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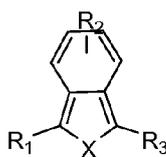
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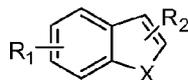
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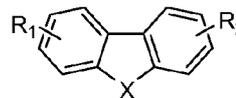
(54) **Title:** BENZO-FUSED THIOPHENE / TRIPHENYLENE HYBRID MATERIALS



Formula (IV)



Formula (V)



Formula (VI)

FIGURE 3

(57) **Abstract:** Triphenylene containing benzo-fused thiophene compounds are provided. Additionally, triphenylene containing benzo-fused furan compounds are provided. The compounds may be useful in organic light emitting devices, particularly as hosts in the emissive layer of such devices, or as materials for enhancement layers in such devices, or both.

BENZO-FUSED THIOPHENE / TRIPHENYLENE HYBRID MATERIALS

[0001] This application claims priority to U.S. Provisional Application Serial No. 60/963,944, filed August 8, 2007, U.S. Provisional Application Serial No. 61/017,506, filed December 28, 2007, and U.S. Provisional Application Serial No. 61/017,391, filed December 28, 2007, the disclosures of which are herein expressly incorporated by reference in their entirety. This application is also related to International Application Serial No. PCT/US07/89131, filed on December 28, 2007.

[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 organic materials having a benzo-fused thiophene and/or a benzo-fused furan and a triphenylene. In particular, the materials have a dibenzothiophene and/or benzofuran and a triphenylene. The materials may be useful in light emitting devices (OLEDs).

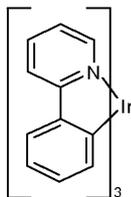
BACKGROUND

[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.

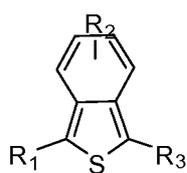
[0012] A ligand is referred to as "photoactive" when it is believed that the ligand contributes to the photoactive properties of an emissive material.

[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.

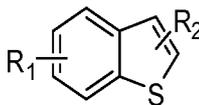
SUMMARY OF THE INVENTION

[0014] Triphenylene containing benzo-fused thiophene compounds are provided. The compounds may be useful in organic light emitting devices. The compounds may be particularly useful as the host of an emissive layer of an organic light emitting device, as a material for an enhancement layer, or both.

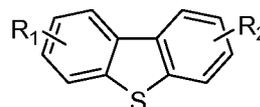
[0015] Examples of triphenylene-containing benzo-fused thiophenes include compounds having the structure of Formula (I), Formula (II), and Formula (III):



Formula (I)



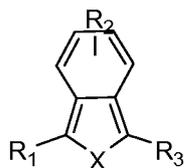
Formula (II)



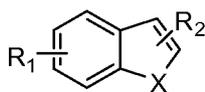
Formula (III)

R_1 , R_2 and R_3 are independently selected from alkyl, alkoxy, amino, alkenyl, alkynyl, arylkyl, aryl, heteroaryl and hydrogen. Each of R_1 , R_2 and R_3 may represent multiple substituents. At least one of R_1 , R_2 and R_3 includes a triphenylene group. The triphenylene group may be linked directly to the structure of Formula (I), (II) or (III), but there may also be a "spacer" in between the triphenylene group and the structure of Formula (I), (II) or (III).

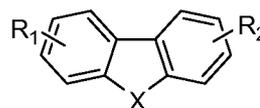
[0016] Examples of triphenylene containing benzo-fused thiophenes or benzo-fused furans include compounds having the structure:



Formula (IV)



Formula (V)



Formula (VI)

X is S or O. Preferably, R_1 , R_2 , and R_3 are unfused substituents that are independently selected from C_nH_{2n+1} , OC_nH_{2n+1} , OAr_1 , $N(C_nH_{2n+1})_2$, $N(Ar_1)(Ar_2)$, $CH=CH-C_nH_{2n+1}$, $C=CHC_nH_{2n+1}$, Ar_1 , Ar_1-Ar_2 , $C_nH_{2n}-Ar_1$, or no substitution. Each of R_1 , R_2 , and R_3 may represent mono, di, tri, or tetra substitutions. n is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10. Ar_1 and Ar_2 are independently selected from the group consisting of benzene, biphenyl, naphthalene, triphenylene, carbazole, and heteroaromatic analogs thereof. At least one of R_1 , R_2 , and R_3 includes a triphenylene group.

[0017] More specific examples of useful triphenylene containing benzo-fused thiophene compounds and triphenylenes containing benzo-fused furan compounds include Compounds 1G-48G and Compounds 1-48, as disclosed herein. The compounds may be useful as the host of an emissive layer of an organic light emitting device, an enhancement layer material of such a device, or both.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] FIG. 1 shows an organic light emitting device.

[0019] FIG. 2 shows an inverted organic light emitting device that does not have a separate electron transport layer.

[0020] FIG. 3 shows triphenylene-containing benzo-fused thiophene and/or benzo-fused furan compounds.

DETAILED DESCRIPTION

[0021] 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.

[0022] 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.

[0023] 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.

[0024] FIG. 1 shows an organic light emitting device 100. The figures are not necessarily drawn to scale. Device 100 may include a substrate 110, an anode 115, a hole injection layer 120, a hole transport layer 125, an electron blocking layer 130, an emissive layer 135, a hole blocking layer 140, an electron transport layer 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.

[0025] 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. 2004/01741 16, which is incorporated by reference in its entirety. A description of protective layers may be found in U.S. Patent Application Publication No. 2004/01741 16, which is incorporated by reference in its entirety. An "enhancement layer" occupies the same position in a device as a blocking layer described above, and may have blocking functionality or other functionality that improves device performance.

[0026] 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.

[0027] 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.

[0028] 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 BuIovio et al., which are incorporated by reference in their entireties.

[0029] 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 (OVDP), 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.

[0030] 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).

[0031] 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.

[0032] The terms halo, halogen, alkyl, cycloalkyl, alkenyl, alkynyl, arylkyl, heterocyclic group, aryl, 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.

[0033] Compounds are provided, comprising a triphenylene-containing benzo-fused thiophene. Triphenylene is a polyaromatic hydrocarbon with high triplet energy, yet high π -conjugation and a relatively small energy difference between the first singlet and first triplet levels. This would indicate that triphenylene has relatively easily accessible HOMO and LUMO levels compared to other aromatic compounds with similar triplet energy (e.g., biphenyl). The advantage of using triphenylene and its derivatives as hosts is that it can accommodate red, green and even blue phosphorescent dopants to give high efficiency without energy quenching. Triphenylene hosts may be used to provide high efficiency and stability PHOLEDs. See Kwong and Alleyene, *Triphenylene Hosts in Phosphorescent Light Emitting Diodes*, 2006, 60 pp, US 2006/0280965 A1. Benzo-fused thiophenes may be used as hole transporting organic conductors. In addition, the triplet energies of benzothiophenes, namely dibenzo[*b*,*i*]thiophene (referred to herein as "dibenzothiophene"), benzo[*b*]thiophene and benzo[*c*]thiophene are relatively high. A combination of benzo-fused thiophenes and

triphenylene as hosts in PHOLED may be beneficial. More specifically, benzo-fused thiophenes are typically more hole transporting than electron transporting, and triphenylene is more electron transporting than hole transporting. Therefore combining these two moieties in one molecule may offer improved charge balance which may improve device performance in terms of lifetime, efficiency and low voltage. Different chemical linkage of the two moieties can be used to tune the properties of the resulting compound to make it the most appropriate for a particular phosphorescent emitter, device architecture, and / or fabrication process. For example, m-phenylene linkage is expected to result in higher triplet energy and higher solubility whereas p-phenylene linkage is expected to result in lower triplet energy and lower solubility.

[0034] Similar to the characterization of benzo-fused thiophenes, benzo-fused furans are also typically hole transporting materials having relatively high triplet energy. Examples of benzo-fused furans include benzofuran and dibenzofuran. Therefore, a material containing both triphenylene and benzofuran may be advantageously used as host or hole blocking material in PHOLED. A compound containing both of these two groups may offer improved electron stabilization which may improve device stability and efficiency with low voltage. The properties of the triphenylene containing benzofuran compounds may be tuned as necessary by using different chemical linkages to link the triphenylene and the benzofuran.

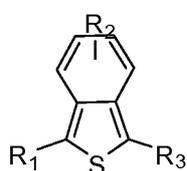
[0035] The compounds may be substituted with groups that are not necessarily triphenylenes, benzo-fused thiophenes, and benzo-fused furans. Preferably, any group that is used as a substituent of the compound has a triplet energy high enough to maintain the benefit of having triphenylene benzo-fused thiophenes or benzo-fused furans (i.e. the triplet energy of the substituent maintains the high triplet energy of benzo-fused thiophenes, benzo-fused furans and triphenylenes). Examples of such groups that may be used as substituents of the compound may include any substituent selected from C_nH_{2n+1} , OC_nH_{2n+1} , OAr_1 , $N(C_nH_{2n+1})_2$, $N(Ar_1)(Ar_2)$, $CH=CH-C_nH_{2n+1}$, $C=CHC_nH_{2n+1}$, Ar_1 , Ar_1-Ar_2 , $C_nH_{2n}-Ar_1$, or no substitution, wherein n is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10, and wherein Ar_1 and Ar_2 are independently selected from the group consisting of benzene, biphenyl, naphthalene, triphenylene, carbazole, and heteroaromatic analogs thereof. The compounds described herein have a high enough triplet energy to be suitable for use in a device having phosphorescent blue emissive materials.

[0036] The substituents of the compounds described herein are unfused such that the substituents are not fused to the triphenylene, benzo-fused furan or benzo-fused thiophene

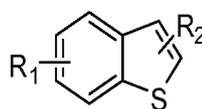
moieties of the compound. The substituents may optionally be inter-fused (i.e. fused to each other).

[0037] In addition to improved device stability and efficiency, the materials provided herein may also offer improved film formation in the device as fabricated by both vapor deposition and solution processing methods. In particular, materials offering improved fabrication have a central pyridine ring to which the benzo-fused thiophenylene and triphenylene, or benzofuran and triphenylene, are attached. The improved film formation is believed to be a result of the combination of polar and non-polar rings in the compound.

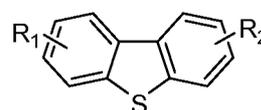
[0038] Examples of triphenylene-containing benzo-fused thiophenes include compounds having the structure of Formula (I), Formula (II), and Formula (III):



Formula (I)



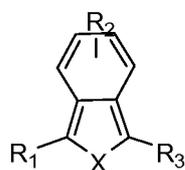
Formula (II)



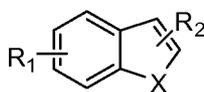
Formula (III)

R_1 , R_2 and R_3 are independently selected from alkyl, alkoxy, amino, alkenyl, alkynyl, arylkyl, aryl, heteroaryl and hydrogen. Each of R_1 , R_2 and R_3 may represent multiple substituents. At least one of R_1 , R_2 and R_3 includes a triphenylene group. The triphenylene group may be linked directly to the structure of Formula (I), (II) or (III), but there may also be a "spacer" in between the triphenylene group and the structure of Formula (I), (II) or (III).

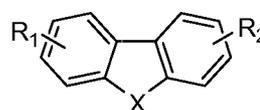
[0039] Examples of triphenylene containing benzo-fused thiophenes or benzo-fused furans include compounds having the structure:



Formula (IV)



Formula (V)

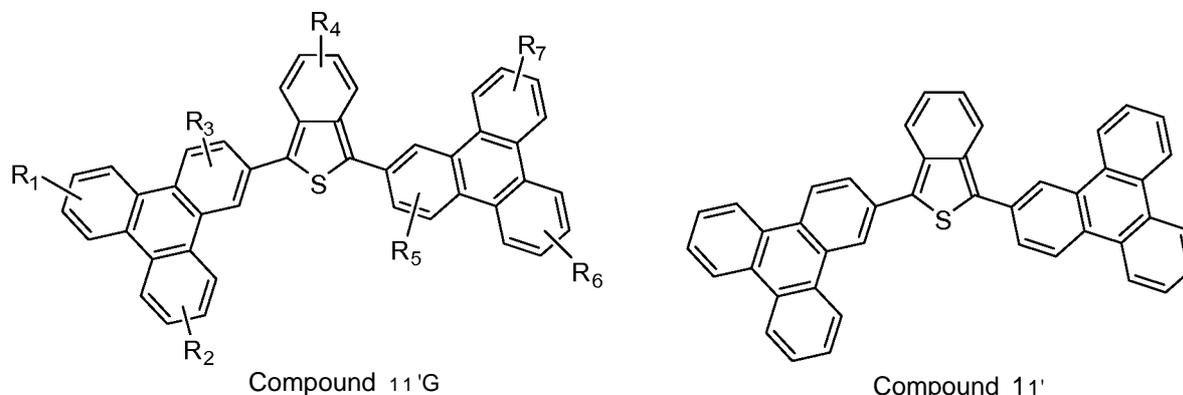


Formula (VI)

X is S or O. Preferably, R_1 , R_2 , and R_3 are unfused substituents that are independently selected from C_nH_{2n+1} , OC_nH_{2n+1} , OAn, $N(C_nH_{2n+1}O_2)$, $N(An)(Ar_2)$, $CH=CH-C_nH_{2n+1}$, $C=CHC_nH_{2n+1}$, Ar_1 , An- Ar_2 , $C_nH_{2n}-Ar_1$, or no substitution. Each of R_1 , R_2 , and R_3 may represent mono, di, tri, or tetra substitutions. n is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10. Ar_1 and Ar_2 are independently selected from the group consisting of benzene, biphenyl, naphthalene,

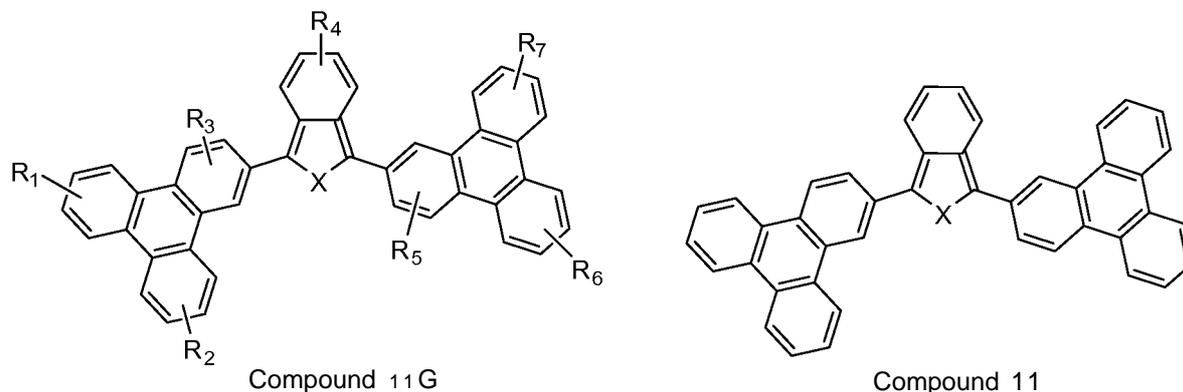
triphenylene, carbazole, and heteroaromatic analogs thereof. At least one of R_1 , R_2 , and R_3 includes a triphenylene group.

[0040] Examples of compounds having the structure of Formula(I) include:



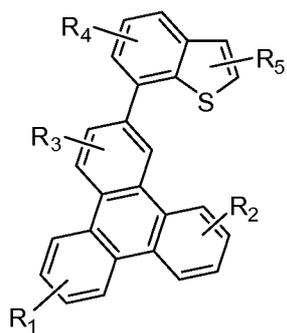
R_1 to R_n represents, independently, mono, di, tri or tetra substitutions selected from alkyl, alkoxy, amino, alkenyl, alkynyl, arylkyl, aryl and heteroaryl, or no substitution.

[0041] Examples of compounds having the structure of Formula(IV) include:

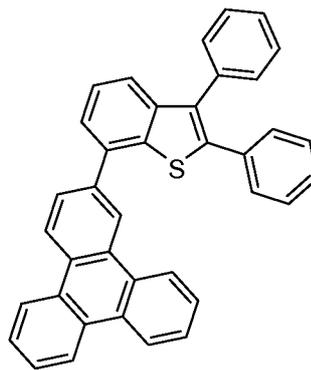


X is S or O. Preferably, X is S. R_1 to R_n are independently selected from the group consisting of C_nH_{2n+1} , OC_nH_{2n+1} , OAn, $N(C_nH_{2n+1}O_2)$, $N(An)(Ar_2)$, $CH=CH-C_nH_{2n+1}$, $C=CHC_nH_{2n+1}$, Ar_1 , An- Ar_2 , $C_nH_{2n}-Ar_1$, or no substitution. Each of R_1 to R_n may represent mono, di, tri, or tetra substitutions.. n is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10. Ar_1 and Ar_2 are independently selected from the group consisting of benzene, biphenyl, naphthalene, triphenylene, carbazole, and heteroaromatic analogs thereof. At least one of R_1 , R_2 , and R_3 includes a triphenylene group.

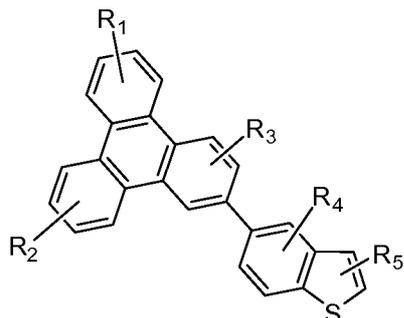
[0042] Examples of compounds having the structure of Formula(II) include:



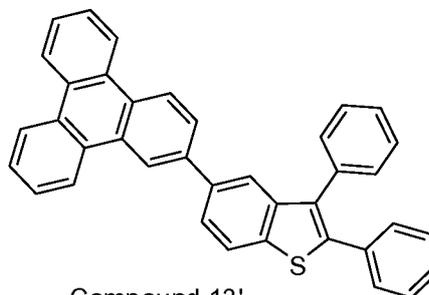
Compound 12'G



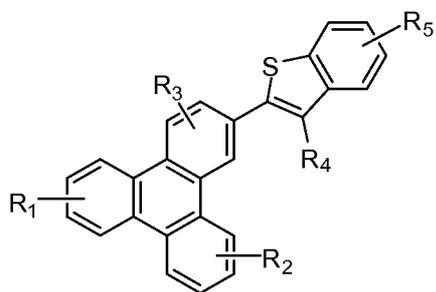
Compound 12'



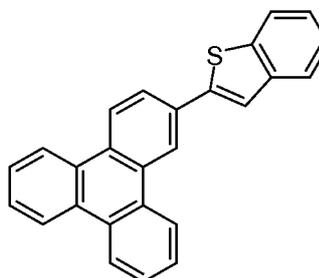
Compound 13'G



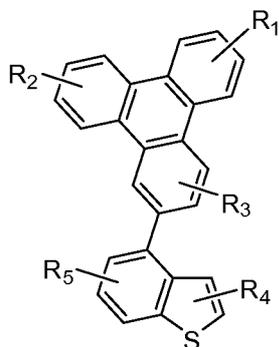
Compound 13'



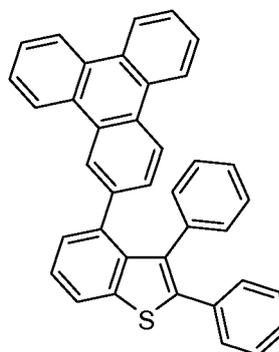
Compound 14'G



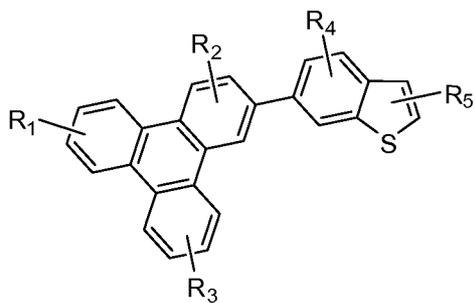
Compound 14'



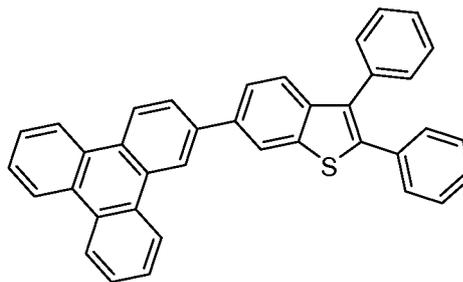
Compound 16'G



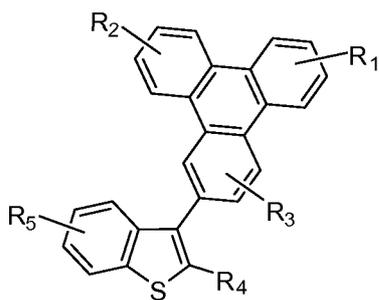
Compound 16'



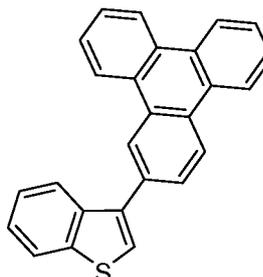
Compound 17'G



Compound 17'



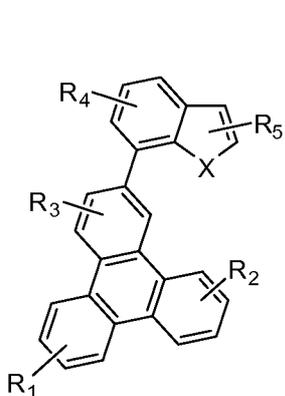
Compound 18'G



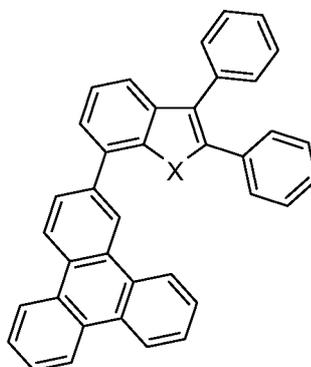
Compound 18'

[0043] R_i to R_n represents, independently, mono, di, tri or tetra substitutions selected from alkyl, alkoxy, amino, alkenyl, alkynyl, arylkyl, aryl and heteroaryl, or no substitution.

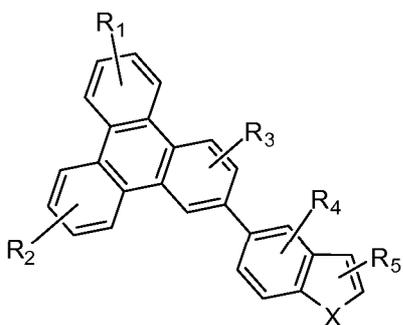
[0044] Examples of compounds having the structure of Formula(V) include:



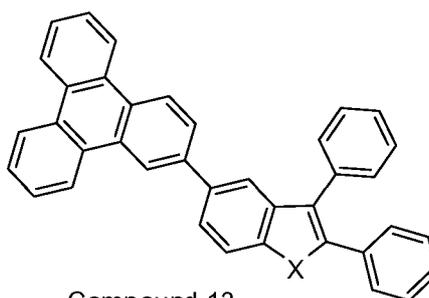
Compound 12G



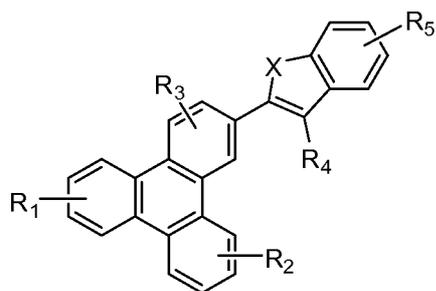
Compound 12



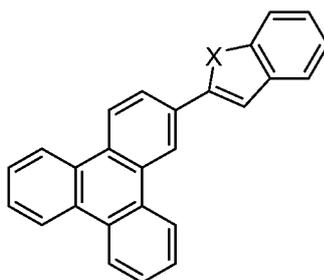
Compound 13G



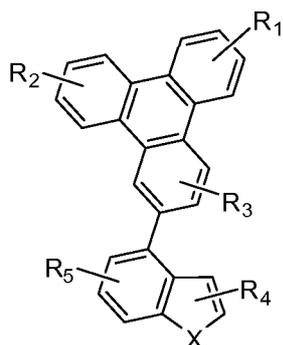
Compound 13



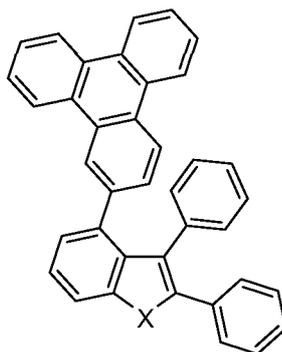
Compound 14G



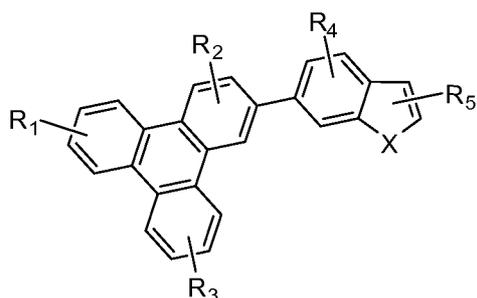
Compound 14



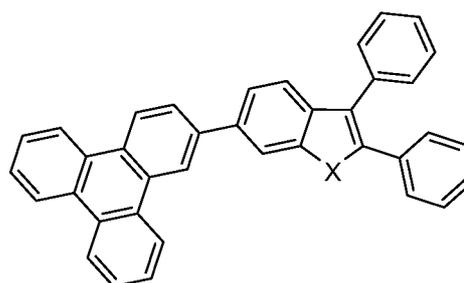
Compound 16G



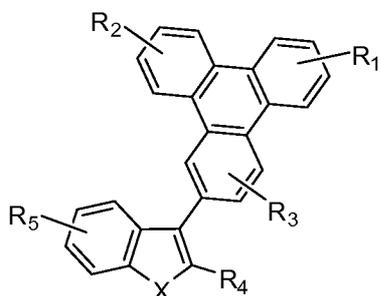
Compound 16



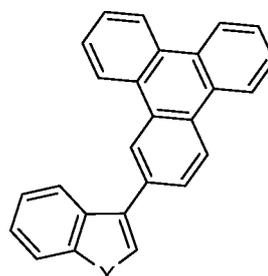
Compound 17G



Compound 17



Compound 18G

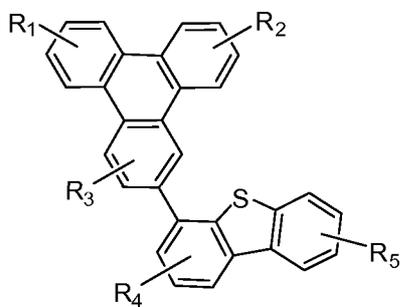


Compound 18

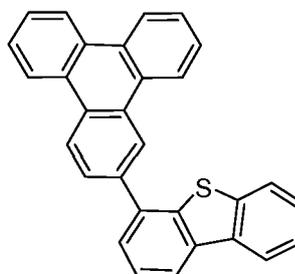
X is S or O. Preferably, X is S. R_1 to R_n are independently selected from the group consisting of C_nH_{2n+1} , OC_nH_{2n+1} , OAn , $N(C_nH_{2n+1})_2$, $N(An)(Ar_2)$, $CH=CH-C_nH_{2n+1}$, $C=CHC_nH_{2n+1}$, Ar_1 , Ar_1-Ar_2 , $C_nH_{2n}-Ar_1$, or no substitution. Each of R_1 to R_n may represent mono, di, tri, or tetra substitutions. n is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10. Ar_1 and Ar_2 are

independently selected from the group consisting of benzene, biphenyl, naphthalene, triphenylene, carbazole, and heteroaromatic analogs thereof. At least one of R_1 , R_2 , and R_3 includes a triphenylene group.

