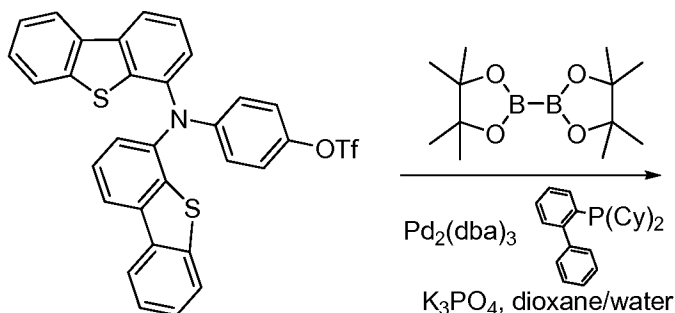
[0065] Synthesis of 4-(bis(dibenzo[b,d]thiophen-4-yl)amino)phenol: N-(dibenzo[b,d]thiophen-4-yl)-N-(4-methoxyphenyl)dibenzo[b,d]thiophen-4-amine (4.6 g, 9.4 mmol) was dissolved in 100 mL of anhydrous dichloromethane. The solution was cooled with a dry ice/isopropanol bath. To the solution was added boron tribromide solution in hexanes (1.0 M solution, 16 mL). The reaction was allowed to warm to room temperature for 6 h. The reaction was quenched with water. The product was purified with column chromatography using dichloromethane as eluent. 4 g of desired product was obtained. (90% yield)



[0066] Synthesis of 4-(bis(dibenzo[b,d]thiophen-4-yl)amino)phenyl trifluoromethanesulfonate: 4-(bis(dibenzo[b,d]thiophen-4-yl)amino)phenol (4.0 g, 8.4 mmol) was dissolved in 60 mL of anhydrous dichloromethane. The solution was cooled with an ice-water bath. To the solution was added pyridine (1.7 mL, 21 mmol) and then triflic anhydride (1.7 mL, 10.1 mmol). The reaction was stirred for 20 minutes and then quenched with water. The

organic layer was separated. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography using 1:3 dichloromethane and hexanes as eluent.

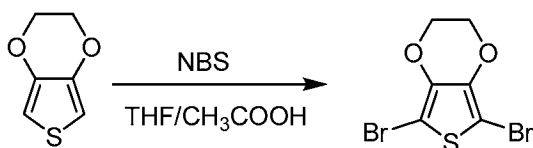
4.15 g of desired product was obtained. (82%



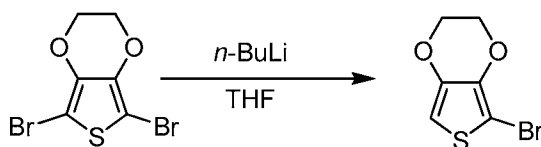
yield)

[0067] Synthesis of C-1, $\text{N}^4, \text{N}^4, \text{N}^{4'}, \text{N}^{4'}$ -tetrakis(dibenzo[b,d]thiophen-4-yl)biphenyl-4,4'-diamine: 4-(bis(dibenzo[b,d]thiophen-4-yl)amino)phenyl trifluoromethanesulfonate (4.0 g, 6.6 mmol), bispinacolatodiboron (0.84 g, 3.3 mmol), biphenyl-2-ylidicyclohexylphosphine (0.09 g, 0.26 mmol), potassium phosphate (3.5 g, 16.5 mmol) were added to a three-neck flask. 100 mL of dioxane and 5 mL of water was then added. The mixture was purged with nitrogen for 30 minutes. $\text{Pd}_2(\text{dba})_3$ (0.06 g, 0.07 mmol) was added. The reaction mixture was heated to 60 °C for 4 h. The reaction mixture was filtered through a magnesium sulfate bed. The solvent was then evaporated. The residue was dissolved in dichloromethane and then precipitated from isopropanol. The solid was collected by filtration. The product was further purified by column using 1:2 to 1:1 of dichloromethane and hexanes as eluent. 2 g of desired product was obtained.

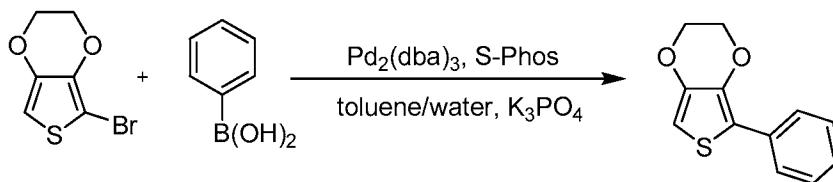
Synthesis of D-1



[0068] Synthesis of 2,5-dibromo-3,4-ethylene dioxythiophene: 3,4-ethylene dioxythiophene (EDOT) (5 g, 35 mmol) was dissolved in the mixture of 70 mL THF and 70 mL acetic acid. NBS (13.2 g, 74 mmol) was slowly added into the solution. The reaction was stirred at room temperature for 2 h, then 350 mL water was added. The precipitation was collected by filtration and washed with water. The collected silver grey solid was dried in a desiccator with applied vacuum overnight and gave 10.3 gram 2,5-dibromo-3,4-ethylene dioxythiophene (33 mmol, yield 94.6%).

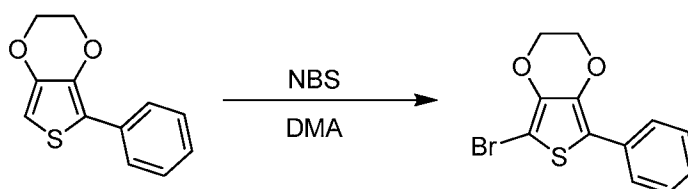


[0069] Synthesis of 2-bromo-3,4-ethylene dioxythiophene: 2,5-dibromo-EDOT (10.3 g, 33 mmol) was dissolved in 200 mL anhydrous THF and cooled to -78°C by acetone/dry ice bath. Then 22.1 mL *n*-BuLi (1.6 M in hexane) was added dropwise into the solution. After warmed to room temperature, the reaction was quenched by 170 mL HCl (1 M) and extracted with methylene chloride (200 mL \times 2). The combined organic layer was dried over MgSO_4 and concentrated by rotovap to get 10.5 gram brown liquid, which was used directly for next step without further purification and without drying to constant weight.

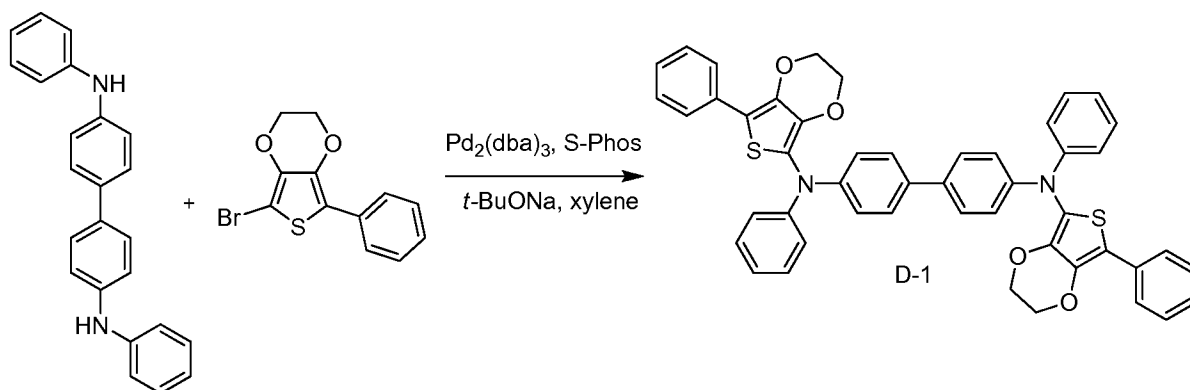


[0070] Synthesis of 2-phenyl-3,4-ethylene dioxythiophene: The mixture of 2-bromo-EDOT (10.5 g, 47 mmol), phenylboronic acid (8.1 g, 66 mmol), potassium phosphate tribasic (30 g, 142.5 mmol), 300 mL toluene and 30 mL water was prepared. Nitrogen was bubbled directly in the mixture for 15 minutes. Then tris(dibenzylideneacetone)dipalladium (435 mg,

0.48 mmol) and S-Phos (788 mg, 1.92 mmol) were added. The nitrogen was bubbled in the mixture for another 15 minutes. The reaction mixture was refluxed overnight under nitrogen. The next day the reaction mixture was cooled to room temperature. The organic layer was separated and the aqueous layer was extracted by dichloromethane. The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulted black oil was distilled by Kugelrohr at 160 °C to get rid of the black color. Then another distillation by Kugelrohr at 100 °C successfully got rid of the impurities. The 6 gram (27.5 mmol, total yield of last two steps: 83%) light yellow oil left in the original flask was used for next step without further purification.



[0071] Synthesis of 2-bromo-5-phenyl-3,4-ethylene dioxothiophene: 2-phenyl-EDOT (6 g, 28 mmol) was dissolved in DMA and cooled to 0 °C by ice bath and was bubbled with nitrogen. NBS (5.4 g, 30.2 mmol) was dissolved in 35 mL DMA and added dropwise into the 2-phenyl-EDOT solution under nitrogen. After all NBS was added, the reaction was warmed to room temperature and stirred for 20 minutes. The mixture then was poured into ice water, extracted by dichloromethane. The combined organic layer was dried over magnesium sulfate, filtered and concentrated by rotovap and Kugelrohr. The red solid was recrystallized from hot methanol to get 5.7 gram grey solid (19 mmol, 70% yield).



[0072] Synthesis of D-1: A mixture of 2-bromo-5-phenyl-EDOT (2 g, 6.7 mmol), diphenylbenzidine (0.57 g, 1.68 mmol), *t*-BuONa (0.48 g, 5.04 mmol) and xylene (80 mL) was prepared. Nitrogen was bubbled directly in the mixture for 15 minutes. Next was added tris(dibenzylideneacetone)dipalladium (23 mg, 1.5% equivalent) and S-Phos (41 mg, 6% equivalent) then the nitrogen was bubbled in the mixture for another 20 minutes. The reaction mixture was refluxed overnight under nitrogen. The next day the reaction mixture was cooled to room temperature, then was filter through a celite plug and washed out with dichloromethane. The filtration was concentrated and purified by column (15% EtOAc in hexanes first, then washed with the solvent of 30% EtOAc and 10% dichloromethane in hexanes). The resulted yellow solid was recrystallized from hot dichloromethane and methanol to give 0.7 g (0.5 mmol, yield 30%) yellow solid.

