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(54) **DEUTERATED COMPOUNDS FOR LUMINESCENT APPLICATIONS**

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(58) **Field of Classification Search** ..... None

See application file for complete search history.

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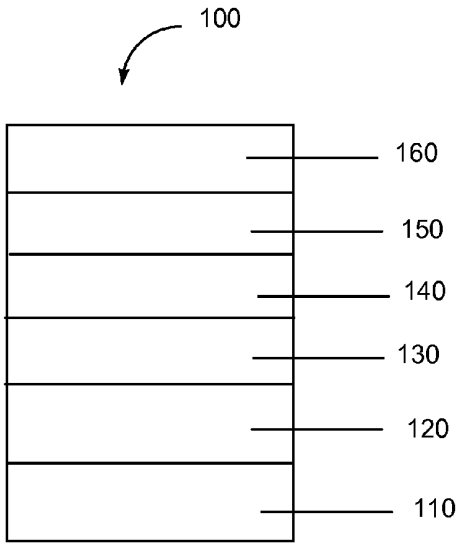
(57) **ABSTRACT**

This invention relates to deuterated compounds that are useful in electroluminescent applications. It also relates to electronic devices in which the active layer includes such a deuterated compound.

4 Claims, 1 Drawing Sheet



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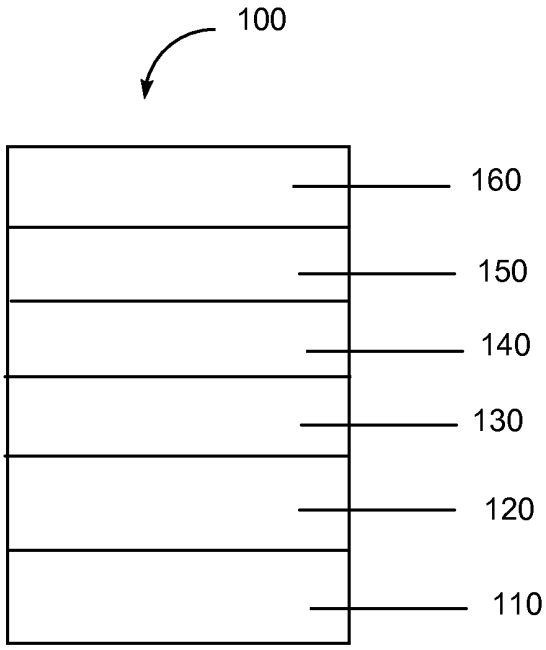
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DEUTERATED COMPOUNDS FOR LUMINESCENT APPLICATIONS

RELATED APPLICATION DATA

This application claims priority under 35 U.S.C. §119(e) from U.S. Provisional Application No. 61/246,563 filed on Sep. 29, 2009, which is incorporated by reference herein in its entirety.

BACKGROUND

1. Field of the Disclosure

This invention relates to electroactive compounds which are at least partially deuterated. It also relates to electronic devices in which the active layers include such a compound.

2. Description of the Related Art

Organic electronic devices that emit light, such as light-emitting diodes that make up displays, are present in many different kinds of electronic equipment. In all such devices, an organic active layer is sandwiched between two electrical contact layers. At least one of the electrical contact layers is light-transmitting so that light can pass through the electrical contact layer. The organic active layer emits light through the light-transmitting electrical contact layer upon application of electricity across the electrical contact layers.

It is well known to use organic electroluminescent compounds as the active component in light-emitting diodes. Simple organic molecules such as anthracene, thiadiazole derivatives, and coumarin derivatives are known to show electroluminescence. Semiconductive conjugated polymers have also been used as electroluminescent components, as has been disclosed in, for example, U.S. Pat. Nos. 5,247,190, 5,408,109, and Published European Patent Application 443 861. In many cases the electroluminescent compound is present as a dopant in a host material.

There is a continuing need for new materials for electronic devices.

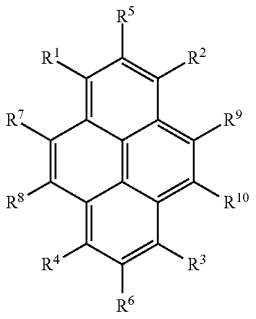
SUMMARY

There is provided a diarylpyrene compound having at least one D substituent.

There is also provided an electronic device comprising an active layer comprising the above compound.

There is also provided a compound having Formula I:

Formula I



wherein:

R^1 through R^4 are the same or different and are selected from the group consisting of H, D, alkyl, alkoxy, oxyalkyl, silyl, siloxane, and aryl, with the proviso that at least two of R^1 through R^4 are aryl; and

R^5 through R^{10} are the same or different and are selected from the group consisting of H and D;

wherein there is at least one D.

There is also provided an electronic device comprising an active layer comprising a compound of Formula I.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments are illustrated in the accompanying figures to improve understanding of concepts as presented herein.

FIG. **1** includes an illustration of one example of an organic electronic device.

Skilled artisans appreciate that objects in the figures are illustrated for simplicity and clarity and have not necessarily been drawn to scale. For example, the dimensions of some of the objects in the figures may be exaggerated relative to other objects to help to improve understanding of embodiments.

DETAILED DESCRIPTION

Many aspects and embodiments are disclosed herein and are exemplary and not limiting. After reading this specification, skilled artisans appreciate that other aspects and embodiments are possible without departing from the scope of the invention.

Other features and benefits of any one or more of the embodiments will be apparent from the following detailed description, and from the claims. The detailed description first addresses Definitions and Clarification of Terms followed by the Electroactive Compound, the Electronic Device, and finally Examples.

1. Definitions and Clarification of Terms

Before addressing details of embodiments described below, some terms are defined or clarified.

As used herein, the term "aliphatic ring" is intended to mean a cyclic group that does not have delocalized pi electrons. In some embodiments, the aliphatic ring has no unsaturation. In some embodiments, the ring has one double or triple bond.

The term "alkoxy" refers to the group RO—, where R is an alkyl.

The term "alkyl" is intended to mean a group derived from an aliphatic hydrocarbon having one point of attachment, and includes a linear, a branched, or a cyclic group. The term is intended to include heteroalkyls. The term is intended to include substituted and unsubstituted groups. The term "hydrocarbon alkyl" refers to an alkyl group having no heteroatoms. The term "deuterated alkyl" is a hydrocarbon alkyl having at least one available H replaced by D. In some embodiments, an alkyl group has from 1-20 carbon atoms.

The term "aryl" is intended to mean a group derived from an aromatic hydrocarbon having one point of attachment. The term "aromatic compound" is intended to mean an organic compound comprising at least one unsaturated cyclic group having delocalized pi electrons. The term is intended to include heteroaryls. The term "hydrocarbon aryl" is intended to mean aromatic compounds having no heteroatoms in the ring. The term aryl includes groups which have a single ring and those which have multiple rings which can be joined by a single bond or fused together. The term "deuterated aryl" refers to an aryl group having at least one of the available H atoms which is bonded directly to the aryl replaced by D. The term "arylene" is intended to mean a group derived from an aromatic hydrocarbon having two points of attachment. Any suitable ring position of the aryl moiety may be covalently

linked to the defined chemical structure. In some embodiments, a hydrocarbon aryl group has from 3-60 carbon atoms; in some embodiments, 6 to 30 carbon atoms. Heteroaryl groups may have from 3-50 carbon atoms; in some embodiments, 3-30 carbon atoms.

The term "branched alkyl" refers to an alkyl group having at least one secondary or tertiary carbon. The term "secondary alkyl" refers to a branched alkyl group having a secondary carbon atom. The term "tertiary alkyl" refers to a branched alkyl group having a tertiary carbon atom. In some embodiments, the branched alkyl group is attached via a secondary or tertiary carbon.

The term "charge transport," when referring to a layer, material, member, or structure is intended to mean such layer, material, member, or structure facilitates migration of such charge through the thickness of such layer, material, member, or structure with relative efficiency and small loss of charge. Hole transport materials facilitate positive charge; electron transport material facilitate negative charge. Although light-emitting materials may also have some charge transport properties, the terms "charge, hole, or electron transport layer, material, member, or structure" are not intended to include a layer, material, member, or structure whose primary function is light emission.

The term "compound" is intended to mean an electrically uncharged substance made up of molecules that further consist of atoms, wherein the atoms cannot be separated by physical means. The phrase "adjacent to," when used to refer to layers in a device, does not necessarily mean that one layer is immediately next to another layer. On the other hand, the phrase "adjacent R groups," is used to refer to R groups that are next to each other in a chemical formula (i.e., R groups that are on atoms joined by a bond).

The term "deuterated" is intended to mean that at least one available H has been replaced by D. A compound or group that is X % deuterated, has X % of the available H replaced by D.

The term "dopant" is intended to mean a material, within a layer including a host material, that changes the electronic characteristic(s) or the targeted wavelength(s) of radiation emission, reception, or filtering of the layer compared to the electronic characteristic(s) or the wavelength(s) of radiation emission, reception, or filtering of the layer in the absence of such material.

The term "electroactive" as it refers to a layer or a material, is intended to indicate a layer or material which electronically facilitates the operation of the device. Examples of active materials include, but are not limited to, materials which conduct, inject, transport, or block a charge, where the charge can be either an electron or a hole, or materials which emit radiation or exhibit a change in concentration of electron-hole pairs when receiving radiation. Examples of inactive materials include, but are not limited to, planarization materials, insulating materials, and environmental barrier materials.

The term "electroluminescence" refers to the emission of light from a material in response to an electric current passed through it. "Electroluminescent" refers to a material that is capable of electroluminescence.

The prefix "hetero" indicates that one or more carbon atoms have been replaced with a different atom. In some embodiments, the different atom is N, O, or S.

The term "host material" is intended to mean a material to which a dopant is added. The host material may or may not have electronic characteristic(s) or the ability to emit, receive, or filter radiation. In some embodiments, the host material is present in higher concentration.

The term "layer" is used interchangeably with the term "film" and refers to a coating covering a desired area. The term is not limited by size. The area can be as large as an entire device or as small as a specific functional area such as the actual visual display, or as small as a single sub-pixel. Layers and films can be formed by any conventional deposition technique, including vapor deposition, liquid deposition (continuous and discontinuous techniques), and thermal transfer. Continuous deposition techniques, include but are not limited to, spin coating, gravure coating, curtain coating, dip coating, slot-die coating, spray coating, and continuous nozzle coating. Discontinuous deposition techniques include, but are not limited to, ink jet printing, gravure printing, and screen printing.

The term "organic electronic device" or sometimes just "electronic device" is intended to mean a device including one or more organic electroactive layers or materials.

The term "oxyalkyl" is intended to mean a heteroalkyl group having one or more carbons replaced with oxygens. The term includes groups which are linked via an oxygen.

The term "silyl" refers to the group R_3Si–, where R is H, D, C1-20 alkyl, fluoroalkyl, or aryl. In some embodiments, one or more carbons in an R alkyl group are replaced with Si. In some embodiments, the silyl groups are $(hexyl)_2Si(Me)CH_2CH_2Si(Me)_2$- and $[CF_3(CF_2)_6CH_2CH_2]_2SiMe$-.

The term "siloxane" refers to the group $(RO)_3Si$—, where R is H, D, C1-20 alkyl, or fluoroalkyl.

The phrase "adjacent to," when used to refer to layers in a device, does not necessarily mean that one layer is immediately next to another layer. On the other hand, the phrase "adjacent R groups," is used to refer to R groups that are next to each other in a chemical formula (i.e., R groups that are on atoms joined by a bond).

All groups can be substituted or unsubstituted unless otherwise indicated. In some embodiments, the substituents are selected from the group consisting of D, halide, alkyl, alkoxy, aryl, and cyano. An optionally substituted group, such as, but not limited to, alkyl or aryl, may be substituted with one or more substituents which may be the same or different. Other suitable substituents include nitro, cyano, hydroxy, carboxy, alkenyl, alkynyl, aryloxy, alkoxycarbonyl, perfluoroalkyl, perfluoroalkoxy, arylalkyl, silyl, siloxane, thioalkoxy, —$S(O)_s$-aryl (where s=0-2) or —$S(O)_s$-heteroaryl (where s=0-2). Each R' and R" is independently an optionally substituted alkyl, cycloalkyl, or aryl group.

As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

Also, use of "a" or "an" are employed to describe elements and components described herein. This is done merely for convenience and to give a general sense of the scope of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention

belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

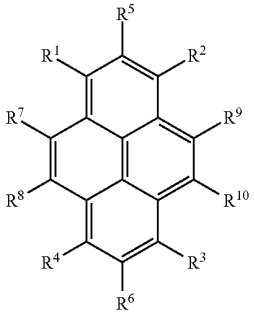
The IUPAC numbering system is used throughout, where the groups from the Periodic Table are numbered from left to right as 1-18 (CRC Handbook of Chemistry and Physics, 81st Edition, 2000).

2. Electroactive Compound

The electroactive compound described herein is a diarylpyrene having at least one D substituent. In some embodiments, the compound is at least 10% deuterated; in some embodiments, at least 20% deuterated; in some embodiments, at least 30% deuterated; in some embodiments, at least 40% deuterated; in some embodiments, at least 50% deuterated; in some embodiments, at least 60% deuterated; in some embodiments, at least 70% deuterated; in some embodiments, at least 80% deuterated; in some embodiments, at least 90% deuterated; in some embodiments, 100% deuterated.

In some embodiments, the electroactive compound has Formula I:

Formula I



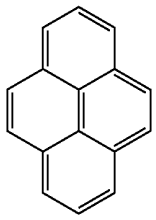
wherein:

R^1 through R^4 are the same or different and are selected from the group consisting of H, D, alkyl, alkoxy, oxyalkyl, silyl, siloxane, and aryl, with the proviso that at least two of R^1 through R^4 are aryl; and

R^5 through R^{10} are the same or different and are selected from the group consisting of H and D;

wherein there is at least one D.

In some embodiments of Formula I, the deuteration is present on the pyrene core. In some embodiments, at least one of R^1 through R^{10} is D. In some embodiments, at least two of R^1 through R^{10} are D; in some embodiments, at least three of R^1 through R^{10} are D; in some embodiments, at least four of R^1 through R^{10} are D; in some embodiments, at least five of R^1 through R^{10} are D; in some embodiments, at least six of R^1 through R^{10} are D; in some embodiments, at least seven of R^1 through R^{10} are D; eight of R^1 through R^{10} are D. The term "pyrene core" refers to the unit:



In some embodiments of Formula I, the deuteration is present on a substituent group on an aryl ring. In some embodiments, the substituent group is selected from alkyl, alkoxy, oxyalkyl, silyl, siloxane, aryl, and aryloxy. In some embodiments, the total of all substituent groups is at least 10% deuterated; in some embodiments, at least 20% deuterated; in some embodiments, at least 30% deuterated; in some embodiments, at least 40% deuterated; in some embodiments, at least 50% deuterated; in some embodiments, at least 60% deuterated; in some embodiments, at least 70% deuterated; in some embodiments, at least 80% deuterated; in some embodiments, at least 90% deuterated; in some embodiments, 100% deuterated.

In some embodiments of Formula I, the deuteration is on any one or more of the aryl groups bonded directly to the pyrene core. In this case, at least one of R^1 through R^4 is a deuterated aryl group. In some embodiments, the aryl groups bonded directly to the pyrene core are at least 10% deuterated. By this it is meant that at least 10% of all the available H bonded to aryl C in the aryl groups bonded directly to the pyrene core are replaced with D. In some embodiments, each aryl ring will have at least one D. In some embodiments, some, and not all of the aryl rings have at least one D. In some embodiments, the aryl groups bonded directly to the pyrene core are at least 20% deuterated; in some embodiments, at least 30% deuterated; in some embodiments, at least 40% deuterated; in some embodiments, at least 50% deuterated; in some embodiments, at least 60% deuterated; in some embodiments, at least 70% deuterated; in some embodiments, at least 80% deuterated; in some embodiments, at least 90% deuterated; in some embodiments, 100% deuterated.