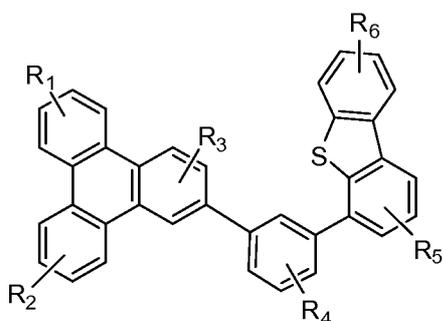
[0045] Examples of compounds having the structure of Formula(III) include:



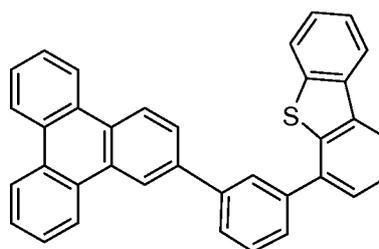
Compound 1'G



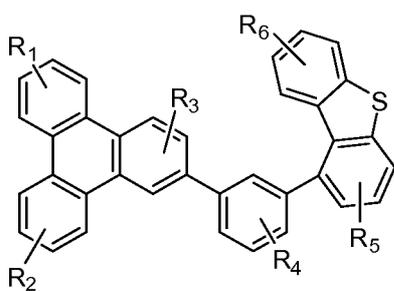
Compound 1'



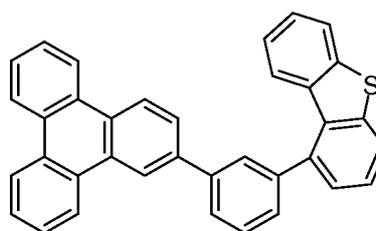
Compound 2'G



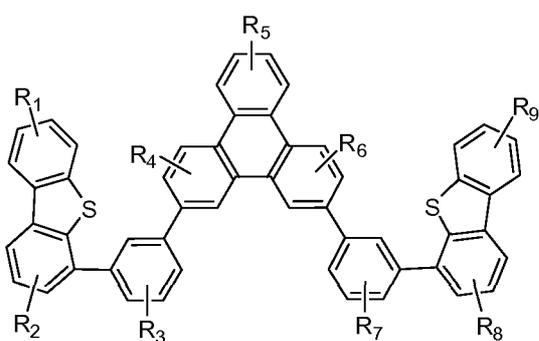
Compound 2'



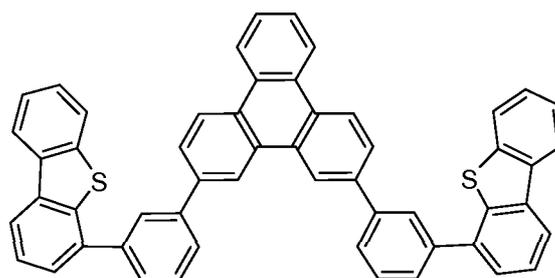
Compound 3'G



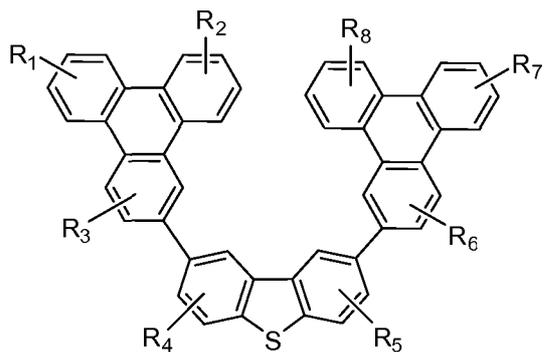
Compound 3'



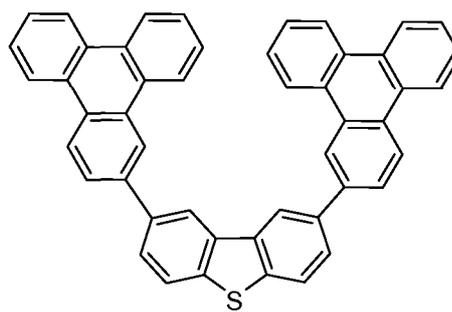
Compound 4'G



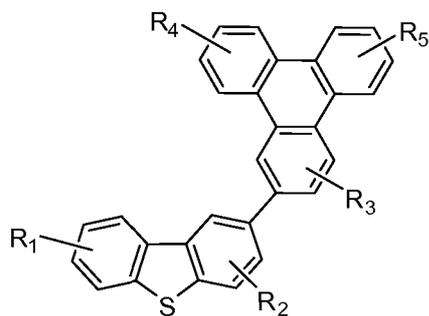
Compound 4'



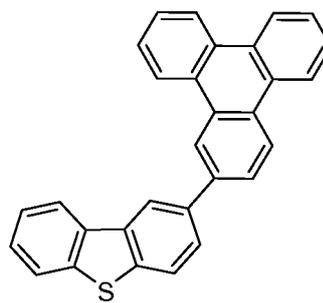
Compound 5'G



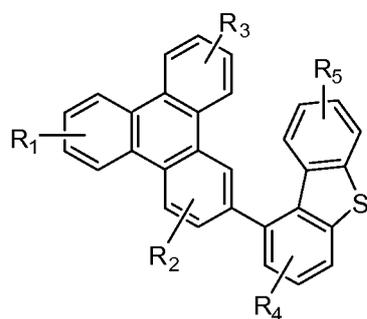
Compound 5'



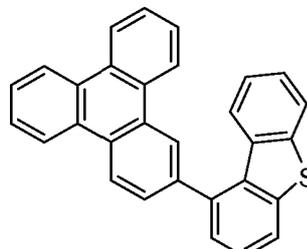
Compound 6'G



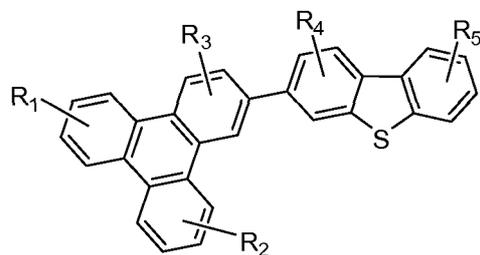
Compound 6'



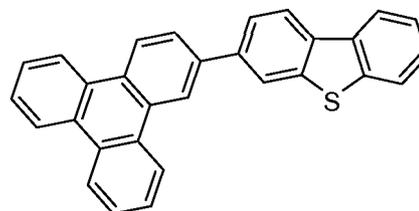
Compound 7'G



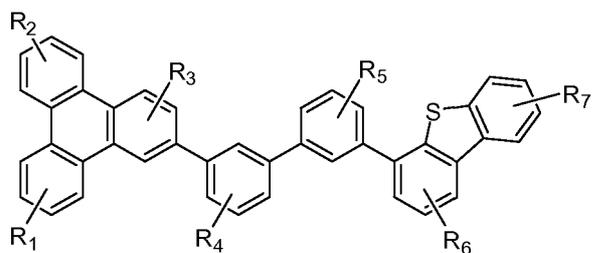
Compound 7'



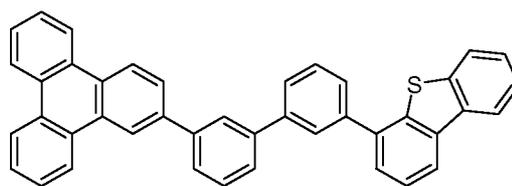
Compound 8'G



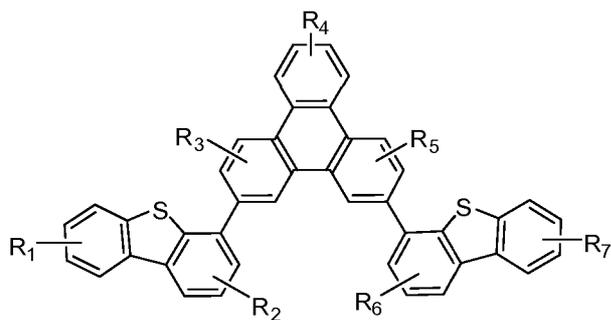
Compound 8'



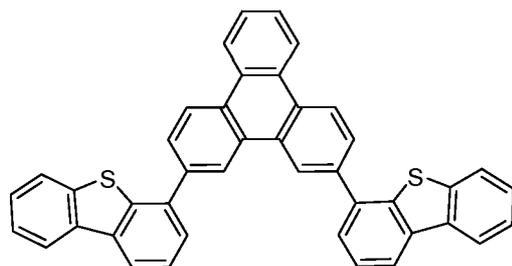
Compound 9'G



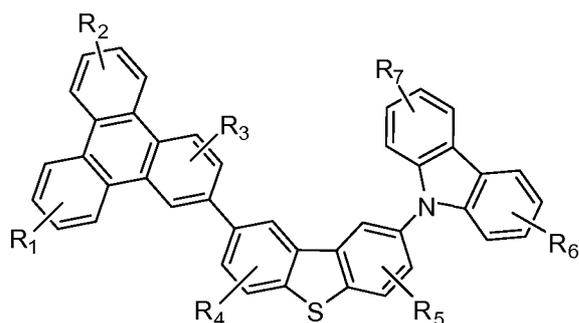
Compound 9'



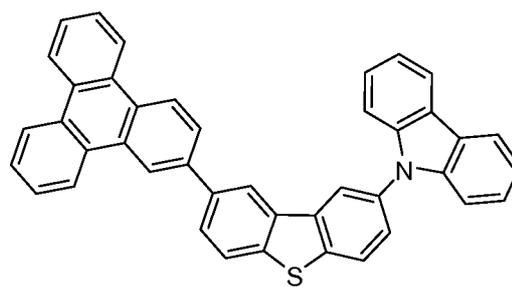
Compound 10'G



Compound 10'



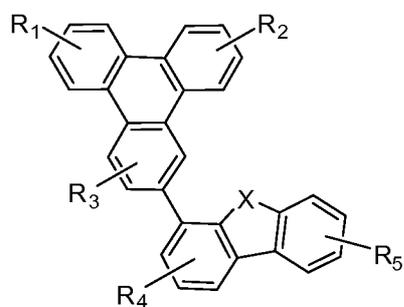
Compound 15'G



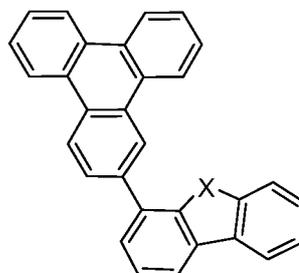
Compound 15'

R_i to R_n represents, independently, mono, di, tri or tetra substitutions selected from alkyl, alkoxy, amino, alkenyl, alkynyl, arylkyl, aryl and heteroaryl, or no substitution.

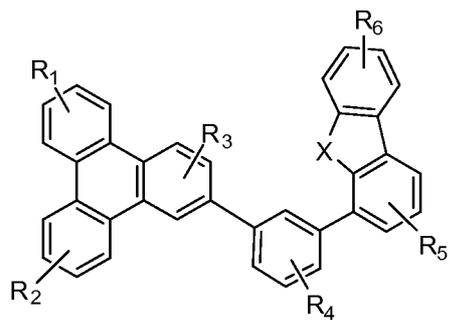
[0046] Examples of compounds having the structure of Formula(VI) include:



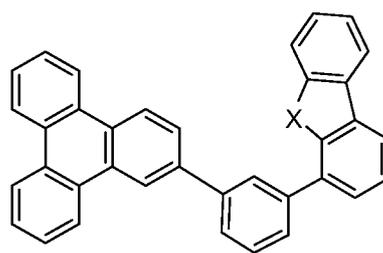
Compound 1G



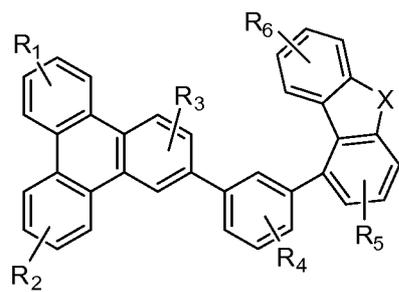
Compound 1



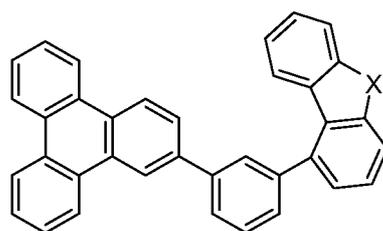
Compound 2G



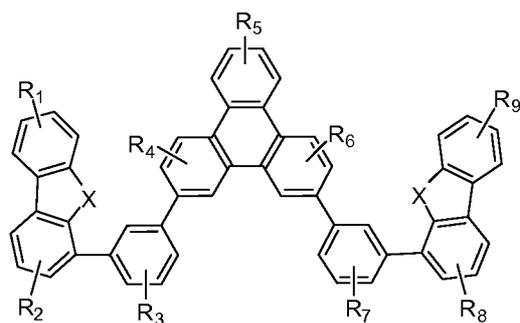
Compound 2



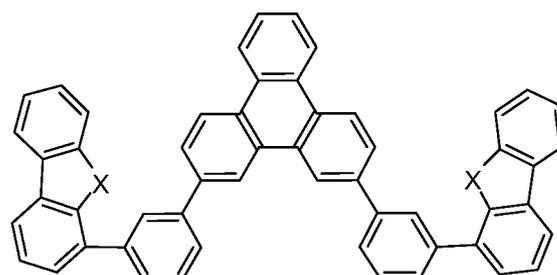
Compound 3G



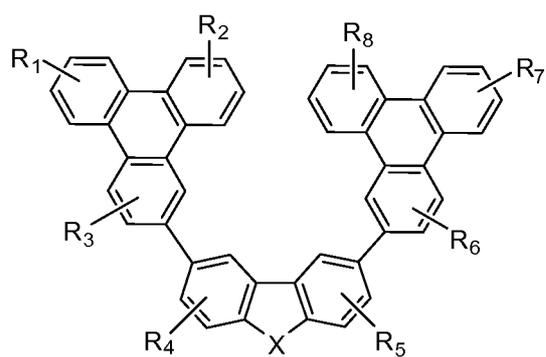
Compound 3



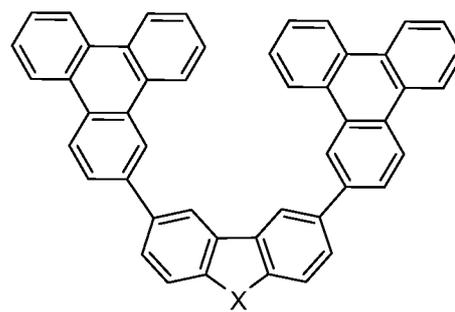
Compound 4G



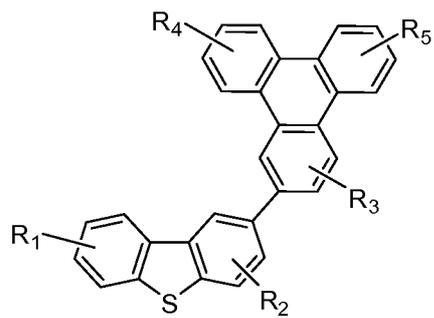
Compound 4



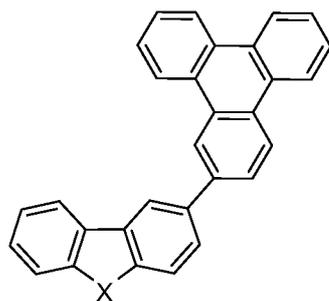
Compound 5G



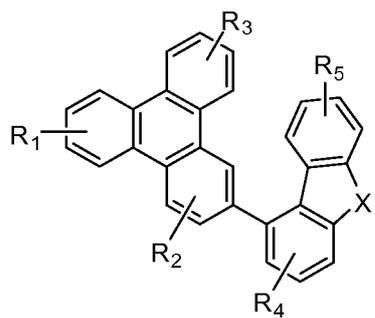
Compound 5



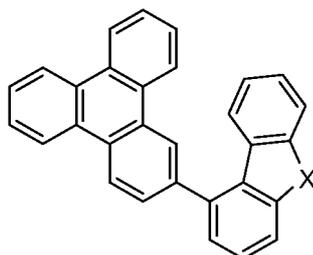
Compound 6G



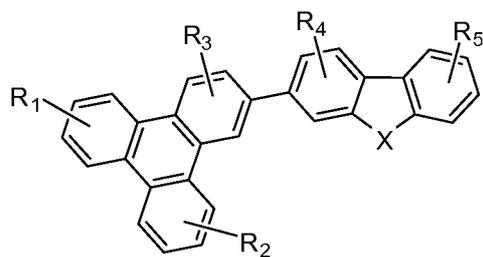
Compound 6



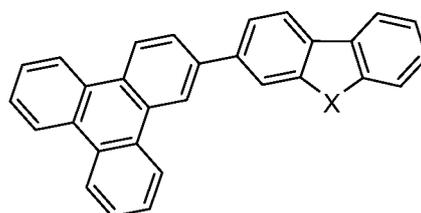
Compound 7G



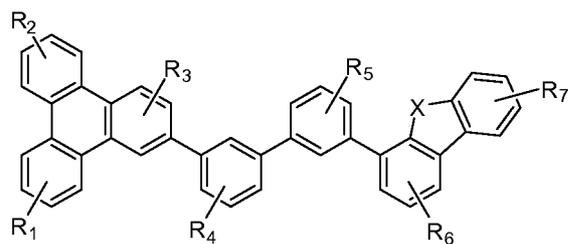
Compound 7



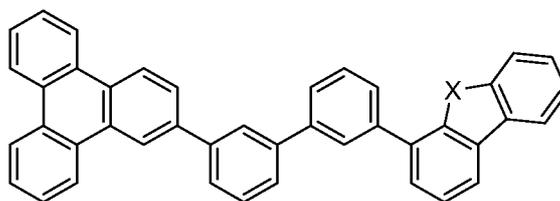
Compound 8G



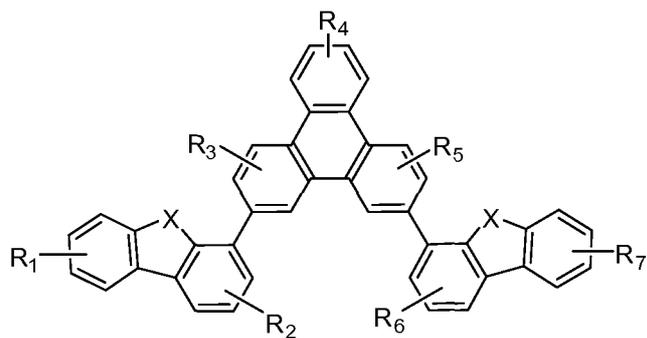
Compound 8



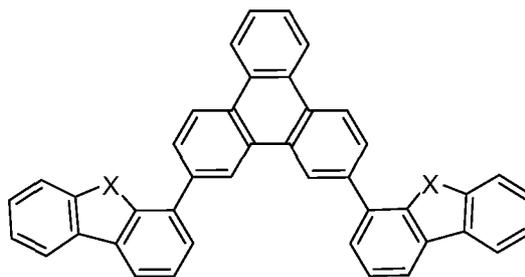
Compound 9G



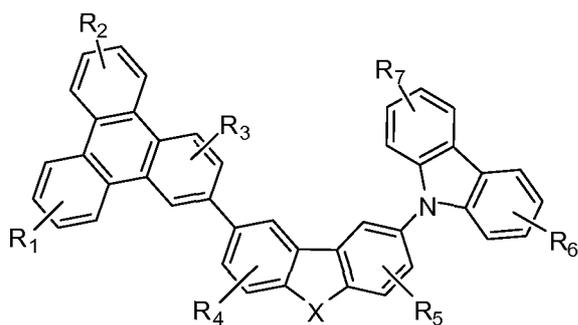
Compound 9



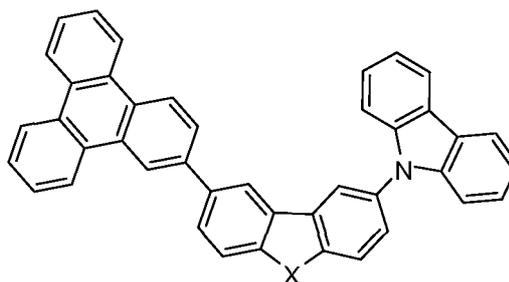
Compound 10G



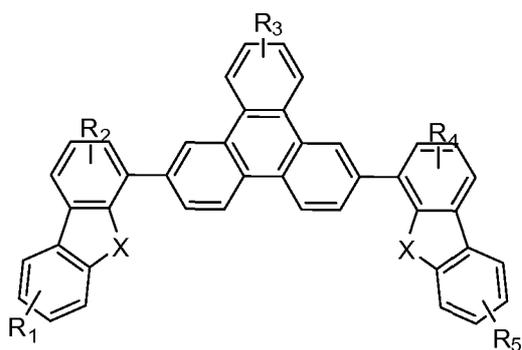
Compound 10



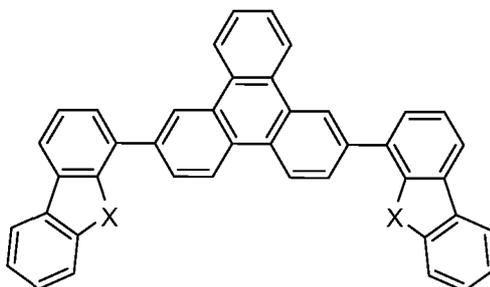
Compound 15G



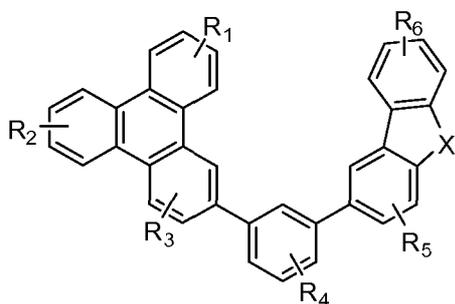
Compound 15



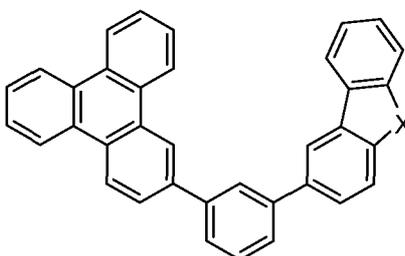
Compound 19 G



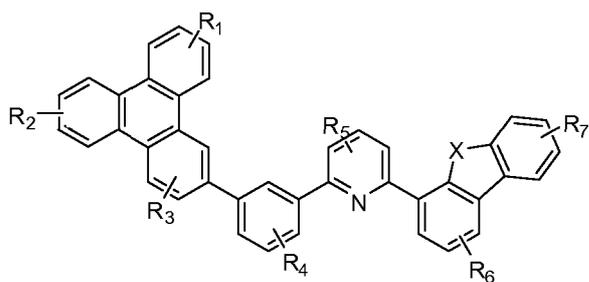
Compound 19



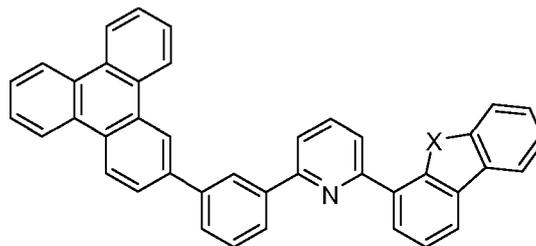
Compound 20 G



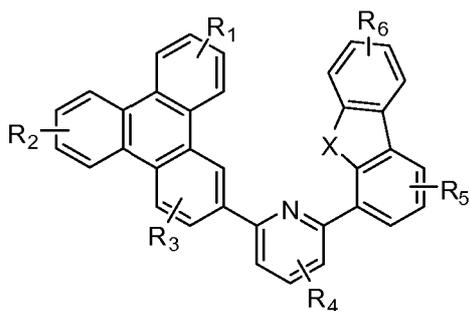
Compound 20



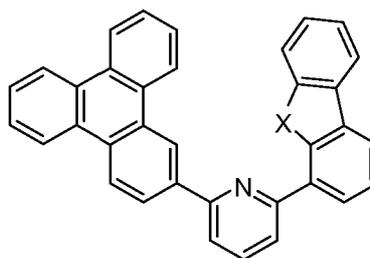
Compound 21 G



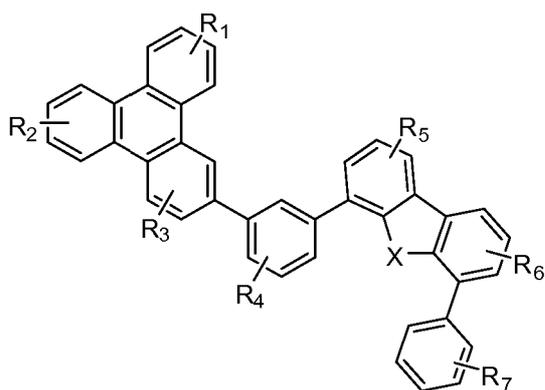
Compound 21



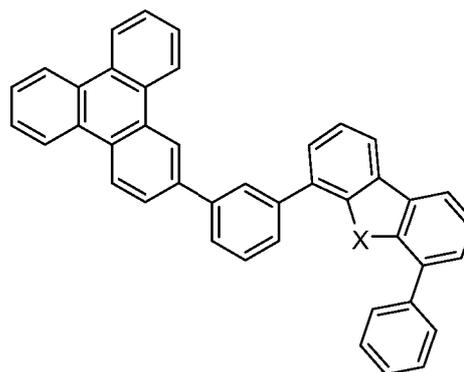
Compound 22 G



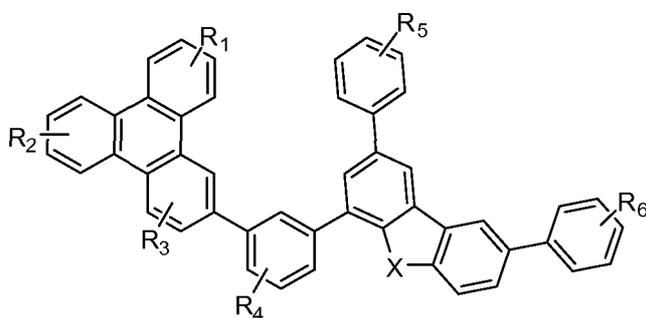
Compound 22



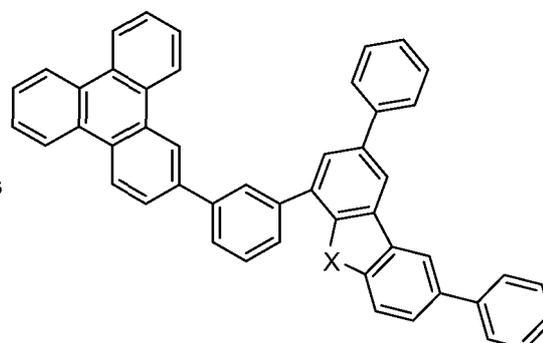
Compound 23 G



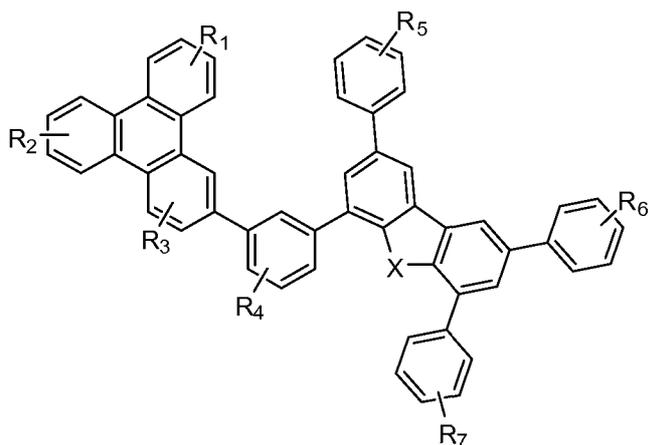
Compound 23



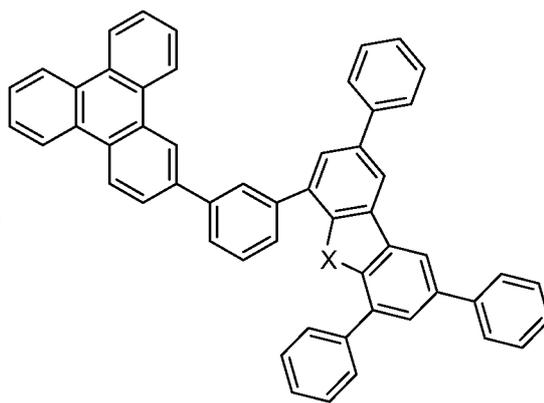
Compound 24 G



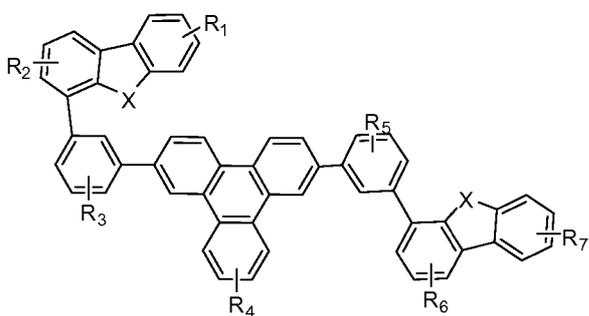
Compound 24



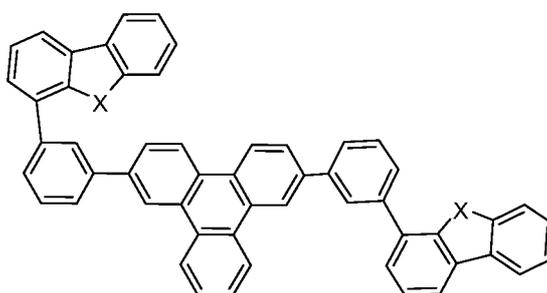
Compound 25 G



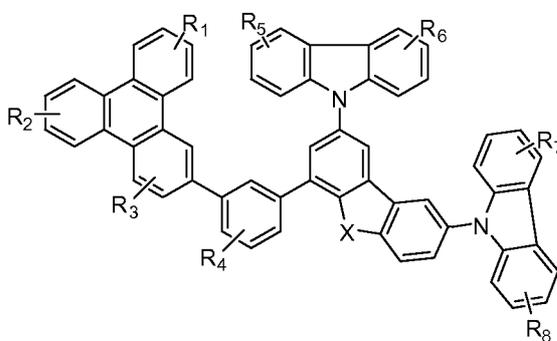
Compound 25



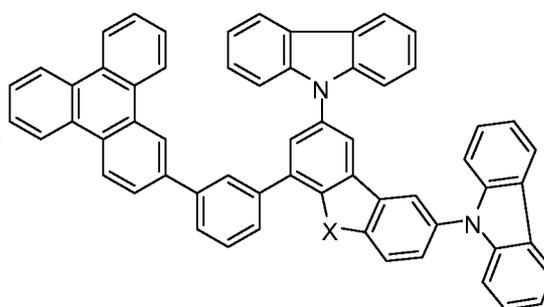
Compound 26 G



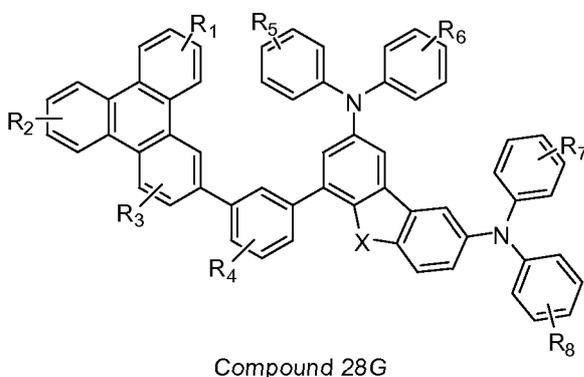
Compound 26



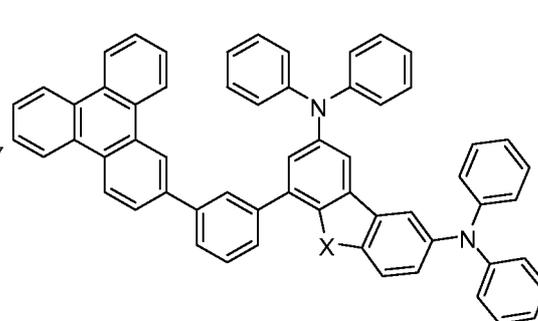
Compound 27 G



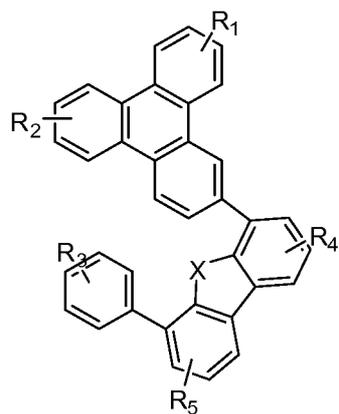
Compound 27



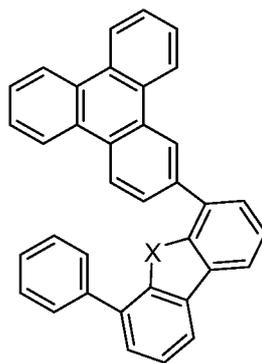
Compound 28 G



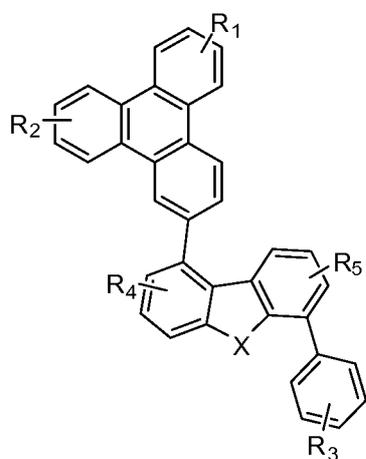
Compound 28



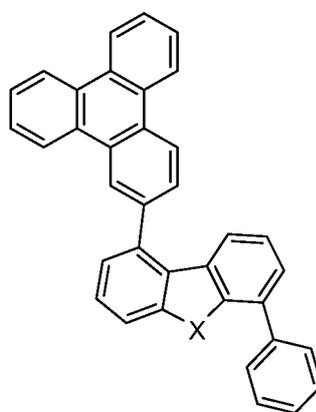
Compound 29G



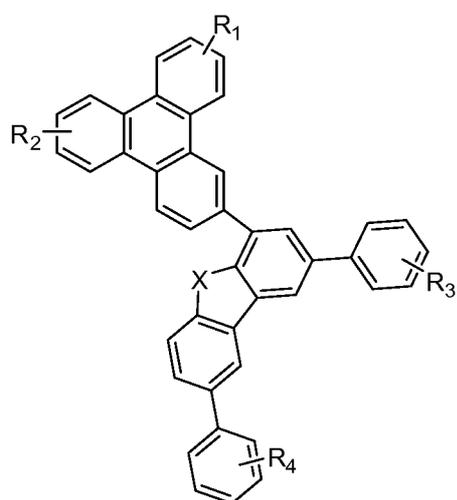
Compound 29



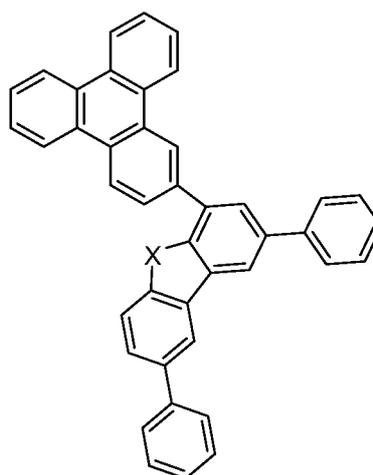
Compound 30G



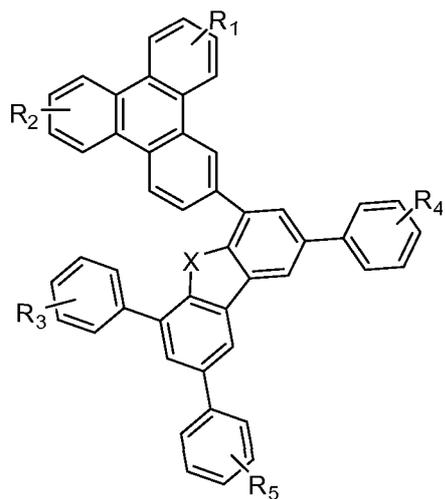
Compound 30



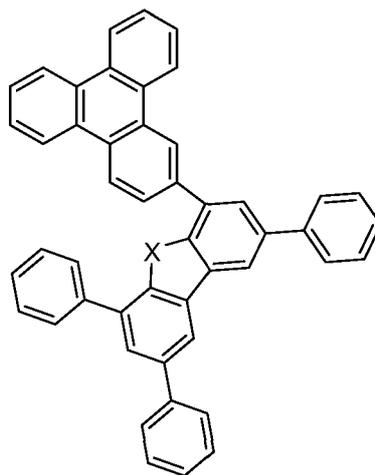
Compound 31G



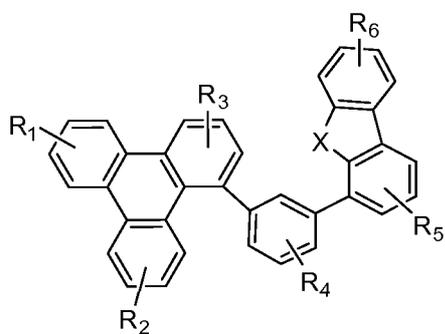
Compound 31



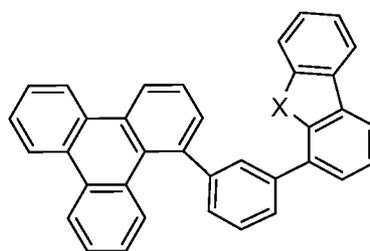
Compound 32G



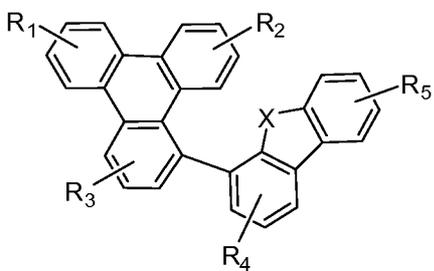
Compound 32



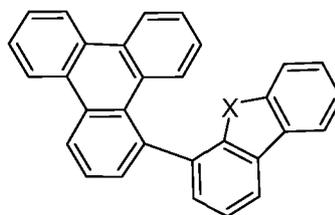
Compound 33G



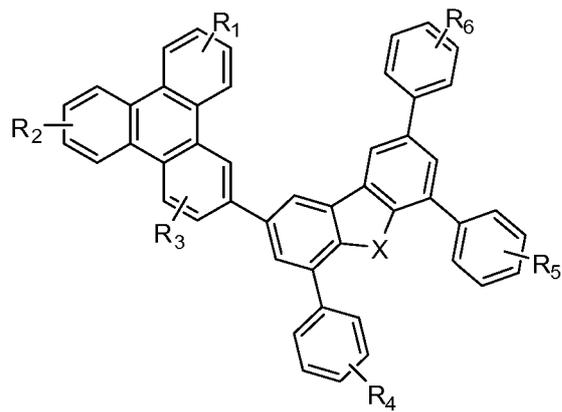
Compound 33



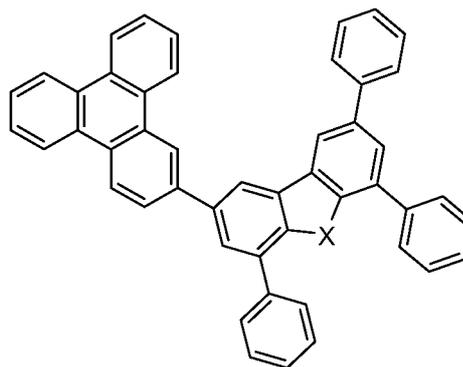
Compound 34G



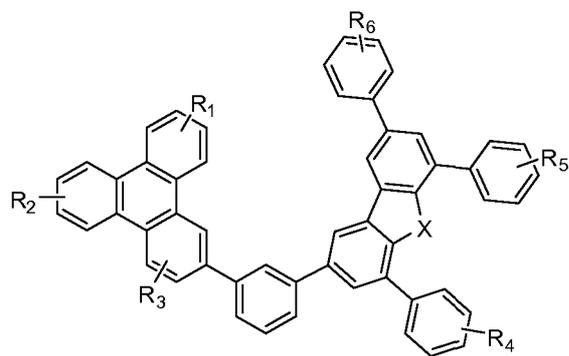
Compound 34



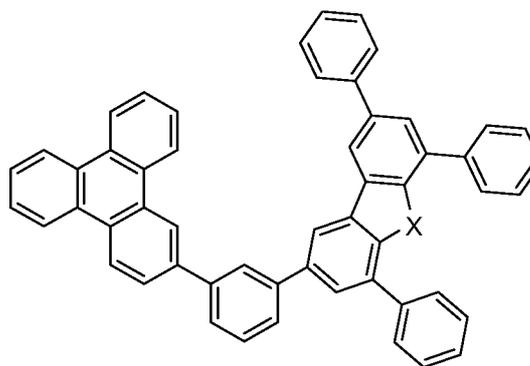
Compound 35G



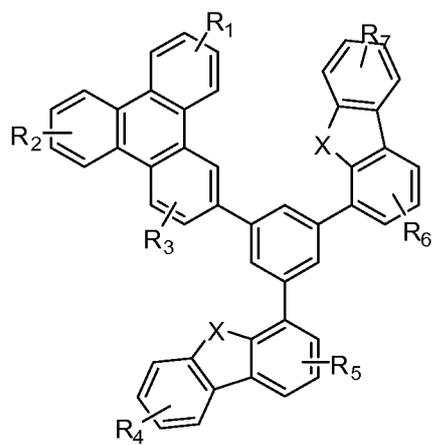
Compound 35



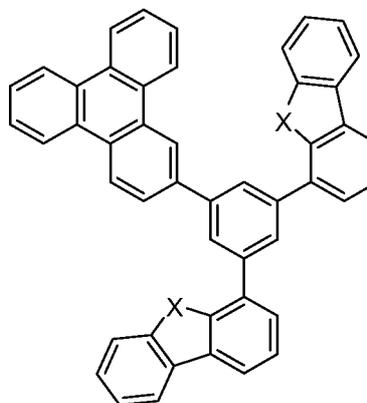
Compound 36G



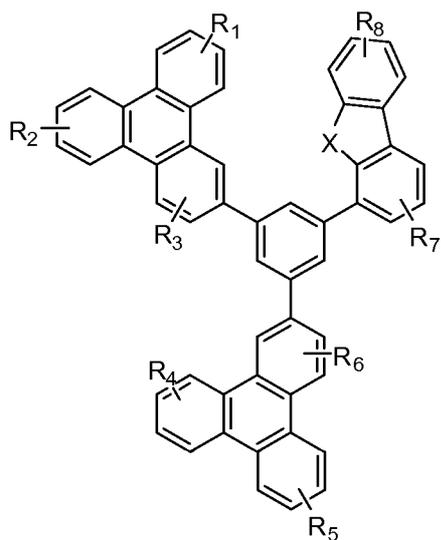
Compound 36



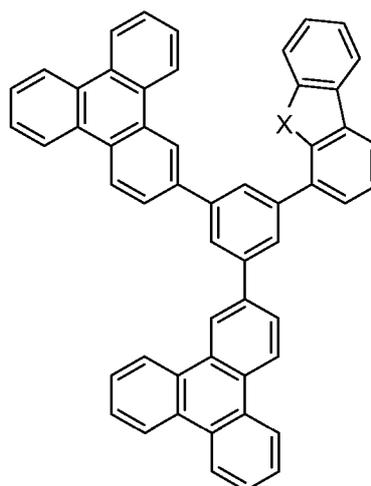
Compound 37G



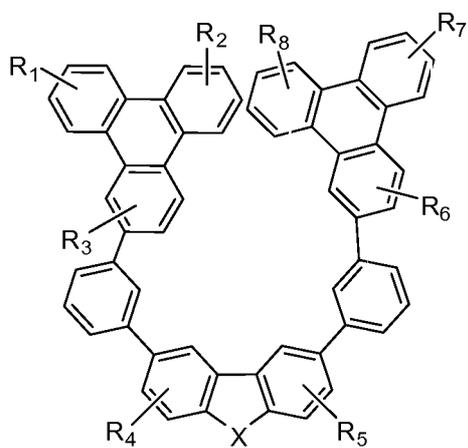
Compound 37



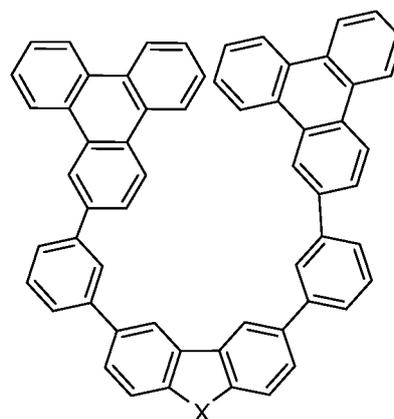
Compound 38G



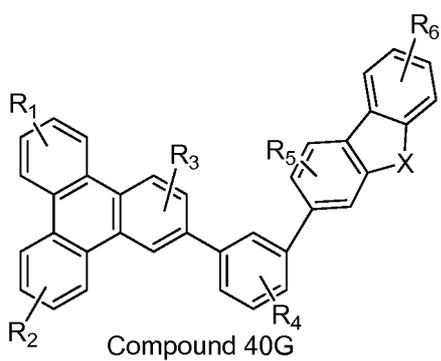
Compound 38



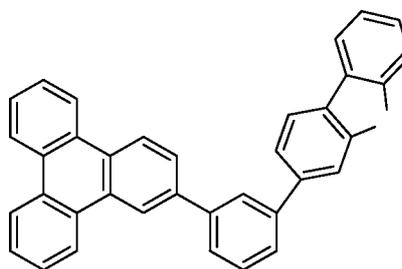
Compound 39G

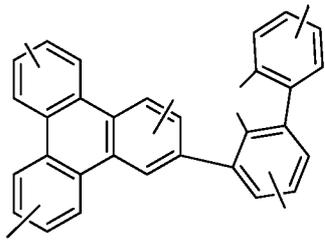
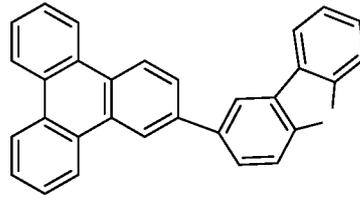
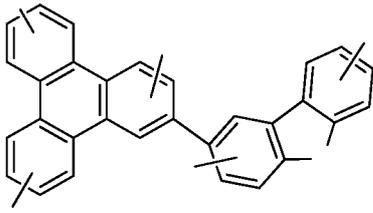


Compound 39

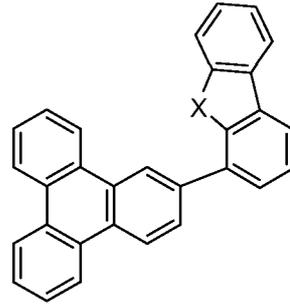


Compound 40G



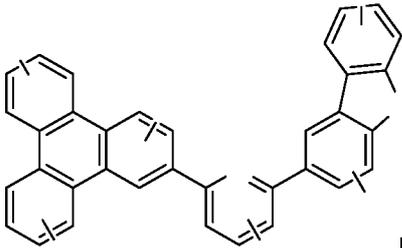


R₁

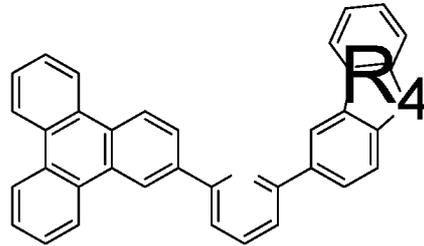


R₃

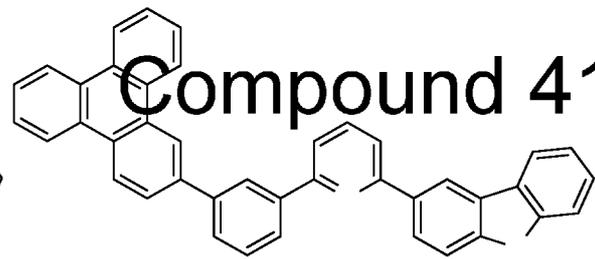
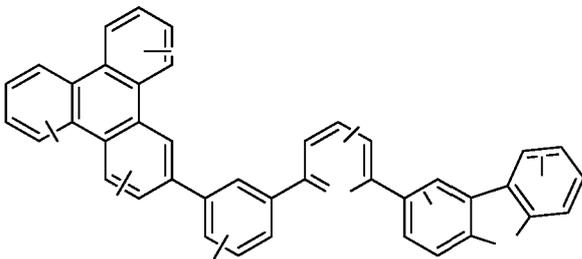
Compound 42



R₂

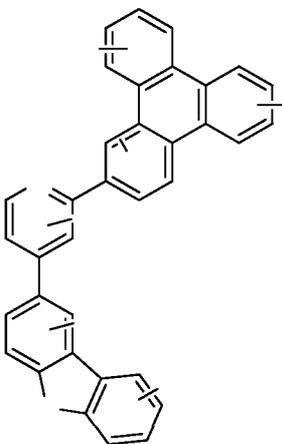
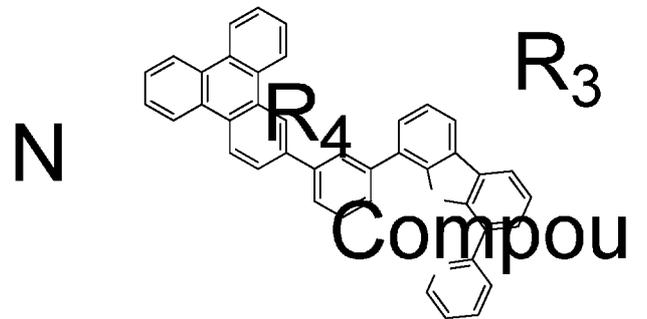
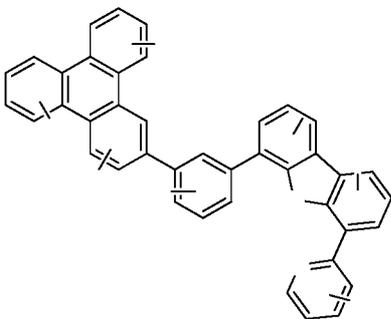
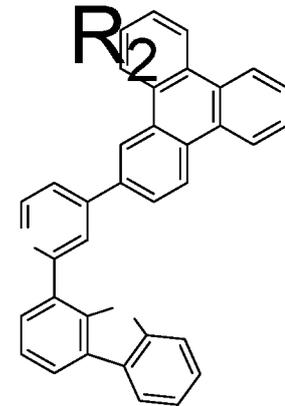
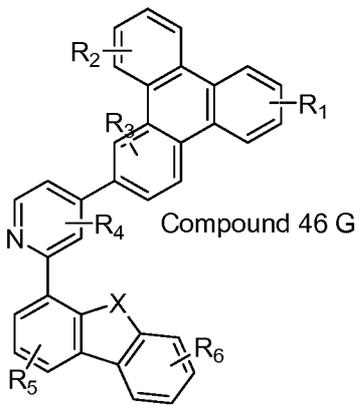
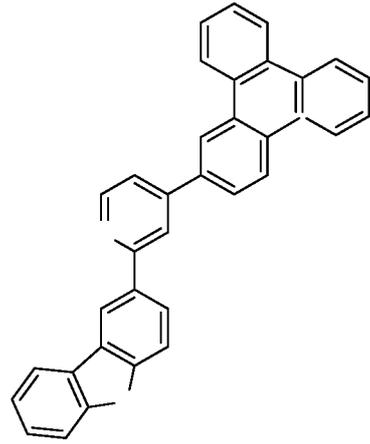
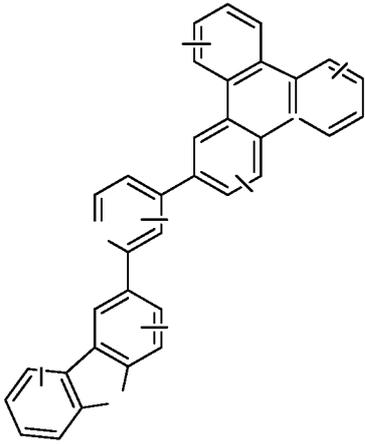


R₄

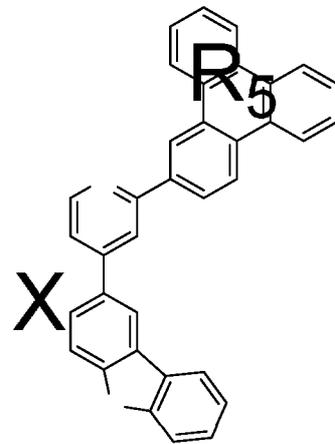


Compound 41G

R₁



R₆



X is S or O. Preferably, X is S. R_1 to R_n are independently selected from the group consisting of C_nH_{2n+1} , OC_nH_{2n+1} , OAn , $N(C_nH_{2n+1}O_2)$, $N(An)(Ar_2)$, $CH=CH-C_nH_{2n+1}$, $C=CHC_nH_{2n+1}$, Ar_1 , $An-Ar_2$, $C_nH_{2n}-Ar_1$, or no substitution. Each of R_1 to R_n may represent mono, di, tri, or tetra substitutions. n is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10. Ar_1 and Ar_2 are independently selected from the group consisting of benzene, biphenyl, naphthalene, triphenylene, carbazole, and heteroaromatic analogs thereof. At least one of R_1 , R_2 , and R_3 includes a triphenylene group.

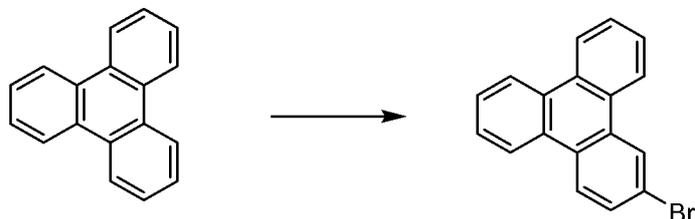
[0047] Each of the triphenylene-containing benzo-fused thiophenes disclosed above may be advantageously used in an organic light emitting device. The compounds are particularly useful for use as the host of an emissive layer in an organic light emissive device, an enhancement layer material of such a device, or both.