DEVICES

[0073] Devices were fabricated using standard techniques. The devices have structures similar to that shown in FIG. 1, but including the specific layers and materials described in the table.

Table 1. Structures of green PHOLEDs with novel HTL materials and novel host/HTL combinations vs comparative examples.

Example	HIL	HTL	Host	Compound 1, %	BL	ETL
1	LG-101 300Å	α -NPD 100Å	Compound 2	10%	Compound 2 100Å	LG-201 300Å
2	LG-101 300Å	B-1 100Å	Compound 2	10%	Compound 2 100Å	LG-201 300Å
3	LG-101 300Å	α -NPD 100Å	Compound 2	10%	Compound 2 100Å	Alq 400Å
4	LG-101 300Å	B-1 100Å	Compound 2	10%	Compound 2 100Å	Alq 400Å

Table 2. Performance of green PHOLEDs with novel HTL materials and novel host/HTL combinations vs. comparative examples.

	CIE		At 1,000 nits					At 40 mA/cm ² LT _{80%} [h]		
Example	x	y	Voltage [V]	LE [cd/A]	EQE [%]	PE [lm/W]	LT _{50%} [h]	Lo [nits]	RT	70°C
1	0.351	0.608	5.6	49.1	13.5	27.5	204,995	14,624	349	65
2	0.347	0.612	5.6	57.7	15.9	23.4		18,163	340	
3	0.351	0.612	5.8	53.5	14.7	29.0	213,955	16,084	372	
4	0.350	0.613	5.7	62.1	17.1	34.2		19,540	265	

[0074] 2 groups of experiments are shown in tables 1 and 2. The superior performance of green PHOLED devices with novel HTL material B-1 is shown relative to devices having an NPD HTL. The desirability of combining HTL materials similar to B-1 with hosts similar to Compound 2 is also shown.

Group 1: Examples 1 and 2

[0075] The difference between Example 1 (comparative) and Example 2 is that Example 1 has an α -NPD HTL, whereas Example 2 has an HTL of Compound B-1. The combination of HTL B-1 with Compound 2 as a host gives results superior to a similar device using an α -NPD HTL. Example 2 shows superior performance in efficiency and the lifetime. Moreover, the results for Example 2 are particularly good for a green-emitting device in general, showing the desirability of combining HTLs with compounds similar to B-1 with hosts similar to Compound 2.

Group 2: Examples 3 and 4

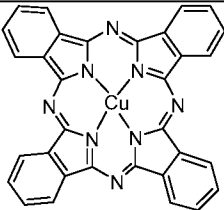
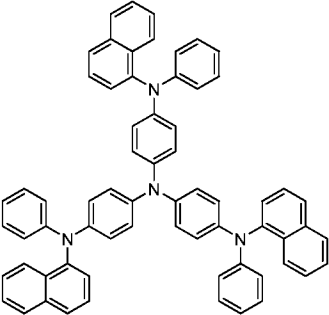
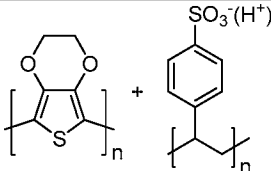
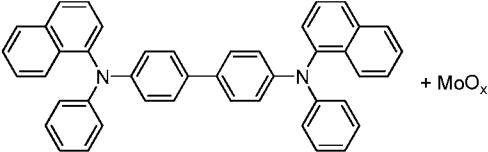
[0076] Group 2 makes a similar comparison to that made in Group 1, except using an ETL of Alq instead of LG-201. The same conclusions can be drawn from Group 2 as from Group 1.

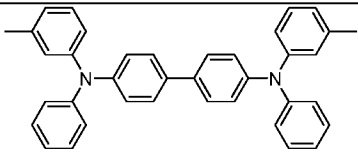
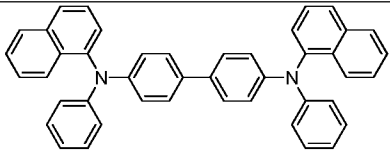
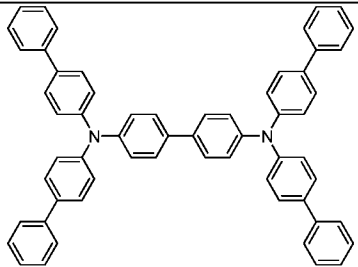
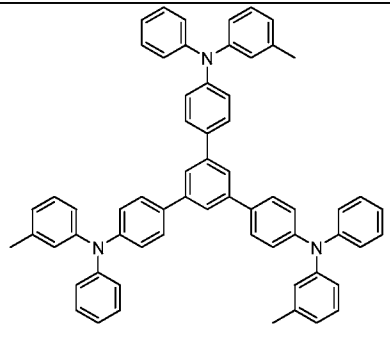
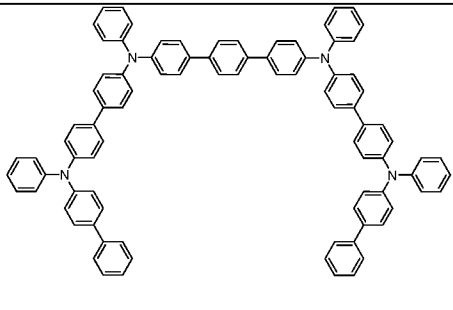
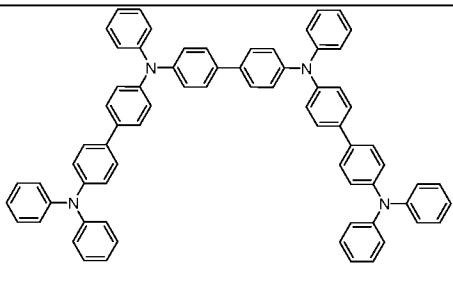
[0077] The materials described herein as useful for a particular layer in an organic light emitting device may be used in combination with a wide variety of other materials present in the device. For example, emissive dopants disclosed herein may be used in conjunction with a wide variety of hosts, transport 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,

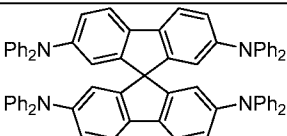
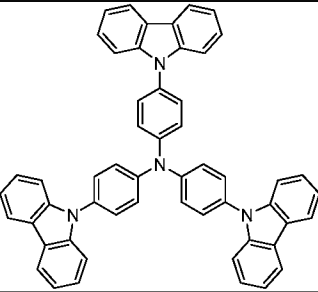
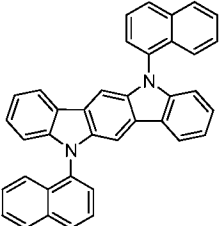
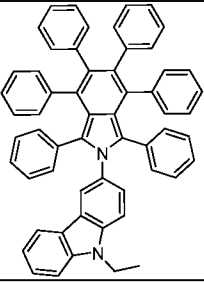
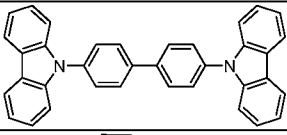
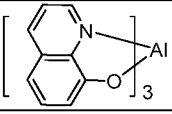
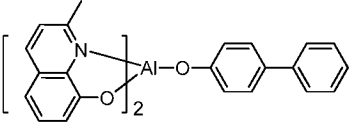
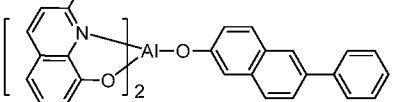
and one of skill in the art can readily consult the literature to identify other materials that may be useful in combination.

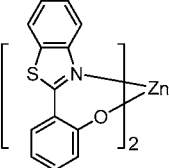
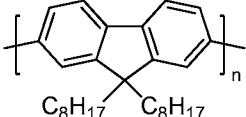
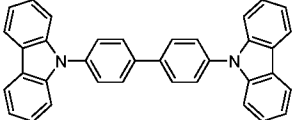
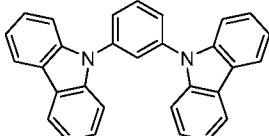
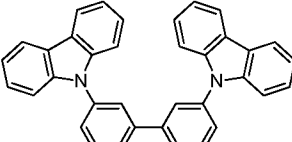
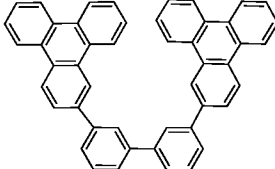
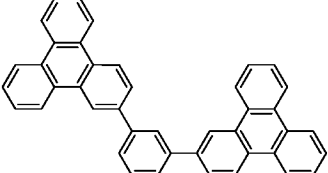
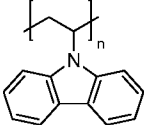
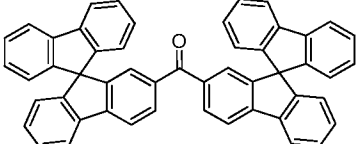
[0078] In addition to and / or in combination with the materials disclosed herein, many hole injection materials, hole transporting materials, host materials, dopant materials, exciton/hole blocking layer materials, electron transporting and electron injecting materials may be used in an OLED. Non-limiting examples of the materials that may be used in an OLED in combination with materials disclosed herein are listed in Table 3 below. Table 3 lists non-limiting classes of materials, non-limiting examples of compounds for each class, and references that disclose the materials.