In some embodiments of Formula I, the deuteration is on any one or more of R^1 through R^4. In some embodiments, each of R^1 through R^4 has at least one D. In some embodiments, R^1 through R^4 taken together are at least 10% deuterated. By this it is meant that at least 10% of all the available H bonded to C are replaced with D. In some embodiments, some, and not all of R^1 through R^4 have at least one D. In some embodiments, R^1 through R^4 taken together are at least 20% deuterated; in some embodiments, at least 30% deuterated; in some embodiments, at least 40% deuterated; in some embodiments, at least 50% deuterated; in some embodiments, at least 60% deuterated; in some embodiments, at least 70% deuterated; in some embodiments, at least 80% deuterated; in some embodiments, at least 90% deuterated; in some embodiments, 100% deuterated.

In some embodiments of Formula I, the deuteration is present on the substituent groups and the aryl groups bonded directly to the pyrene core. In some embodiments, the deuteration is present on the substituent groups and the pyrene core. In some embodiments, the deuteration is present on the pyrene core and the aryl groups bonded directly to the pyrene core. In some embodiments, the deuteration is present on the pyrene core, the aryl groups bonded directly to the pyrene core, and the substituent groups.

In some embodiments, the compound of Formula I is at least 10% deuterated; in some embodiments, at least 20% deuterated; in some embodiments, at least 30% deuterated; in some embodiments, at least 40% deuterated; in some embodiments, at least 50% deuterated; in some embodiments, at least 60% deuterated; in some embodiments, at least 70% deuterated; in some embodiments, at least 80% deuterated; in some embodiments, at least 90% deuterated; in some embodiments, 100% deuterated.

In some embodiments of Formula I, R^1 and R^4 are aryl and R^2 and R^3 are selected from H and D. In some embodiments, R^1 and R^3 are aryl and R^2 and R^4 are selected from H and D. In some embodiments, R^1, R^2, and R^4 are aryl and R^4 is selected from H and D. In some embodiments, R^1 through R^4 are all aryl.

Examples of aryl groups include, but are not limited to Ar1 through Ar93, shown in Table 1. The groups may be non-deuterated, as shown, or may have from one D up to full deuteration.

TABLE 1

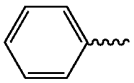
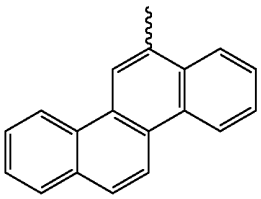
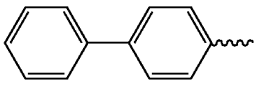
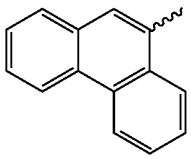
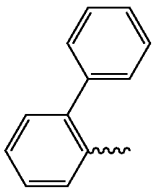
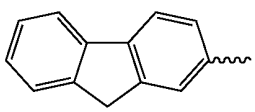
Ar groups	
Ar	Chemical Structure of substituent
Ar1	
Ar2	
Ar3	
Ar4	
Ar5	
Ar6	

TABLE 1-continued

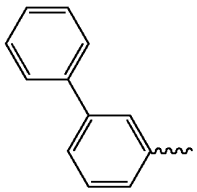
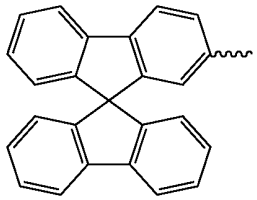
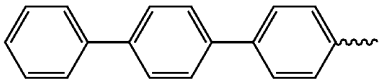
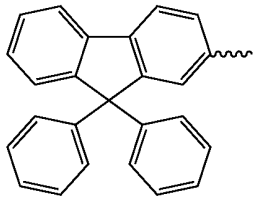
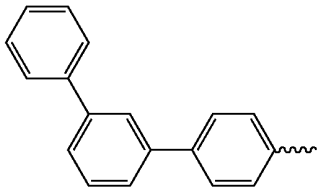
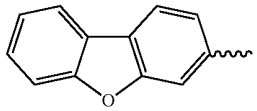
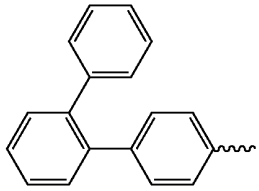
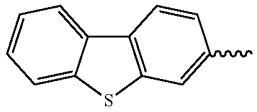
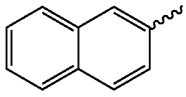
Ar groups	
Ar	Chemical Structure of substituent
Ar7	
Ar8	
Ar9	
Ar10	
Ar11	
Ar12	
Ar13	
Ar14	
Ar15	

TABLE 1-continued

Ar groups

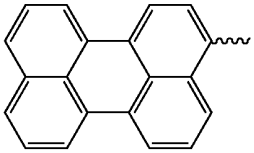
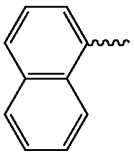
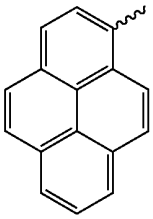
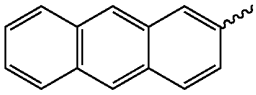
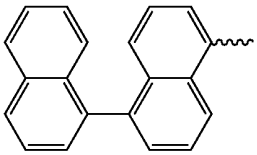
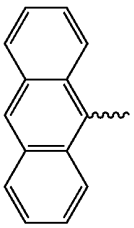
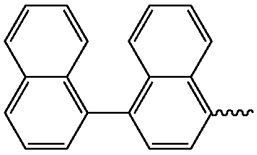
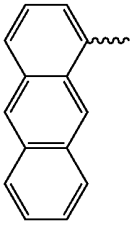
Ar	Chemical Structure of substituent
Ar16	
Ar17	
Ar18	
Ar19	
Ar20	
Ar21	
Ar22	
Ar23	

TABLE 1-continued

Ar groups

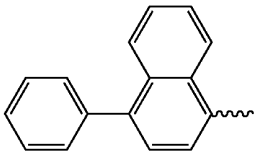
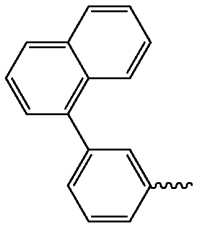
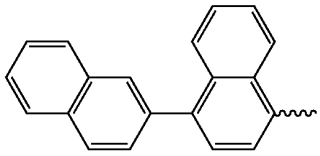
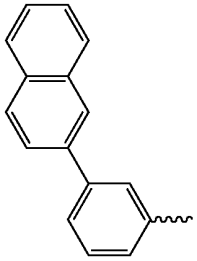
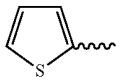
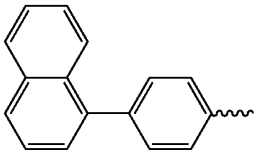
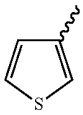
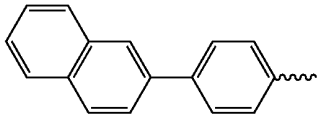
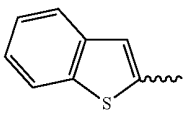
Ar	Chemical Structure of substituent
Ar24	
Ar25	
Ar26	
Ar27	
Ar28	
Ar29	
Ar30	
Ar31	
Ar32	

TABLE 1-continued

Ar groups

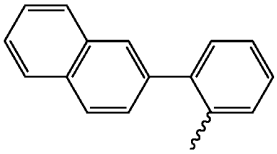
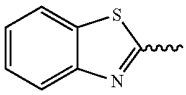
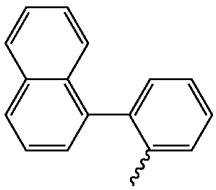
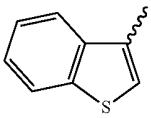
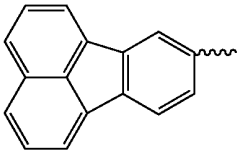
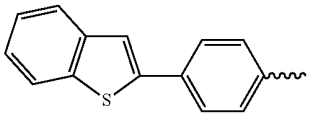
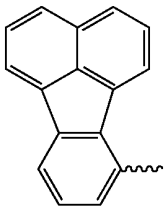
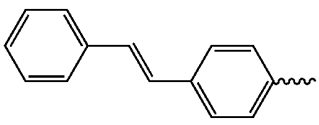
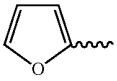
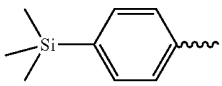
Ar	Chemical Structure of substituent
Ar33	
Ar34	
Ar35	
Ar36	
Ar37	
Ar38	
Ar39	
Ar40	
Ar41	
Ar42	

TABLE 1-continued

Ar groups

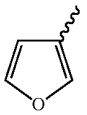
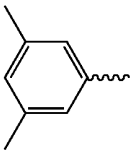
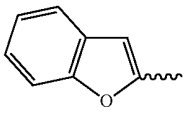
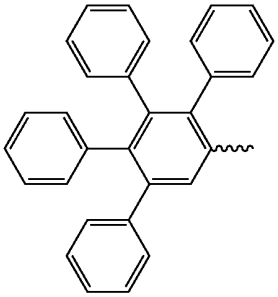
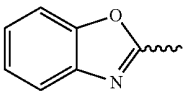
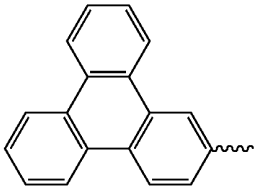
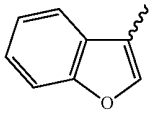
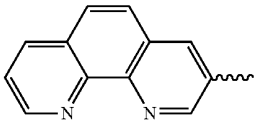
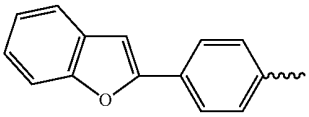
Ar	Chemical Structure of substituent
Ar43	
Ar44	
Ar45	
Ar46	
Ar47	
Ar48	
Ar49	
Ar50	
Ar51	

TABLE 1-continued

Ar groups

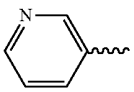
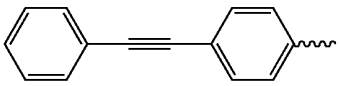
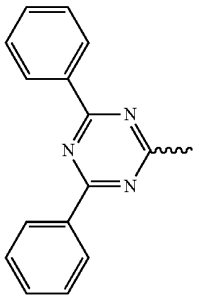
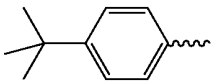
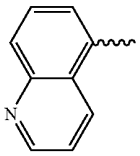
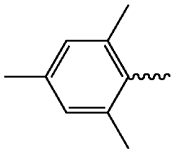
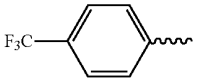
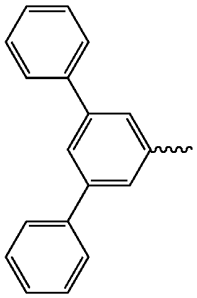
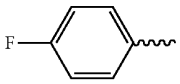
Ar	Chemical Structure of substituent
Ar52	
Ar53	
Ar54	
Ar55	
Ar56	
Ar57	
Ar58	
Ar59	
Ar60	

TABLE 1-continued

Ar groups

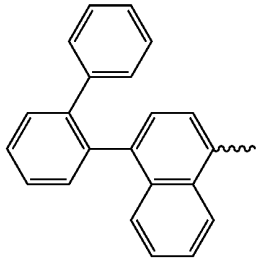
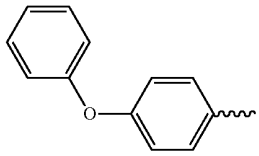
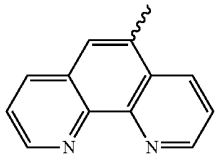
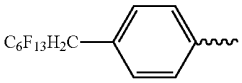
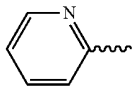
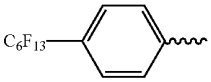
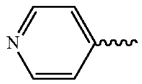
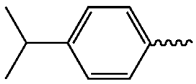
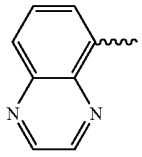
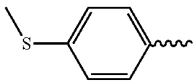
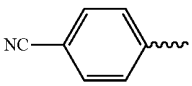
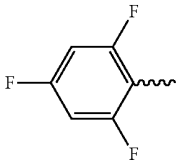
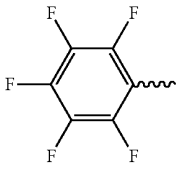
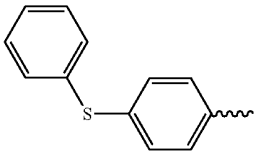
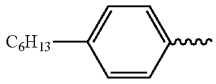
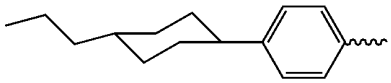
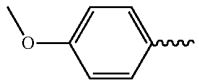
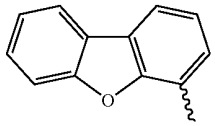
Ar	Chemical Structure of substituent
Ar61	
Ar62	
Ar63	
Ar64	
Ar65	
Ar66	
Ar67	
Ar68	
Ar69	
Ar70	
Ar71	

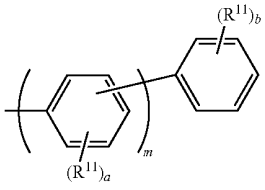
TABLE 1-continued

Ar g oups

Ar	Chemical Structure of substituent
Ar72	
Ar73	
Ar74	
Ar75	
Ar76	
Ar77	
Ar78	

In some embodiments, at least one of R^1 through R^4 has Formula II

Formula II



where:

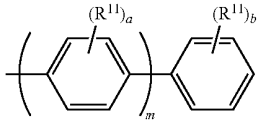
R^{11} is the same or different at each occurrence and is selected from the group consisting of D, alkyl, alkoxy, aryl, silyl, and siloxane, or adjacent R^{11} groups can be joined to form an aromatic ring;

a is the same or different at each occurrence and is an integer from 0-4; b is the same or different at each occurrence and is an integer from 0-5; and

m is the same or different at each occurrence and is an integer from 0 to 6.

In some embodiments, at least one of R^1 through R^4 has Formula IIa:

Formula IIa

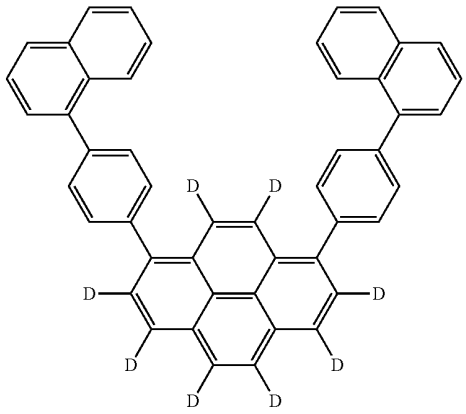


where R^{11}, a, b, and m are as defined above for Formula II.

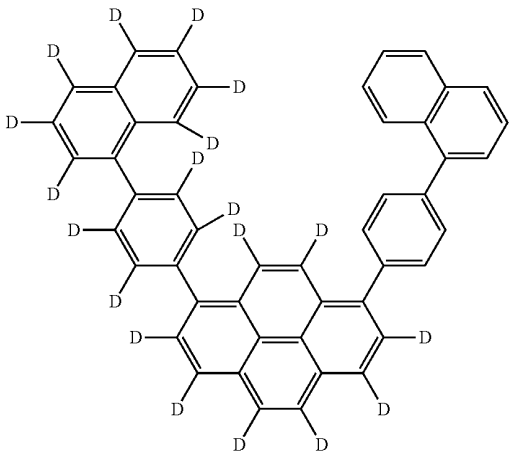
In some embodiments, at least one of R^1 through R^4 is selected from the group consisting of phenyl, naphthyl, phenylnaphthyl, naphthylphenyl, fluorenyl, dibenzofuranyl, substituted analogs thereof, and deuterated analogs thereof. In some embodiments, at least one of R^1 through R^4 is selected from the group consisting of 3-naphthalen-1-yl-phenyl, 3-naphthalen-2-yl-phenyl, 1-naphthalen-2-yl-6-(4-naphthalen-1-yl-phenyl), 4-naphthalen-1-yl-phenyl, 4-dibenzofuranyl, and deuterated analogs thereof.

In some embodiments, the electroactive compound is selected from A1 through A34 below.