EXPERIMENTAL

Compound Examples

Example 1 4-(triphenylen-2-yl)dibenzothiophene (**Compound IS**)

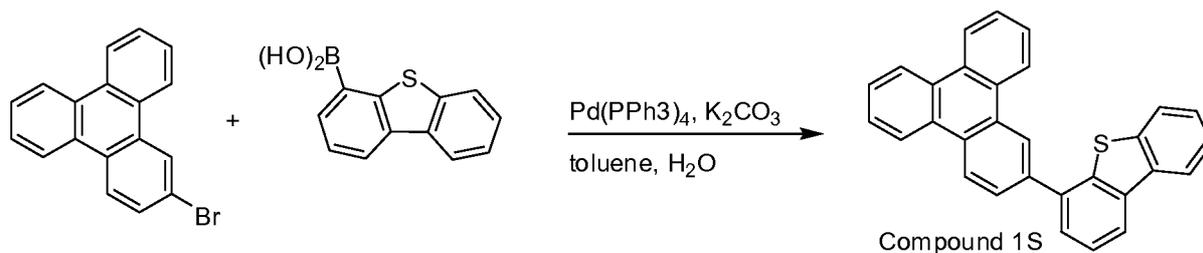
1. Synthesis of 2-Bromotriphenylene



[0048] The synthesis of the compound above was described in US20060280965.

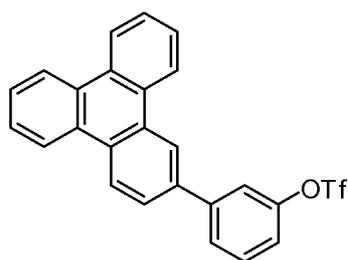
2. Synthesis of 4-(triphenylen-2-yl)dibenzothiophene.

[0049] 4.4 g (14.6 mmol) of 2-bromotriphenylene, 4.0 g (17.5 mmol) of 4-dibenzothiopheneboronic acid, 0.51 g (0.44 mmol) of tetrakis(triphenyl)phosphinepalladium, and 4.0 g (43.4 mmol) of potassium carbonate were charged in a 250 mL round bottom flask with solvent 90 mL of toluene and 10 mL of water. The reaction mixture was purged with nitrogen for 30 min and then was heated up to reflux for overnight under nitrogen with stirring. The reaction mixture was cooled and the organic extracts were purified by column chromatography and recrystallization with toluene. 5.1 g (86%) of white solid was obtained as the product which was confirmed by proton NMR.



Example 2 4-(3-(triphenylene-2-yl)phenyl)dibenzothiophene (Compound 2S)

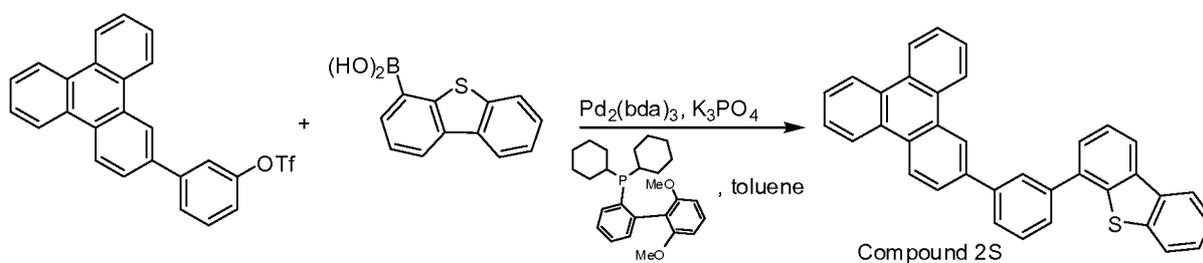
1. Synthesis of 3-(2-(triphenylene)phenyl) trifluoromethanesulfonate



[0050] The synthesis of the above compound was described Provisional Application No: 60/963,944.

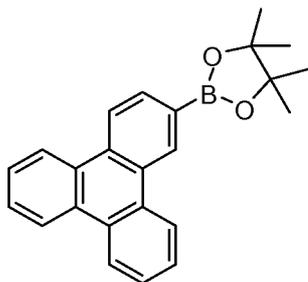
2. Synthesis of 4-(3-(triphenylene-2-yl)phenyl)dibenzothiophene

[0051] 4.52 g (10.0 mmol) of 3-(triphenylene-2-yl)phenyl trifluoromethanesulfonate, 3.0 g (13.0 mmol) of 4-dibenzothiopheneboronic acid, 0.46 g (0.5 mmol) of $\text{Pd}_2(\text{dba})_3$, 0.82 g (2.0 mmol) of 2-dicyclohexylphosphino-2', 6'-dimethoxybiphenyl, 12.7 g (60.0 mmol) OfK_3PO_4 and 150 mL of toluene and 15 mL of water were charged in a 250 mL round bottom flask. The reaction mixture was heated up to reflux under nitrogen for overnight. The reaction mixture was cooled and the organic extracts were purified by column chromatography and recrystallization. 4.3 g (88%) of white solid was obtained as product which was confirmed by proton NMR.



Example 3 2,8-di(triphenylene-2-yl)dibenzothiophene (Compound 5S)

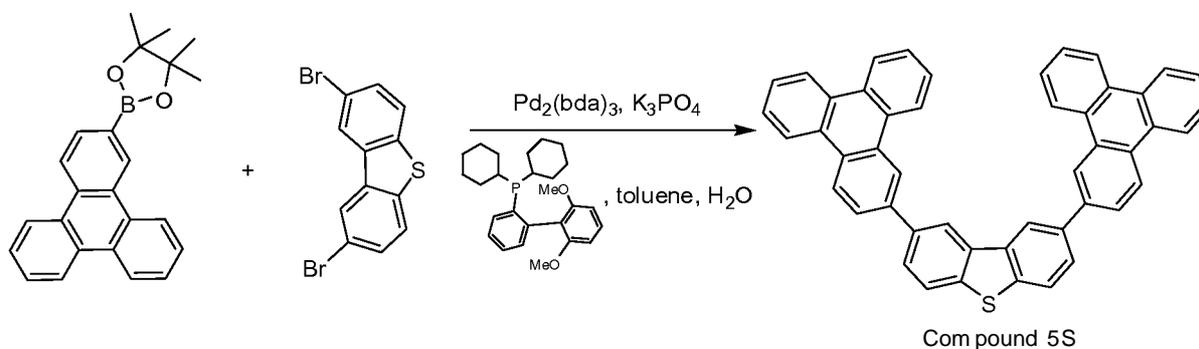
1. Synthesis of 4,4,5,5-tetramethyl-2-(triphenylene-2-yl)-1,3,2-dioxaborolane



[0052] The synthesis of this compound was described in US2006/0280965.

1. Synthesis of 2,8-di(triphenylen-2-yl)dibenzothiophene

[0053] 2.25 g (6.3 mmol) of 4,4,5,5-tetramethyl-2-(triphenylen-2-yl)-1,3,2-dioxaborolane, 0.92 g (2.7 mmol) of 2,8-dibromodibenzothiophene, 0.12 g (0.14 mmol) of $\text{Pd}_2(\text{dba})_3$, 0.22 g (0.53 mmol) of 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl, 3.4 g (16.0 mmol) of K_3PO_4 , 100 mL of toluene and 10 mL of water were charged in a 250 mL round bottom flask. The reaction mixture was purged with nitrogen for 20 min and then heated up to reflux for overnight with stirring. The reaction mixture was cooled and filtered. The white solid was washed with methanol 3 times (3x100 mL) and methylene chloride (2x100 mL). 1.6 g of (94% yield) solid was obtained as the product which was further purified by recrystallization with toluene and sublimation. The product was confirmed by solid probe MS.



Example 4 Compound 20S

1. Synthesis of 2-bromodibenzothiophene

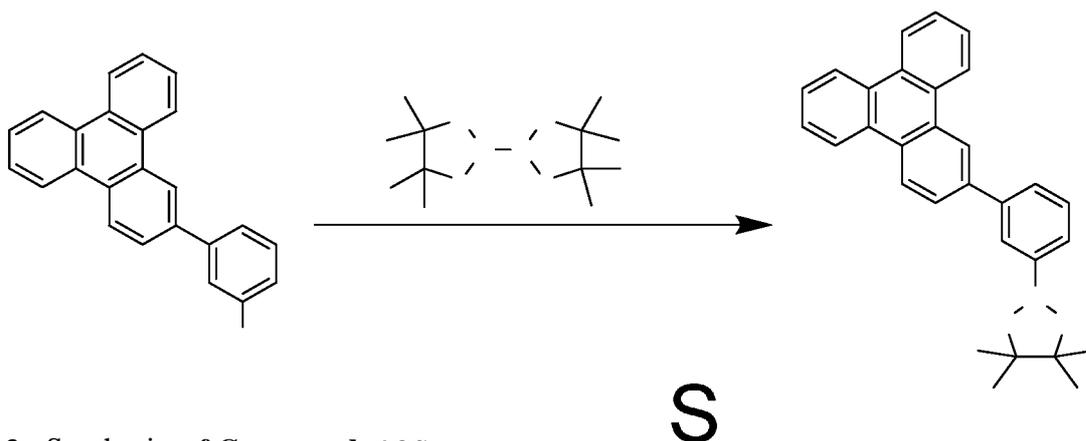
[0054] 15 g (79.9 mmol) dibenzothiophene was dissolved in 1.5 L chloroform. To the solution, 12.76 g (79.9 mmol) bromine was added dropwise. The reaction mixture was vigorously stirred for 2 days at room temperature and then treated with sodium sulfite water solution. The organic phase was evaporated 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.



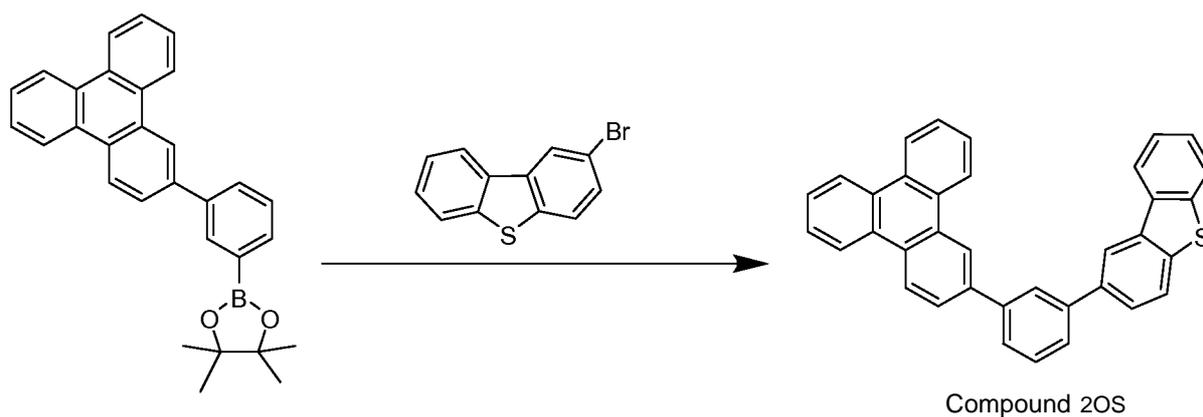
2. Synthesis of boron ester product

[0055] 8 g (17.5 mmol) 3-(2-triphenylene)phenyl trifluoromethanesulfonate, 9.1 g (35.2 mmol) bis(pinacolato)diboron, 290 mg (0.35 mmol) Pd(dffp)₂Cl₂, 5.2 g (52.5 mmol) KOAc and 150 mL anhydrous dioxane were charged in a 250 mL three-necked flask. The reaction mixture was heated up to 90 °C under nitrogen for 20 hours. 7.0 g white solid was obtained after column with 30% ethyl acetate in hexane as elute. The product was confirmed by proton NMR.



3. Synthesis of Compound 2OS.

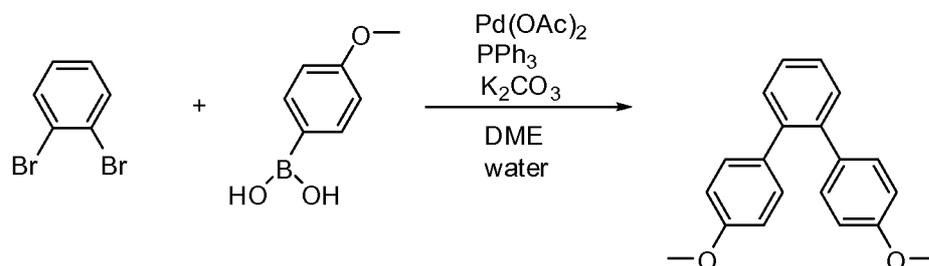
[0056] 2 g (7.1 mmol) 2-bromodibenzothiophene, 4.0 g (9.3 mmol) boron ester product in Step 2, 325 mg (0.355 mmol) Pd₂(dba)₃, 582 g (1.4 mmol) S-phose, 9 g (42 mmol) K₃PO₄, 90 mL toluene and 10 mL water were charged in a 250 mL flask. The reaction mixture was heated up to reflux under nitrogen for overnight. The reaction mixture was extracted with methylene chloride and the organic extracts were purified by silica gel column chromatography and recrystallization. ~ 2.9 g (85%) white solid was obtained as product which was confirmed by proton NMR.



Example 5 Compound 10S

1. Synthesis of 4,4'-dimethoxy-o-terphenyl.

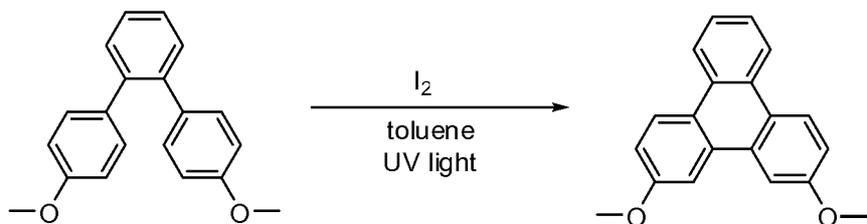
[0057] A mixture was prepared consisting of 1,2-dibromobenzene (50 g, 212 mmol), 4-methoxyphenylboronic acid (78 g, 513 mmol), triphenylphosphine (11.12 g, 42.2 mmol), potassium carbonate (73.25 g, 530 mmol), dimethoxyethane (290 mL), and water (290 mL). Nitrogen was bubbled directly into the mixture for 20 minutes. Palladium acetate was added (4.76 g, 21.2 mmol) and the mixture was heated to reflux overnight under nitrogen. The reaction mixture was cooled and water and dichloromethane was added. The layers were separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were filtered through Celite and washed with brine, dried over magnesium sulfate, filtered, evaporated to yield a black oil. The crude material was purified by column chromatography eluting with 0 to 100% dichloromethane in hexane. The major fractions were purified by distillation using Kugelrohr at 200 to 220 °C. 49 g (80%) product was obtained.



2. Synthesis of 2,11-dimethoxytriphenylene.

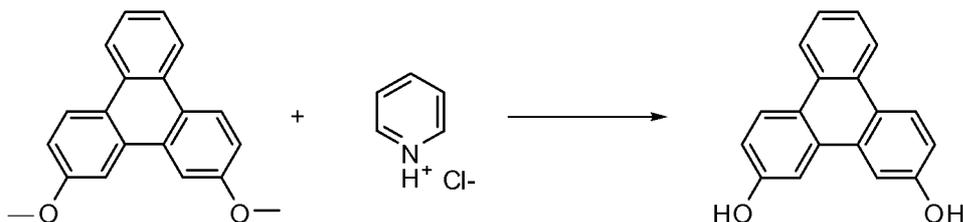
[0058] 12.4 g (42.7 mmol) of 4,4'-dimethoxy-o-terphenyl and 16g (63.0 mmol) iodine chips was placed in a 250 mL reaction vessel. 200 mL of toluene was added followed by 30 mL of propylene oxide. The photoreactor was set up with a condenser cooled by a circulating

chiller. A 400 W medium pressure mercury lamp was used as the light source. The reaction vessel was placed in a cabinet. The lamp was ignited and the chiller temperature was set such that the water exiting the reactor was maintained at between 20°C and 25°C (monitored by a thermocouple attached the exit stream). The reaction was left on for 18 hours. A solid was filtered off and washed with hexanes, only recovered 2.2g of material. The filtrate was diluted with toluene and washed with sodium sulfate solution. The aqueous layer was back extracted with toluene and the organic layers were dried over magnesium sulfate, filtered, and evaporated. Material was dissolved in toluene and added sodium sulfite solution and stirred. The layers were separated, the aqueous layer extracted with toluene and the combined organic layers were dried over magnesium sulfate, filtered, and evaporated. The residue was purified by column chromatography eluting with 0 to 100% ethyl acetate/hexane. 8.8g material (72%) was obtained.



3. Synthesis of triphenylene-2,11-diol.

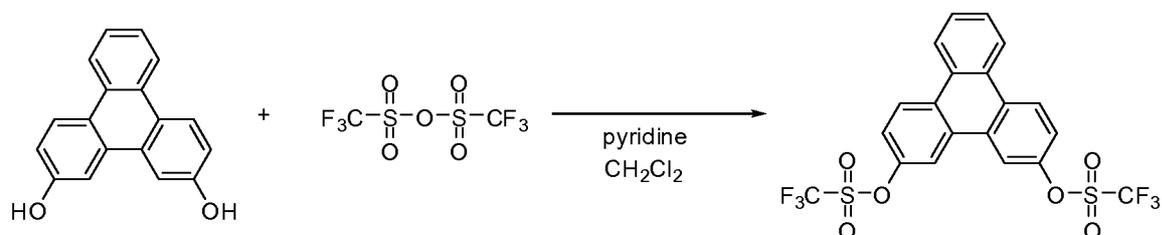
[0059] A mixture of 2,1,1-dimethoxytriphenylene (8.8g, 30.5 mmol) and pyridine hydrochloride (3.173g, 274.6 mmol) was heated to 220 °C for 2 hours. The mixture was cooled and water was added. The resulting solid was filtered off, washed with water, and dried under high vacuum. 7.45g (94%) desired product was obtained.



4. Synthesis of triphenylene-2,11-diol bis(trifluoromethanesulfonate).

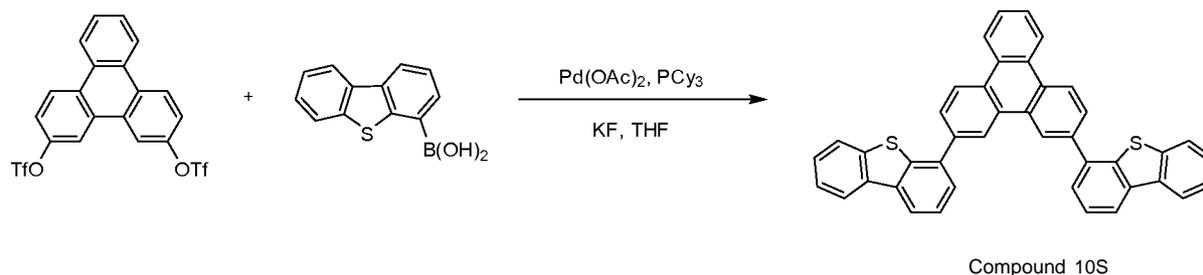
[0060] Triphenylene-2,1,1-diol (7.45g, 28.62 mmol) was added to 100 mL dichloromethane and 13 mL pyridine and the solution was cooled in an ice salt bath. Trifluoromethanesulfonic anhydride (19 mL, 114.49 mmol) in 70 mL of dichloromethane was added dropwise to the solution under nitrogen. The reaction was allowed to proceed for 2 hours and quenched by adding by adding methanol and water followed by dilution with dichloromethane. A tan

solid was filtered off and washed with dichloromethane and water. The layers in the filtrate were separated and the aqueous layer was extracted with dichloromethane. The organic extracts were dried over magnesium sulfate, filtered, and evaporated to yield a brown solid. The brown solid was purified by column chromatography eluting with 0 to 100% dichloromethane/hexane following sublimation at 170 °C and recrystallization twice from 300 mL boiling toluene. 11A g product was obtained (76%).



5. Synthesis of Compound 10S.

[0061] A mixture of triphenylene-2,11-diyl bis(trifluoromethanesulfonate) (1.5 g, 2.9 mmol), dibenzothiophene-4-boronic acid (2.6 g, 11.4 mmol), potassium fluoride (1.1 g, 19 mmol) and THF 50 mL was prepared. Nitrogen was bubbled directly in the mixture for 1 hour. Next potassium acetate (13 mg, 0.06 mmol) and triscyclohexyl phosphine (19 mg, 0.07 mmol) was added, and then nitrogen was bubbled in the mixture for another 30 minutes. The mixture was heated at 50 °C overnight. Then the reaction was cooled to room temperature. The precipitation was collected by filtration. The white solid was put in one soxhlet extractor and washed by refluxing THF overnight. The solid in the extractor was collect to provide 0.9 gram white solid (yield 53%).

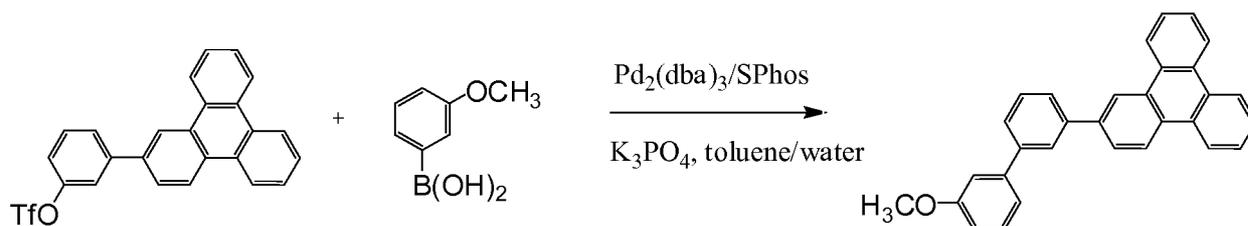


Example 6 Compound 9S

1. Synthesis of 2-(3'-methoxybiphenyl-3-yl)triphenylene

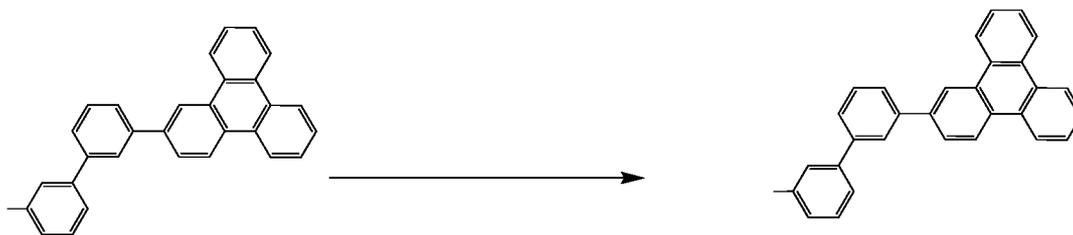
[0062] 12.9 g (28.5 mmol) 3-(triphenylene-2-yl)phenyl trifluoromethanesulfonate, 6.5 g (42.8 mmol) 3-methoxyphenylboronic acid, 0.47 g (1.1 mmol) 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos) and 18.2 g (85.5 mmol) potassium phosphate tribasic

(K₃PO₄) were weighed in a round bottom flask. 150 mL toluene and 80 mL water were added to the flask as solvent. The solution was purged with nitrogen and 0.26 g (0.28 mmol) of tris(dibenzylideneacetone)dipalladium (0) [Pd₂(dba)₃] was added. The solution was heated to reflux for twelve hours. Upon cooling, the organic layer was separated, and dried with MgSO₄. The product was readily separated by column chromatography using hexane/dichloromethane as eluent (1/0 gradient to 3/2). The solvent was removed by rotary evaporation resulting in 11.7 g (28 mmol) of the product, 2-(3'-methoxybiphenyl-3-yl)triphenylene.



2. Synthesis of 3'-(triphenylen-2-yl)biphenyl-3-ol

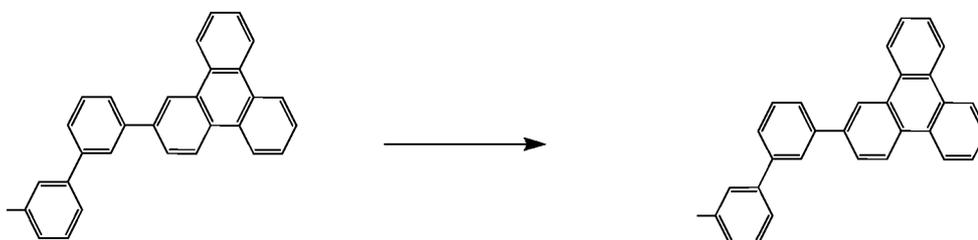
[0063] In a round bottom flask under nitrogen, 11.5 g (28 mmol) 2-(3'-methoxybiphenyl-3-yl)triphenylene and 21.1 g (183 mmol) pyridine hydrochloride were heated to 204°C. Upon cooling, water was added and extracted with dichloromethane. The combined organic fractions were washed with additional water and the solvent was removed by rotary evaporation. The solid was drypacked on celite and the product purified by column chromatography using hexanes:dichloromethane (1:4) as eluent. The solvent was removed by rotary evaporation resulting in 8.6 g (22 mmol) of the product, 3'-(triphenylen-2-yl)biphenyl-3-ol.



3. Synthesis of 3'-(triphenylen-2-yl)biphenyl-3-yl trifluoromethanesulfonate

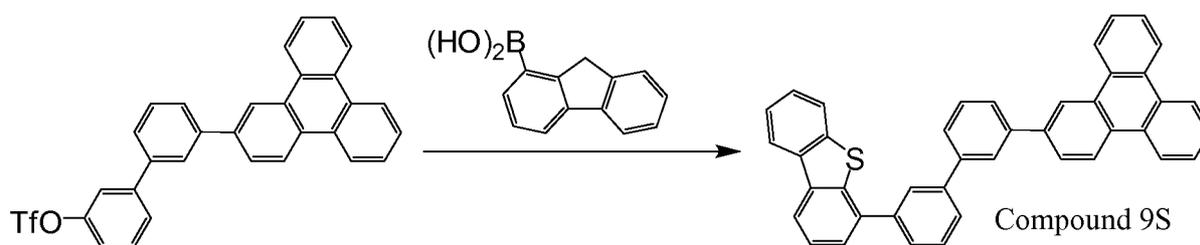
[0064] 8.6 g (22 mmol) of 3'-(triphenylen-2-yl)biphenyl-3-ol was added to a flask under nitrogen with 3.4 g (43.4 mmol) anhydrous pyridine and 450 mL anhydrous dichloromethane. The solution was cooled in an ice bath and 12.2 g (43.4 mmol) trifluoromethanesulfonic anhydride (Tf₂O) was added slowly via syringe. The solution was warmed to room

temperature and stirred overnight. The solution was washed with water, dried with MgSO_4 and solvent was removed by rotary evaporation. The product, 3'-(triphenylen-2-yl)biphenyl-3-yl trifluoromethanesulfonate, was purified by column chromatography using hexane/dichloromethane as eluent (1/0 to 1/1 gradient) resulting in 10.7 g (20.2 mmol).