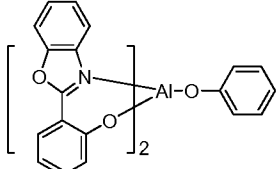
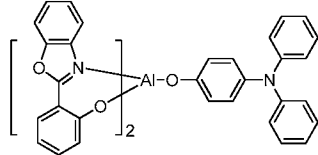
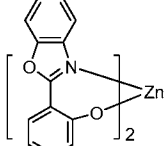
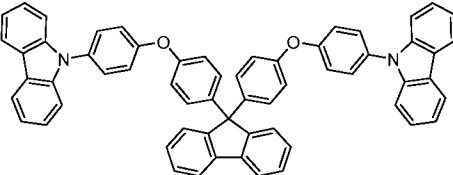
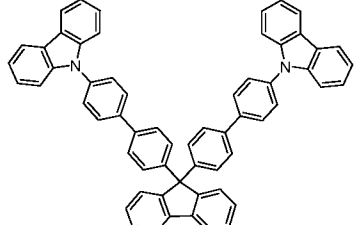
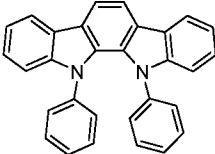
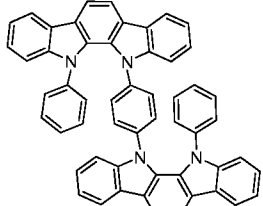
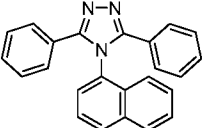
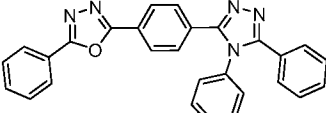
TABLE 3

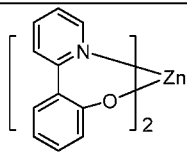
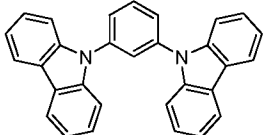
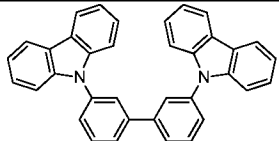
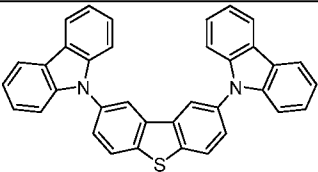
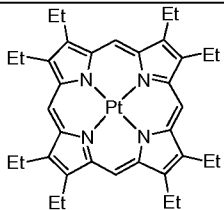
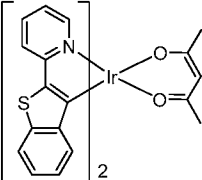
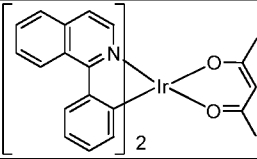
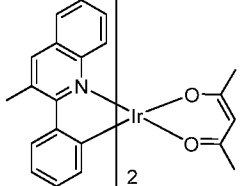
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Hole injection materials		
Phthalocyanine and porphyrin compounds		Appl. Phys. Lett. 69, 2160 (1996)
Starburst triarylamines		J. Lumin. 72-74, 985 (1997)
CF _x Fluorohydrocarbon polymer	$\left[\text{CH}_x\text{F}_y \right]_n$	Appl. Phys. Lett. 78, 673 (2001)
Conducting polymers (e.g., PEDOT:PSS, polyaniline, polythiophene)		Synth. Met. 87, 171 (1997)
Arylamines complexed with metal oxides such as molybdenum and tungsten oxides		SID Symposium Digest, 37, 923 (2006)
Hole transporting materials		

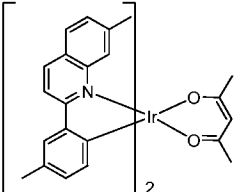
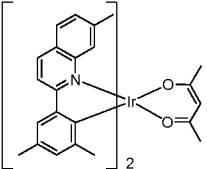
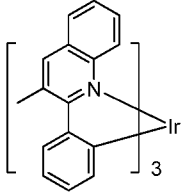
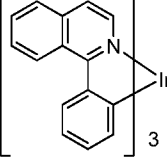
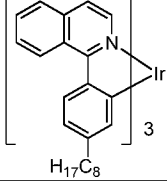
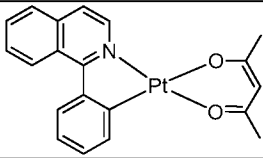
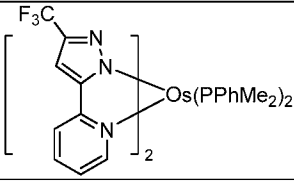
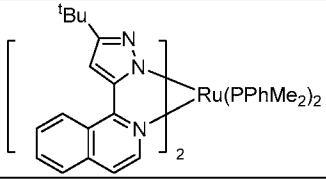
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Triarylamines (e.g., TPD, α -NPD)		Appl. Phys. Lett. 51, 913 (1987)
		US5061569
		EP650955
		J. Mater. Chem. 3, 319 (1993)
		Appl. Phys. Lett. 90, 183503 (2007)
		Appl. Phys. Lett. 90, 183503 (2007)

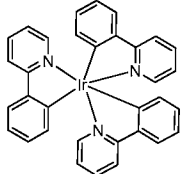
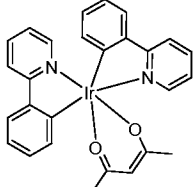
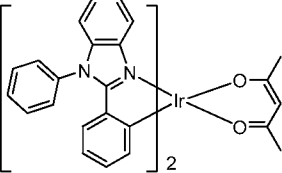
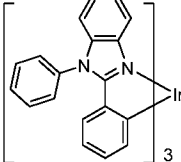
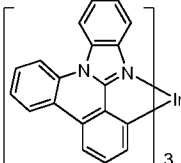
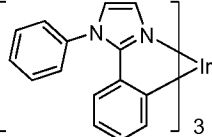
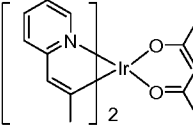
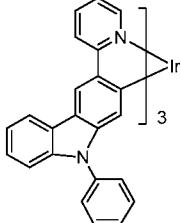
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Triarylamine on spirofluorene core		Synth. Met. 91, 209 (1997)
Arylamine carbazole compounds		Adv. Mater. 6, 677 (1994)
Indolocarbazoles		Synth. Met. 111, 421 (2000)
Isoindole compounds		Chem. Mater. 15, 3148 (2003)
Phosphorescent OLED host materials		
Red hosts		
Arylcarbazoles		Appl. Phys. Lett. 78, 1622 (2001)
Metal 8-hydroxyquinolates (e.g., Alq ₃ , BAlq)		Nature 395, 151 (1998)
		US20060202194
		WO2005014551

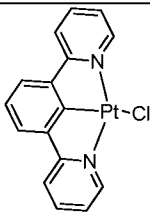
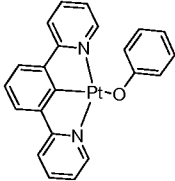
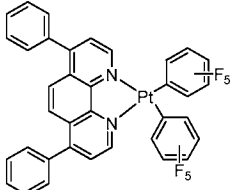
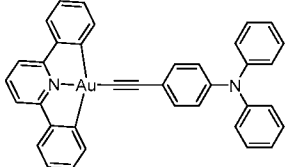
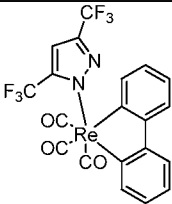
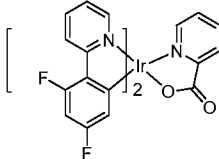
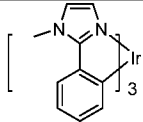
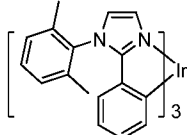
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Metal phenoxybenzothiazole compounds		Appl. Phys. Lett. 90, 123509 (2007)
Conjugated oligomers and polymers (e.g., polyfluorene)		Org. Electron. 1, 15 (2000)
Green hosts		
Arylcarbazoles		Appl. Phys. Lett. 78, 1622 (2001)
		US2003175553
		WO2001039234
Aryltriphenylene compounds		US20060280965
		US20060280965
Polymers (e.g., PVK)		Appl. Phys. Lett. 77, 2280 (2000)
Spirofluorene compounds		WO2004093207

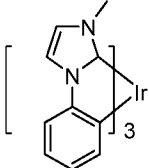
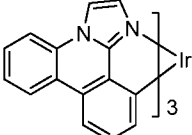
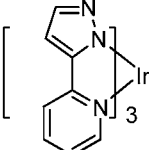
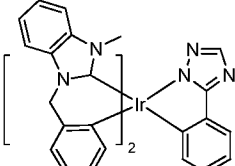
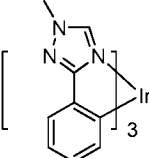
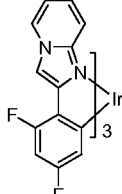
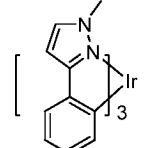
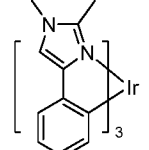
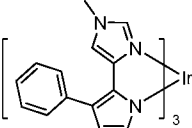
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Metal phenoxybenzoxazole compounds		WO05089025
		WO06132173
		JP200511610
Spirofluorene-carbazole compounds		JP2007254297
		JP2007254297
Indolocabazoles		WO07063796
		WO07063754
5-member ring electron deficient heterocycles (e.g., triazole, oxadiazole)		J. Appl. Phys. 90, 5048 (2001)
		WO04107822

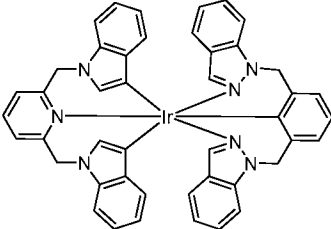
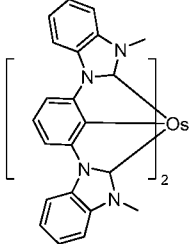
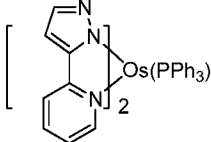
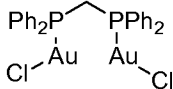
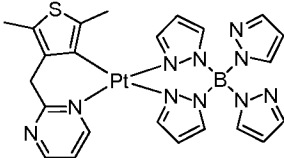
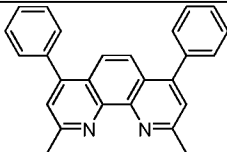
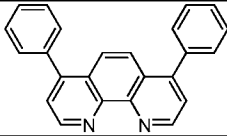
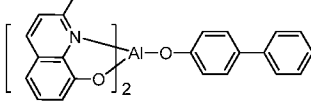
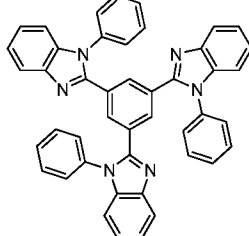
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Metal phenoxypyridine compounds		WO05030900
Blue hosts		
Arylcarbazoles		Appl. Phys. Lett, 82, 2422 (2003)
		US20070190359
Dibenzothiophene-carbazole compounds		WO2006114966
Phosphorescent dopants		
Red dopants		
Heavy metal porphyrins (e.g., PtOEP)		Nature 395, 151 (1998)
Iridium(III) organometallic complexes		Appl. Phys. Lett. 78, 1622 (2001)
		US06835469
		US06835469