A1



A2



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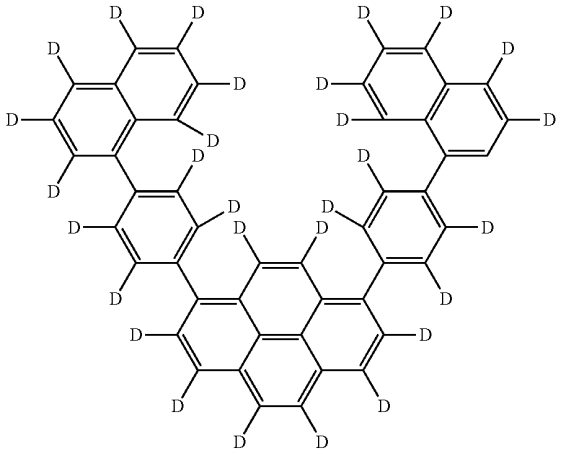
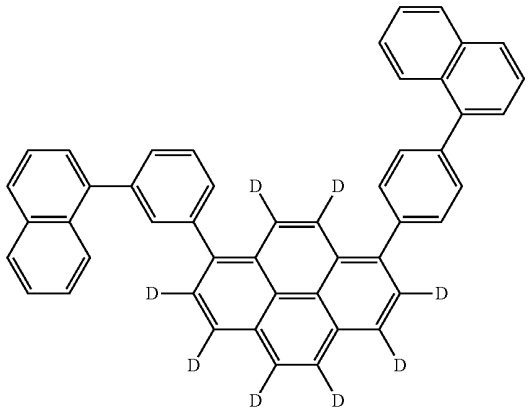
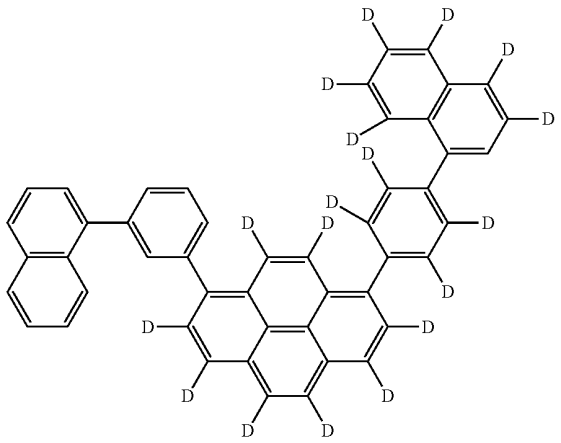
A3



A4



A5



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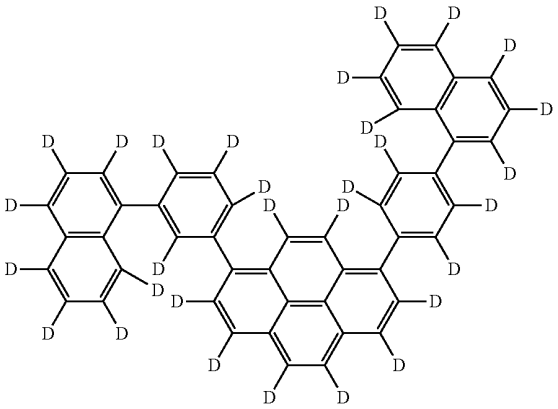
A6



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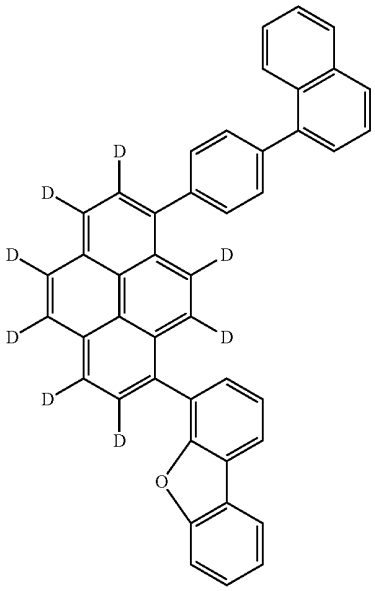

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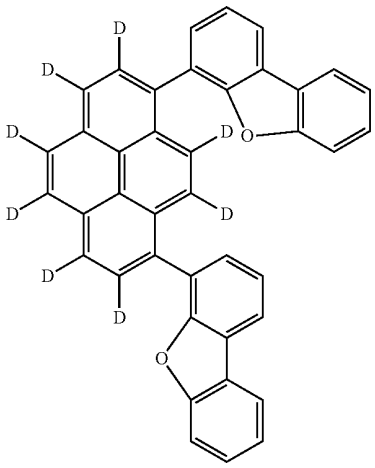

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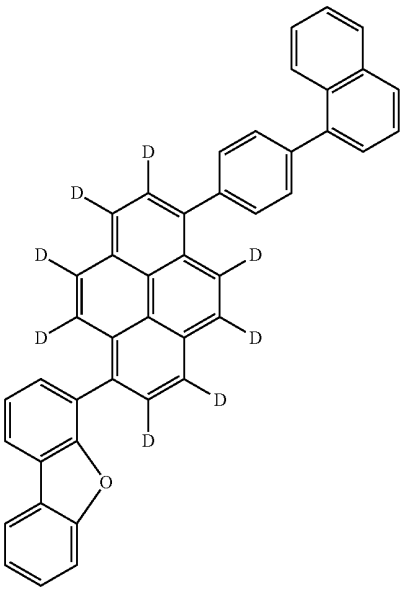

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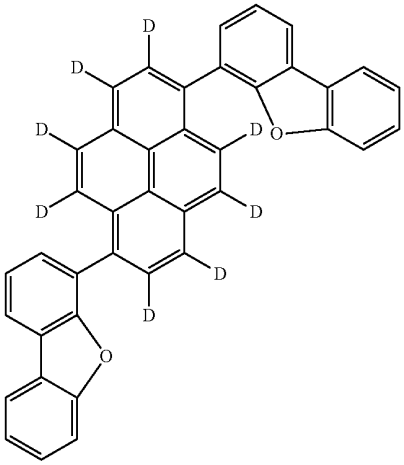

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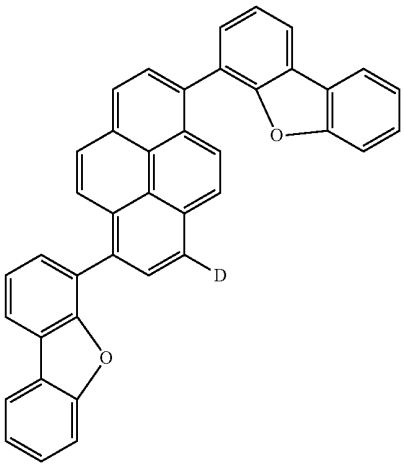

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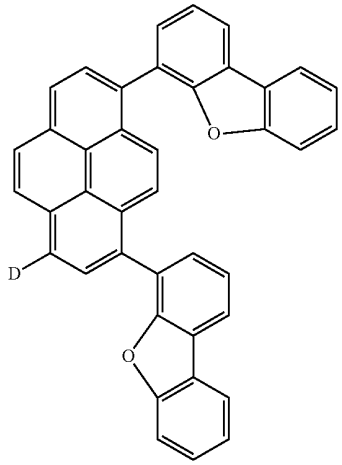

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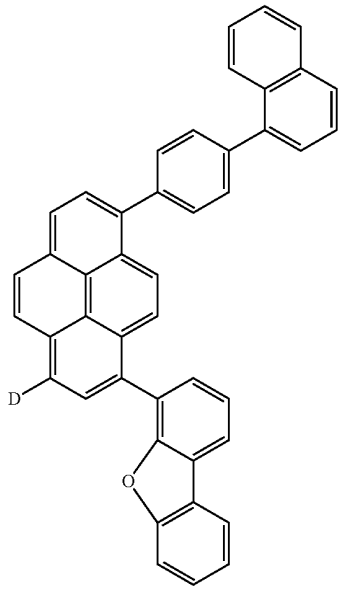

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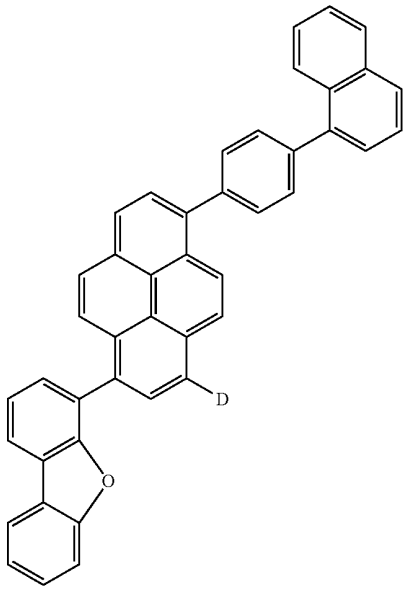

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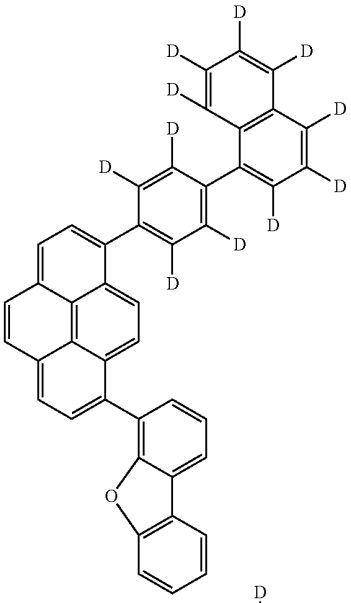

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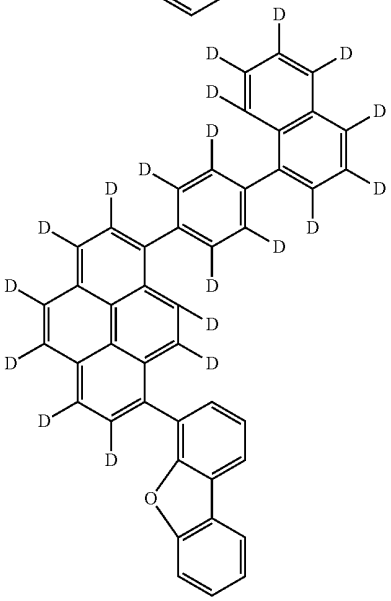

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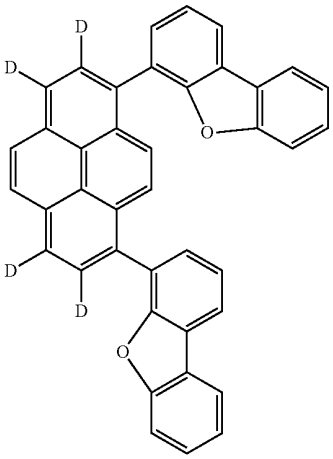

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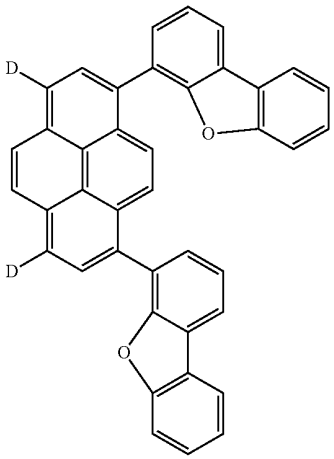

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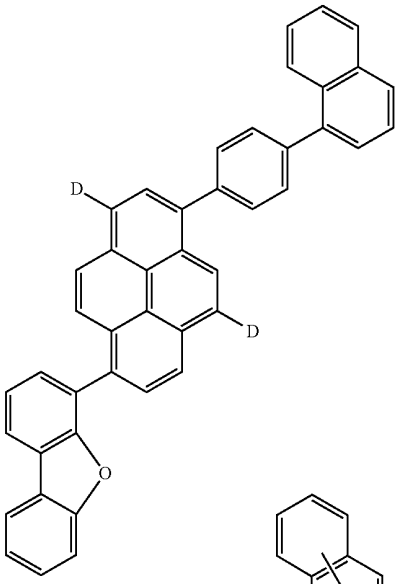

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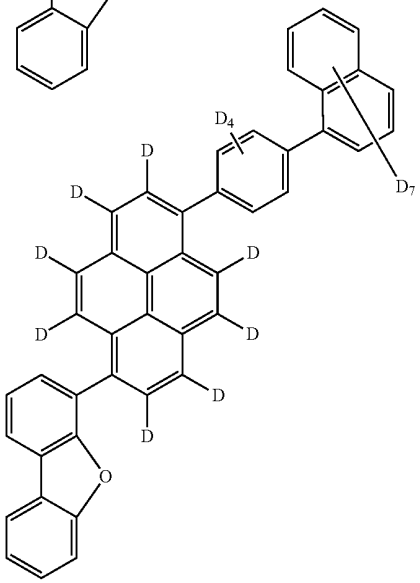

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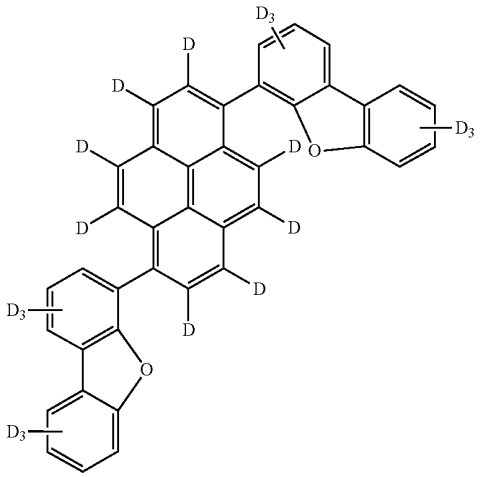

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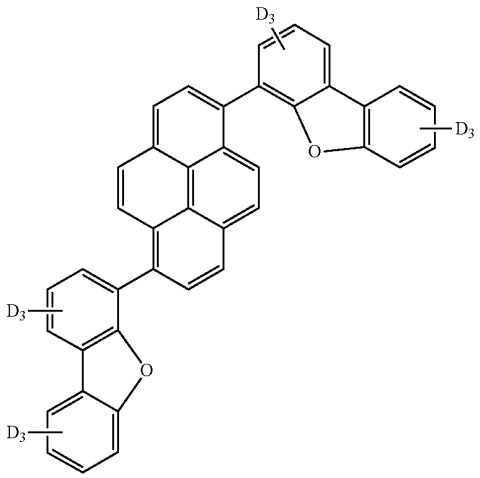

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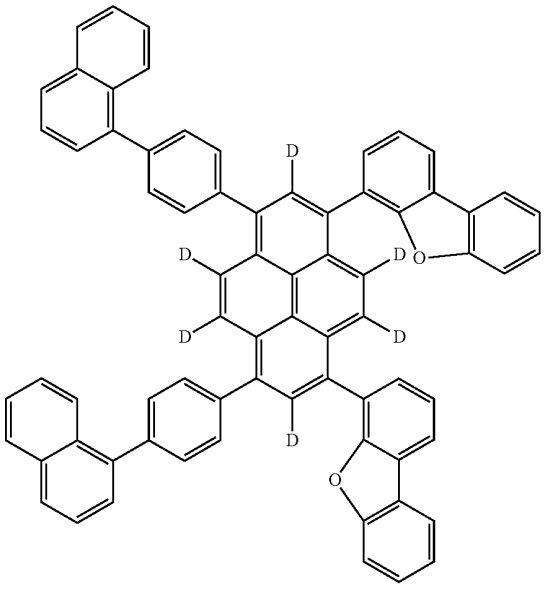

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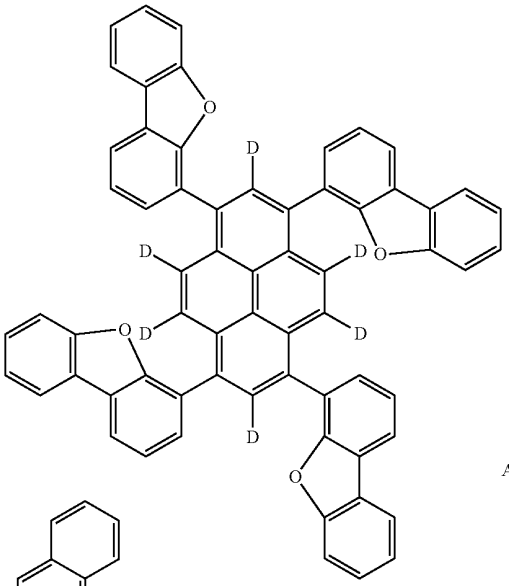