4. Synthesis of Compound 9S

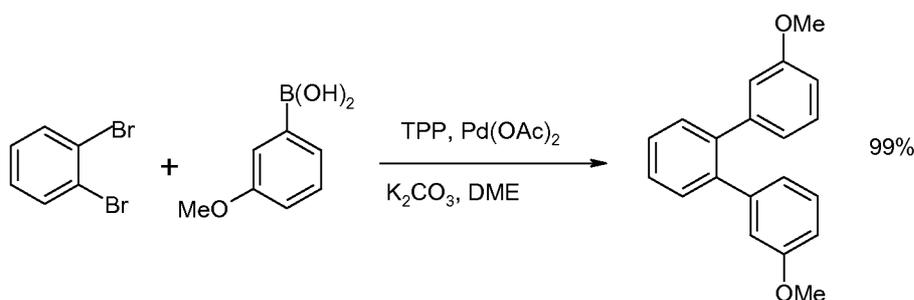
[0065] 5.5 g (10.4 mmol) product in above Step 3, 3.0 g (13.5 mmol) 4-boronic acid dibenzothiophene, 458 mg (0.5 mmol) $\text{Pd}_2(\text{dba})_3$, 820 mg (2 mmol) S-phose, 12.7 g (60 mmol) potassium phosphate and 150 mL toluene were added in a 250 flask. The reaction mixture was heated up to reflux under nitrogen overnight. Then it was cooled down and worked up. ~ 5 g white product was obtained after silica gel column chromatography with 20% methylene chloride in hexane as elute and following with washing with methanol. The product was confirmed by proton NMR.



Example 7 Compound 19S

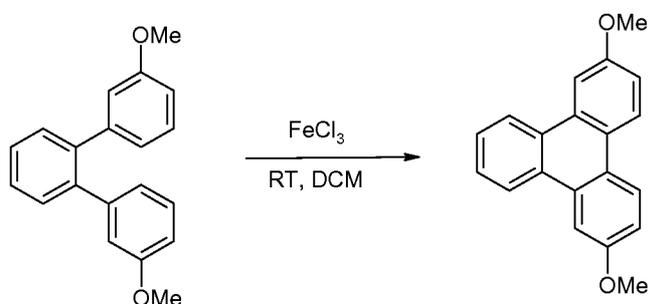
1. Synthesis of 3,3'-dimethoxy- ϕ -terphenyl

[0066] 1,2-dibromobenzene (50.0 g, 0.212 mol), 3-methoxyphenylboronic acid (77.3 g, 0.509 mol), palladium acetate (1.2 g, 5.33 mmol), triphenylphosphine (21.4 mmol), sodium carbonate (78.9 g, 0.744 mol) were combined with dimethoxyethane (430 mL) and water (290 mL) in a 2000 mL round-bottom flask equipped with a stir bar, reflux condenser, and a nitrogen inlet and heated at reflux for 4 days. Ethyl acetate (500 mL) was added and the organic layer was separated, dried over magnesium sulfate, and evaporated to dryness to yield 61.3 g (99.7 %) of 3,3'-dimethoxy- ϕ -terphenyl as a white solid.



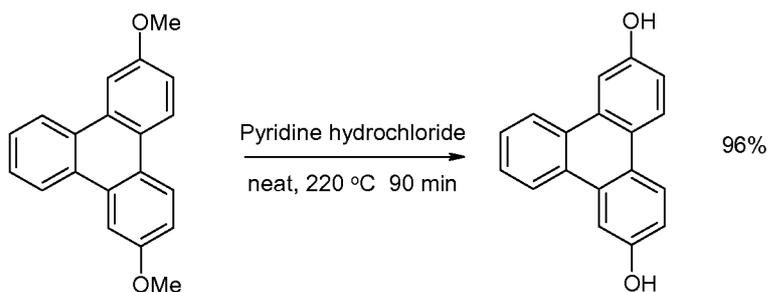
2. Synthesis of 2,9-dimethoxytriphenylene

[0067] In a 2000 mL round-bottom flask equipped with a nitrogen inlet and a stir bar, 3,3'-dimethoxy-o-terphenyl (61.3 g, 0.211 mol) was dissolved in anhydrous methylene chloride (1000 mL). Iron (III) chloride (68.6 g, 0.423 mol) was then added, and the mixture was stirred overnight. In the morning an additional two equivalents of iron (III) chloride were added, and the reaction reached completion within one hour. Methanol and water were added to the mixture and the organic layer was separated, dried over magnesium sulfate, and evaporated to dryness. The crude product was purified by silica gel column chromatography with 60/40 methylene chloride/hexane as the eluent to give 50.7 g of a light yellow solid that was recrystallized from 700 mL of acetonitrile to yield 49.1 g of 2,9-dimethoxytriphenylene.



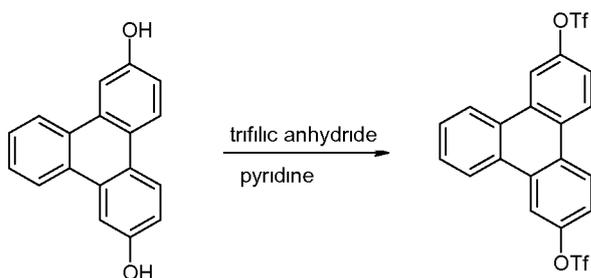
3. Synthesis of 2,9-dihydroxytriphenylene.

[0068] 2,9-dimethoxytriphenylene (49.1 g, 0.170 mol) and pyridine hydrochloride (200 g, 1.70 mol) were placed in a 500 mL round-bottom flask equipped with a stir bar, reflux condenser, and a nitrogen inlet and heated at 220 °C for 90 minutes. The solution was cooled and water was added, resulting in the formation of a white precipitate, which was collected by vacuum filtration, washed with water, and dried *in vacuo* to yield 43.7 g (96 %) of 2,9-dihydroxytriphenylene.



4. Synthesis of triphenylene-2,7-diyl bis(trifluoromethanesulfonate).

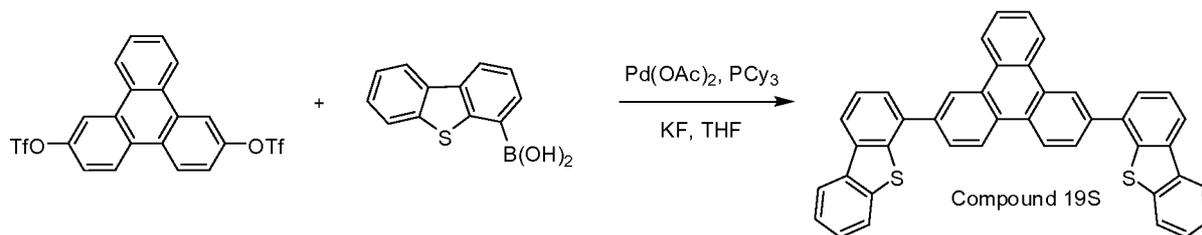
[0069] To a cooled solution (0 °C) of 2,9-dihydroxytriphenylene (17.5 g, 65 mmol) and pyridine (300 mL) in a 1000 mL round bottom flask equipped with a stir bar and nitrogen inlet was added dropwise trifluoromethanesulfonyl anhydride (38.7 g, 137 mmol). The reaction mixture was allowed to stir overnight at room temperature. After evaporation of the pyridine, the resulting solid was stirred with methanol (500 mL) and collected by vacuum filtration to afford 32 g of a white powder that was recrystallized from 500 mL of 30/70 heptane/dichloroethane, yielding 28.3 g (82 %) of 2,9-bis(trifluoromethanesulfonyl) triphenylene.



5. Synthesis of Compound 19S.

[0070] A mixture of triphenylene-2,7-diyl bis(trifluoromethanesulfonate) (2 g, 3.8 mmol), dibenzothiophene-4-boronic acid (3.5 g, 15 mmol), potassium fluoride (1.5 g, 25 mmol) and THF 100 mL was prepared. Nitrogen was bubbled directly in the mixture for 1 hour. Next potassium acetate (17 mg, 0.08 mmol) and triscyclohexyl phosphine (26 mg, 0.09 mmol) were added, and then the nitrogen was bubbled in the mixture for another 30 minutes. The mixture was stirred at room temperature for two days. Then the reaction was cooled to room temperature. The precipitation was collected by filtration. Potassium acetate (17 mg, 0.08 mmol) and triscyclohexyl phosphine (26 mg, 0.09 mmol) were added and then the nitrogen was bubbled in the mixture for another 15 minutes. The mixture was stirred at room temperature for another two days. The grey solid was put in one soxlet extractor and washed

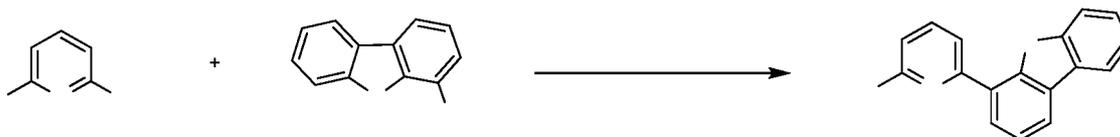
by refluxing THF overnight. The solid in the extractor was collect to provide 2.1 gram white solid (yield 92%).



Example 8 Compound 22S

Step 1

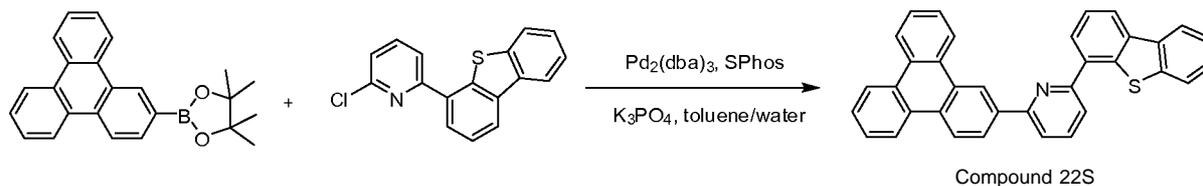
[0071] A mixture of 2,6-dichloropyridine (13 g, 88 mmol), dibenzothiophene-4-boronic acid (5 g, 22 mmol), potassium phosphate tribasic (28 g, 132 mmol), toluene 300 mL and water 30 mL was prepared. Nitrogen was bubbled directly in the mixture for 1 hour. Next tris dibenzylideneacetone (0.54 g, 1.3 mmol) was added, and then nitrogen was bubbled into the mixture for another 20 minutes. The mixture was stirred at room temperature for two days. Then the organic layer was collected and the aqueous layer was extracted by dichloromethane. The combined organic layers were dried over magnesium sulfate and concentrated. The crude product was purified by silica gel flash chromatography with up to 10% ethyl acetate in hexanes to give 5 grams of yellow solid. It was further recrystallized from dichloroethane/heptane to obtain 2.5 grams of white sold (39%).



2. Synthesis of Compound 22S.

[0072] A mixture of 4,4,5,5-tetramethyl-2-(triphenylen-2-yl)-1,3,2-dioxaborolane (2.2 g, 6.1 mmol), 2-chloro-6-(dibenzothiophen-4-yl)pyridine (1.5 g, 5.1 mmol), potassium phosphate tribasic (3.3 g, 15.3 mmol), toluene 150 mL and water 15 mL was prepared. Nitrogen was bubbled directly in the mixture for 40 minutes. Next tris dibenzylideneacetone dipalladium (56 mg, 0.06 mmol) and bis(cyclohexyl)-2-biphenylphosphine (100 mg, 0.24 mmol) were added, and then nitrogen was bubbled in the mixture for another 17 minutes. The reaction mixture was refluxed overnight under nitrogen. The precipitation was collected by filtration and washed by toluene, dichloromethane and methanol. Then the product was dissolved in 250 mL boiling xylene, filtered through a small magnesium sulfate plug. The

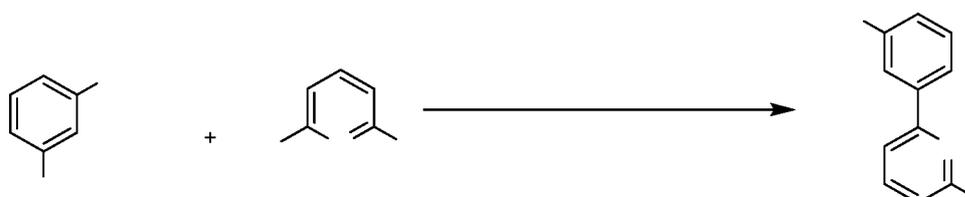
filtration was heated to reflux to dissolve all the solid and allowed to slowly cool down. The recrystallized product was obtained as 2.3 gram white solid (93%).



Example 9 Compound 21S

1. Synthesis of 2-chloro-6-(3-methoxyphenyl)pyridine.

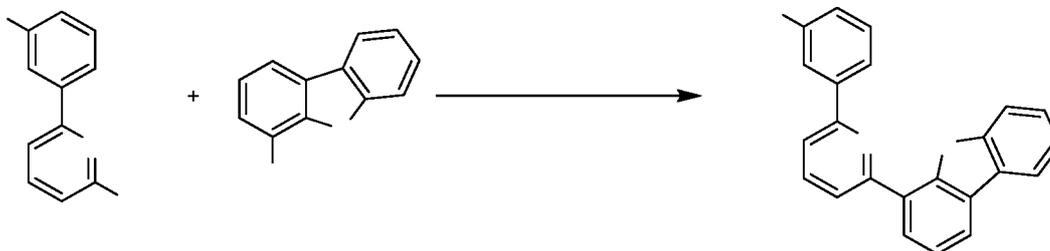
[0073] A mixture of m-methoxy-phenylboronic acid (10 g, 65.8 mmol), 2,6-dichloropyridine (9.7 g, 65.8 mmol), potassium carbonate (27.3 g, 197.4 mmol), triphenylphosphine (2.07 g, 7.9 mmol), dimethoxyethane 250 mL and water 80mL was prepared. Nitrogen was bubbled directly in the mixture for 20 minutes. Then palladium acetate was added (0.44 g, 2.0 mmol). Nitrogen was bubbled again in the mixture for another 10 minutes. The mixture was heated to reflux under nitrogen overnight. The reaction mixture was cooled to room temperature. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over magnesium sulfate, filtered and evaporated. The mixture was purified by silica column with up to 10% ethyl acetate in hexanes to gain 6.5 g colorless oil (45%).



2. Synthesis of 2-(dibenzo[*b*,*c'*]thiophen-4-yl)-6-(3-methoxyphenyl)pyridine.

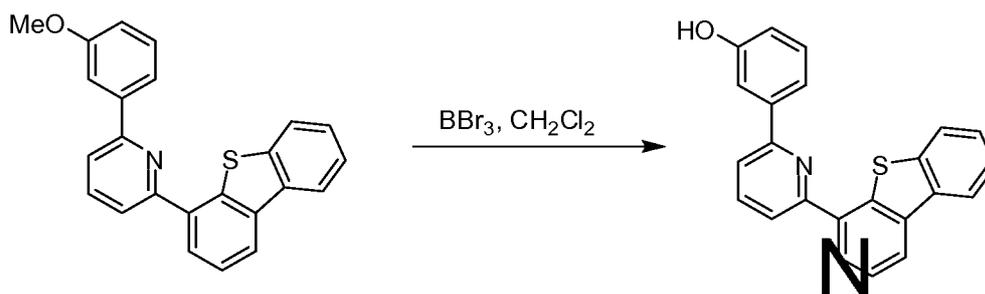
[0074] A mixture of 2-chloro-6-(3-methoxyphenyl)pyridine (3.5 g, 16 mmol), dibenzothiophene-4-boronic acid (4g, 17.5 mmol), potassium phosphate (10.2 g, 48mmol), dimethoxyethane 500 mL and water 50 mL was prepared. Nitrogen was bubbled directly in the mixture for 15 minutes. Next tris dibenzylideneacetone dipalladium (147 mg, 0.16 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (263 mg, 0.64 mmol) were added, and then nitrogen was bubbled in the mixture for another 15 minutes. The reaction mixture was heated to reflux 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 with

dichloromethane. The combined organic layers were dried over magnesium sulfate, filtered and evaporated. The mixture was purified by silica column with up to 10% ethyl acetate in hexanes to gain 3.8 g yellow solid (65%).



3. Synthesis of 3-(6-(dibenzo[6, J]thiophen-4-yl)pyridin-2-yl)phenol

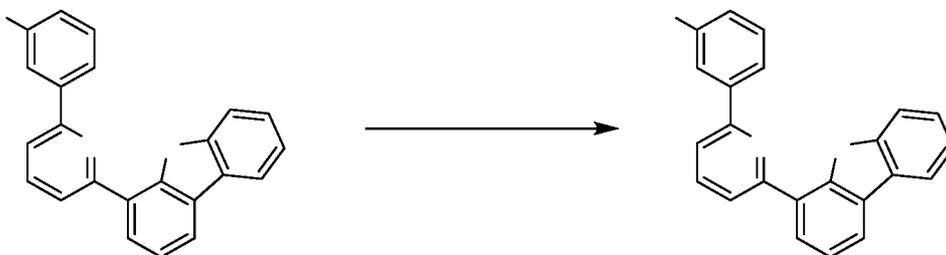
[0075] 2-(dibenzo[*b,d*]thiophen-4-yl)-6-(3-methoxyphenyl)pyridine (3.8 g, 10.3 mmol) was dissolved in 120 mL dichloromethane. The solution was cooled to 0 °C under nitrogen. BBr₃ (22.8 mL, 1M in hexane) was slowly added in at 0 °C and then was slowly brought up to room temperature. The mixture was stirred at room temperature overnight. A brown solid was observed to form. The reaction was quenched by adding 100 mL water slowly. The dichloromethane was removed by rotovap. Then the mixture was refluxed for three hours. Saturated sodium bicarbonate solution was added to neutralize the mixture, which was extracted by dichloromethane and ethyl acetate. The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure to obtain 4 gram glassy dark brown solid. The product was used for next step without further purification.



4. Synthesis of 3-(6-(dibenzo[6, J]thiophen-4-yl)pyridin-2-yl)phenyl trifluoromethanesulfonate.

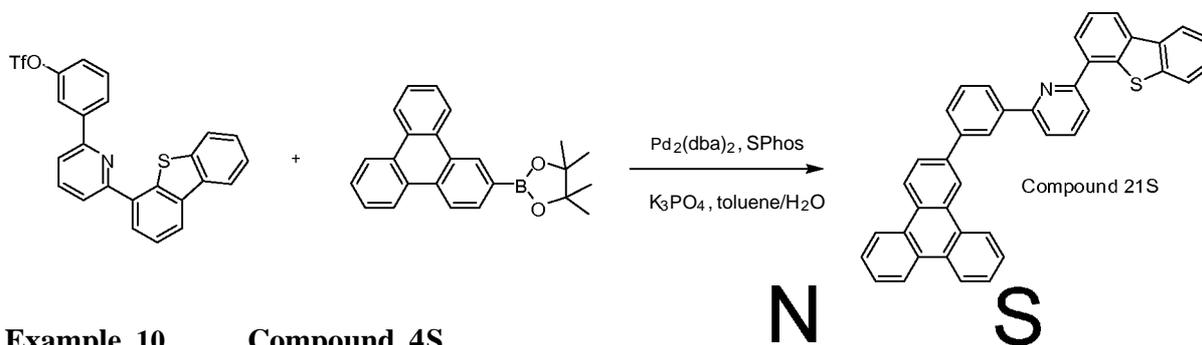
[0076] 3-(6-(dibenzo[6, J]thiophen-4-yl)pyridin-2-yl)phenol (4 g, 11.1 mmol) was suspended in 100 mL pyridine, cooled to -10 °C with acetone/ice bath. Triflate anhydride (2.29 mL, 13.6 mmol) was slowly added under nitrogen. The mixture was stirred at 0 °C for two hours then poured into saturated sodium bicarbonate solution 200 mL. The mixture was extracted by ethyl acetate. The combined organic layers were dried over magnesium sulfate,

filtered and evaporated. The mixture was purified by silica column twice with up to 15% ethyl acetate in hexanes. The product was then precipitated from its dichloromethane solution by adding hexanes to gain 1.8 gram white color solid (the combined yield of last two steps is 36%).



5. Synthesis of Compound 21S.

[0077] A mixture of 3-(6-(dibenzo[*b,d*]thiophen-4-yl)pyridin-2-yl)phenyl trifluoromethanesulfonate (1.65 g, 3.4 mmol), 4,4,5,5-tetramethyl-2-(triphenylen-2-yl)-1,3,2-dioxaborolane (1.32 g, 3.7 mmol), potassium phosphate (2.16 g, 10.2 mmol), toluene 100 mL and water 10 mL was prepared. Nitrogen was bubbled directly in the mixture for 25 minutes. Next tris dibenzylideneacetone dipalladium (31 mg, 0.034 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (55 mg, 0.14 mmol) were added, and then nitrogen was bubbled in the mixture for another 15 minutes. The reaction mixture was heated to reflux for eight hours under nitrogen. The next day the reaction mixture was cooled to room temperature. The residue was collected by filtration, washed by toluene, dichloromethane and methanol px| e/si\ely to get 1.8 gram grey solid, which was sublimed at 260 °C twice before used for device raorication.

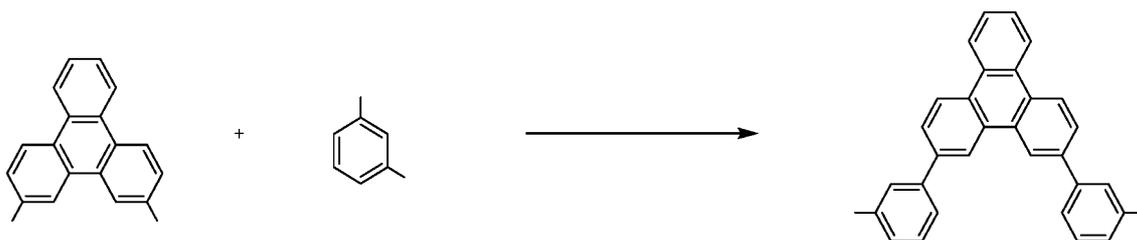


Example 10 Compound 4S

1. Synthesis of 2,11-bis(3-methoxyphenyl)triphenylenes.

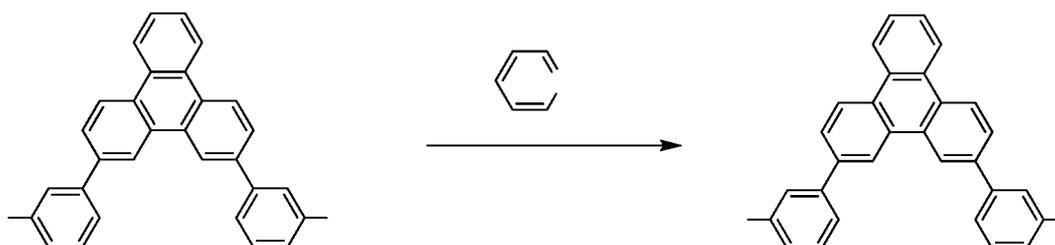
[0078] A mixture of triphenylene-2,11-diyl bis(trifluoromethanesulfonate) (2 g, 3.8 mmol), 3-methoxyphenylboronic acid (2.3 g, 15 mmol), potassium phosphate tribasic (4.8 g, 23

mmol), toluene 100 mL and water 10 mL was prepared. Nitrogen was bubbled directly in the mixture for 30 minutes. Next tris(dibenzylideneacetone)dipalladium (70 mg, 0.076 mmol) and bis(cyclohexyl)-2-biphenylphosphine (125 mg, 0.30 mmol) were added, and then nitrogen was bubbled in the mixture for another 15 minutes. The reaction was refluxed under nitrogen for three hours. After cooled to room temperature, the organic layer of the reaction mixture was collected, dried over magnesium sulfate, and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography to give 1.6 g white solid (yield 95%).



2. Synthesis of 3,3'-(triphenylene-2,11-diyl)diphenole.

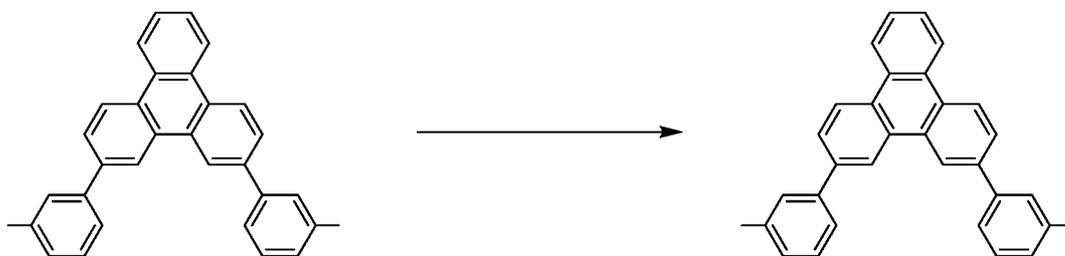
[0079] A mixture of 2,11-bis(3-methoxyphenyl)triphenylene (1.6 g, 3.7 mmol) and pyridine hydrochloride (4.3 g, 37 mmol) was heated to 220 °C under nitrogen for two and half hours. The reaction was cooled to room temperature, and washed with water. The 1.6 g brown residue was collected by filtration, dried under vacuum and was used without further purification for next step.



3. Synthesis of 3,3'-(triphenylene-2,11-diyl) bis(3,1-phenylene) bis(trifluoromethanesulfonate).

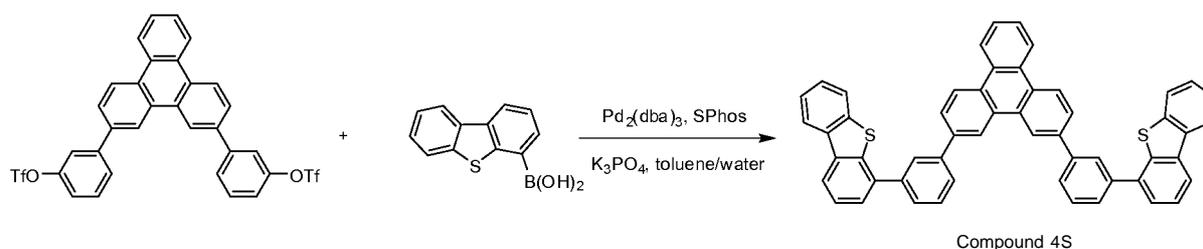
[0080] The 3,3'-(triphenylene-2,11-diyl)diphenole (1.6 g, 3.9 mmol) was suspended in a mixture of 50 mL dichloromethane and 5 mL pyridine. The mixture was cooled to 0 °C by ice/water bath. Triflate anhydride (1.44 mL, 8.5 mmol) was dissolved in 30 mL dichloromethane and slowly added into the reaction mixture under nitrogen at 0 °C. Then the reaction was stirred at room temperature under nitrogen overnight. Methanol 20 mL was added to the reaction. The mixture was concentrated by rotovap. The residue was suspended

in water then was collected by filtration. After washed with water, the residue was dried under vacuum. The crude product was purified by silica flash chromatograph with up to 30% dichloromethane in hexanes to give white solid 1.6 gram (combined yield of last two steps: 65 %).