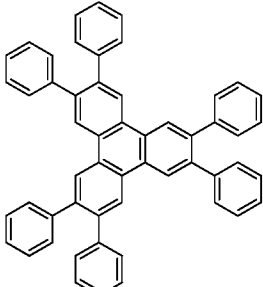
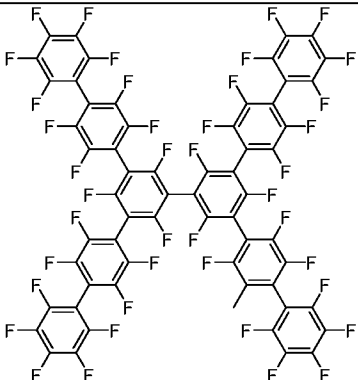
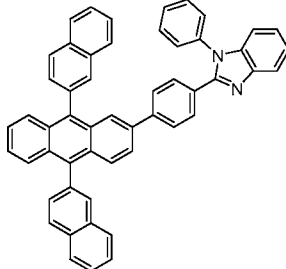
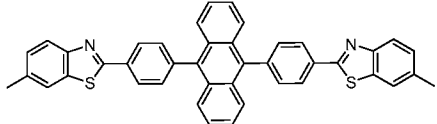
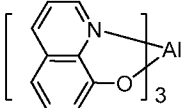
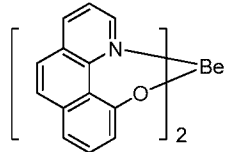
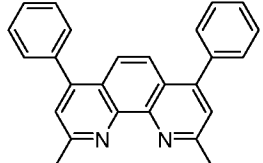
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		US20060202194
		US20060202194
		US07087321
		US07087321
		Adv. Mater. 19, 739 (2007)
Platinum(II) organometallic complexes		WO2003040257
Osmium(III) complexes		Chem. Mater. 17, 3532 (2005)
Ruthenium(II) complexes		Adv. Mater. 17, 1059 (2005)
Green dopants		

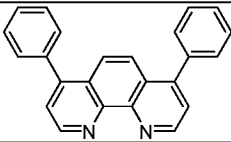
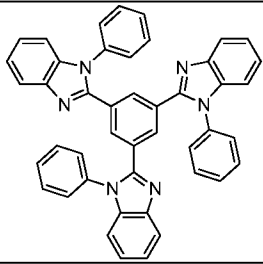
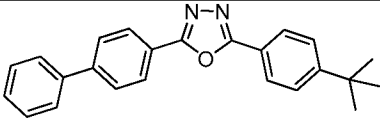
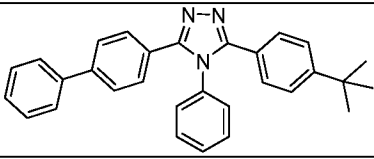
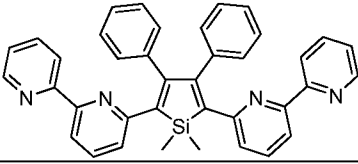
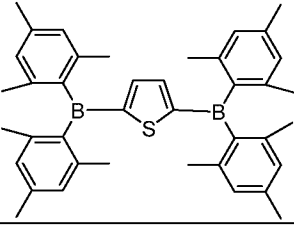
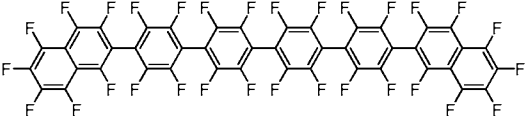
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Iridium(III) organometallic complexes	 <p>and its derivatives</p>	Inorg. Chem. 40, 1704 (2001)
		US2002034656
		US06687266
		Chem. Mater. 16, 2480 (2004)
		US2007190359
		US 2006008670 JP2007123392
		Adv. Mater. 16, 2003 (2004)
		Angew. Chem. Int. Ed. 2006, 45, 7800

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Pt(II) organometallic complexes		Appl. Phys. Lett. 86, 153505 (2005)
		Appl. Phys. Lett. 86, 153505 (2005)
		Chem. Lett. 34, 592 (2005)
Gold complexes		Chem. Commun. 2906 (2005)
Rhenium(III) complexes		Inorg. Chem. 42, 1248 (2003)
Blue dopants		
Iridium(III) organometallic complexes		WO2002002714
		WO2006009024
		US2006251923

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)
		WO05123873
		WO05123873
		WO07004380

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		WO06082742
Osmium(II) complexes		US2005260449
		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., BAQ)		Appl. Phys. Lett. 81, 162 (2002)
5-member ring electron deficient heterocycles such as triazole, oxadiazole, imidazole, benzoimidazole		Appl. Phys. Lett. 81, 162 (2002)

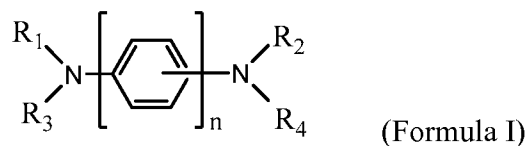
MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
Triphenylene compounds		US20050025993
Fluorinated aromatic compounds		Appl. Phys. Lett. 79, 156 (2001)
Electron transporting materials		
Anthracene-benzimidazole compounds		WO03060956
Anthracene-benzothiazole compounds		Appl. Phys. Lett. 89, 063504 (2006)
Metal 8-hydroxyquinolates (e.g., Alq ₃)		Appl. Phys. Lett. 51, 913 (1987)
Metal hydroxybenzoquinolates		Chem. Lett. 5, 905 (1993)
Bathocuprine compounds such as BCP, BPhen, etc		Appl. Phys. Lett. 91, 263503 (2007)

MATERIAL	EXAMPLES OF MATERIAL	PUBLICATIONS
		Appl. Phys. Lett. 79, 449 (2001)
5-member ring electron deficient heterocycles (e.g., triazole, oxadiazole, imidazole, benzoimidazole)		Appl. Phys. Lett. 74, 865 (1999)
		Appl. Phys. Lett. 55, 1489 (1989)
		Jpn. J. Apply. Phys. 32, L917 (1993)
Silole compounds		Org. Electron. 4, 113 (2003)
Arylborane compounds		J. Am. Chem. Soc. 120, 9714 (1998)
Fluorinated aromatic compounds		J. Am. Chem. Soc. 122, 1832 (2000)

[0079] 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.

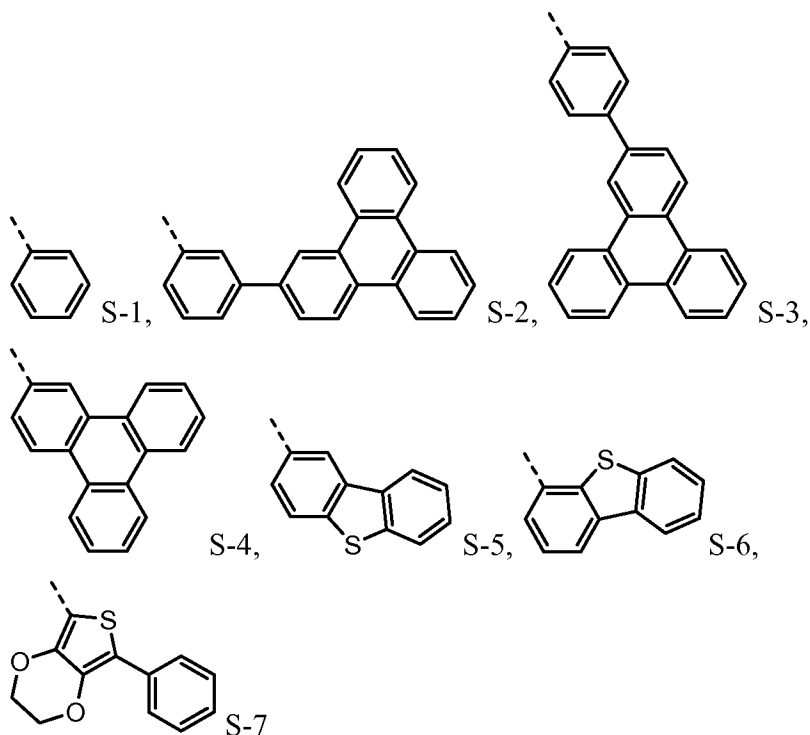
CLAIMS

1. A composition of matter having the chemical structure:



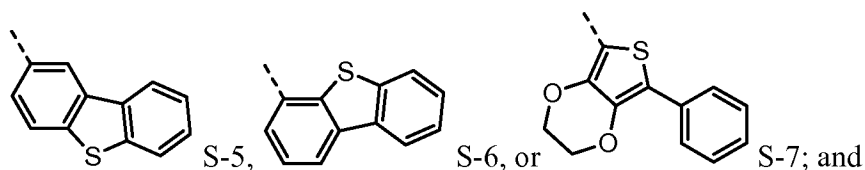
wherein n is 1, 2 or 3, and the phenyl rings between the nitrogen atoms may be attached to each other and to the nitrogen atoms in a para or meta configuration independently selected for each attachment;

wherein each of R₁, R₂, R₃ and R₄ are independently selected from the group consisting of:



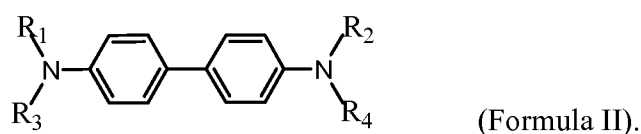
wherein the dotted line shows the point of attachment to an N atom of Formula I;

wherein at least one of R₁, R₂, R₃ and R₄ is selected from the group consisting of:

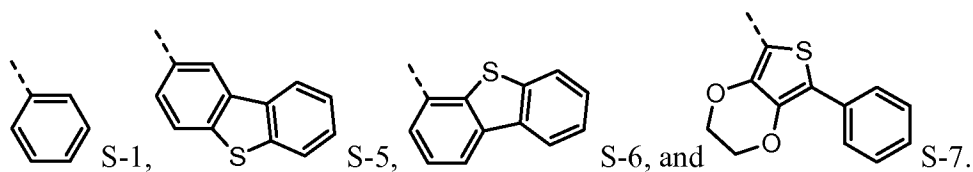


wherein each of R_1 , R_2 , R_3 and R_4 may be further substituted with substituents that are not fused to R_1 , R_2 , R_3 and R_4 .