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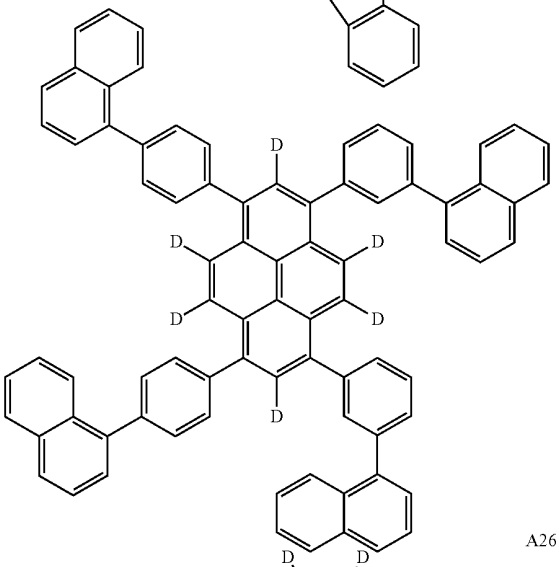

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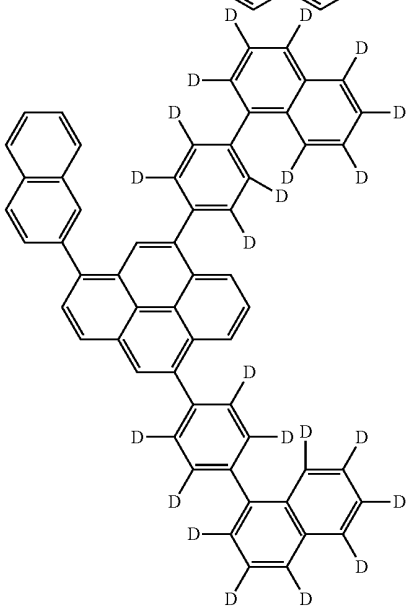

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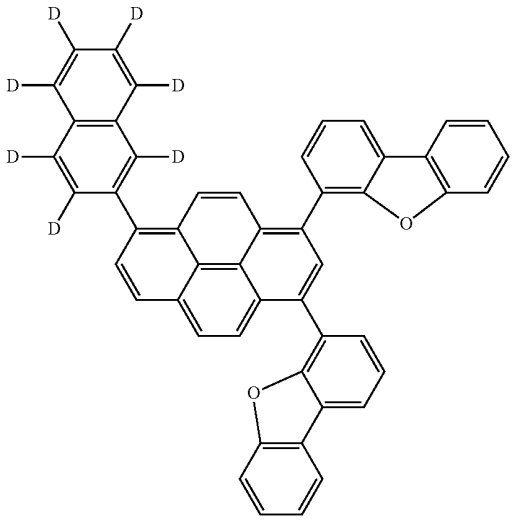

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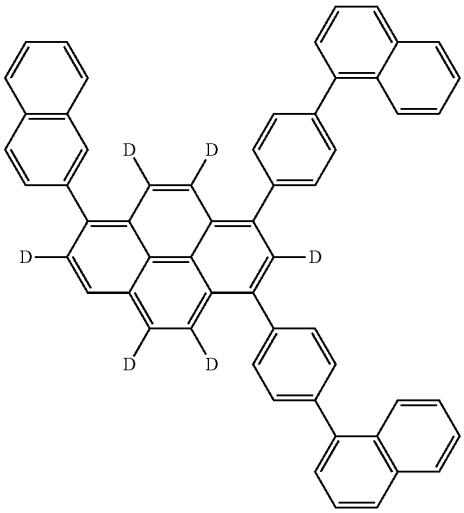

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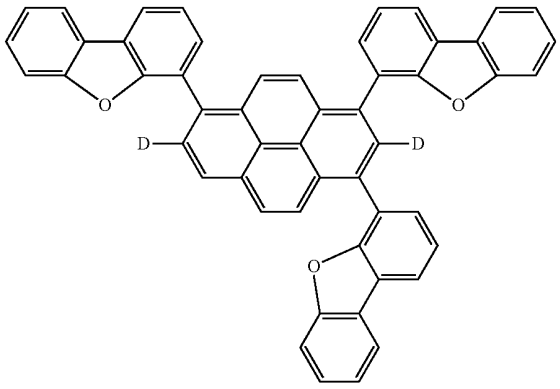

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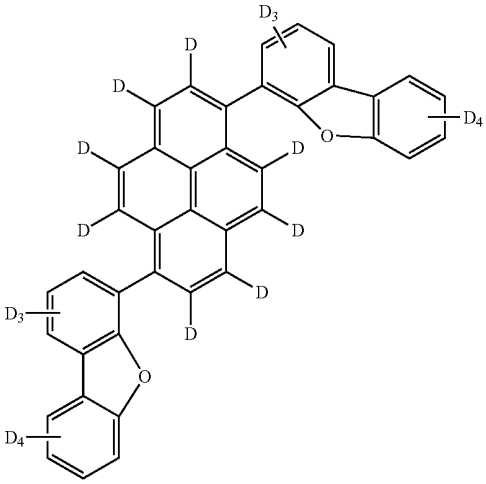
A30



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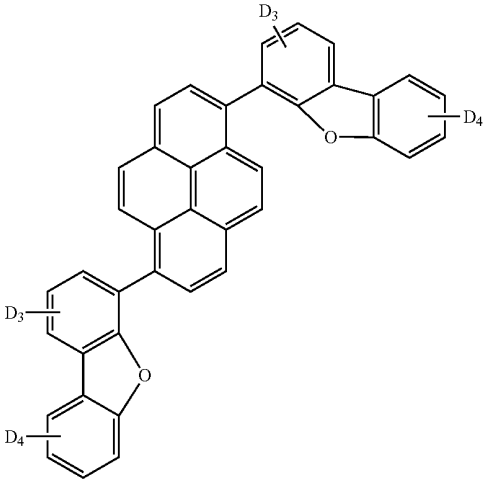

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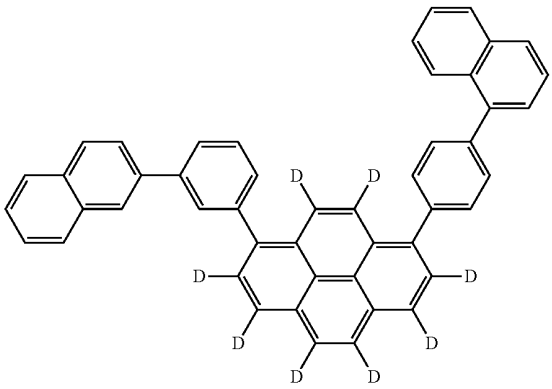

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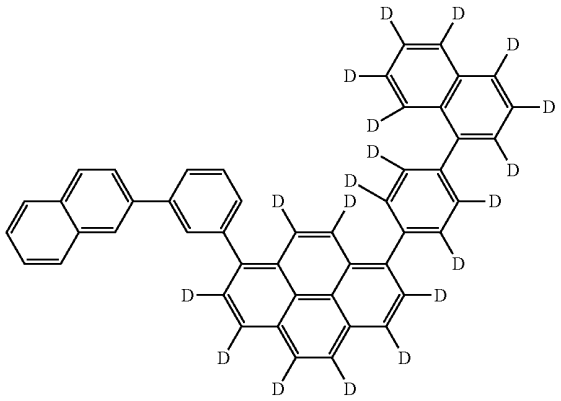
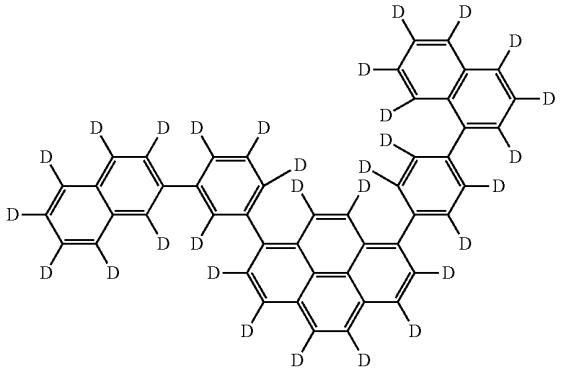


A34



The non-deuterated analog compounds can be made using any technique that will yield a C—C bond. A variety of such techniques are known, such as Suzuki, Yamamoto, Stille, and Pd- or Ni-catalyzed C—C couplings. The new deuterated compound can then be prepared in a similar manner using deuterated precursor materials or, more generally, by treating the non-deuterated compound with deuterated solvent, such as d6-benzene, in the presence of a Lewis acid H/D exchange catalyst, such as aluminum trichloride or ethyl aluminum chloride. Exemplary preparations are given in the Examples. The level of deuteration can be determined by NMR analysis and by mass spectrometry, such as Atmospheric Solids Analysis Probe Mass Spectrometry (ASAP-MS).

The compounds described herein can be formed into films using liquid deposition techniques. Surprisingly and unexpectedly, these compounds have greatly improved properties when compared to analogous non-deuterated compounds. Electronic devices including an active layer with the compounds described herein, have greatly improved lifetimes. In addition, the lifetime increases are achieved without sacrificing other device properties. Furthermore, the deuterated compounds described herein have greater air tolerance than the non-deuterated analogs. This can result in greater processing tolerance both for the preparation and purification of the materials and in the formation of electronic devices using the materials.

The new deuterated compounds described herein have utility as hole transport materials, as electroluminescent materials, and as hosts for electroluminescent materials.

3. Electronic Device

Organic electronic devices that may benefit from having one or more layers comprising the electroluminescent materials described herein include, but are not limited to, (1) devices that convert electrical energy into radiation (e.g., a light-emitting diode, light emitting diode display, or diode laser), (2) devices that detect signals through electronics processes (e.g., photodetectors, photoconductive cells, photoresistors, photoswitches, phototransistors, phototubes, IR detectors), (3) devices that convert radiation into electrical energy, (e.g., a photovoltaic device or solar cell), and (4) devices that include one or more electronic components that include one or more organic semi-conductor layers (e.g., a transistor or diode).

One illustration of an organic electronic device structure is shown in FIG. **1**. The device **100** has a first electrical contact layer, an anode layer **110** and a second electrical contact layer, a cathode layer **160**, and an electroactive layer **140** between them. Adjacent to the anode is a hole injection layer **120**. Adjacent to the hole injection layer is a hole transport layer **130**, comprising hole transport material. Adjacent to the cathode may be an electron transport layer **150**, comprising an electron transport material. As an option, devices may use one or more additional hole injection or hole transport layers (not shown) next to the anode **110** and/or one or more additional electron injection or electron transport layers (not shown) next to the cathode **160**.

Layers **120** through **150** are individually and collectively referred to as the active layers.

In one embodiment, the different layers have the following range of thicknesses: anode **110**, 500-5000 Å, in one embodiment 1000-2000 Å; hole injection layer **120**, 50-2000 Å, in one embodiment 200-1000 Å; hole transport layer **130**, 50-2000 Å, in one embodiment 200-1000 Å; electroactive layer **140**, 10-2000 Å, in one embodiment 100-1000 Å; layer **150**, 50-2000 Å, in one embodiment 100-1000 Å; cathode **160**, 200-10000 Å, in one embodiment 300-5000 Å. The location of the electron-hole recombination zone in the device, and thus the emission spectrum of the device, can be affected by the relative thickness of each layer. The desired ratio of layer thicknesses will depend on the exact nature of the materials used.

Depending upon the application of the device **100**, the electroactive layer **140** can be a light-emitting layer that is activated by an applied voltage (such as in a light-emitting diode or light-emitting electrochemical cell), or a layer of material that responds to radiant energy and generates a signal with or without an applied bias voltage (such as in a photodetector). Examples of photodetectors include photoconductive cells, photoresistors, photoswitches, phototransistors, and phototubes, and photovoltaic cells, as these terms are described in Markus, John, *Electronics and Nucleonics Dictionary,* 470 and 476 (McGraw-Hill, Inc. 1966).

One or more of the new deuterated materials described herein may be present in one or more of the active layers of a device. The deuterated materials may be used alone or in combination with non-deuterated materials.

In some embodiments, the new deuterated compounds are useful as hole transport materials in layer **130**. In some embodiments, at least one additional layer includes a deuterated material. In some embodiments, the additional layer is the hole injection layer **120**. In some embodiments, the additional layer is the electroactive layer **140**. In some embodiments, the additional layer is the electron transport layer **150**.

In some embodiments, the new deuterated compounds are useful as host materials for electroluminescent dopant materials in electroactive layer **140**. In some embodiments, the

dopant material is also deuterated. In some embodiments, at least one additional layer includes a deuterated material. In some embodiments, the additional layer is the hole injection layer **120**. In some embodiments, the additional layer is the hole transport layer **130**. In some embodiments, the additional layer is the electron transport layer **150**.

In some embodiments, the new deuterated compounds are useful as electroluminescent materials in electroactive layer **140**. In some embodiments, a host is also present in the electroactive layer. In some embodiments, the host material is also deuterated. In some embodiments, at least one additional layer includes a deuterated material. In some embodiments, the additional layer is the hole injection layer **120**. In some embodiments, the additional layer is the hole transport layer **130**. In some embodiments, the additional layer is the electron transport layer **150**

In some embodiments, the new deuterated compounds are useful as electron transport materials in layer **150**. In some embodiments, at least one additional layer includes a deuterated material. In some embodiments, the additional layer is the hole injection layer **120**. In some embodiments, the additional layer is the hole transport layer **130**. In some embodiments, the additional layer is the electroactive layer **140**.

In some embodiments, an electronic device has deuterated materials in any combination of layers selected from the group consisting of the hole injection layer, the hole transport layer, the electroactive layer, and the electron transport layer.

In some embodiments, the devices have additional layers to aid in processing or to improve functionality. Any or all of these layers can include deuterated materials. In some embodiments, all the organic device layers comprise deuterated materials. In some embodiments, all the organic device layers consist essentially of deuterated materials.

a. Electroactive Layer

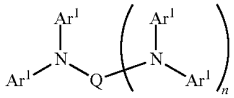
The new deuterated compounds of Formula I are useful as host materials for electroactive dopant materials in layer **140**. The compounds can be used alone, or in combination with a second host material. The new deuterated compounds can be used as a host for dopants with any color of emission. In some embodiments, the new deuterated compounds are used as hosts for green- or blue-emissive materials.

In some embodiments, the electroactive layer consists essentially of a host material having Formula I and one or more electroactive dopants. In some embodiments, the electroactive layer consists essentially of a first host material having Formula I, a second host material, and an electroactive dopant. Examples of second host materials include, but are not limited to, chrysenes, phenanthrenes, triphenylenes, phenanthrolines, naphthalenes, anthracenes, quinolines, isoquinolines, quinoxalines, phenylpyridines, benzodifurans, and metal quinolinate complexes.

The amount of dopant present in the electroactive composition is generally in the range of 3-20% by weight, based on the total weight of the composition; in some embodiments, 5-15% by weight. When a second host is present, the ratio of first host having Formula I to second host is generally in the range of 1:20 to 20:1; in some embodiments, 5:15 to 15:5. In some embodiments, the first host material having Formula I is at least 50% by weight of the total host material; in some embodiments, at least 70% by weight.

In some embodiments, the second host material has Formula III:

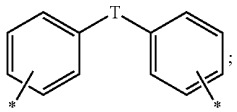
Formula III



where:

Ar^1 is the same or different at each occurrence and is an aryl group;

Q is selected from the group consisting of multivalent aryl groups and



T is selected from the group consisting of $(CR')_a$, SiR_2, S, SO_2, PR, PO, PO_2, BR, and R;

R is the same or different at each occurrence and is selected from the group consisting of alkyl, and aryl;

R' is the same or different at each occurrence and is selected from the group consisting of H, D, and alkyl;

a is an integer from 1-6; and

n is an integer from 0-6.