4. Synthesis of Compound 4S.

[0081] The mixture of 3,3'-(triphenylene-2,11-diyl) bis(3,1-phenylene) bis(trifluoromethanesulfonate) (1.6 g, 2.4 mmol), dibenzothiophene-4-boronic acid (2.7 g, 12 mmol), potassium phosphate tribasic (3.4 mmol, 16 mmol), toluene 100 mL and water 50 mL was prepared. Nitrogen was bubbled directly in the mixture for 1 hour. Next tris dibenzylideneacetone dipalladium (44 mg, 0.048 mmol) and bis(cyclohexyl)-2-biphenylphosphine (78 mg, 0.19 mmol) were added, and then nitrogen was bubbled in the mixture for another 30 minutes. The reaction was refluxed overnight. After the reaction was cooled to room temperature, the residue was collected by filtration and washed by methanol and dichloromethane to provide final product.



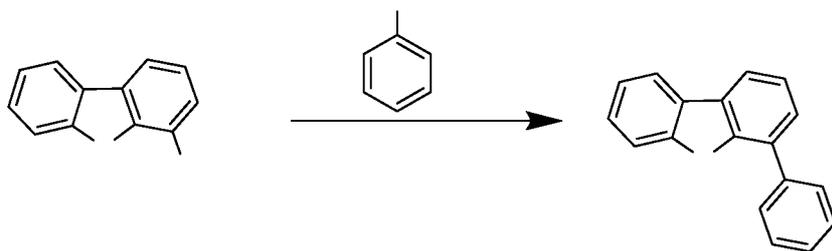
Example 11 Compound 23S

1. Synthesis of 4-phenyldibenzothiophene.

[0082] 10 g (41.6 mmol) 4-dibenzothiophene boronic acid, 6.25 g (39.6 mmol) bromobenzene, 366 mg (0.39 mmol) $\text{Pd}_2(\text{dba})_3$, 656 mg (1.6 mmol) S-phose, 25.4 g (120 mmol) K_3PO_4 , 180 mL toluene and 20 mL water were charged in a 500 mL flask. The mixture was heated up to reflux under nitrogen for overnight. The reaction mixture was

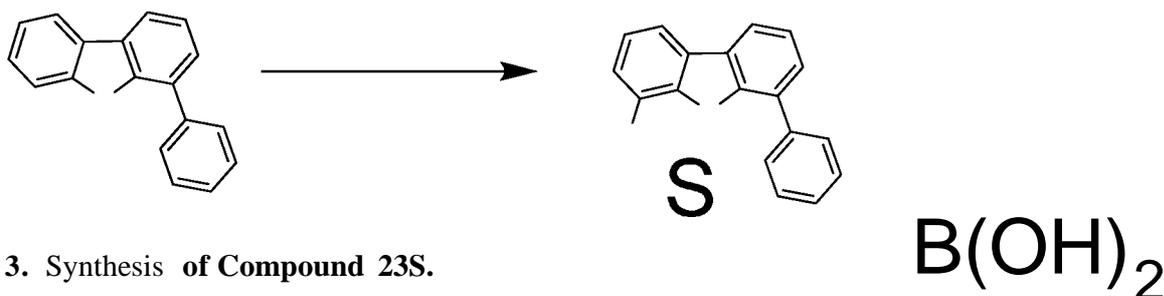
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purified by silica gel column chromatography with pure hexane as elute. ~ 8.5 g (83%) white solid was obtained as product which was confirmed by MS.



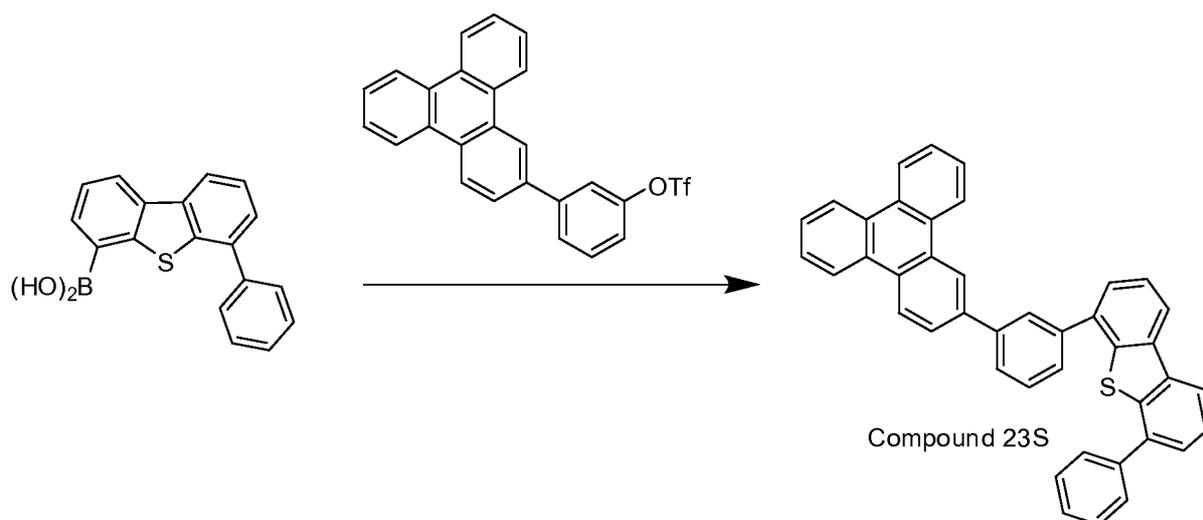
2. Synthesis of 4-phenyldibenzothiophene-6-boronic acid.

[0083] 3.5 g (13.4 mmol) 4-phenyldibenzothiophene was dissolved in ~30 mL anhydrous THF in a three necked 250 mL flask and cooled down to -78°C . To the mixture, 17 mL (27 mmol) 1.6 M BuLi in hexane was added and stirred for 30 minutes. The cooling bath was removed and let reaction kept stirring for overnight. The reaction mixture was cooled down again to -78°C and 4.5 mL (40 mmol) trimethyl borate was added and stirred at room temperature for 4 hours. ~ 100 mL 1 M HCl was added and kept stirring for 1 hour. The mixture was extracted by ethyl acetate and the organic extracts were combined. The solvent was evaporated to dryness. The solid was added with ~ 100 mL 20% ethyl acetate in hexane was stirred for few hours and then filtered. The filtered solid washed by hexane few times. ~ 2.5 g white solid was obtained as product which was confirmed by proton NMR.



3. Synthesis of Compound 23S.

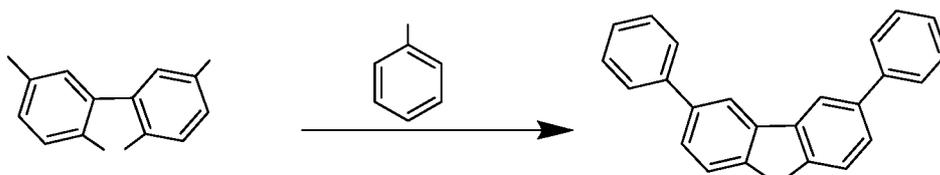
[0084] 2.4 g (7.89 mmol) above boronic acid, 3.3 g (7.2 mmol) 3-(triphenyl-2-yl)phenyl trifluoromethanesulfonate, 67 mg (0.08 mmol) $\text{Pd}_2(\text{dba})_3$, 120 mg (0.3 mmol) S-phose, 4.6 g (21.7 mmol) K_3PO_4 , 90 mL toluene and 10 mL water were charged in a 250 mL flask. The mixture was heated up to reflux under nitrogen for 6.5 hours. The reaction mixture was separated with separation funnel and the organic phase was purified by silica gel column chromatography using 20% dichloromethane in hexane as elute and recrystallization from toluene and hexane mixture. ~ 3.8 g (94%) white solid was obtained as product which was confirmed by proton NMR.



Example 12 Compound 24S

1. Synthesis of 2,8-diphenylbenzothiophene.

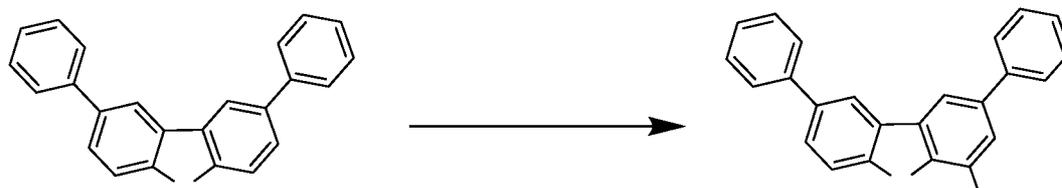
[0085] 7.0 g (20.4 mmol) 2,8-dibromodibenzothiophene, 6.4 g (51.1 mmol) phenylboronic acid, 187 mg (0.2 mmol) $\text{Pd}_2(\text{dba})_3$, 335 mg (0.8 mmol) S-phase, 13 g (61.2 mmol) K_3PO_4 , 90 mL toluene and 10 mL water were charged in a 250 mL flask. The mixture was heated up to reflux under nitrogen for 4 hours. The reaction mixture was separated with separation funnel and the organic phase was purified by silica gel column chromatography using 20% dichloromethane in hexane as elute. ~ 6.6 g (96%) white solid was obtained as product which was confirmed by GC-MS.



2. Synthesis of 2,8-diphenyldibenzothiophene-4-boronic acid.

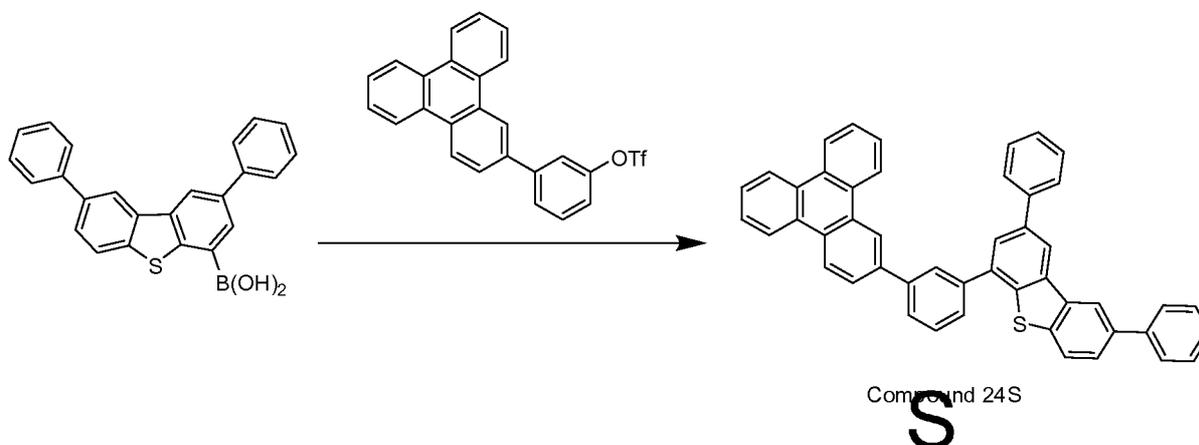
[0086] 3.8 g (11.3 mmol) 2,8-diphenylbenzothiophene was dissolved in ~ 30 mL anhydrous THF in a 250 mL three necked flask. To the mixture, ~18 mL (28.3 mmol) 1.6 M BuLi in hexane was added at $-78\text{ }^\circ\text{C}$ under nitrogen. The mixture was warmed up to room temperature and kept stirring for 18 hours. The reaction mixture cooled down to $-78\text{ }^\circ\text{C}$ again and 3.8 mL (34 mmol) trimethyl borate was added and kept mixture stirred for 4 hours at room temperature then added ~ 60 mL IM HCl with stirring for 1 hour. The mixture was extracted by ethyl acetate and the organic phases were combined. The solvent was evaporated to dryness. The solid was added with ~ 100 mL 20% ethyl acetate in hexane. It was stirred for

few hours and then filtered. The filtered solid was washed with hexane 3 times. ~ 2.2 g white solid was obtained as product which was confirmed by proton NMR.



3. Synthesis of Compound 24S.

[0087] 2.0 g (5.26 mmol) 2,8-diphenyldibenzothiophene-4-boronic acid, 2.18 g (4.78 mmol) 3-(triphenyl-2-yl)phenyl trifluoromethanesulfonate, 45 mg (0.05 mmol) $\text{Pd}_2(\text{dba})_3$, 80 mg (0.19 mmol) *S*-phose, 3.2 g (14 mmol) K_3PO_4 , 90 mL toluene and 10 mL water were charged in a 250 mL flask. The mixture was heated up to reflux under nitrogen for overnight. The reaction mixture was separated with separation funnel and the organic phase was purified by silica gel column chromatography using 20% dichloromethane in hexane as elute and recrystallization from toluene and hexane mixture. ~ 2.52 g (84%) white solid was obtained as product which was confirmed by proton NMR.

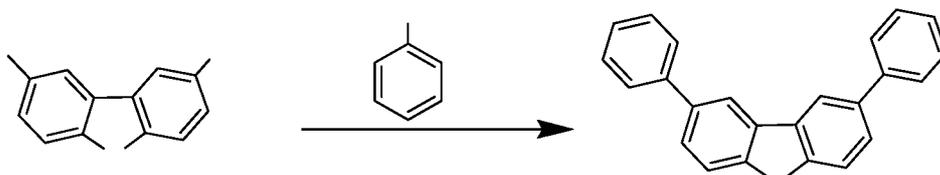


Example 13 Compound 25S

1. Synthesis of 2,8-diphenylbenzothiophene.

[0088] 7.0 g (20.4 mmol) 2,8-dibromodibenzothiophene, 6.4 g (51.1 mmol) phenylboronic acid, 187 mg (0.2 mmol) $\text{Pd}_2(\text{dba})_3$, 335 mg (0.8 mmol) *S*-phose, 13 g (61.2 mmol) K_3PO_4 , 90 mL toluene and 10 mL water were charged in a 250 mL flask. The mixture was heated up to reflux under nitrogen for 4 hours. The reaction mixture was separated with separation funnel and the organic phase was purified by silica gel column chromatography using 20%

dichloromethane in hexane as elute. ~ 6.6 g (96%) white solid was obtained as product which was confirmed by GC-MS.



2. Synthesis of 2,8-diphenyldibenzothiophene-4-boronic acid.

[UDC please verify the name that we assigned to the above intermediate.]

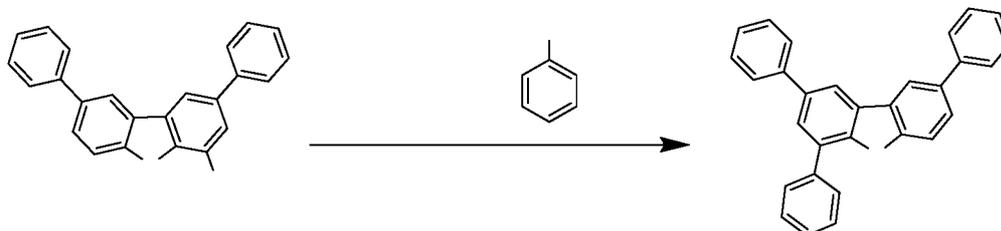
[0089] 3.8 g (11.3 mmol) 2,8-diphenylbenzothiophene was dissolved in ~ 30 mL anhydrous THF in a 250 mL three necked flask. To the mixture, ~18 mL (28.3 mmol) 1.6 M BuLi in hexane was added at -78 °C under nitrogen. The mixture was warmed up to room temperature and was kept stirring for 18 hours. The reaction mixture was cooled down to -78 °C again and 3.8 mL (34 mmol) trimethyl borate was added and the mixture was kept stirring for 4 hours at room temperature. ~ 60 mL IM HCl was then added with continuous stirring for 1 hour. The mixture was extracted by ethyl acetate and the organic phases were combined. The solvent was evaporated to dryness. The solid was added with ~ 100 mL 20% ethyl acetate in hexane was stirred for a few hours and then filtered. The filtered solid washed with hexane. ~ 2.2 g white solid was obtained as product which was confirmed by proton NMR.



3. Synthesis of 2,4,8-triphenylbenzothiophene.

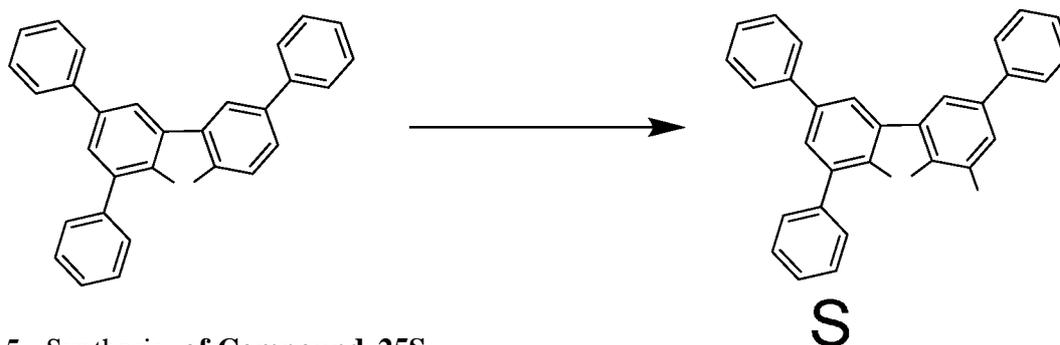
[0090] 5.5 g (14.5 mmol) 2,8-diphenyldibenzothiophene-4-boronic acid, 2.3 g (14.5 mmol) bromobenzene, 135 mg (0.15 mmol) Pd₂(dba)₃, 238 mg (0.58 mmol) S-phase, 9.2 g (43.2 mmol) K₃PO₄, 180 mL toluene and 20 mL water were charged in a 500 mL flask. The mixture was heated up to reflux under nitrogen for overnight. The reaction mixture was separated with separation funnel and the organic phase was purified by silica gel column chromatography using 20% ethyl acetate in hexane as elute. ~ 5.1 g 2,4,8-

triphenylbenzothiophene white solid was obtained as product which was confirmed by proton NMR.



4. Synthesis of 2,4,8-triphenyldibenzothiophene-6-boronic acid.

[0091] 5.0 g (12.13 mmol) 2,4,8-triphenylbenzothiophene was dissolved in ~ 100 mL anhydrous THF in a 250 mL three necked flask. To the mixture, ~19 mL (30.3 mmol) 1.6 M BuLi in hexane was added at -78 °C under nitrogen. The mixture was warmed up to room temperature and kept stirring for 18 hours. The reaction mixture was cooled down to -78 °C again and 3.8 mL (34 mmol) trimethyl borate was added and kept mixture stirred for 4 hours at room temperature then added ~ 100 mL 1M HCl with stirring for 1.5 hour. The mixture was extracted by ethyl acetate and the organic phases were combined. The solvent was evaporated to dryness. The solid was added with ~ 150 mL 20% ethyl acetate in hexane. The mixture was stirred for few hours and then filtered. The filtered solid was washed with hexane 3 times. - 4.5 g white solid was obtained as product which was confirmed by proton NMR.



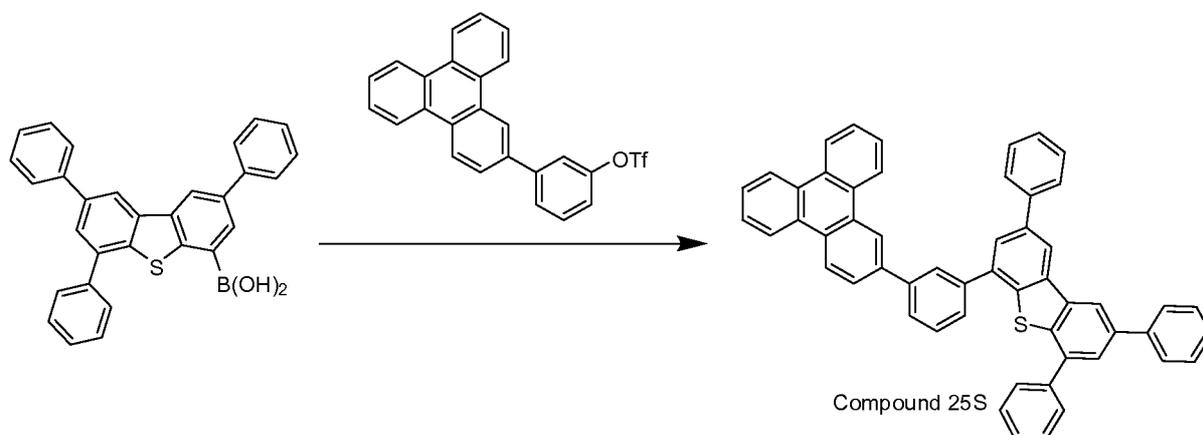
5. Synthesis of Compound 25S.

[0092] 3.5 g (7.67 mmol) 2,4,8-triphenyldibenzothiophene-6-boronic acid, 3.2 g (6.98 mmol) 3-(triphenyl-2-yl)phenyl trifluoromethanesulfonate, 64 mg (0.077 mmol) Pd₂(dba)₃, 115 mg (0.30 mmol) S-phase, 4.5 g (22 mmol) K₃PO₄, 90 mL toluene and 10 mL water were charged in a 250 mL flask. The mixture was heated up to reflux under nitrogen for overnight.



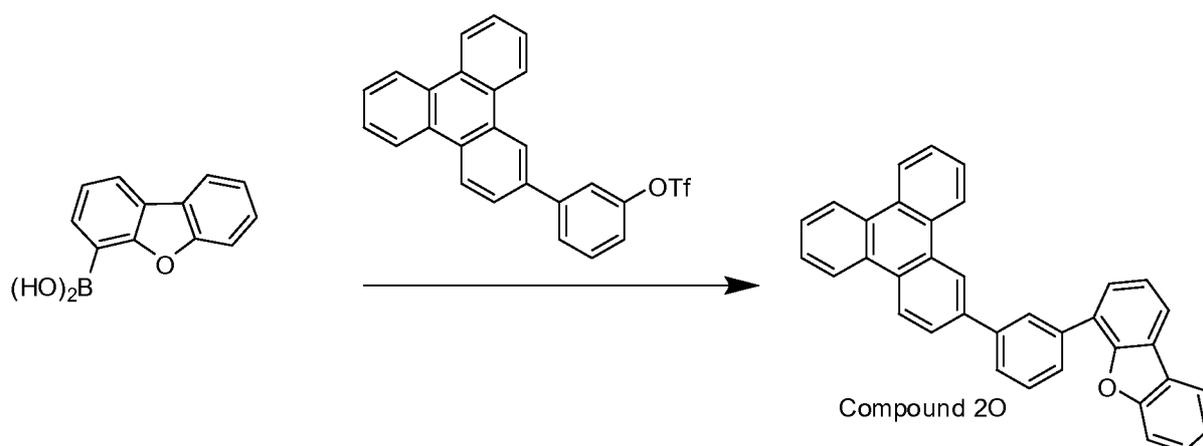
S

The reaction mixture was separated with separation funnel and the organic phase was purified by silica gel column chromatography using 25% dichloromethane in hexane as elute and recrystallization from toluene and hexane mixture. ~ 4.5 g (92%) white solid was obtained as product which was confirmed by proton NMR.



Example 14 Compound 20

[0093] 3.9 g (18.4 mmol) dibenzofuran-4-boronic acid, 7.0 g (15.4 mmol) 3-(triphenylen-2-yl)phenyl trifluoromethanesulfonate, 141 mg (0.154 mmol) $\text{Pd}_2(\text{dba})_3$, 252 mg (0.46 mmol) *S*-phose, 9.8 g (46 mmol) K_3PO_4 , 180 mL toluene and 20 mL water were charged in a 500 mL flask. The mixture was heated up to reflux under nitrogen for overnight. The reaction mixture was separated with separation funnel and the organic phase was purified by silica gel column chromatography using 20% dichloromethane in hexane as elute. ~ 6.2 g (87%) white solid was obtained as product which was confirmed by proton NMR.



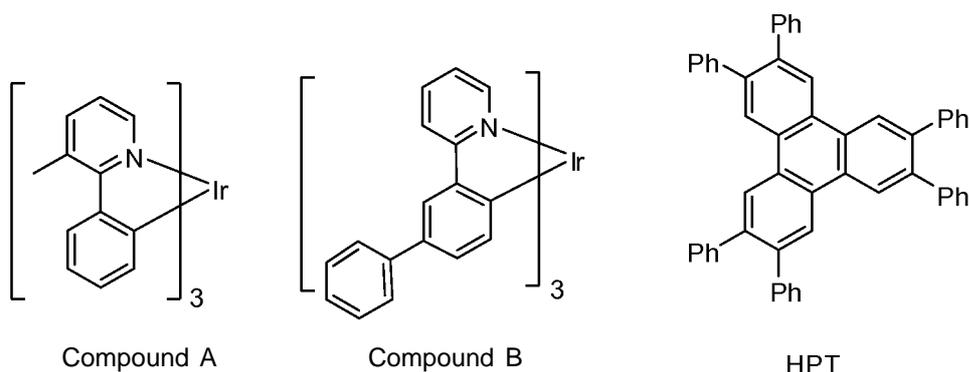
Device Examples

[0094] All example devices were fabricated by high vacuum ($<10^{-7}$ Torr) thermal evaporation. The anode electrode is -800 or 1200 Å of indium tin oxide (ITO). The cathode consisted of 10 Å of LiF followed by 1,000 Å of Al. All devices are encapsulated with a glass lid sealed with an epoxy resin in a nitrogen glove box (<1 ppm of H_2O and O_2) immediately after fabrication, and a moisture getter was incorporated inside the package.

[0095] The organic stack of Device Examples 1-30 in Tables 1 and 2 consisted of sequentially, from the ITO surface, 100 Å of Compound A as the hole injection layer (HIL), 300 Å of 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (α -NPD) as the hole transporting layer (HTL), 300 Å of the invention compound doped with 10 or 15 wt% of an Ir phosphorescent compound as the emissive layer (EML), 50 or 100 Å of HPT or the invention compound as the ETL2 and 400 or 450 Å of Alq_3 (tris-8-hydroxyquinoline aluminum) as the ETL1.

[0096] Comparative Examples 1 and 2 were fabricated similarly to the Device Examples except that the CBP is used as the host.

[0097] The device structures and data are summarized in Tables 1 through 5. Table 1 shows device structure and Table 2 shows corresponding measured results for those devices, whereas each of Tables 3 through 5 show both the device structure and measured experimental results. As used herein, Compound A, Compound B, NPD and HPT, have the following structures:



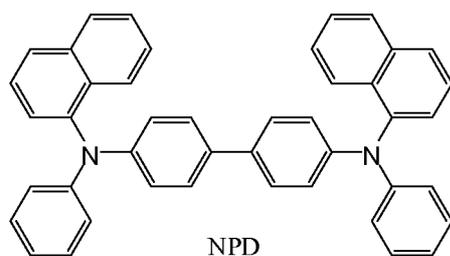


Table 1.