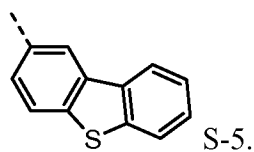
2. The composition of matter of claim 1, wherein the part of the composition represented by Formula I is more specifically:



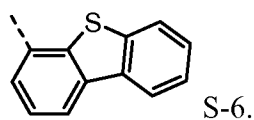
3. The composition of matter of claim 1, wherein each of R_1 , R_2 , R_3 and R_4 are independently selected from the group consisting of:



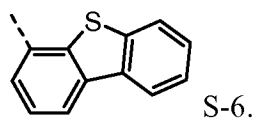
4. The composition of matter of claim 1, wherein at least one of R_1 , R_2 , R_3 and R_4 is



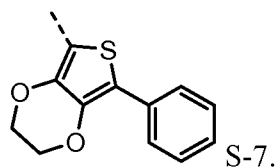
5. The composition of matter of claim 1, wherein at least one of R_1 , R_2 , R_3 and R_4 is



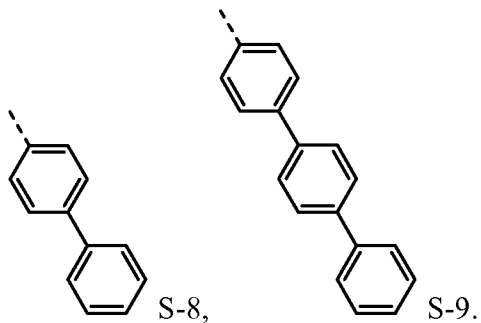
6. The composition of matter of claim 1, wherein both R_1 and R_2 are



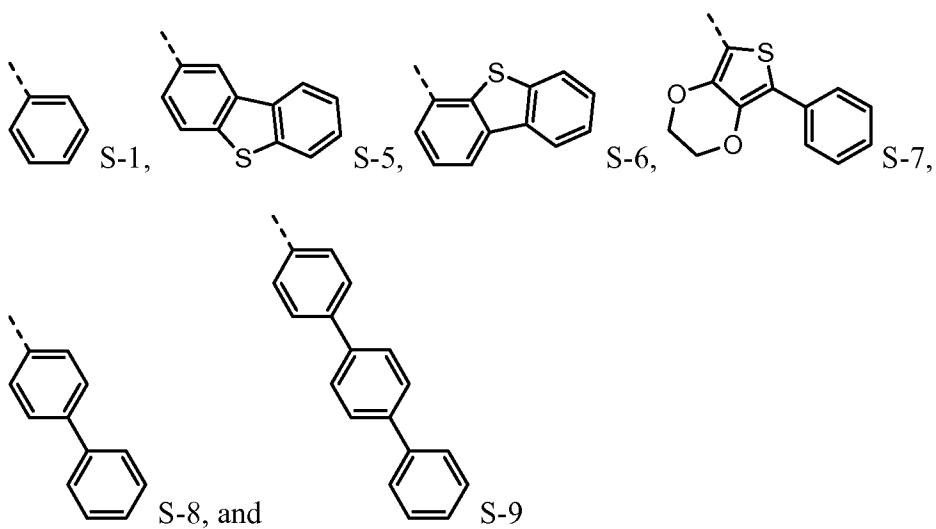
7. The composition of matter of claim 1, wherein at least one of R_1 , R_2 , R_3 and R_4 is



8. The composition of matter of claim 1, wherein at least one of R_1 , R_2 , R_3 and R_4 is selected from the group consisting of:

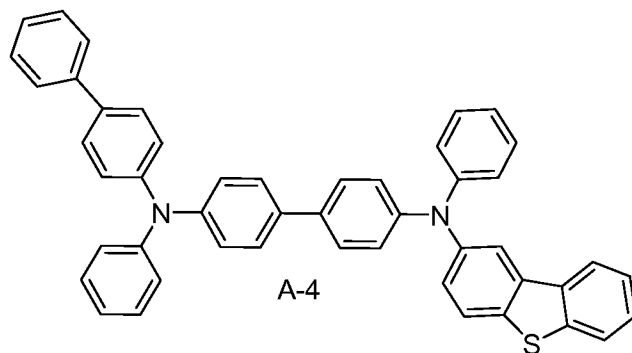
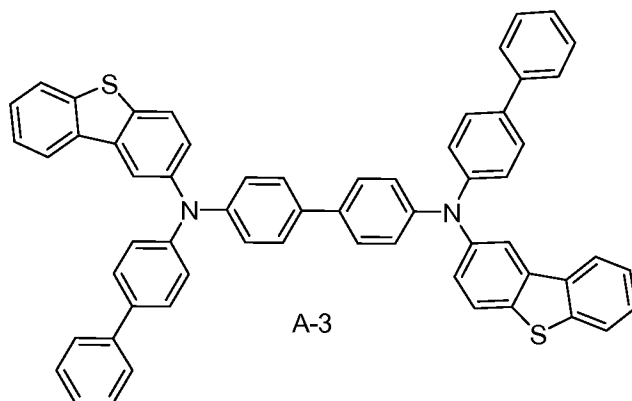
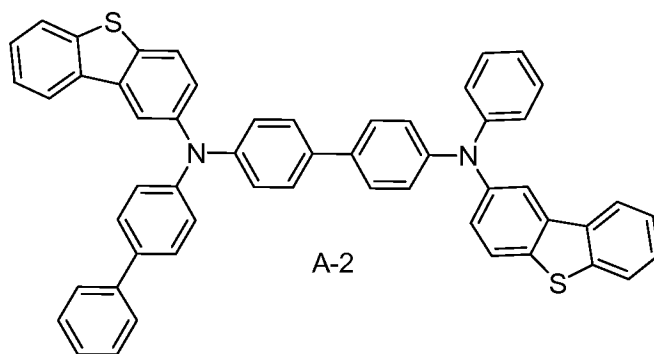
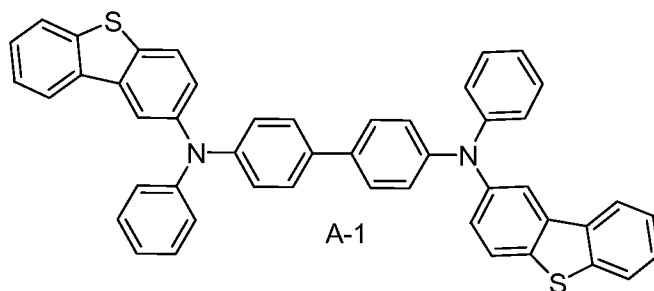


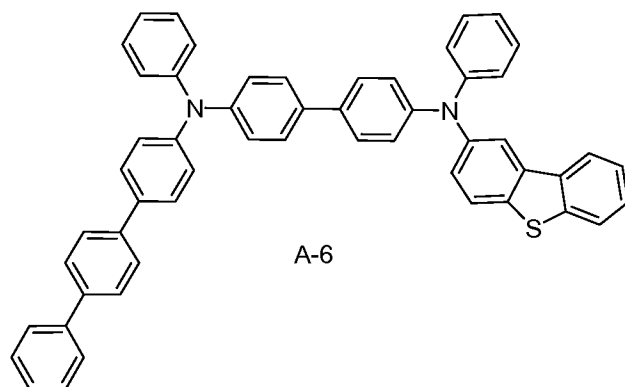
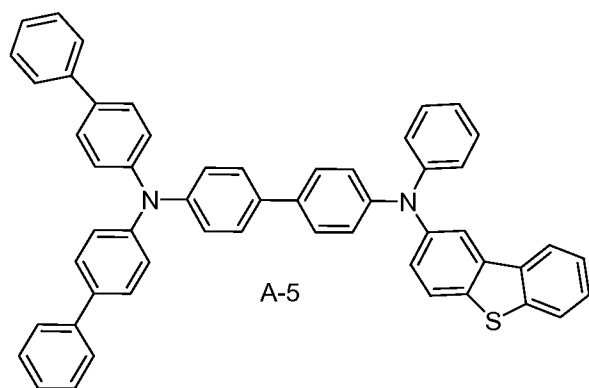
9. The composition of matter of claim 1, wherein each of R_1 , R_2 , R_3 and R_4 is independently selected from the group consisting of:



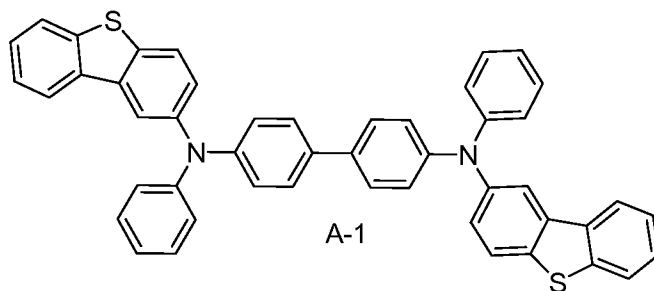
and there are no further substitutions to R₁, R₂, R₃ and R₄.

10. The composition of matter of claim 4, wherein the composition of matter has a structure selected from the group consisting of:

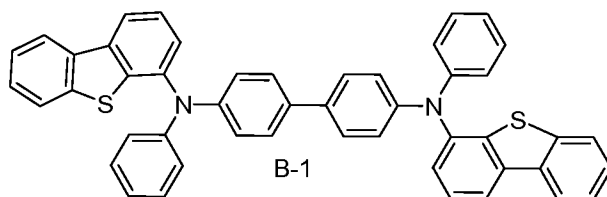


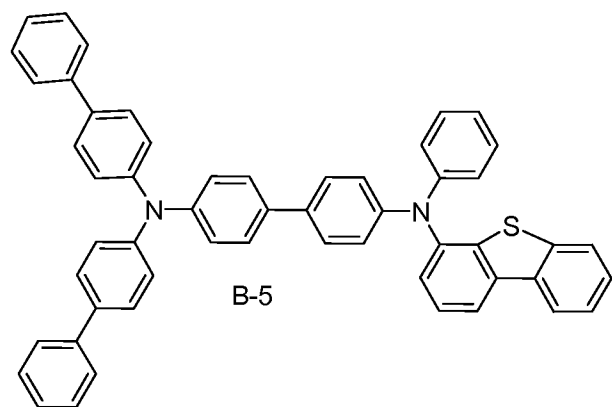
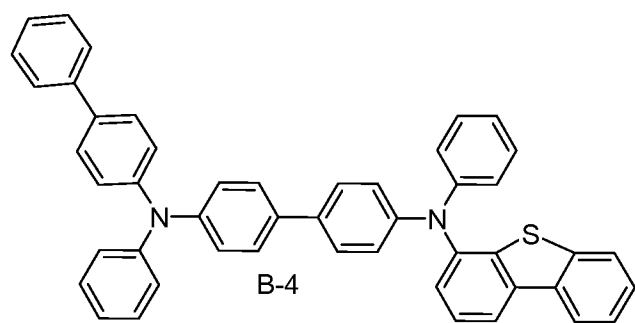
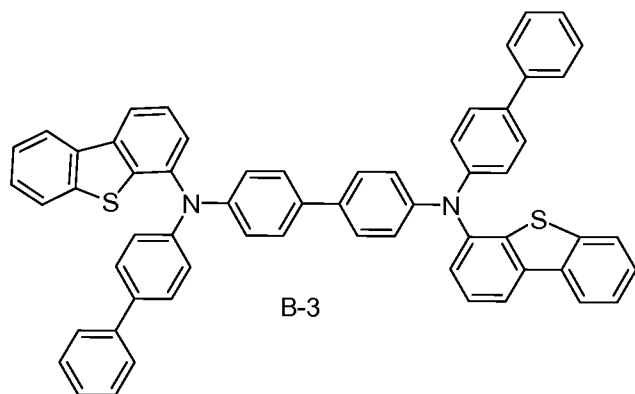
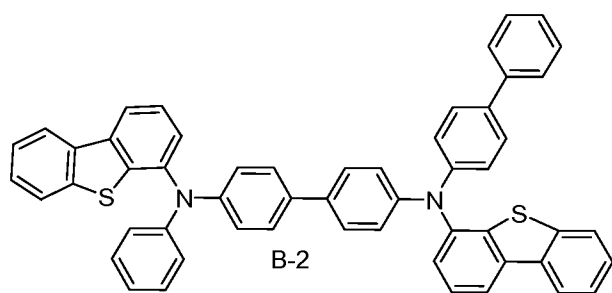