While n can have a value from 0-6, it will be understood that for some Q groups the value of n is restricted by the chemistry of the group. In some embodiments, n is 0 or 1. In some embodiments, Q is an aryl group having at least two fused rings. In some embodiments, Q has 3-5 fused aromatic rings. In some embodiments, Q is selected from the group consisting of chrysene, phenanthrene, triphenylene, phenanthroline, naphthalene, anthracene, quinoline and isoquinoline.

The dopant is an electroactive material which is capable of electroluminescence having an emission maximum between 380 and 750 nm. In some embodiments, the dopant emits red, green, or blue light.

Electroluminescent ("EL") materials which can be used as a dopant in the electroactive layer, include, but are not limited to, small molecule organic luminescent compounds, luminescent metal complexes, conjugated polymers, and mixtures thereof. Examples of small molecule luminescent compounds include, but are not limited to, chrysenes, pyrenes, perylenes, rubrenes, coumarins, anthracenes, thiadiazoles, derivatives thereof, and mixtures thereof. Examples of metal complexes include, but are not limited to, metal chelated oxinoid compounds. Examples of conjugated polymers include, but are not limited to poly(phenylenevinylenes), polyfluorenes, poly(spirobifluorenes), polythiophenes, poly (p-phenylenes), copolymers thereof, and mixtures thereof.

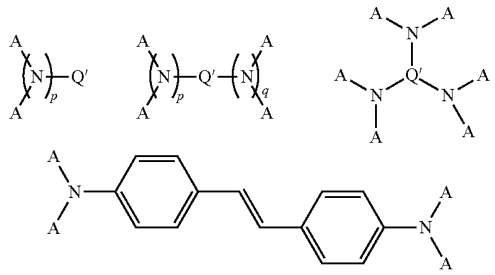
Examples of red light-emitting materials include, but are not limited to, periflanthenes, fluoranthenes, and perylenes. Red light-emitting materials have been disclosed in, for example, U.S. Pat. No. 6,875,524, and published US application 2005-0158577.

Examples of green light-emitting materials include, but are not limited to, diaminoanthracenes, and polyphenylenevinylene polymers. Green light-emitting materials have been disclosed in, for example, published PCT application WO 2007/021117.

Examples of blue light-emitting materials include, but are not limited to, diarylanthracenes, diaminochrysenes, diaminopyrenes, and polyfluorene polymers. Blue light-emitting materials have been disclosed in, for example, U.S. Pat. No. 6,875,524, and published US applications 2007-0292713 and 2007-0063638.

In some embodiments, the dopant is an organic compound. In some embodiments, the dopant is selected from the group consisting of a non-polymeric spirobifluorene compound and a fluoranthene compound.

In some embodiments, the dopant is a compound having aryl amine groups. In some embodiments, the electroactive dopant is selected from the formulae below:



where:

A is the same or different at each occurrence and is an aromatic group having from 3-60 carbon atoms;

Q' is a single bond or an aromatic group having from 3-60 carbon atoms;

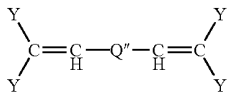
p and q are independently an integer from 1-6.

In some embodiments of the above formula, at least one of A and Q' in each formula has at least three condensed rings. In some embodiments, p and q are equal to 1.

In some embodiments, Q' is a styryl or styrylphenyl group. In some embodiments, Q' is an aromatic group having at least two condensed rings. In some embodiments, Q' is selected from the group consisting of naphthalene, anthracene, chrysene, pyrene, tetracene, xanthene, perylene, coumarin, rhodamine, quinacridone, and rubrene.

In some embodiments, A is selected from the group consisting of phenyl, biphenyl, tolyl, naphthyl, naphthylphenyl, and anthracenyl groups.

In some embodiments, the dopant has the formula below:



where:

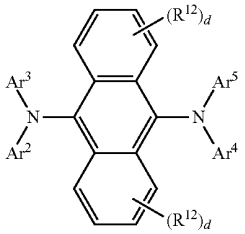
Y is the same or different at each occurrence and is an aromatic group having 3-60 carbon atoms;

Q" is an aromatic group, a divalent triphenylamine residue group, or a single bond.

In some embodiments, the dopant is an aryl acene. In some embodiments, the dopant is a non-symmetrical aryl acene.

In some embodiments, the dopant is an anthracene derivative having Formula IV:

Formula IV



wherein:

R^{12} is the same or different at each occurrence and is selected from the group consisting of D, alkyl, alkoxy and aryl, where adjacent R^{12} groups may be joined together to form a 5- or 6-membered aliphatic ring;

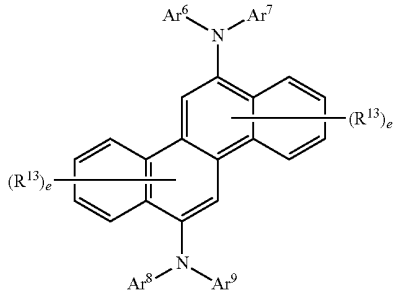
Ar^2 through Ar^5 are the same or different and are selected from the group consisting of aryl groups;

d is the same or different at each occurrence and is an integer from 0 to 4; and

In some embodiments, the dopant of Formula IV is deuterated. In some embodiments, the aryl groups are deuterated. In some embodiments, the alkyl groups are deuterated. In some embodiments, the dopant is at least 20% deuterated; in some embodiments, at least 30% deuterated; in some embodiments, at least 40% deuterated; in some embodiments, at least 50% deuterated in some embodiments, at least 60% deuterated; in some embodiments, at least 70% deuterated; in some embodiments, at least 80% deuterated; in some embodiments, at least 90% deuterated; in some embodiments, 100% deuterated.

In some embodiments, the dopant is a chrysene derivative having Formula V:

Formula V



wherein:

R^{13} is the same or different at each occurrence and is selected from the group consisting of D, alkyl, alkoxy aryl, fluoro, cyano, nitro,

SO_2R^{12}, where R^{12} is alkyl or perfluoroalkyl, where adjacent R^{11} groups may be joined together to form a 5- or 6-membered aliphatic ring;

Ar^6 through Ar^9 are the same or different and are selected from the group consisting of aryl groups; and

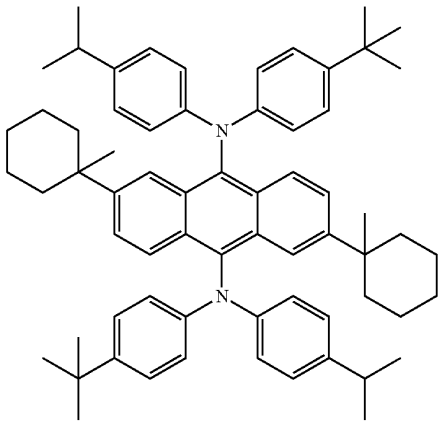
e is the same or different at each occurrence and is an integer from 0 to 5

In some embodiments, the dopant of Formula V is deuterated. In some embodiments, the aryl groups are deuterated. In some embodiments, the alkyl groups are deuterated. In some embodiments, the dopant is at least 30% deuterated; in some embodiments, at least 40% deuterated; in some embodiments, at least 50% deuterated in some embodiments, at least

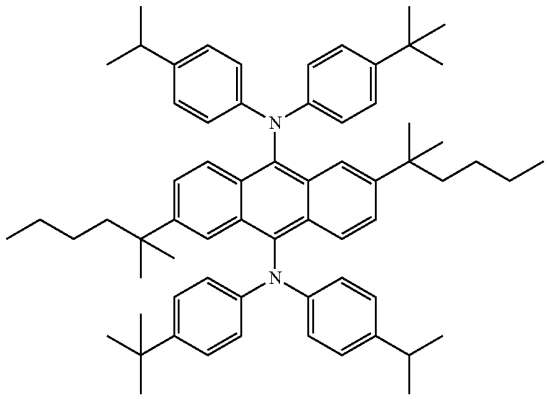
60% deuterated; in some embodiments, at least 70% deuterated; in some embodiments, at least 80% deuterated; in some embodiments, at least 90% deuterated; in some embodiments, 100% deuterated.

Some non-limiting examples of green dopants are compounds D1 through D8 shown below.

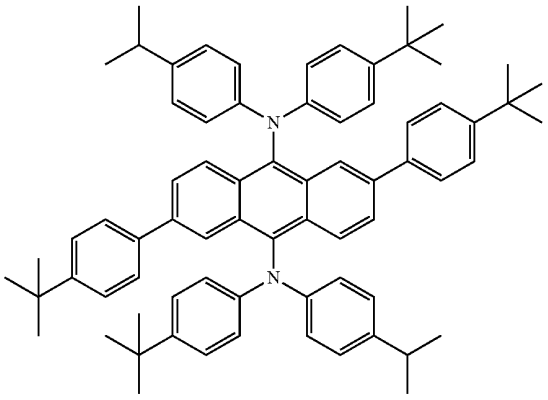
D1:



D2:



D3:



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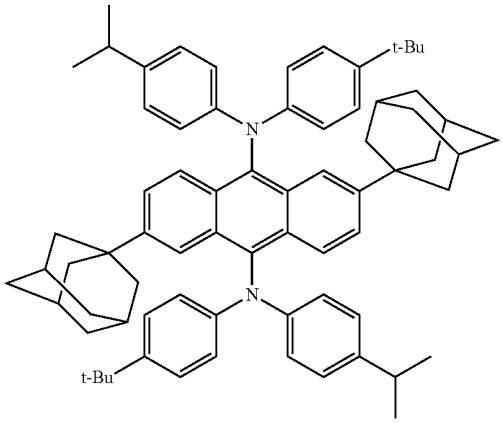
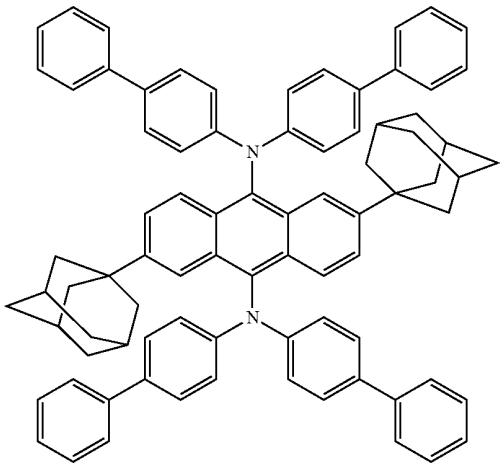
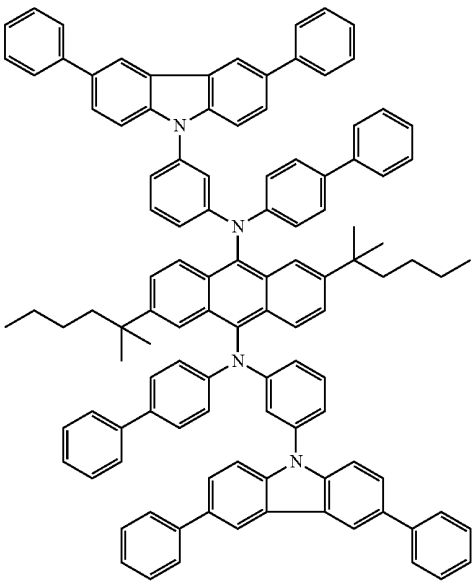
D4:



D5:



D6:



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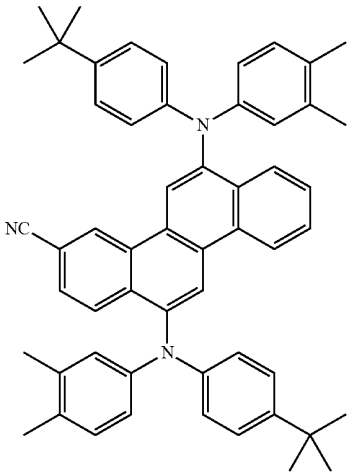
D7:



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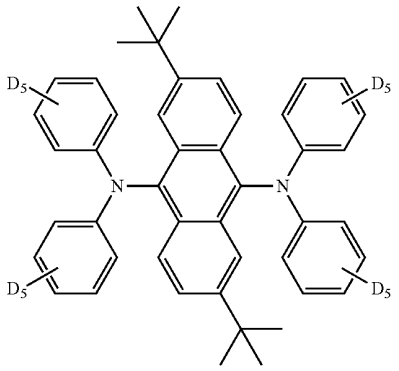
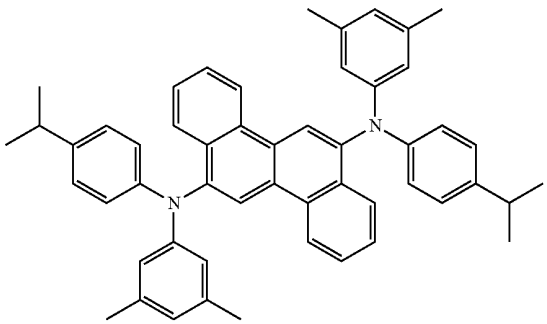
D8:

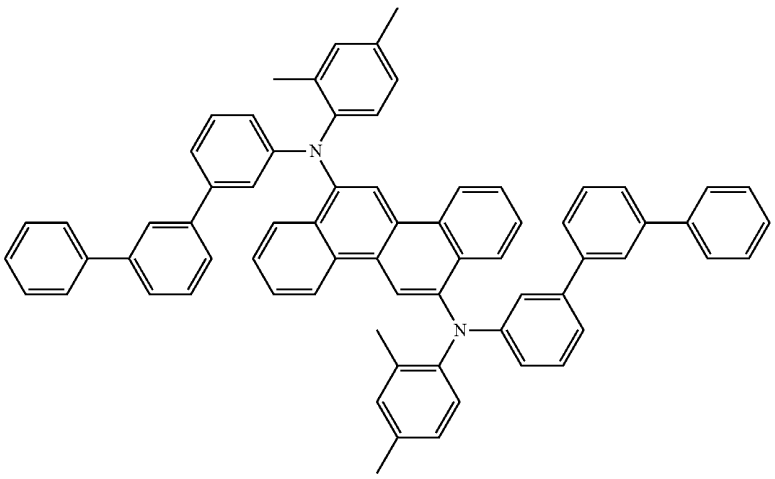


Some non-limiting examples of blue dopants are compounds D9 through D16 shown below.