Device Example	Host	Dopant %	ETL2 (Å)	ETL1 (Å)	ITO thickness (nm)
Comparative 1	CBP	B 10%	HPT (50)	Alq ₃ (450)	120
Comparative 2	CBP	A 10%	HPT (50)	Alq ₃ (450)	120
1	1S	A 10%	HPT (50)	Alq ₃ (450)	120
2	1S	A 10%	1S (100)	Alq ₃ (400)	120
3	1S	A 15%	HPT (50)	Alq ₃ (450)	120
4	1S	A 15%	1S (100)	Alq ₃ (400)	120
5	2S	A 10%	HPT (50)	Alq ₃ (450)	120
6	2S	A 10%	2S (100)	Alq ₃ (400)	120
7	2S	A 15%	HPT (50)	Alq ₃ (450)	120
8	2S	A 15%	2S (100)	Alq ₃ (400)	120
9	2S	B 10%	HPT (50)	Alq ₃ (450)	120
10	2S	B 10%	2S (100)	Alq ₃ (400)	120
11	2S	B 15%	HPT (50)	Alq ₃ (450)	120
12	2S	B 15%	2S (100)	Alq ₃ (400)	120
13	20S	A 10%	20S (100)	Alq ₃ (400)	120
14	20S	A 10%	HPT (50)	Alq ₃ (450)	120
15	9S	A 10%	20S (100)	Alq ₃ (400)	120
16	9S	A 10%	HPT (50)	Alq ₃ (450)	120
17	22S	A 10%	22S (100)	Alq ₃ (400)	120
18	22S	A 10%	HPT (50)	Alq ₃ (450)	120
19	21S	A 10%	21S (100)	Alq ₃ (400)	120
20	21S	A 10%	HPT (50)	Alq ₃ (450)	120
21	23S	A 15%	23S (100)	Alq ₃ (400)	120
22	23S	A 15%	HPT (50)	Alq ₃ (450)	120
23	23S	A 10%	23S (100)	Alq ₃ (400)	120
24	23S	A 10%	HPT (50)	Alq ₃ (450)	120
25	24S	A 10%	24S (100)	Alq ₃ (400)	120
26	24S	A 10%	HPT (50)	Alq ₃ (450)	120
27	5S	A 10%	5S (100)	Alq ₃ (400)	120
28	5S	A 10%	HPT (50)	Alq ₃ (450)	120
29	2O	A 10%	2O (100)	Alq ₃ (400)	120
30	2O	A 10%	HPT (50)	Alq ₃ (450)	120

Table 2.

Device Example	CIE		Emission max (nm)	FWHM (nm)	At L=1000 cd/m ²				At J=40 mA/cm ²	
	X	Y			V (V)	LE (cd/A)	EQE (%)	PE (lm/W)	L ₀ (cd/m ²)	LT _{80%} (hr)
Comparative 1	0 331	0 627	521	67	6 1	61 0	17	31 4	16,935	87
Comparative 2	0 346	0 613	522	75	6 2	57 0	16	28 9	13,304	105
1	0 347	0 610	526	76	5 9	60 6	17	32 3	14,083	270
2	0 345	0 612	526	75	6 4	54 9	15	26 9	14,028	310
3	0 348	0 609	526	76	5 9	60 1	17	32 0	14,092	288
4	0 346	0 611	526	75	6 4	54 0	14 8	26 5	13,946	306
5	0 347	0 612	526	75	5 5	67 1	18	38 3	16,615	244
6	0 346	0 612	527	74	6 2	59 6	16	30 2	16,160	300
7	0 352	0 608	527	77	5 6	62 5	17	35 0	15,726	224
8	0 350	0 609	526	76	6 2	57 1	16	28 9	15,716	260
9	0 341	0 619	525	69	6 2	59 9	16 2	30 3	14,641	380
10	0 343	0 618	525	72	6 8	50 2	13 6	23 2	14,069	450
11	0 343	0 620	527	69	5 9	54 3	14 6	28 9	17,088	194
12	0 341	0 620	527	68	6 5	40 5	10 9	19 6	13,744	620
13	0 356	0 607	528	76	6 4	60 9	16 8	29 8	15,974	150
14	0 356	0 607	528	76	5 7	66 6	18 4	38 1	15,414	134
15	0 366	0 600	528	75	6 0	52	14 2	25	15,950	60
16	0 357	0 608	528	75	6 0	60	16 4	31 2	17,100	70
17	0 375	0 587	532	78	8	29 3	8 2	11 5	8,755	91
18	0 374	0 590	532	76	7 5	39 2	11	16 4	10,865	82
19	0 367	0 597	532	82	8 5	35 4	9 8	13 1	10,058	338
20	0 364	0 600	532	82	7 9	44 5	12 3	17 7	11,682	240
21	0 365	0 601	528	76	6 9	49 5	13 7	22 5	14,135	620
22	0 363	0 603	528	76	6 2	56 5	15 7	28 6	15,067	457
23	0 362	0 602	529	77	7 2	52 4	14 6	22 9	14,186	378
24	0 364	0 601	529	77	6 6	55 1	15 4	26 2	13,810	343
25	0 363	0 603	530	78	6 8	52 3	14 5	29 8	14,994	175
26	0 363	0 602	530	78	6 3	51 9	14 4	36 7	14,061	150
27	0 385	0 588	538	86	7 4	30 7	8 6	13 0	10,211	1 3
28	0 382	0 590	538	86	6 8	36 4	10 2	16 8	11,305	2 0
29	0 352	0 609	528	79	6 6	56 8	15 7	27 0	15,207	305
30	0 355	0 607	528	78	6	63 3	17 4	33 1	15,219	240

[0098] From Device Examples 1-30, it can be seen that Compounds IS, 2S, 20S, 9S, 23S, 24S and 20 as hosts in green phosphorescent OLEDs give high device efficiency (LE>40 cd/A at 1000 cd/m²), indicating the triphenylene and benzothiophene combinations, either directly linked or m-phenylene-linked have triplet energy high enough for efficient green electrophosphorescence.

[0099] The high stability of devices incorporating Compounds IS, 2S, 21S, 23S and 20 as the host is notable. Device Example 1 and Comparative Example 2 are only different in the host. Device Example 1 uses Compound 1 as the host whereas Comparative Example 2 uses

the commonly used host CBP. The lifetime, $T_{80\%}$ (defined as the time required for the initial luminance, L_0 , to decay to 80% of its value, at a constant current density of 40 mA/cm² at room temperature) are 270 hours and 105 hours respectively, with Device Example 1 having a slightly higher L_0 . This translates to almost a 3 fold improvement in the device stability. Similarly, Device Example 5 using Compound 2S as the host, is at least 2.5 times more stable than Comparative Example 2. Device Example 9 using Compound 2S as the host, is at least 3 times more stable than Comparative Example 1 with CBP as the host. It is also notable that the compounds may function very well as an enhancement layer material (ETL2). Device Example 10 and Device Example 9 both have Compound 2S as the host, but Compound 2 and HPT as the enhancement layer respectively. Device Example 10 and Device Example 9 have $T_{0.8}$ of 450 and 380 hours respectively, indicating the good performance of Compound 2S as the enhancement layer material. Device Example 21 has $T_{0.8}$ of 620 hours which is significantly higher than the lifetime of Comparative Example 1 or 2 device with CBP.

[0100] The data suggest that triphenylene containing benzothiophenes, particularly triphenylene containing dibenzothiophenes, are excellent host and enhancement layer materials for phosphorescent OLEDs, providing as least the same efficiency and multiple times of improvement in stability compared to the commonly used CBP as the host. More conjugated versions of triphenylene containing benzothiophenes, for example triphenylene and benzothiophene units linked via -phenylene (such as 4,4'-biphenyl) may be very suitable for lower energy (yellow to red) phosphorescent OLEDs.

[0101] Table 3 shows device structures and measured experimental results for some devices having an emissive layer with an interface between a first organic layer and a second organic layer, where the host and the dopant, i.e., the non-emissive material is the same material in both layers and the phosphorescent material is the same material in both layers, but the concentrations are different. All of the devices in Table 3 had a 100 Å hole injection layer of Compound A, a 100 Å enhancement layer (ETL2) of different materials depending on the specific device, a 400 Å electron transport layer (ETL1), and an LiF / Al cathode. The emissive layer included a first organic layer and a second organic layer with an interface between them, where the first organic layer was 300 Å of a non-emissive material (the "host" in Table 3) at a concentration of 70 wt% and a phosphorescent material (the "dopant" of Table 3) at a concentration of 30 wt%, and the second organic layer was 300 Å of the same non-emissive material (the "host" in Table 3) but at a concentration of 90 wt% and the same phosphorescent material (the "dopant" of Table 3) but at a concentration of 10 wt%. The

specific host and dopant for each device are identified in Table 3. Thus, the general device structure for the devices of Table 3 was: ITO (1200Å) / Compound A (100Å) / host (70 wt%):dopant (30 wt%) (300Å) / host (90 wt%):dopant (10 wt%) (300Å) / ETL2 (100Å) / Alq₃ (400Å) / LiF / AL

Table 3.

Example				CIE		At 1,000 nits				At 40mA/cm ²	
	Host	Dopant	ETL2	X	Y	V (V)	L.E. [cd/A]	E.Q.E. [%]	P.E. [lm/W]	Lo [nits]	LT80% [h]
A	Cmpd. 2S	A	Cmpd. 2S	0.36	0.61	6.4	57.5	15.9	28.2	17,225	1060
B	Cmpd. 2S	A	HPT	0.36	0.61	5.8	60.4	16.6	32.7	16,732	1000
C	Cmpd. 2S	B	Cmpd. 2S	0.34	0.62	8.4	46.4	12.5	17.3	15,184	2100
D	Cmpd. 2S	B	HPT	0.35	0.62	7.8	54.7	14.8	22.0	15,04	1350

[0102] The devices in Table 3, using Compound 2S as the host and Compound 2S or HPT as the enhancement layer material show high efficiency (>46 cd/A at 1000 cd/m²). Even more notable are the stabilities of LT_{80%} of 1000 hours (Device Examples A, B and D) or even 2000 hours (Device Example C), rendering these devices among the most long-lived green phosphorescent OLEDs to date.

[0103] The good performance and high stability of the devices with triphenylene-benzothiophene hybrids is believed to be a result of the good charge balance provided by the triphenylene and benzothiophene charge transporting units, and the stabilization of the oxidized/reduced states of the molecule by the π -conjugation provided by the benzothiophene and triphenylene units.

[0104] Table 4 and Table 5 show device structures and measured experimental results for devices having an emissive layer containing triphenylene and benzo-fused thiophene attached to a central pyridine.

[0105] All of the devices in Table 4 had a IOOA hole injection layer of Compound A, a 300 Å hole transport layer of NPD, a 300Å emissive layer with Compound 21S as the host and Compound A as the dopant, a blocking layer (BL) having materials and thicknesses identified in Table 4, an electron transport layer (ETL) of Alq having a thickness identified in Table 4, and a LiF / Al cathode. In particular, the BL thickness and the ETL thickness have a sum total of 500Å. The emissive layer was a single layer including the host and dopant. The specific percentage of dopant for each device is identified in Table 4. Thus, the general

device structure for Table 4 was: ITO(1200Å)/ Compound A (100Å)/ NPD (300Å)/ Compound 21S:Compound A x% (300Å)/BL/Alq(500Å - BL)ZLiF(IO)ZAl(IOOO).

Table 4.

Example					CIE		At 1,000 nits				At 40mA/cm ²	
	Host	Dopant x %	BL	ETL (Å)	X	Y	V (V)	L.E. [Cd/A]	EQE [%]	P.E. [lm/W]	Lo [nits]	RT 80%
E	21S	A, 10%	21S 100Å	Alq 400	0.367	0.597	8.5	35.4	9.8	13.1	10,058	338
F	21S	A, 15%	21S 100Å	Alq 400	0.370	0.594	8.1	34	9.5	13.2	10,189	335
G	21S	A, 10%	HPT 50Å	Alq 450	0.364	0.600	7.9	44.5	12.3	17.7	11,682	240
H	21S	A, 15%	HPT 50Å	Alq 450	0.369	0.597	7.5	44.3	12.3	18.5	12,377	235

[0106] All of the devices of Table 5 had a 100Å hole injection layer of Compound A, a 300Å hole transport layer having materials identified in Table 5, a 300Å emissive layer with Compound 22S as the host and Compound A as the dopant, a blocking layer (BL) having materials and thicknesses identified in Table 5, an electron transport layer having a thickness that is 500Å minus the thickness (Å) of the blocking layer (BL), and a LiFZAl cathode. In particular, the BL thickness and the ETL thickness have a sum total of 500Å. The emissive layer was a single layer including the host and dopant. The specific percentages for each device is identified in Table 5. Thus, the general device structure for Table 5 was: ITO(120 Å)Z Compound A 100(A)ZHPT(300Å)ZCompound 22S:Compound A x% (300Å)ZBLZAlq(500Å -BL)ZLiF(IO)Z Al(IOOO).

Table 5.

Example	HTL, 300Å	Host	Dopant x %	BL (Å)	ETL (Å)	CIE		At 1,000 nits				At 40 mA/cm ²	
						X	Y	V (V)	L.E. [cd/A]	E.Q.E. [%]	P.E. [lm/W]	Lo [nits]	RT 80% [hr]*
I	NPD 300Å	22S	A 10%	22S 100	Alq 400	0.375	0.587	8	29.3	8.2	11.5	8,755	91
J	NPD 300Å	22S	A 10%	HPT 50	Alq 450	0.374	0.590	7.5	39.2	11	16.4	10,865	82
K	NPD 300Å	22S	A 15%	22S 100	Alq 400	0.374	0.590	7.9	31.2	8.7	12.4	9,222	120
L	NPD 300Å	22S	A 15%	HPT 50	Alq 450	0.373	0.594	7.4	42.4	11.7	18.0	11,522	110
M	22S:A 30%	22S	A 10%	22S 100	Alq 400	0.398	0.579	9.5	16.4	4.7	5.4	5,959	>600
N	22S:A 30%	22S	A10%	HPT 50	Alq 450	0.393	0.583	9.3	20.2	5.8	6.8	6,863	>600

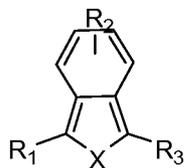
*extrapolated data

[0107] 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. Particularly, the triphenylene containing group may be attached to any position of benzothiophene or benzofuran. It is understood that various theories as to why the invention works are not intended to be limiting.

CLAIMS:

1. A compound comprising a triphenylene containing benzo-fused thiophene or benzo-fused furan, wherein any substituent in the compound is an unfused substituent independently selected from the group consisting of C_nH_{2n+1} , OC_nH_{2n+1} , OAr_1 , $N(C_nH_{2n+1})_2$, $N(Ar_1)(Ar_2)$, $CH=CH-C_nH_{2n+1}$, $C=CHC_nH_{2n+1}$, Ar_1 , Ar_1-Ar_2 , $C_nH_{2n}-Ar_1$, or no substitution, wherein n is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10, and wherein Ar_1 and Ar_2 are independently selected from the group consisting of benzene, biphenyl, naphthalene, triphenylene, carbazole, and heteroaromatic analogs thereof.

2. The compound of claim 1, wherein the compound is represented by the structure of Formula (IV):



Formula (IV)

wherein X is S or O;

wherein R_1 , R_2 , and R_3 are unfused substituents independently selected from the group consisting of C_nH_{2n+1} , OC_nH_{2n+1} , OAr_1 , $N(C_nH_{2n+1})_2$, $N(Ar_1)(Ar_2)$, $CH=CH-C_nH_{2n+1}$, $C=CHC_nH_{2n+1}$, Ar_1 , Ar_1-Ar_2 , $C_nH_{2n}-Ar_1$, or no substitution, and wherein each of R_1 , R_2 , and R_3 may represent mono, di, tri, or tetra substitutions;

wherein n is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10;

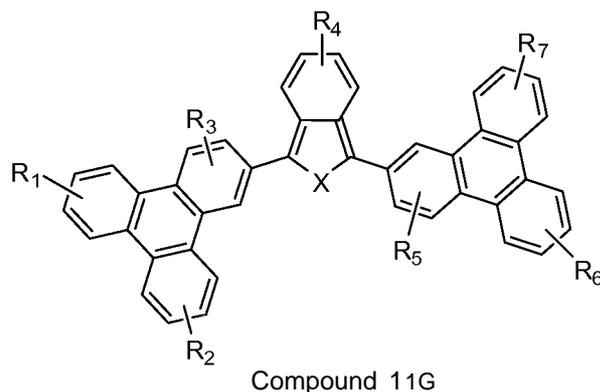
wherein Ar_1 and Ar_2 are independently selected from the group consisting of benzene, biphenyl, naphthalene, triphenylene, carbazole, and heteroaromatic analogs thereof; and

wherein at least one of R_1 , R_2 , and R_3 includes a triphenylene group.

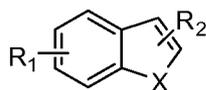
3. The compound of claim 2, wherein X is S.

4. The compound of claim 2, wherein X is O.

5. The compound of claim 2, wherein the compound is represented by the structure:



6. The compound of claim 5, wherein X is S.
7. The compound of claim 5, wherein X is O.
8. The compound of claim 1, wherein the compound is represented by the structure of Formula (V):



Formula (V)

wherein X is S or O;

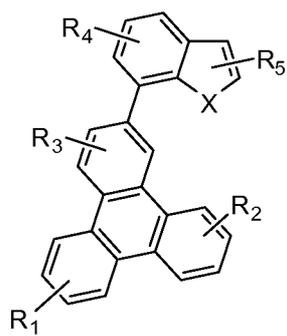
wherein R_1 , R_2 , and R_3 are unfused substituents independently selected from the group consisting of C_nH_{2n+1} , OC_nH_{2n+1} , OAr_1 , $N(C_nH_{2n+1}O_2)$, $N(Ar_1)(Ar_2)$, $CH=CH-C_nH_{2n+1}$, $C=CHC_nH_{2n+1}$, Ar_1 , $Ari-Ar_2$, $C_nH_{2n}-Ar_1$, or no substitution, and wherein each of R_1 , R_2 , and R_3 may represent mono, di, tri, or tetra substitutions;

wherein n is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10;

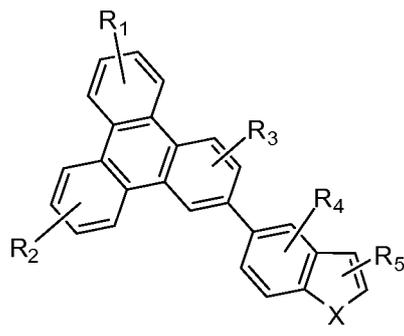
wherein Ar_1 and Ar_2 are independently selected from the group consisting of benzene, biphenyl, naphthalene, triphenylene, carbazole, and heteroaromatic analogs thereof; and

wherein at least one of R_1 , R_2 , and R_3 includes a triphenylene group.

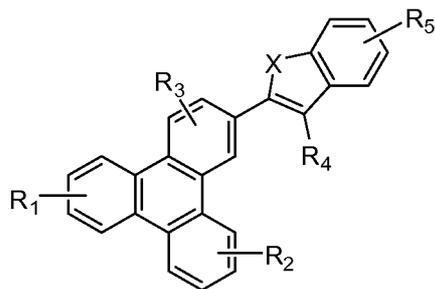
9. The compound of claim 8, wherein X is S.
10. The compound of claim 8, wherein X is O.
11. The compound of claim 8, wherein the compound is selected from the group consisting of:



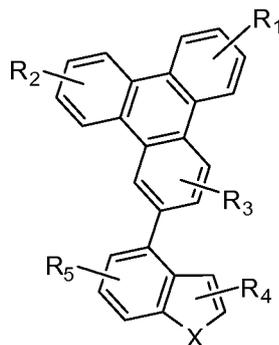
Compound 12G



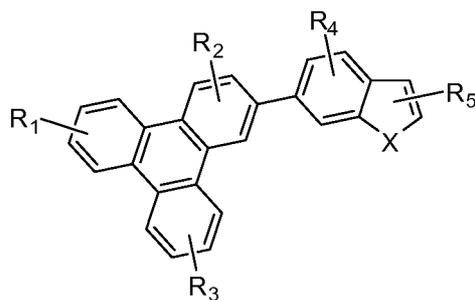
Compound 13G



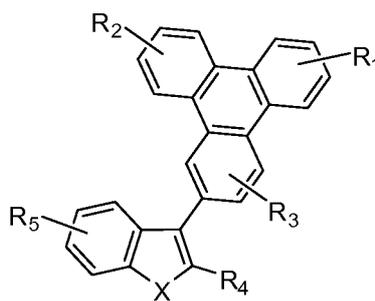
Compound 14G



Compound 16G

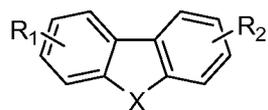


Compound 17G



Compound 18G

12. The compound of claim 11, wherein X is S.
13. The compound of claim 11, where X is O.
14. The compound of claim 1, wherein the compound is represented by structure of Formula (VI):



Formula (VI)

wherein X is S or O;

wherein R_1 and R_2 are unfused substituents independently selected from the group consisting of C_nH_{2n+1} , OC_nH_{2n+1} , OAr_1 , $N(C_nH_{2n+1})_2$, $N(Ar_1)(Ar_2)$, $CH=CH-C_nH_{2n+1}$, $C=CHC_nH_{2n+1}$, Ar_1 , $Ari-Ar_2$, $C_nH_{2n}-Ar_1$, or no substitution, and wherein each of R_1 and R_2 may represent mono, di, tri, or tetra substitutions;

wherein n is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10;

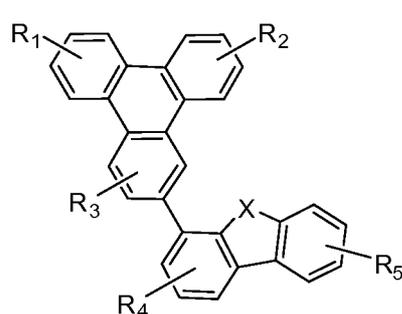
wherein Ar_1 and Ar_2 are independently selected from the group consisting of benzene, biphenyl, naphthalene, triphenylene, carbazole, and heteroaromatic analogs thereof; and

wherein at least one of R_1 and R_2 includes a triphenylene group.

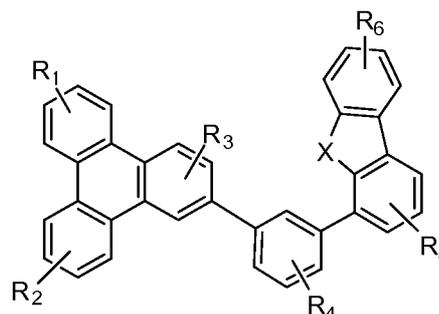
15. The compound of claim 14, wherein X is S.

16. The compound of claim 14, wherein X is O.

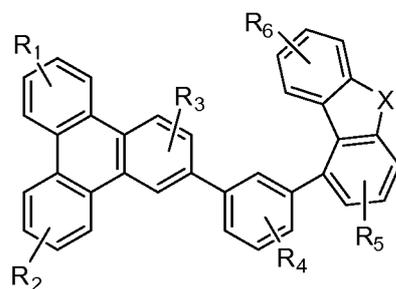
17. The compound of claim 14, wherein the compound is selected from the group consisting of:



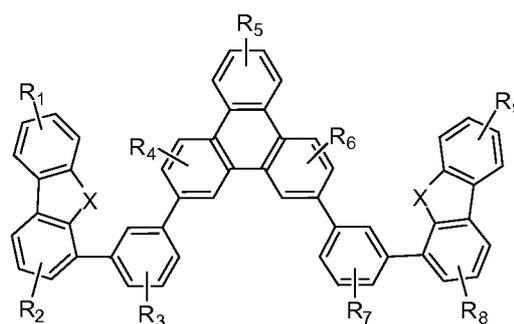
Compound 1G



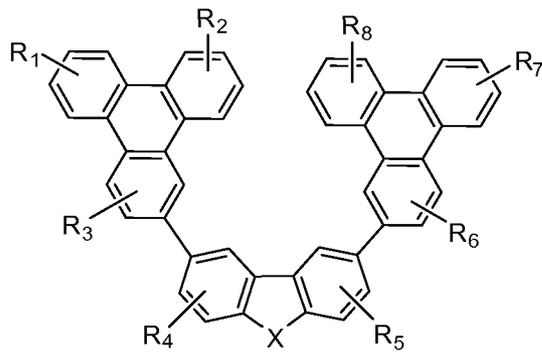
Compound 2G



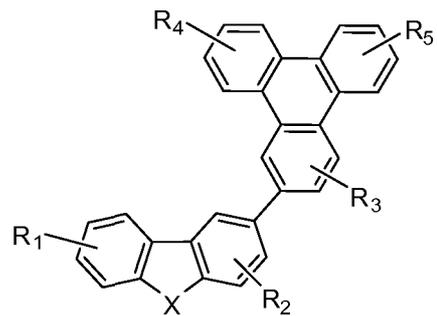
Compound 3G



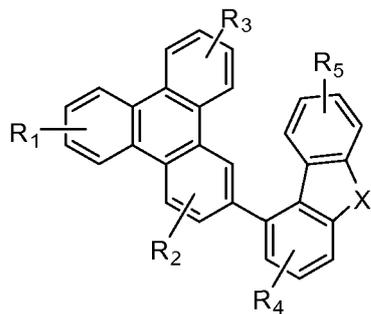
Compound 4G



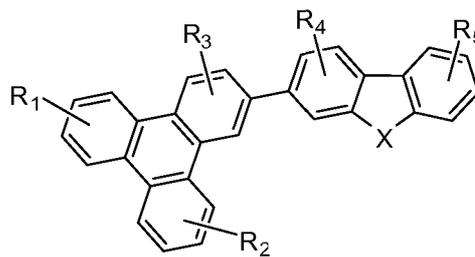
Compound 5G



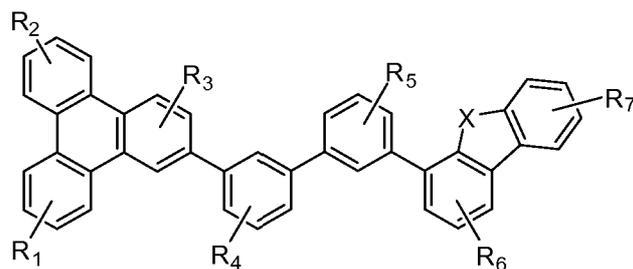
Compound 6G



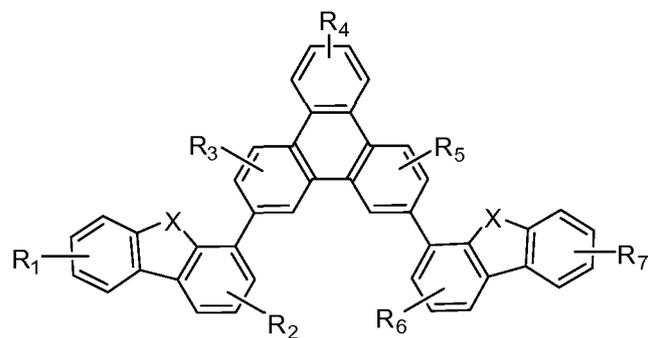
Compound 7G



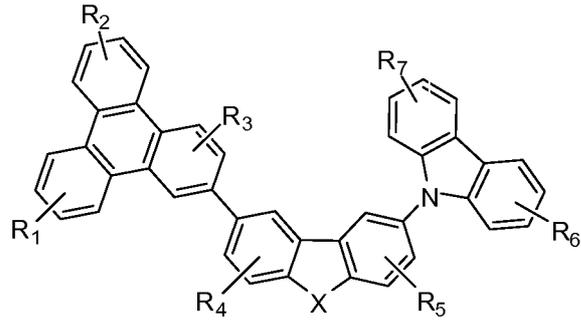
Compound 8G



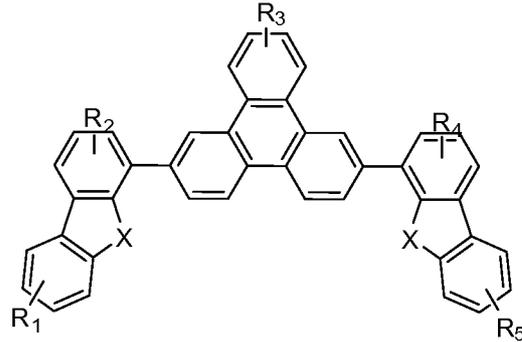
Compound 9G



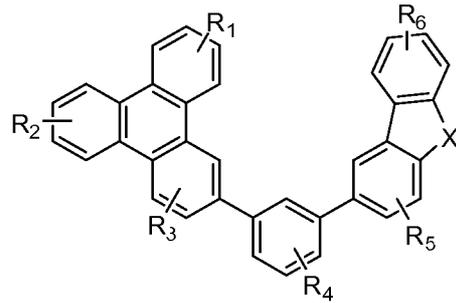
Compound 10G



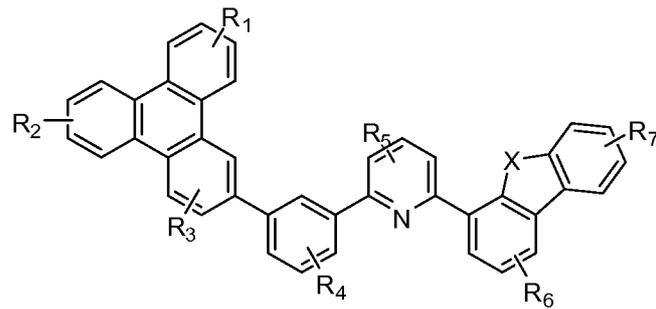
Compound 15G



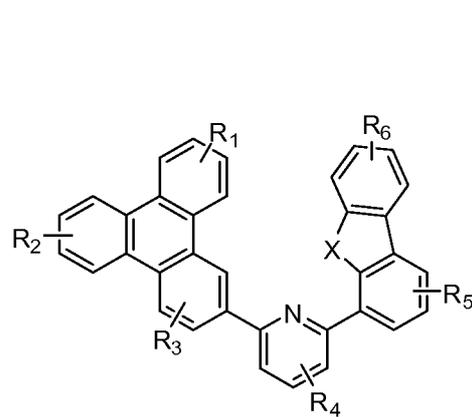
Compound 19 G



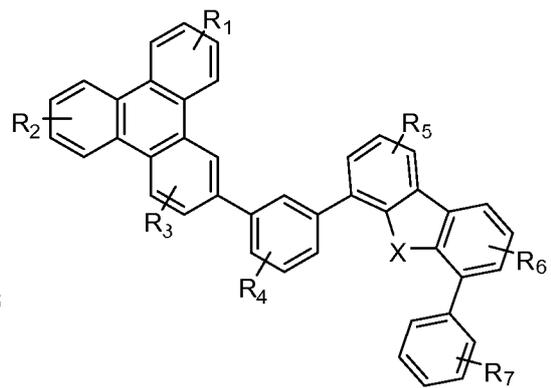
Compound 20 G



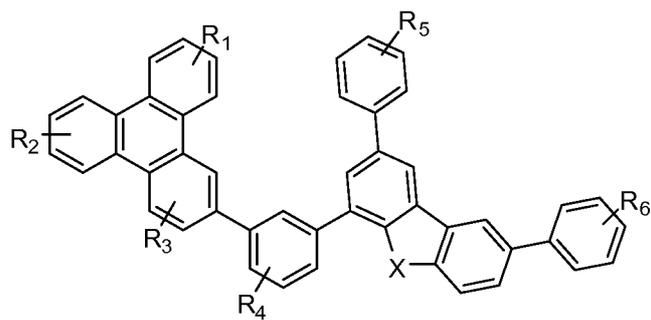
Compound 21 G



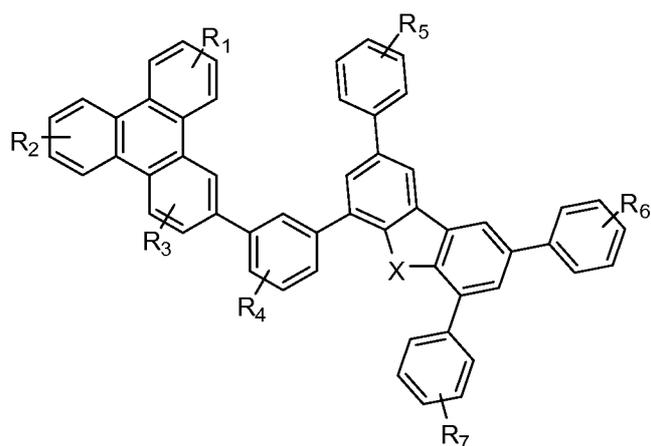
Compound 22 G



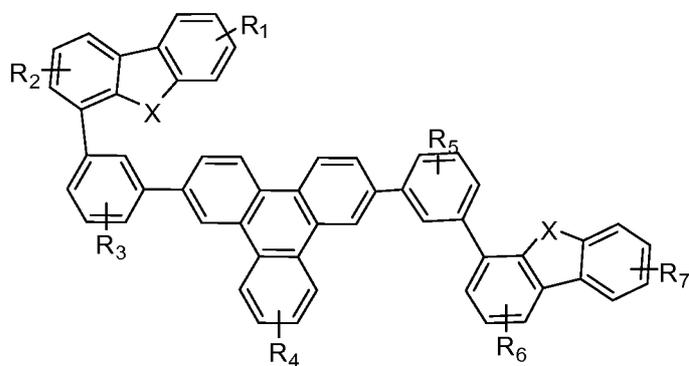
Compound 23 G



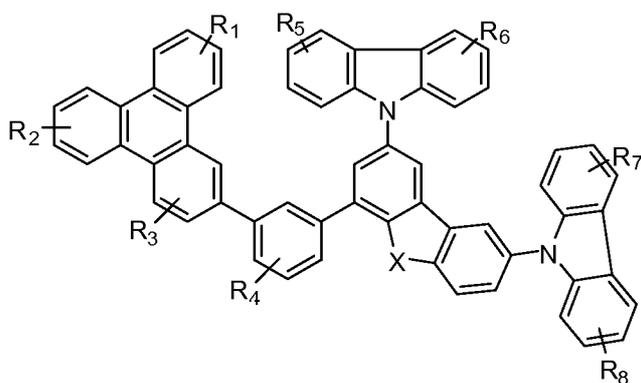
Compound 24 G



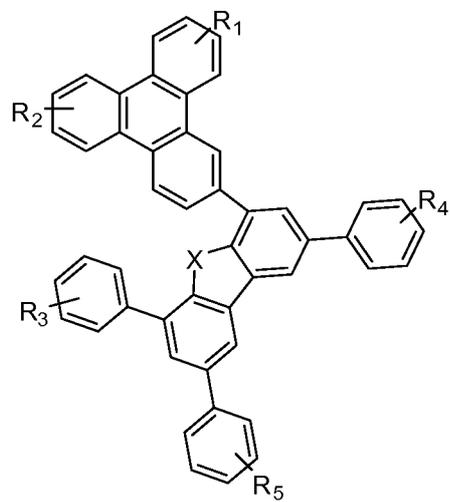
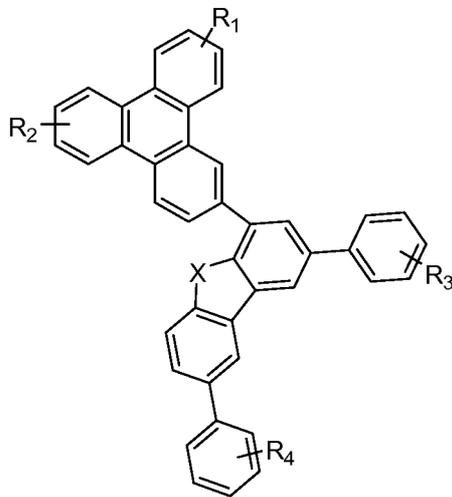
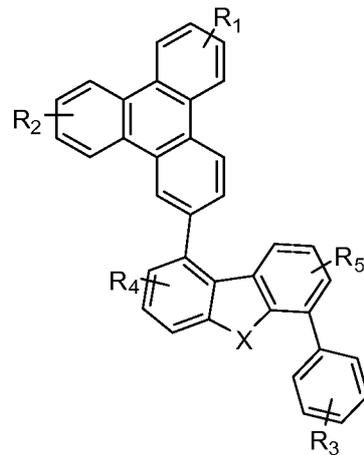
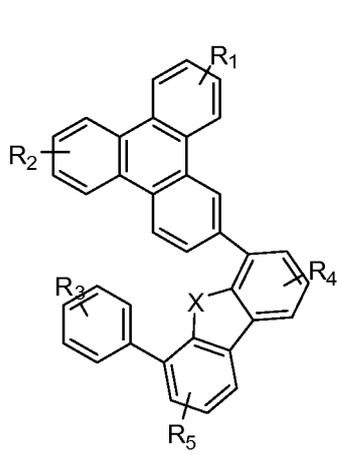
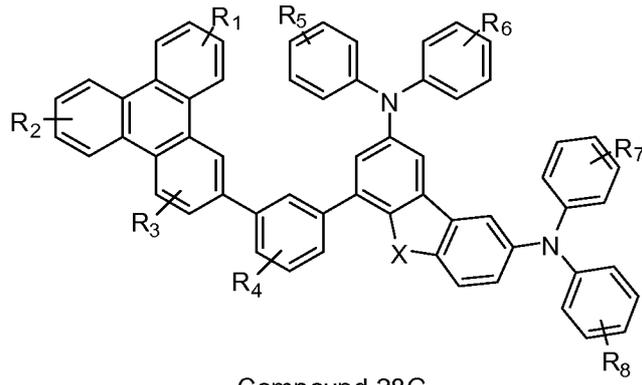
Compound 25 G

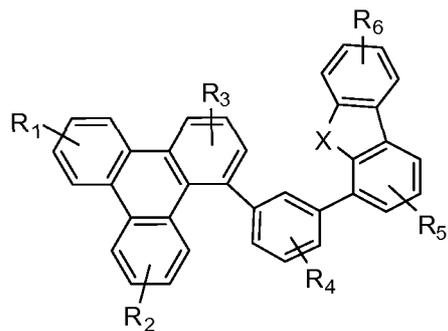


Compound 26 G

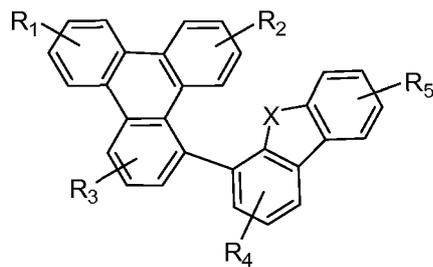


Compound 27 G

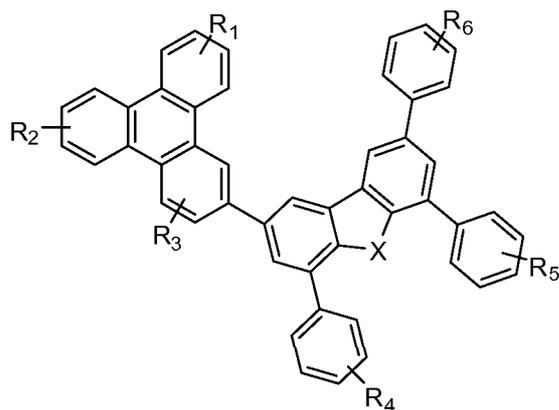




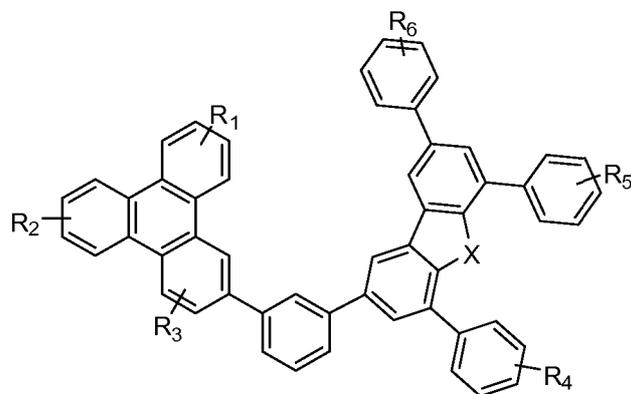
Compound 33G



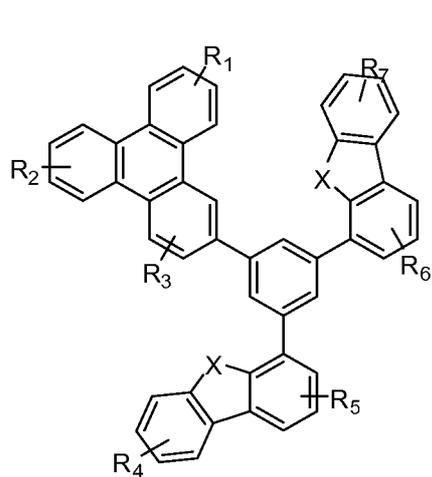
Compound 34G



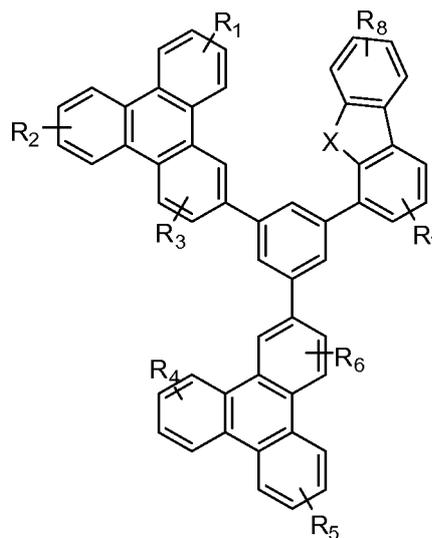
Compound 35G



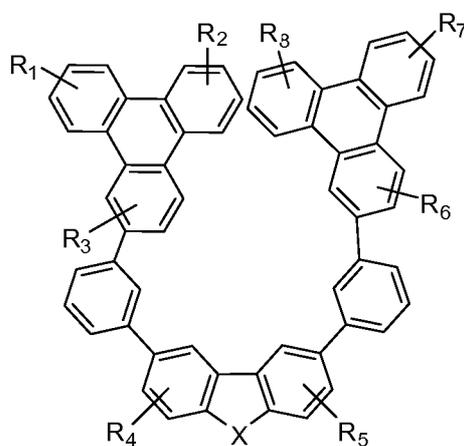
Compound 36G



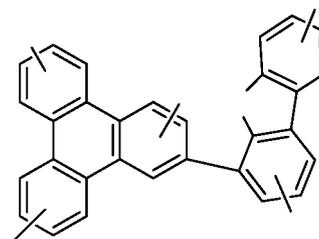
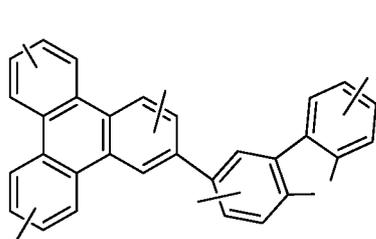
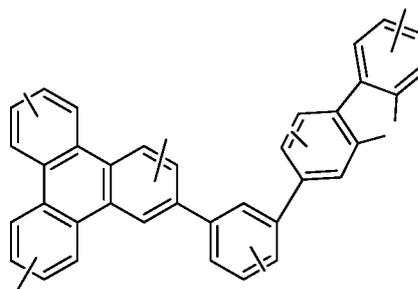
Compound 37G

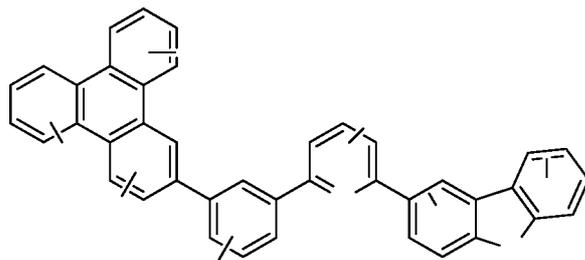
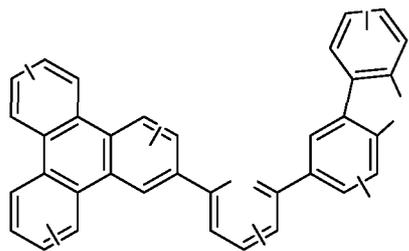


Compound 38G

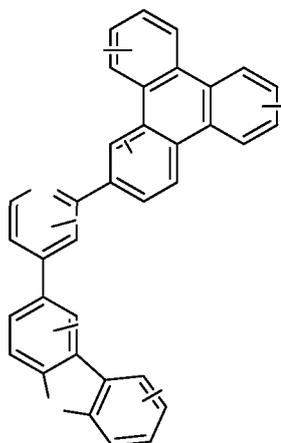
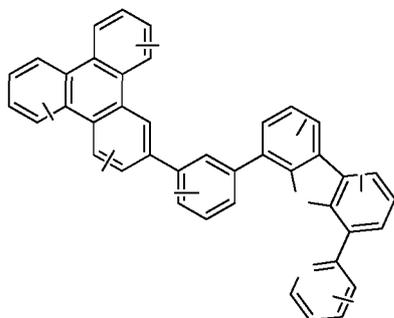
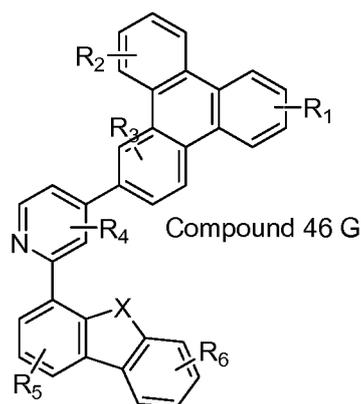
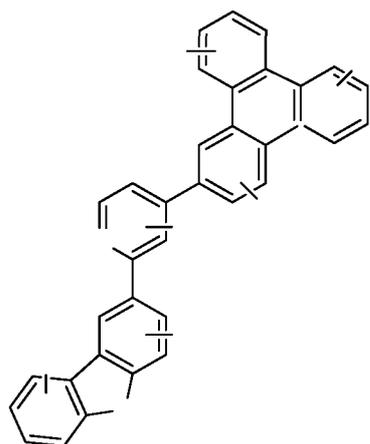


Compound 39G





R₁



R₂

18. The compound of claim 17, wherein X is S.
19. The compound of claim 17, wherein X is O.

20. The compound of any of claims 1-19, wherein Ar_1 and Ar_2 are independently selected from the group consisting of benzene, biphenyl, naphthalene, triphenylene, and carbazole.
21. An organic light emitting device, comprising:
an anode;
a cathode; and
an organic layer disposed between the anode and the cathode, wherein the organic layer comprises a compound comprising a triphenylene containing benzo-fused thiophene or benzo-fused furan, wherein any substituent in the compound is an unfused substituent independently selected from the group consisting of C_nH_{2n+1} , OC_nH_{2n+1} , OAr_1 , $N(C_nH_{2n+1})_2$, $N(Ar_1)(Ar_2)$, $CH=CH-C_nH_{2n+1}$, $C=CHC_nH_{2n+1}$, Ar_1 , Ar_1-Ar_2 , $C_nH_{2n}-Ar_1$, or no substitution, wherein n is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10, and wherein Ar_1 and Ar_2 are independently selected from the group consisting of benzene, biphenyl, naphthalene, triphenylene, carbazole, and heteroaromatic analogs thereof.
22. The device of claim 21, wherein the organic layer is an emissive layer.
23. The device of claim 22, wherein the organic layer further comprises a phosphorescent emitter.
24. The device of claim 23, wherein the phosphorescent emitter is an iridium complex.
25. The device of claim 21, wherein the organic layer comprises Compound 2S and an iridium complex.
26. The device of any of claims 21-25, wherein Ar_1 and Ar_2 are independently selected from the group consisting of benzene, biphenyl, naphthalene, triphenylene, and carbazole.

1 / 3

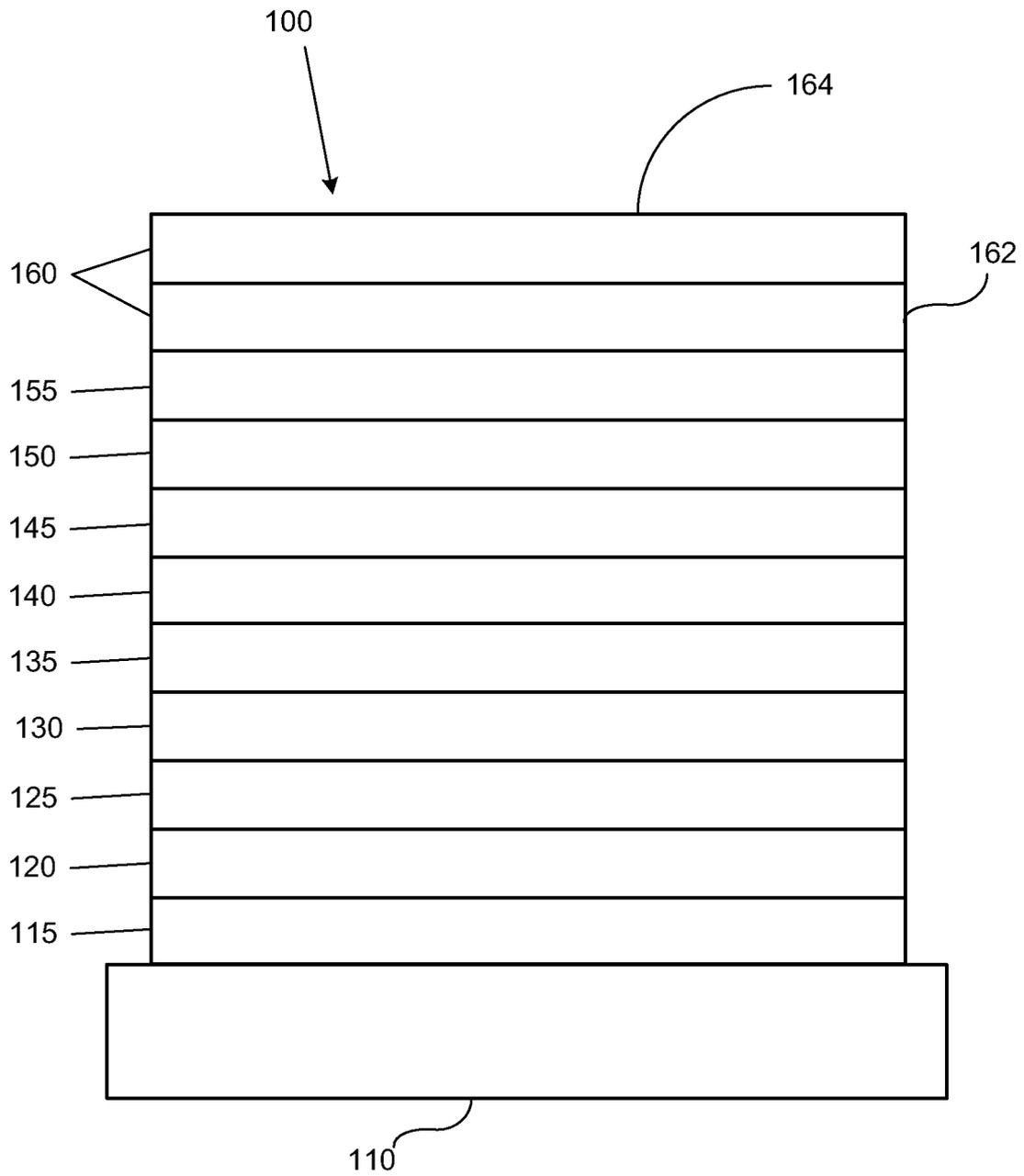


FIGURE 1

2 / 3

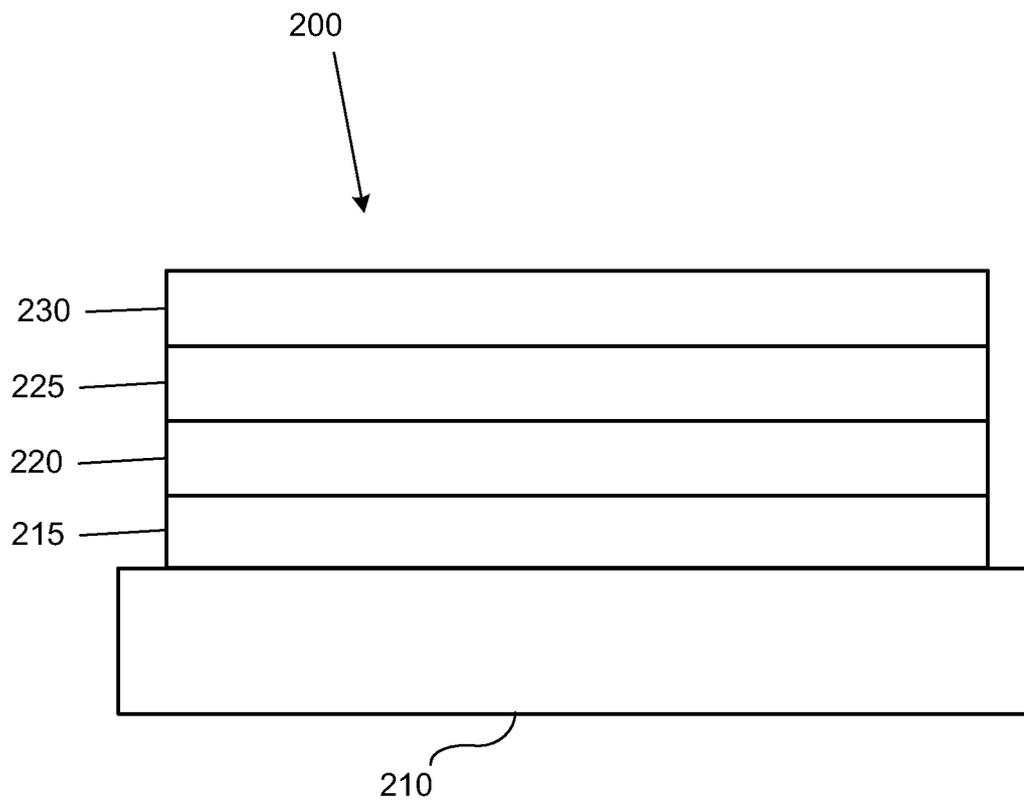
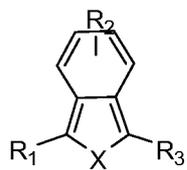
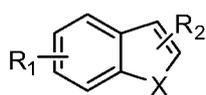


FIGURE 2

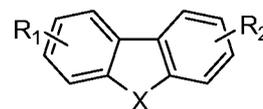
3 / 3



Formula (IV)



Formula (V)



Formula (VI)

FIGURE 3