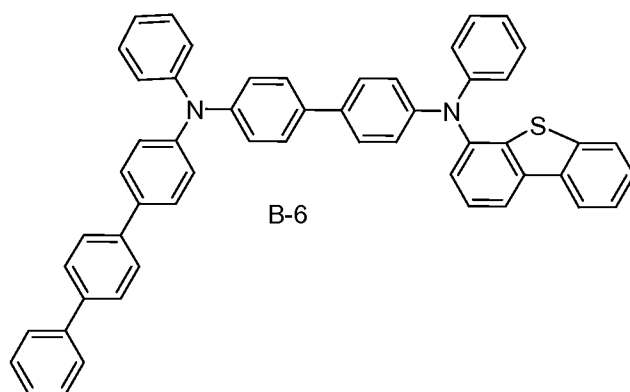
11. The composition of matter of claim 10, wherein the composition of matter has the structure:



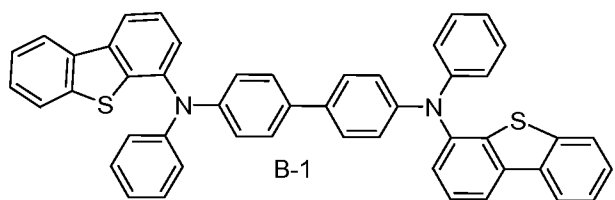
12. The composition of matter of claim 5, wherein the composition of matter has a structure selected from the group consisting of:



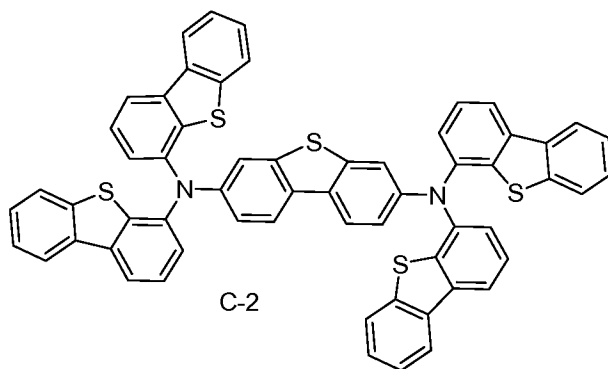
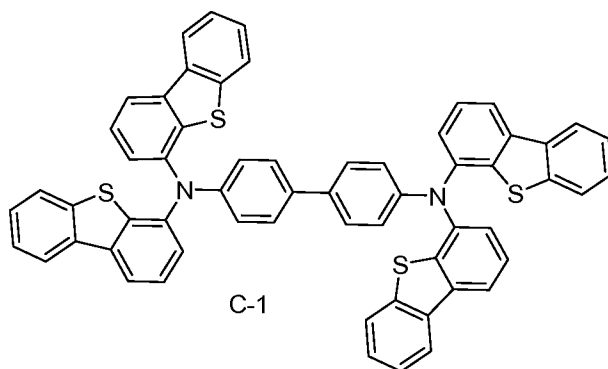


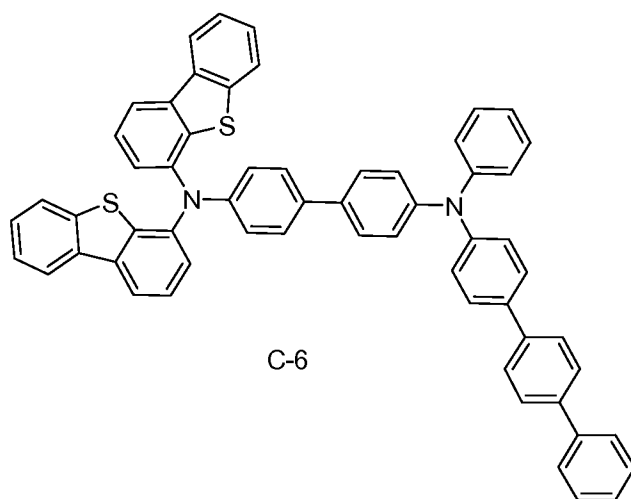
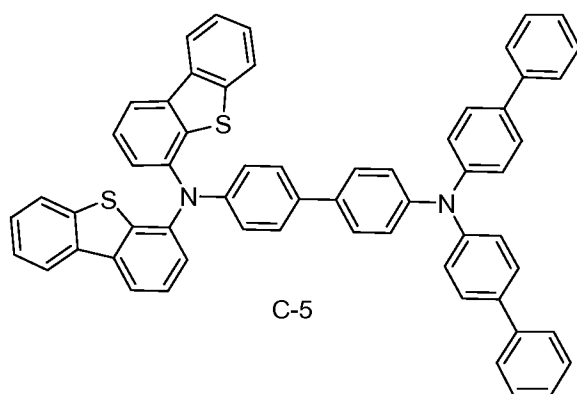
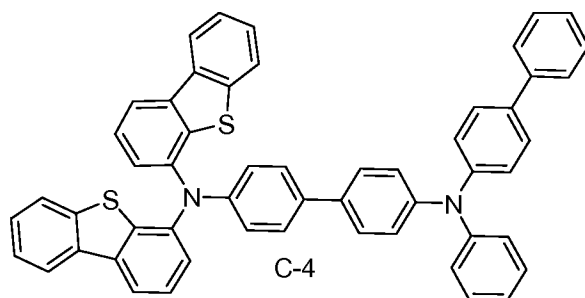
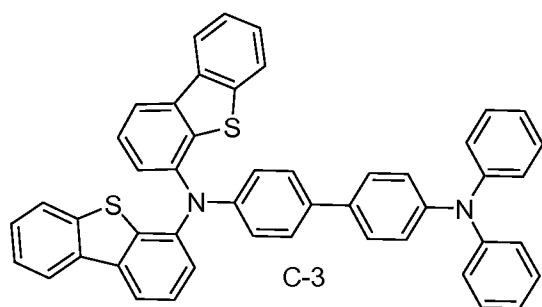


13. The composition of matter of claim 12, wherein the composition of matter has the structure:

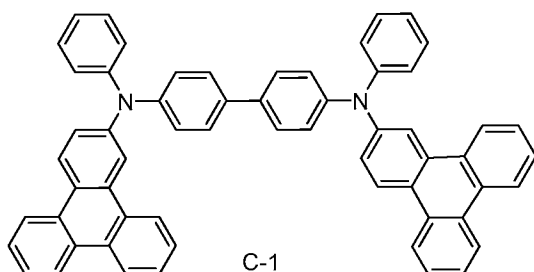


14. The composition of matter of claim 6, wherein the composition of matter has a structure selected from the group consisting of:

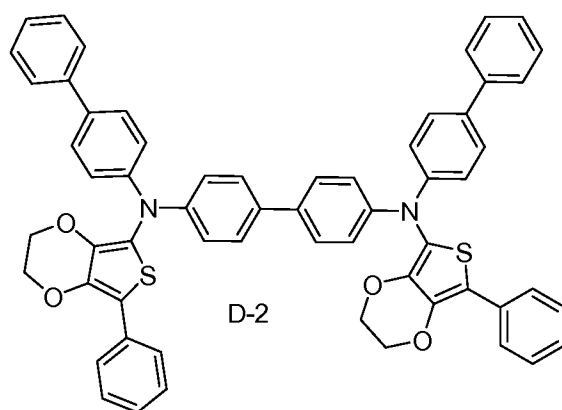
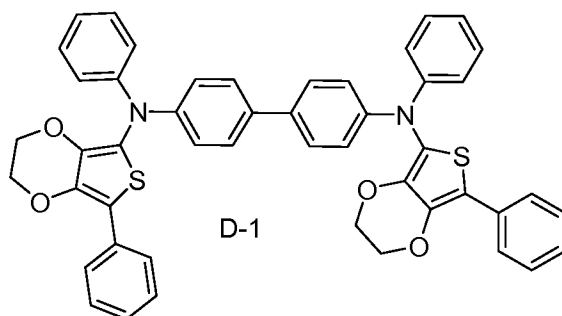