D9:



D10:



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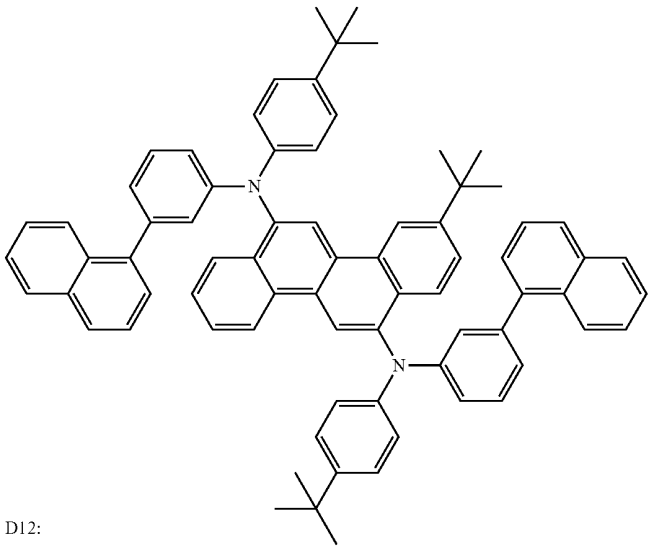
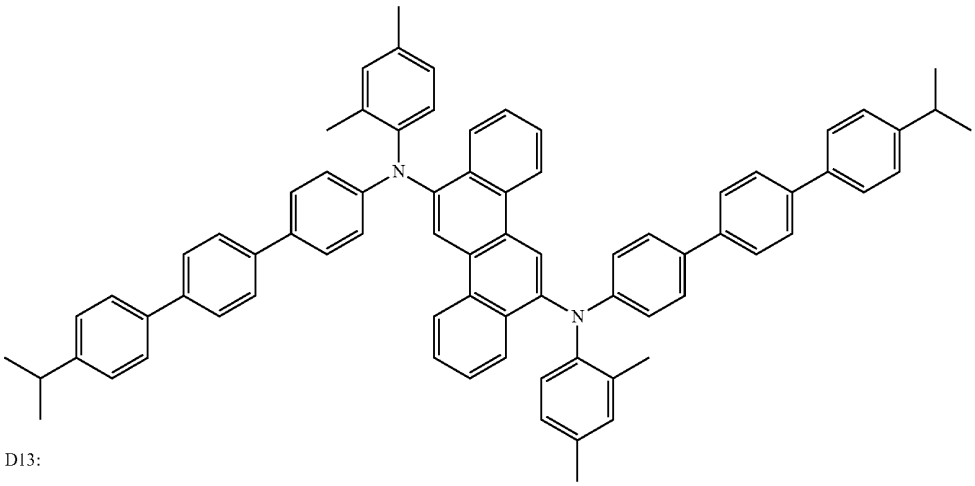
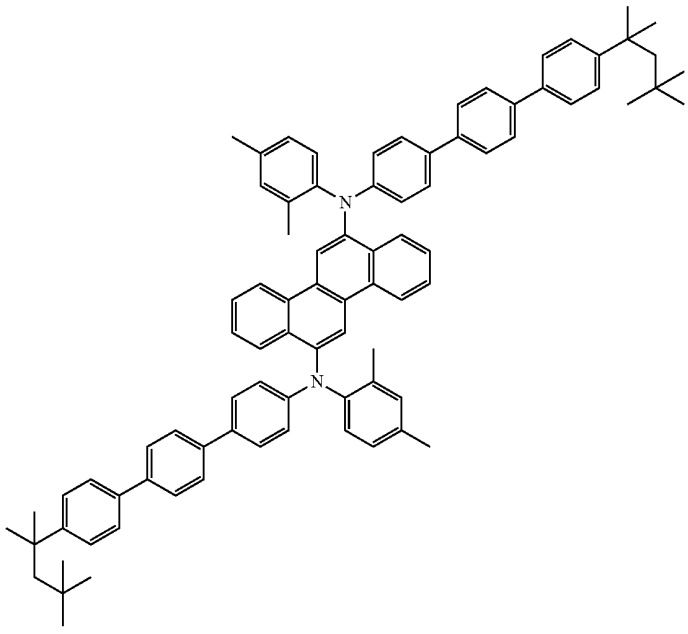
D11:



D12:



D13:



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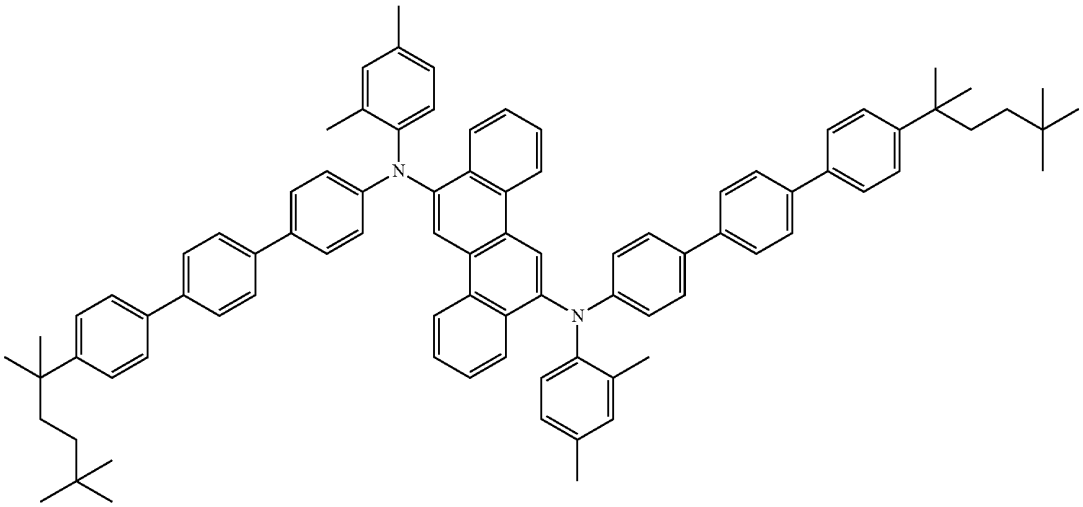
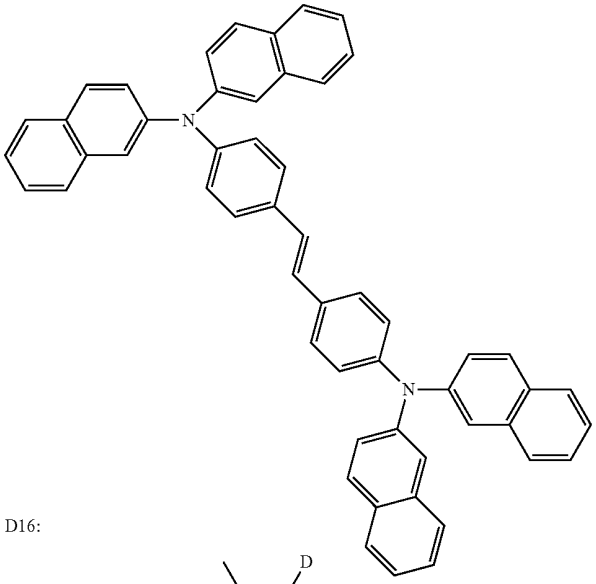
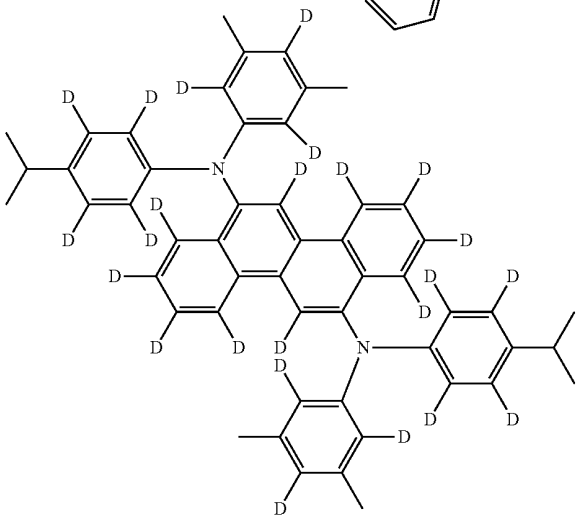
D14:



D15:



D16:



In some embodiments, the electroactive dopant is selected from the group consisting of amino-substituted chrysenes and amino-substituted anthracenes.

In some embodiments, the new deuterated compound described herein is an electroluminescent material and is present as an electroactive material.

b. Other Device Layers

The other layers in the device can be made of any materials that are known to be useful in such layers.

The anode **110**, is an electrode that is particularly efficient for injecting positive charge carriers. It can be made of, for example, materials containing a metal, mixed metal, alloy, metal oxide or mixed-metal oxide, or it can be a conducting polymer, or mixtures thereof. Suitable metals include the Group 11 metals, the metals in Groups 4-6, and the Group 8-10 transition metals. If the anode is to be light-transmitting, mixed-metal oxides of Groups 12, 13 and 14 metals, such as indium-tin-oxide, are generally used. The anode **110** can also comprise an organic material such as polyaniline as described in "Flexible light-emitting diodes made from soluble conducting polymer," *Nature* vol. 357, pp 477-479 (11 Jun. 1992). At least one of the anode and cathode is desirably at least partially transparent to allow the generated light to be observed.

The hole injection layer **120** comprises hole injection material and may have one or more functions in an organic electronic device, including but not limited to, planarization of the underlying layer, charge transport and/or charge injection properties, scavenging of impurities such as oxygen or metal ions, and other aspects to facilitate or to improve the performance of the organic electronic device. Hole injection materials may be polymers, oligomers, or small molecules. They may be vapour deposited or deposited from liquids which may be in the form of solutions, dispersions, suspensions, emulsions, colloidal mixtures, or other compositions.

The hole injection layer can be formed with polymeric materials, such as polyaniline (PANI) or polyethylenedioxythiophene (PEDOT), which are often doped with protonic acids. The protonic acids can be, for example, poly(styrenesulfonic acid), poly(2-acrylamido-2-methyl-1-propanesulfonic acid), and the like.

The hole injection layer can comprise charge transfer compounds, and the like, such as copper phthalocyanine and the tetrathiafulvalene-tetracyanoquinodimethane system (TTF-TCNQ).

In some embodiments, the hole injection layer comprises at least one electrically conductive polymer and at least one fluorinated acid polymer. Such materials have been described in, for example, published U.S. patent applications 2004-0102577, 2004-0127637, and 2005/205860 In some embodiments, the hole transport layer **130** comprises the new deuterated compound of Formula I. Examples of other hole transport materials for layer **130** have been summarized for example, in Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Vol. 18, p. 837-860, 1996, by Y. Wang. Both hole transporting molecules and polymers can be used. Commonly used hole transporting molecules are: N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD), 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC), N,N'-bis(4-methylphenyl)-N,N'-bis(4-ethylphenyl)-[1,1'-(3,3'-dimethyl)biphenyl]-4,4'-diamine (ETPD), tetrakis-(3-methylphenyl)-N,N,N',N'-2,5-phenylenediamine (PDA), a-phenyl-4-N,N-diphenylaminostyrene (TPS), p-(diethylamino)benzaldehyde diphenylhydrazone (DEH), triphenylamine (TPA), bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methane (MPMP), 1-phenyl-3-[p-(diethylamino)styryl]-5-[p-(diethylamino)phenyl] pyrazoline (PPR or DEASP), 1,2-trans-bis(9H-carbazol-9-yl)cyclobutane (DCZB), N,N,N',N'-tetrakis(4-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TTB), N,N'-bis(naphthalen-1-yl)-N,N'-bis-(phenyl)benzidine (-NPB), and porphyrinic compounds, such as copper phthalocyanine. Commonly used hole transporting polymers are polyvinylcarbazole, (phenylmethyl)-polysilane, and polyaniline. It is also possible to obtain hole transporting polymers by doping hole transporting molecules such as those mentioned above into polymers such as polystyrene and polycarbonate. In some cases, triarylamine polymers are used, especially triarylamine-fluorene copolymers. In some cases, the polymers and copolymers are crosslinkable. Examples of crosslinkable hole transport polymers can be found in, for example, published US patent application 2005-0184287 and published PCT application WO 2005/052027. In some embodiments, the hole transport layer is doped with a p-dopant, such as tetrafluorotetracyanoquinodimethane and perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride.

In some embodiments, the electron transport layer **150** comprises the new deuterated compound of Formula I. Examples of other electron transport materials which can be used in layer **150** include metal chelated oxinoid compounds, such as tris(8-hydroxyquinolato)aluminum (Alq_3); bis(2-methyl-8-quinolinolato)(para-phenyl-phenolato)aluminum(III) (BAlQ); and azole compounds such as 2-(4-biphenylyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole (PBD) and 3-(4-biphenylyl)-4-phenyl-5-(4-t-butylphenyl)-1,2,4-triazole (TAZ), and 1,3,5-tri(phenyl-2-benzimidazole)benzene (TPBI); quinoxaline derivatives such as 2,3-bis(4-fluorophenyl)quinoxaline; phenanthroline derivatives such as 9,10-diphenylphenanthroline (DPA) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (DDPA); and mixtures thereof. The electron-transport layer may also be doped with n-dopants, such as Cs or other alkali metals. Layer **150** can function both to facilitate electron transport, and also serve as a buffer layer or confinement layer to prevent quenching of the exciton at layer interfaces. Preferably, this layer promotes electron mobility and reduces exciton quenching.

The cathode **160**, is an electrode that is particularly efficient for injecting electrons or negative charge carriers. The cathode can be any metal or nonmetal having a lower work function than the anode. Materials for the cathode can be selected from alkali metals of Group 1 (e.g., Li, Cs), the Group 2 (alkaline earth) metals, the Group 12 metals, including the rare earth elements and lanthanides, and the actinides. Materials such as aluminum, indium, calcium, barium, samarium and magnesium, as well as combinations, can be used. Li- or Cs-containing organometallic compounds, LiF, CsF, and Li_2O can also be deposited between the organic layer and the cathode layer to lower the operating voltage.

It is known to have other layers in organic electronic devices. For example, there can be a layer (not shown) between the anode **110** and hole injection layer **120** to control the amount of positive charge injected and/or to provide band-gap matching of the layers, or to function as a protective layer. Layers that are known in the art can be used, such as copper phthalocyanine, silicon oxy-nitride, fluorocarbons, silanes, or an ultra-thin layer of a metal, such as Pt. Alternatively, some or all of anode layer **110**, active layers **120**, **130**, **140**, and **150**, or cathode layer **160**, can be surface-treated to increase charge carrier transport efficiency. The choice of materials for each of the component layers is preferably determined by balancing the positive and negative charges in the emitter layer to provide a device with high electroluminescence efficiency.

It is understood that each functional layer can be made up of more than one layer.

The device can be prepared by a variety of techniques, including sequential vapor deposition of the individual layers on a suitable substrate. Substrates such as glass, plastics, and metals can be used. Conventional vapor deposition techniques can be used, such as thermal evaporation, chemical vapor deposition, and the like. Alternatively, the organic layers can be applied from solutions or dispersions in suitable solvents, using conventional coating or printing techniques, including but not limited to spin-coating, dip-coating, roll-to-roll techniques, ink-jet printing, screen-printing, gravure printing and the like.

The present invention also relates to an electronic device comprising at least one active layer positioned between two electrical contact layers, wherein the at least one active layer of the device includes the anthracene compound of Formula 1. Devices frequently have additional hole transport and electron transport layers.

To achieve a high efficiency LED, the HOMO (highest occupied molecular orbital) of the hole transport material desirably aligns with the work function of the anode, and the LUMO (lowest un-occupied molecular orbital) of the electron transport material desirably aligns with the work function of the cathode. Chemical compatibility and sublimation temperature of the materials are also important considerations in selecting the electron and hole transport materials.

It is understood that the efficiency of devices made with the anthracene compounds described herein, can be further improved by optimizing the other layers in the device. For example, more efficient cathodes such as Ca, Ba or LiF can be used. Shaped substrates and novel hole transport materials that result in a reduction in operating voltage or increase quantum efficiency are also applicable. Additional layers can also be added to tailor the energy levels of the various layers and facilitate electroluminescence.

The compounds of the invention often are photoluminescent and can be useful in applications other than OLEDs, such as oxygen sensitive indicators and as luminescent indicators in bioassays.

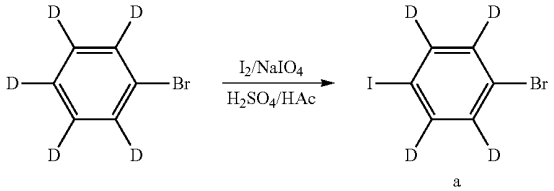
EXAMPLES

The following examples illustrate certain features and advantages of the present invention. They are intended to be illustrative of the invention, but not limiting. All percentages are by weight, unless otherwise indicated.

Example 1

This example illustrates the preparation of a deuterated diarylpyrene compound having Formula I, Compound A3.

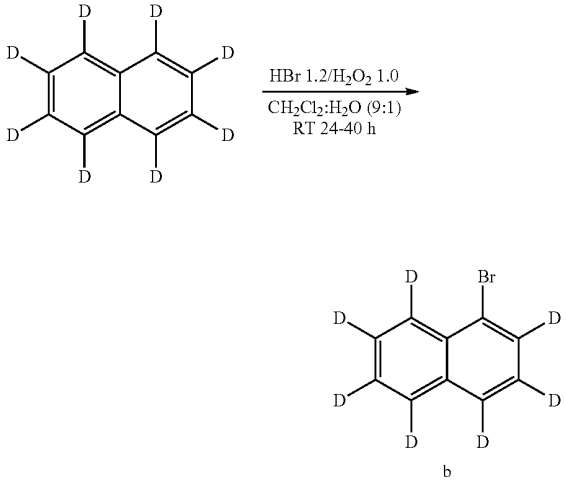
Intermediate a:



a

To d5-bromobenzene (MW 162, 100 g, 0.617 mol), was added a mixture solvents of 93 mL of 50% H_2SO_4, and 494 mL of HOAc at rt. Then a pulverized I_2 (MW 254, 61.7 g, 0.243 mol) was added followed by pulverized $NaIO_4$ (MW 214, 26.4 g, 0.123 mol). The mixture was vigorously stirred and heated to 90° C. for 4 h. The dark purple color solution changed to a pale-orange-colored mixture containing a very fine white precipitate. The mixture was allowed to cool to rt overnight. During this time, the product precipitated as microcrystalline plates. The mixture was filtered and was washed twice 10% sodium thiosulfate $Na_2S_2O_3$ (50 mL) and then with water. It was dissolved in CH_2Cl_2 and run flash column. The light yellow, crystalline material was obtained 124 g (70%). The filtrate was extracted with CH_2Cl_2 (50 mL ×3) and combined the CH_2Cl_2 washed twice 10% sodium thiosulfate $Na_2S_2O_3$ (50 mL) and then with water. After dried and evaporated the solvent and run flash column to give another 32 g of pure product (17.5%). Total is 156 g (yield 88%).

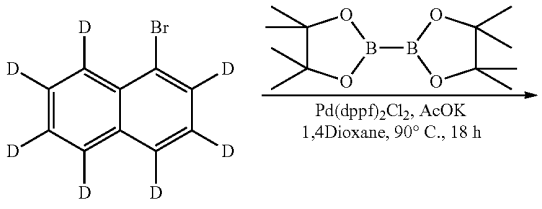
Intermediate b:



b

To a stirred solution of naphalene-d8 (MW 136, 68 g, 0.5 mole) in CH2Cl2 (800 mL): H20 (80 mL) and hydrobromic acid (MW: 81, d=1.49, 100 g; 67.5 mL of a 49% aq. solution; 0.6 mol) was slowly added hydrogen peroxide (FW: 34, d=1.1 g/mL, 56 g; 51.5 mL of a 30% aq. solution; 0.5 mol) over a period of 30 min at 10-15° C. The reaction was left at room temperature for 40 h whilst monitoring its progress by TLC. After the completion of bromination, the solvent was removed under reduced pressure and the crude product was washed twice 10% sodium thiosulfate Na2S2O3 (50 mL) and then with water.The pure product was isolated by flash column chromatography on silica gel (100-200 mesh) using hexane (100%) followed by distillation to give pure 1-bromonaphthene-d7 as a clear liquid 85 g, the yield is around 80%.

Intermediate c:



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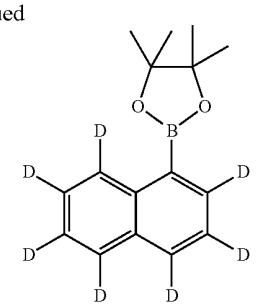
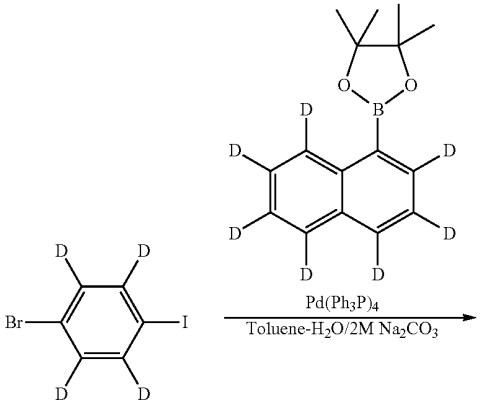


c

The mixture of 1-bromonaphthalene-d7 (21.4 g, 0.10 mol), bis(pinacolato)diboron (38 g, 0.15 mol), potassium acetate (19.6 g, 0.20 mol) in 300 ml of dry 1,4-dioxane was bubbled with nitrogen for 15 min. Then $Pd(dppf)_2Cl_2$—CH_2Cl_2(1.63 g, 0.002 mol) was added. The mixture was heated at 100° C. (oil bath) for 18 h. After cooling down the mixture was filtered through CELIT and then concentrated to 50 mL, then added water and extracted with ether for three times (100 mL ×3). The organic layer was washed with water (3×) and brine (1×), dried over $MgSO_4$, filtered and concentrated. The residue was submitted to a silica gel column (eluent: hexane) to give a white liquid which has by products of naphalene, and diboronic ester. Thus futher purification was conducted by distilliation to give a viscous clear liquid. Yield 21 g, 82%.

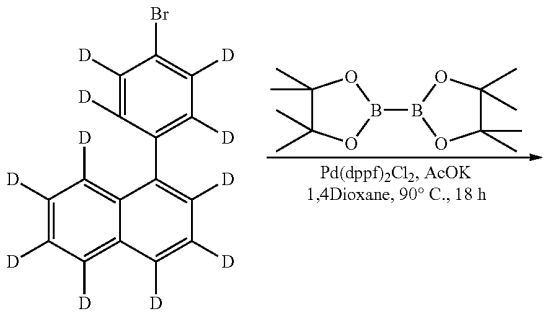
Intermediate d:

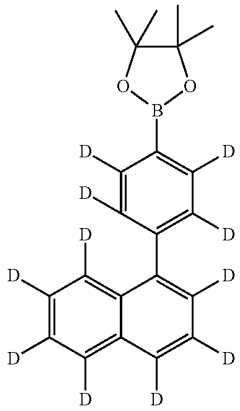


d

To a mixture of 1-bromo-4-iodo-benzene-D4 (10.95 g, 0.0382 mole) and 1-naphaleneboronic ester-D7 (10.0 g, 0.0383 mole) in Toluene (300 mL) was added Na_2CO_3 (12.6 g, 0.12 mole) and H_2O (50 mL), aliquant (3 g). The mixture was bubbled with nitrogen for 15 min. Then Pd(PPh3)4 (0.90 g, 2%) was added. The mixture was refluxed for 12 h under a nitrogen atmosphere. After cooling down the reaction mixture was separated, the organic layer was washed with water and separated, dried and concentrated. Silica was added and concentrated. After evaporation the residue solvent, it was subject to run flash column using hexane as eluent to give crude product. Further purification was conducted by distillation (collect 135-140° C./100 mtorr) to give clear viscous liquid (8.76 g, yield 78%).

Intermediate e:

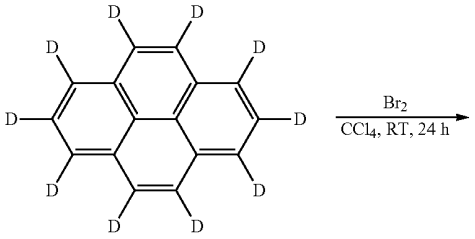


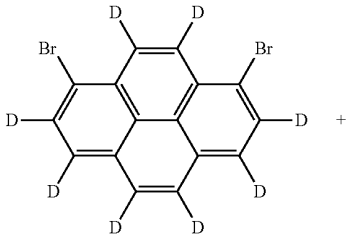


e

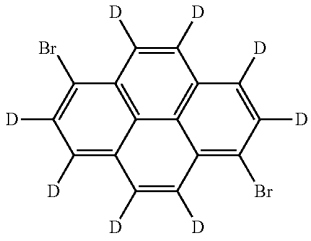
The mixture of 1-bromo-phenyl-4-naphthalene-d11 (22 g, 0.075 mole), bis(pinacolato)diboron (23 g, 0.090 mol), potassium acetate 22 g, 0.224 mol) in 200 ml of dry 1,4-dioxane was bubbled with nitrogen for 15 min. Then $Pd(dppf)_2Cl_2.CH_2Cl_2$(1.20 g, 0.00147 mol) was added. The mixture was heated at 100° C. (oil bath) for 18 h. After cooling down the mixture was filtered through CELIT and then concentrated to 50 mL, then added water and extracted with ether for three times (100 mL ×3). The organic layer was washed with water (3×) and brine(1×), dried over $MgSO_4$, filtered and concentrated. The residue was submitted to a silica gel column (eluent: hexane) to give a white liquid which has by products of naphalene, and diboronic ester. Thus further purification was conducted by run silica gel column again using hexane as eluent . After evaporate the solvent and concentrated to around 80 mL hexane and white crystal product was formed, it was filtrate to give 20.1 g of product, yield 81%.

Intermediate f:





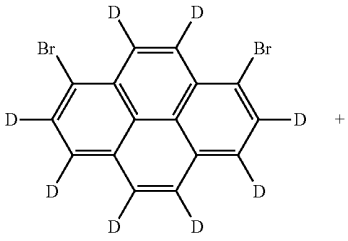
f



g

To a stirred solution of pyrene-d10 (25 g, 0.12 mol) in CCl_4 (1500 mL) was added Br_2 (35.8 g, 0.22 mol)/CCl_4 (150 mL) drop-wise at RT. After addition the mixture was stirred for 24 h. The solid was filtered and washed with MeOH to give a solid 32.21 g, which was stirred with 634 mL of THF at RT for 1-2 days. The mixture was filtered to give a solid A, 16 g (1,6-dibromopyrene). The filtrate was put in the refrigerator for 1 day. The solid was then filtered to give a solid (~0.6 g, 1.6:1.8=~1:1). The filtrate was concentrated to ~150 mL, put in the refrigerator for 1 day. The solid was filtered to give 10.3 g, which was recrystallized from toluene (260 mL) to give 5.2 g. 5.2 g of solid was heated to dissolve in 50 mL of THF. After cooling down the solid was filtered to give Intermediate B, 4.21 g, 10%, HPLC 98.5%.

Compound A3:



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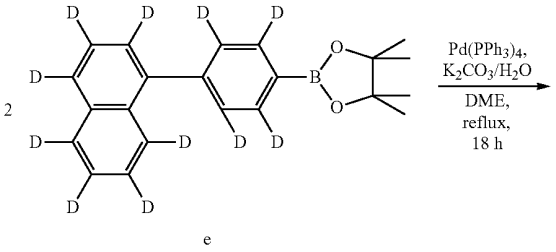

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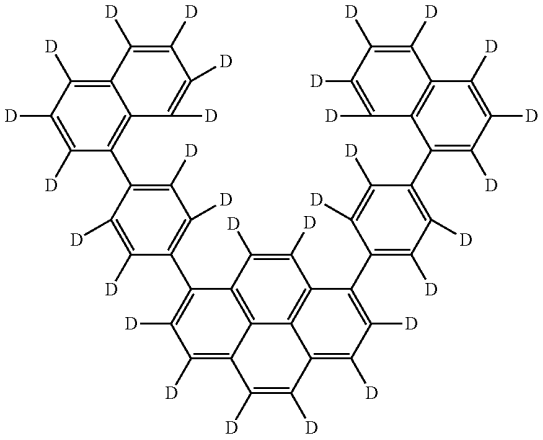
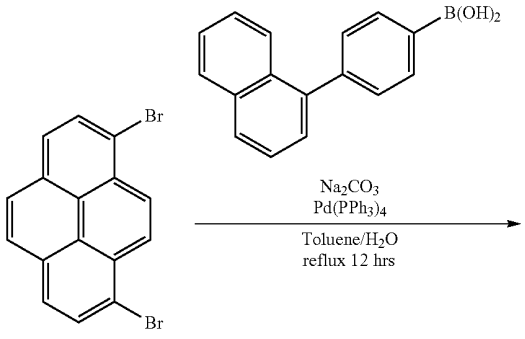


Compound A3

To a mixture of f (2.94 g, 0.008 mol) and e (6.28 g, 0.018 mol) in DME (100 mL) was added K_2CO_3 (6.63 g, 0.048 mol) and H_2O (16 mL). The mixture was bubbled with nitrogen for 15 min. Then $Pd(PPh_3)_4$ (0.46 g, 0.4 mmol) was added. The mixture was refluxed for 18 h under a nitrogen atmosphere. After cooling down the mixture was poured into MeOH. The solid was filtered and purified by Isolera, Florisil column, recrystallized from $CHCl_3/CH_3CN$ (2:1) to give product Compound A3, 1.45 g, 28%, HPLC 98.2%.

Comparative Example A

This comparative example illustrates the preparation of 1,8-Bis-(4-naphthalen-1-yl-phenyl)-pyrene, Comparative X. This comparative compound is the non-deuterated analog of Compound A3.



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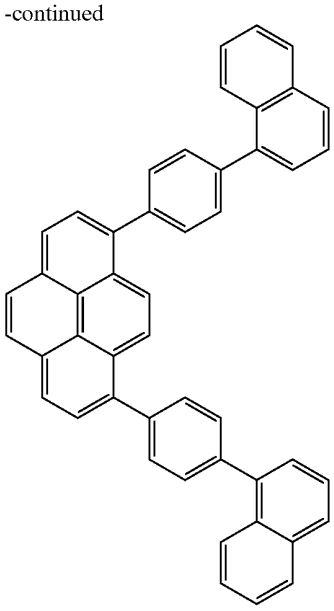


Comparative X

Into a RBF (500 mL) was added 1,8-dibromopyrene (10 g, 27.6 mmol), 3-(2-naphthenylphenylboronic acid (16.5 g, 66.3 mmol), followed by the addition of toluene (300 mL). The mixture was purged with N2 for 10 min. Then Na_2CO_3 (14.6 g, 138 mmole) dissolved in the water (70 mL) was added. The mixture was continued to be purged with N_2 for 10 min. A catalytic amount of $Pd(PPh_3)_4$ (0.16 g) was added. The mixture was refluxed for 4 h. First, a clear solution was formed (in about 2 h). Then 2 h later a light white precipitate was formed. Continued reflux overnight. A slightly white precipitate was formed. Filtered through silica pad at 70-90° C. to remove black Pd. After concentration, the solid was slurried with hot THF/Acetone(100 ml/100 ml) for 12 hrs. Filtered and washed with THF and dried. An off-white powder was formed (11.55 g, yield: 68.8%). Further purification of the compound by train submission affords 7.4 g pure compound (purity 99.9%). The ^1H NMR spectrum was consistent with the structure of Comparative X.

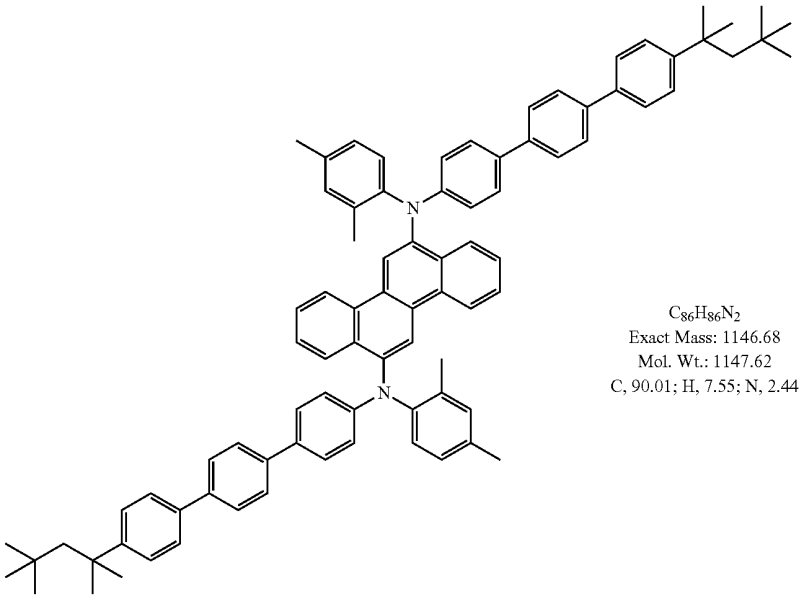
Example 2 and Comparative Example B

This example demonstrates the fabrication and performance of a device having deep blue emission.

In Example 2, the host material was Compound A3. In Comparative Example B, the host material was Comparative X.

The electroluminescent material E1 had the structure given below.

E1



$C_{86}H_{86}N_2$
Exact Mass: 1146.68
Mol. Wt.: 1147.62
C, 90.01; H, 7.55; N, 2.44

Compound E1 is made by combining 6,12-dibromochrysene, N-(2,4-dimethylphenyl)-N-(4"-tertoctylterphenyl-4-yl) amine, tris(tert-butyl)phosphine, and tris(dibenzylideneacetone) dipalladium(0) in a 20:40:2:1 molar ratio, respectively, in dry toluene in an inert atmosphere. To this solution is added sodium tert-butoxide (~45 relative molar ratio) followed by heating at 60° C. for 3 days. The reaction product is recovered as a solid and purified by silica gel column chromatography and recrystallization from DCM and acetonitrile.