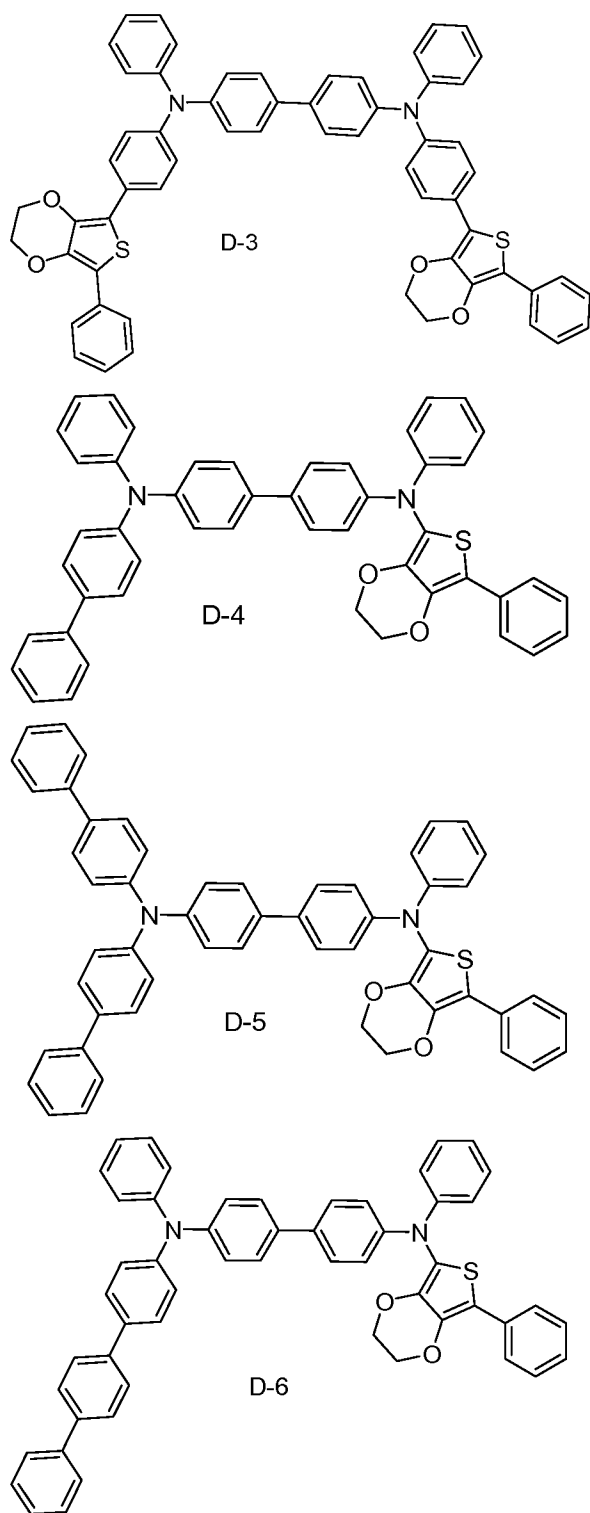


15. The composition of matter of claim 14, wherein the composition of matter has the structure:

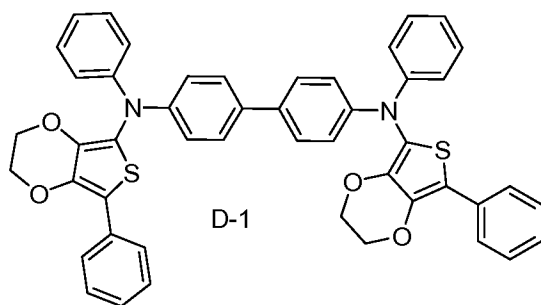


16. The composition of matter of claim 7, wherein the composition of matter has a structure selected from the group consisting of:



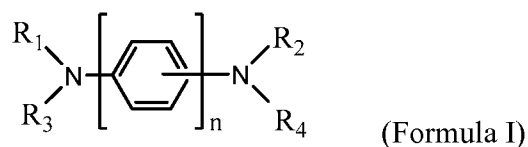


17. The composition of matter of claim 16, wherein the composition of matter has the structure:



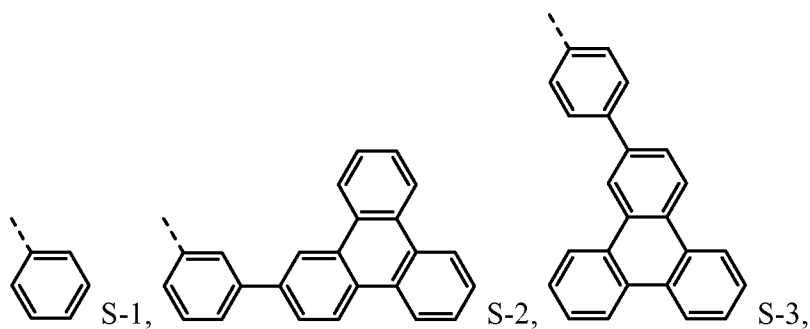
18. An organic light emitting device comprising:
 an anode;
 a cathode;
 an organic emissive layer, disposed between the anode and the cathode, the organic emissive layer further comprising a host and a phosphorescent dopant,
 an organic hole transport layer comprising a hole transport material, disposed between the organic emissive layer and the anode, and in direct contact with the organic emissive layer;

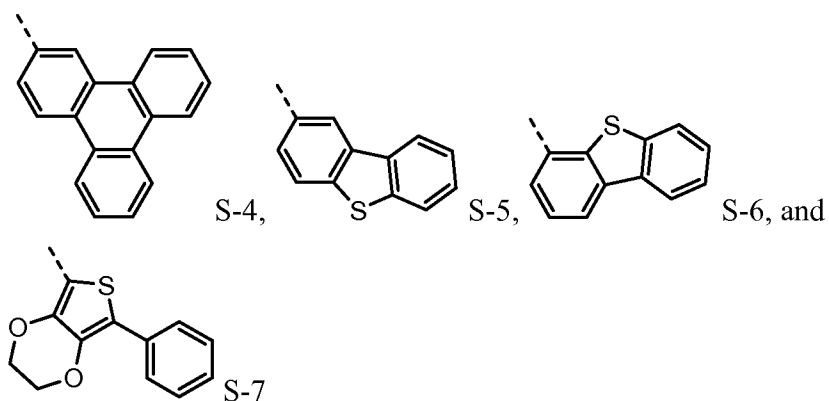
wherein the hole transport material has the structure:



wherein n is 1, 2 or 3, and the phenyl rings between the nitrogen atoms may be attached to each other and to the nitrogen atoms in a para or meta configuration independently selected for each attachment;

wherein each of R₁, R₂, R₃ and R₄ are independently selected from the group consisting of:



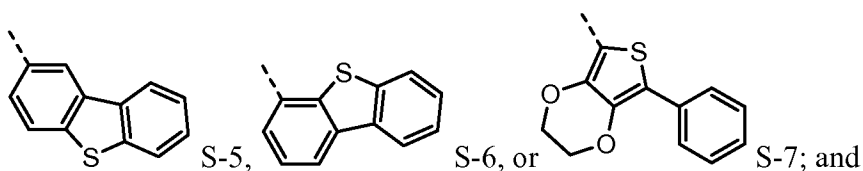


wherein the dotted line shows the point of attachment to an N atom of Formula

I;

wherein at least one of R_1 , R_2 , R_3 and R_4 is selected from the group consisting

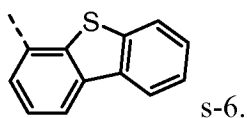
of:



wherein each of R_1 , R_2 , R_3 and R_4 may be further substituted with substituents that are not fused to R_1 , R_2 , R_3 and R_4 .

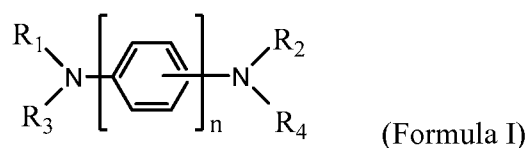
19. The device of claim 18, wherein the dopant is an organo-metallic iridium material.

20. The device of claim 18, wherein at least one of R_1 , R_2 , R_3 and R_4 is



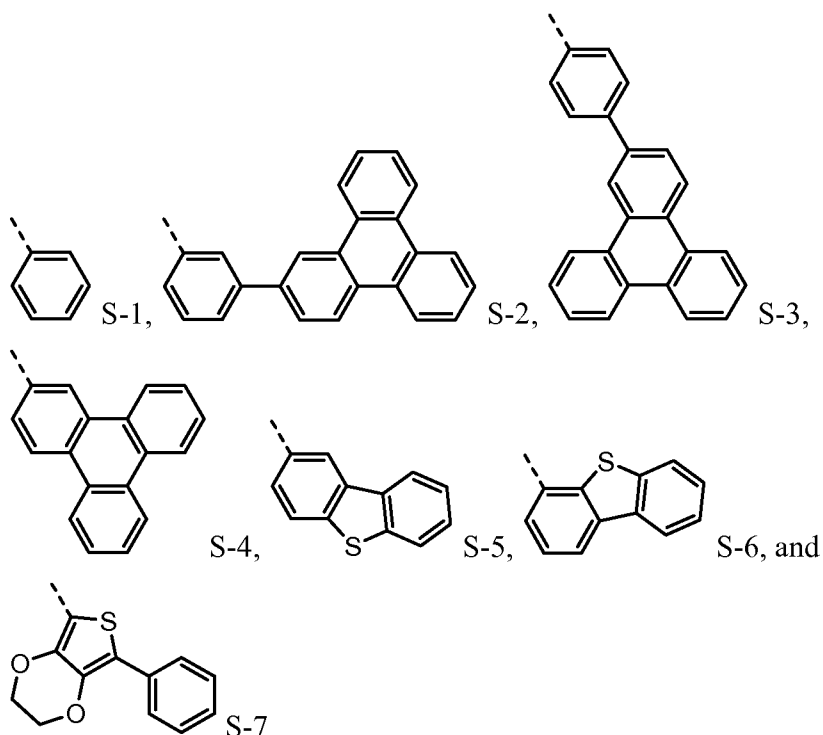
21. The device of claim 20, wherein the host is a compound comprising a triphenylene containing benzo-fused thiophene.

22. A consumer product, wherein the consumer product includes an organic light emitting device that further includes a composition of matter having the chemical structure:



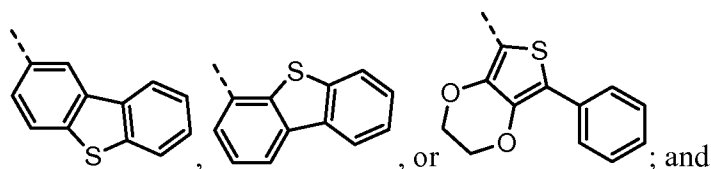
wherein n is 1, 2 or 3, and the phenyl rings between the nitrogen atoms may be attached to each other and to the nitrogen atoms in a para or meta configuration independently selected for each attachment;

wherein each of R₁, R₂, R₃ and R₄ are independently selected from the group consisting of:



wherein the dotted line shows the point of attachment to an N atom of Formula I;

wherein at least one of R₁, R₂, R₃ and R₄ is selected from the group consisting of:



wherein each of R₁, R₂, R₃ and R₄ may be further substituted with substituents that are not fused to R₁, R₂, R₃ and R₄.

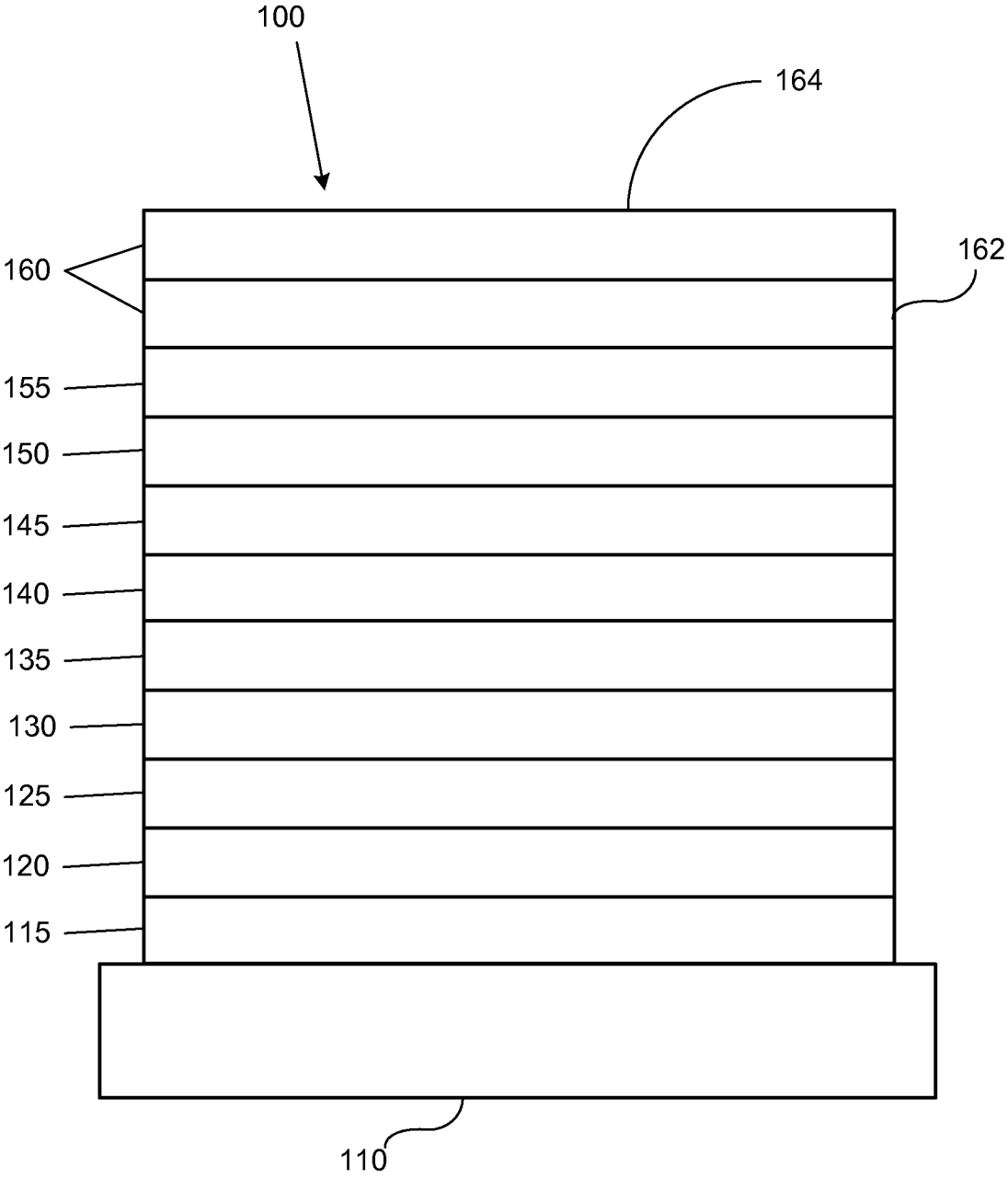


FIGURE 1

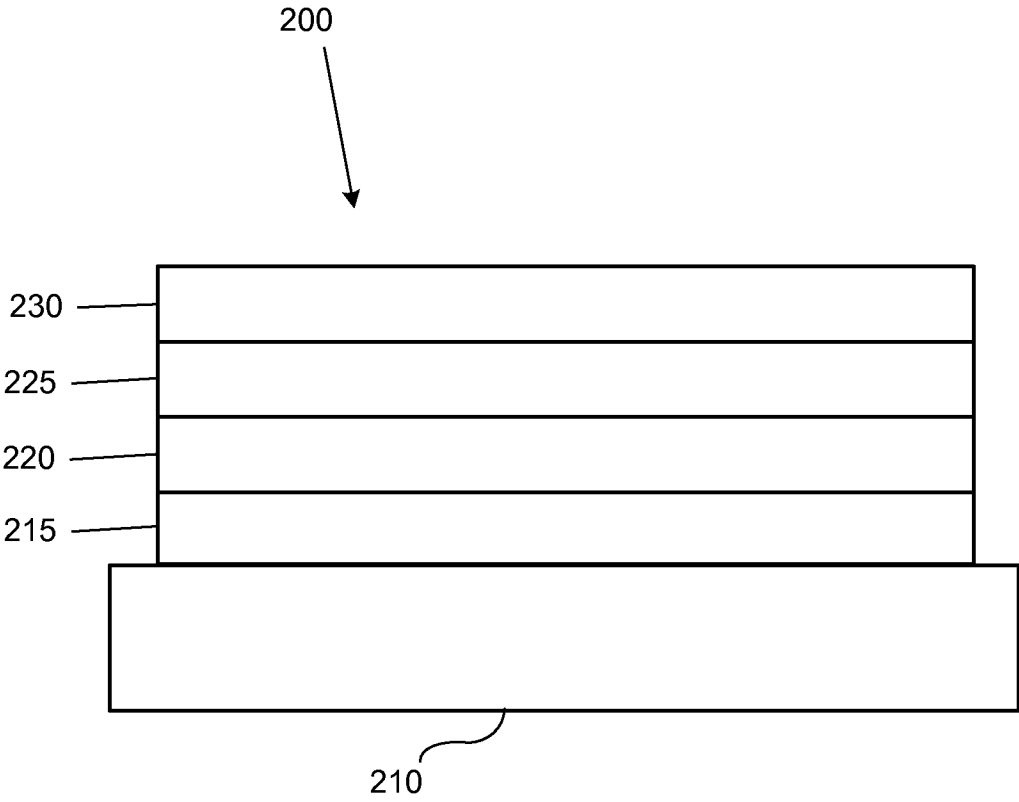
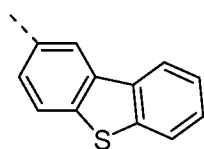
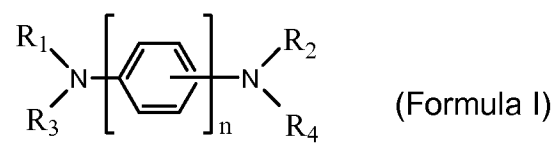
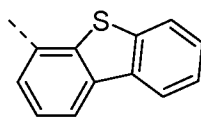


FIGURE 2

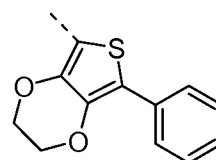
3 / 3



S-5



S-6



S-7

FIGURE 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/049186

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/06 H05B33/14 H01L51/00

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)
H01L C09K H05B

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007/088167 A1 (LIN CHUN [US] ET AL) 19 April 2007 (2007-04-19) abstract table 3 examples 1-20 table 4 examples A-F	1-14, 16-22
A	WO 03/064373 A (SYNTEC GES FUER CHEMIE UND TEC [DE]; RICHTER ANDREAS M [DE]; LISCHEWSK) 7 August 2003 (2003-08-07) abstract page 2 compound 24 the whole document	1-14, 16-22

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * & * document member of the same patent family

Date of the actual completion of the international search

26 August 2009

Date of mailing of the international search report

11/09/2009

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
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Authorized officer

Heer, Stephan

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2009/049186

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-9 (part), 15, 18-22 (part)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers allsearchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search reportcovers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-9 (part), 15, 18-22 (part)

The present independent claim 1 relates to an extremely large number of possible compositions of matter. Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of the compositions of matter claimed, see the synthetic examples to produce compounds A-1, B-1, C-1 and D-1 and the organic light emitting device examples 2 and 4. The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of independent claim 1 (PCT Guidelines 9.19 and 9.23).

A similar argumentation applies for claims 2-9 and 18-22.

Dependent claim 15 was not searched, since it appears that there is neither a support nor a disclosure how to produce such a structure.

The search of independent claim 1 was restricted to those compositions of matter which appear to be supported and a generalisation of their structural formulae. The restricted subject-matter can be defined as follows:

Independent claim 1, wherein

- formula I is replaced by formula II defined in dependent claim 2
- R1, R2, R3 and R4 are selected from the formulas S-1, S-5, S-6, S-7, S-8 and S-9 as defined in dependent claim 9.
- R1, R2, R3 and R4 are unsubstituted

The claims 2-9 and 18-22 were restricted accordingly.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2)PCT declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2009/049186

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007088167 A1	19-04-2007	WO 2008054584 A1	08-05-2008
WO 03064373 A	07-08-2003	CN 1602293 A	30-03-2005
		DE 10203328 A1	07-08-2003
		EP 1470100 A1	27-10-2004
		JP 2005516059 T	02-06-2005
		US 2005067951 A1	31-03-2005

专利名称(译)	具有含硫基团的空穴传输材料		
公开(公告)号	EP2321376A1	公开(公告)日	2011-05-18
申请号	EP2009774299	申请日	2009-06-30
[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	LIN CHUN MA BIN XIA CHUANJUN WU YONGGANG KWONG RAYMOND		
发明人	LIN, CHUN MA, BIN XIA, CHUANJUN WU, YONGGANG KWONG, RAYMOND		
IPC分类号	C09K11/06 H05B33/14 H01L51/00		
CPC分类号	C09K11/06 C07D333/76 C07D495/04 C07D519/00 C09K2211/1007 C09K2211/1011 C09K2211/1014 C09K2211/1018 C09K2211/1092 H01L51/0037 H01L51/004 H01L51/0052 H01L51/0059 H01L51/006 H01L51/0061 H01L51/0071 H01L51/0074 H01L51/0078 H01L51/0085 H01L51/0086 H01L51/0087 H01L51/0088 H01L51/5048		
代理机构(译)	MAIWALD专利ADVOCATE GMBH		
优先权	61/077073 2008-06-30 US		
其他公开文献	EP2321376B1		
外部链接	Espacenet		

摘要(译)

提供了具有单个苯基或苯基链的新型材料，其中在单个苯基或苯基链的每个末端上存在氮原子。氮原子可以进一步被特定的噻吩，苯并噻吩和三亚苯基取代。还提供了有机发光器件，其中新型材料用作器件中的空穴传输材料。还提供了空穴传输材料与特定主体材料的组合。