The device had the following structure on a glass substrate:

anode=Indium Tin Oxide (ITO): 50 nm

hole injection layer=HIJ 1 (50 nm), which is an aqueous dispersion of an electrically conductive polymer and a polymeric fluorinated sulfonic acid. Such materials have been described in, for example, published U.S. patent applications US 2004/0102577, US 2004/0127637, and US 2005/0205860.

hole transport layer=a non-crosslinked arylamine polymer (20 nm)

electroactive layer=13:1 host:dopant E1 (40 nm), as shown in Table 1

electron transport layer=a metal quinolate derivative (10 nm)

cathode=CsF/Al (1.0/100 nm)

OLED devices were fabricated by a combination of solution processing and thermal evaporation techniques. Patterned indium tin oxide (ITO) coated glass substrates from Thin Film Devices, Inc were used. These ITO substrates are based on Corning 1737 glass coated with ITO having a sheet resistance of 30 ohms/square and 80% light transmission. The patterned ITO substrates were cleaned ultrasonically in aqueous detergent solution and rinsed with distilled water. The patterned ITO was subsequently cleaned ultrasonically in acetone, rinsed with isopropanol, and dried in a stream of nitrogen.

Immediately before device fabrication the cleaned, patterned ITO substrates were treated with UV ozone for 10 minutes. Immediately after cooling, an aqueous dispersion of Buffer 1 was spin-coated over the ITO surface and heated to remove solvent. After cooling, the substrates were then spin-coated with a solution of a hole transport material, and then heated to remove solvent. After cooling the substrates were spin-coated with the emissive layer solution, and heated to remove solvent. The substrates were masked and placed in a vacuum chamber. The electron transport layer was deposited by thermal evaporation, followed by a layer of CsF. Masks were then changed in vacuo and a layer of Al was deposited by thermal evaporation. The chamber was vented, and the devices were encapsulated using a glass lid, dessicant, and UV curable epoxy.

The OLED samples were characterized by measuring their (1) current-voltage (I-V) curves, (2) electroluminescence radiance versus voltage, and (3) electroluminescence spectra versus voltage. All three measurements were performed at the same time and controlled by a computer. The current efficiency of the device at a certain voltage is determined by dividing the electroluminescence radiance of the LED by the current density needed to run the device. The unit is a cd/A.

The results are given in Table 1.

TABLE 1

Device Results						
Example	Host	CE [cd/A]	Voltage [V]	CIE [x]	CIE [y]	Lifetime T50 [h]
Comparative B	Comparative X	7.2	4.9	0.1325	0.1579	4547
Example 2	Compound A3	7.1	5.0	0.1329	0.1542	7490

All data @ 1000 nits, CE = current efficiency; CIEx and CIEy are the x and y color coordinates according to the C.I.E. chromaticity scale (Commission Internationale de L'Eclairage, 1931); T50 is the time to reach half the initial luminance.

Note that not all of the activities described above in the general description or the examples are required, that a portion of a specific activity may not be required, and that one or more further activities may be performed in addition to those described. Still further, the order in which activities are listed are not necessarily the order in which they are performed.

In the foregoing specification, the concepts have been described with reference to specific embodiments. However, one of ordinary skill in the art appreciates that various modifications and changes can be made without departing from the scope of the invention as set forth in the claims below. Accordingly, the specification and figures are to be regarded in an illustrative rather than a restrictive sense, and all such modifications are intended to be included within the scope of invention.

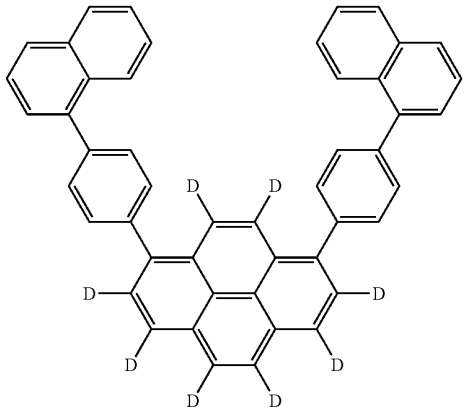
Benefits, other advantages, and solutions to problems have been described above with regard to specific embodiments. However, the benefits, advantages, solutions to problems, and any feature(s) that may cause any benefit, advantage, or solution to occur or become more pronounced are not to be construed as a critical, required, or essential feature of any or all the claims.

It is to be appreciated that certain features are, for clarity, described herein in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any subcombination. Further, reference to values stated in ranges include each and every value within that range.

What is claimed is:

1. A compound selected from A1 through A34.

A1



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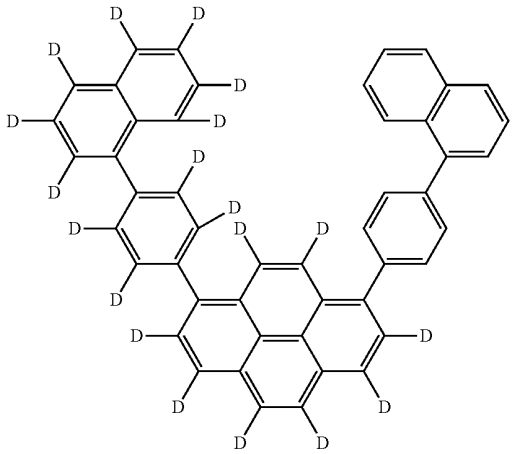
A2



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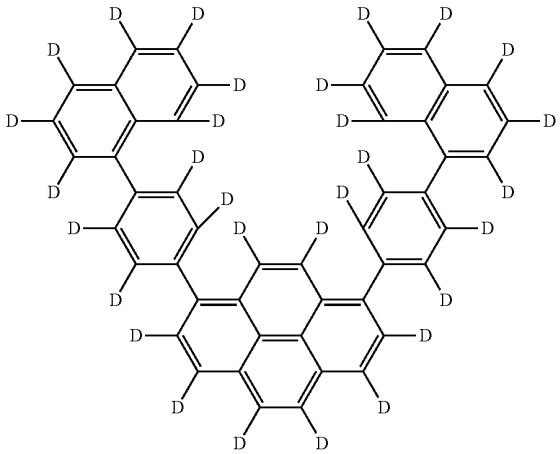

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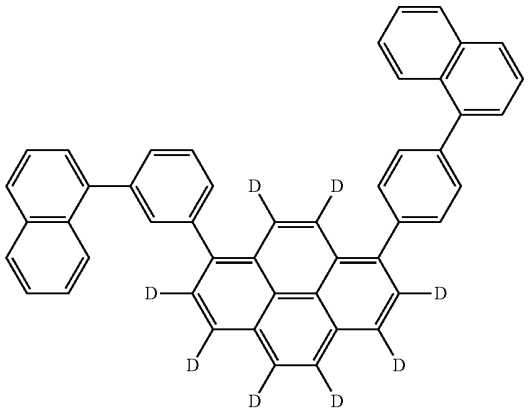

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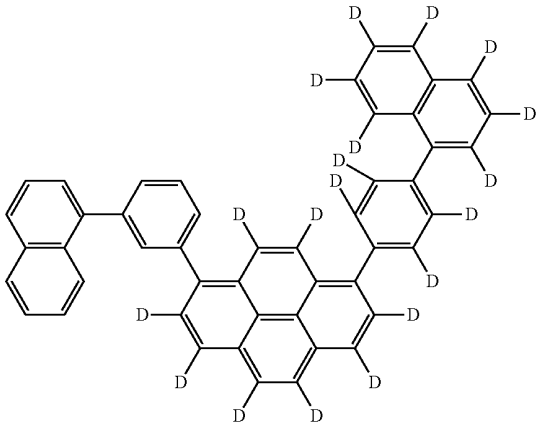

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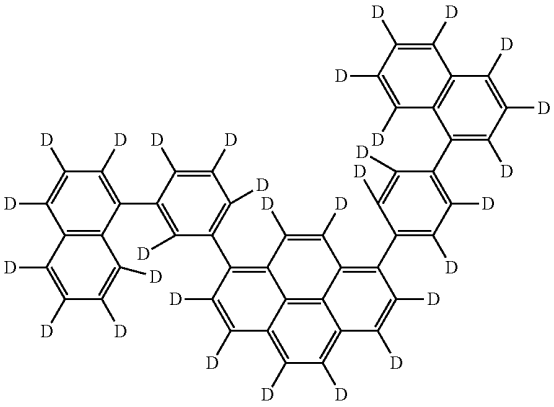

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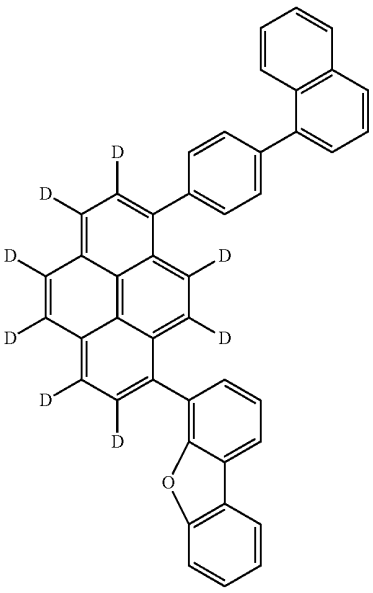

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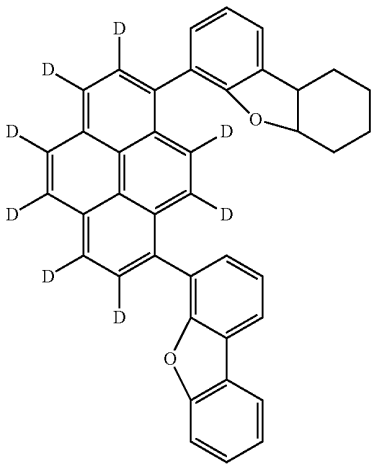

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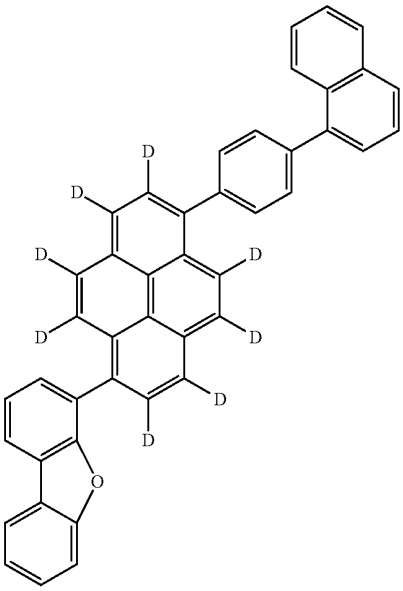

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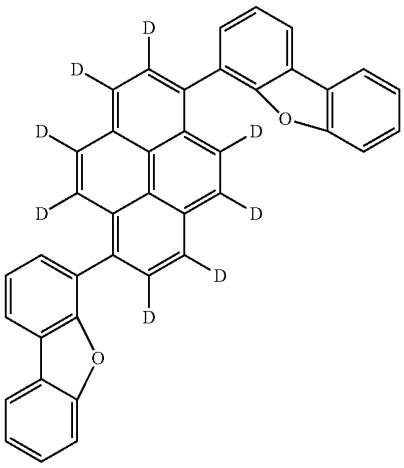

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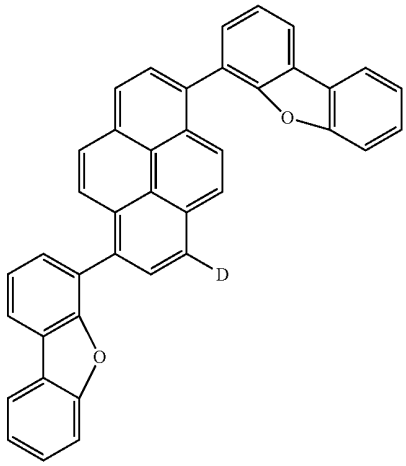

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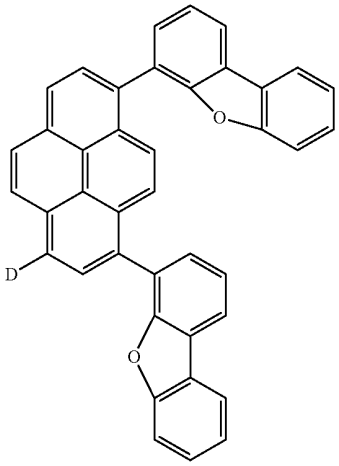

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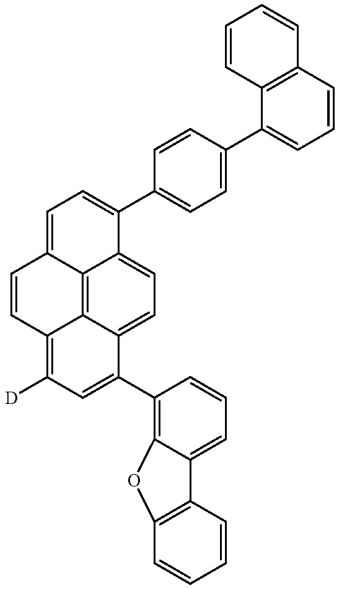

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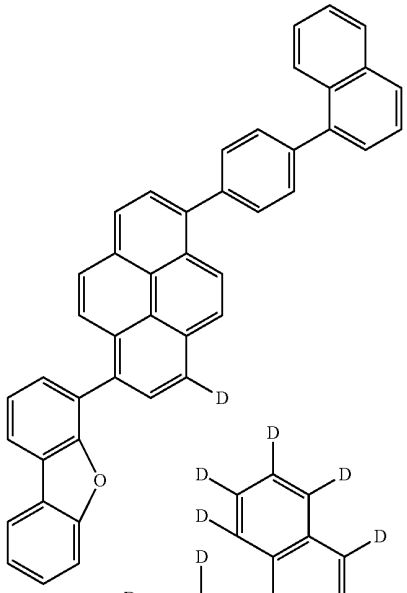

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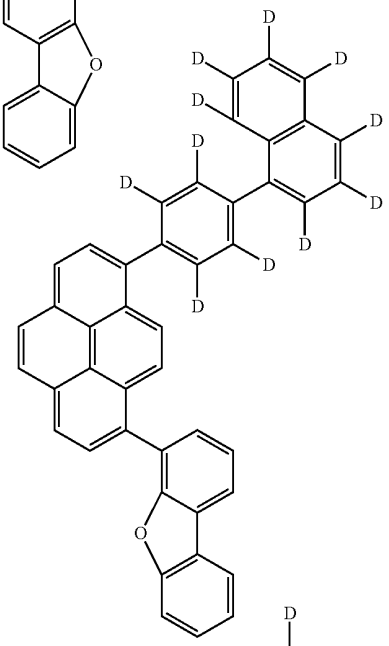

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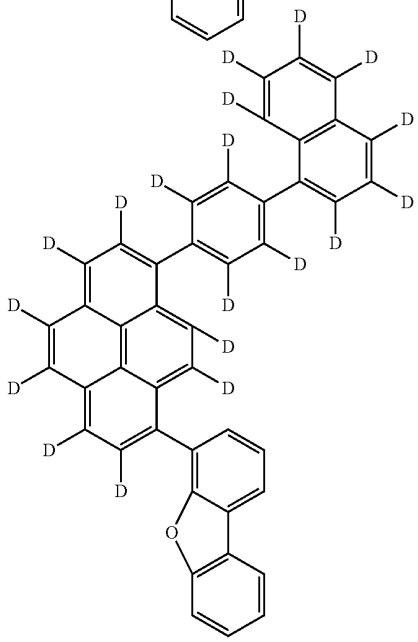

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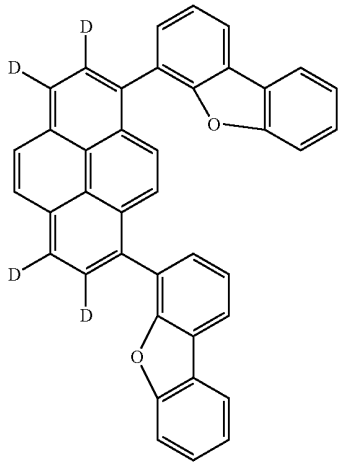

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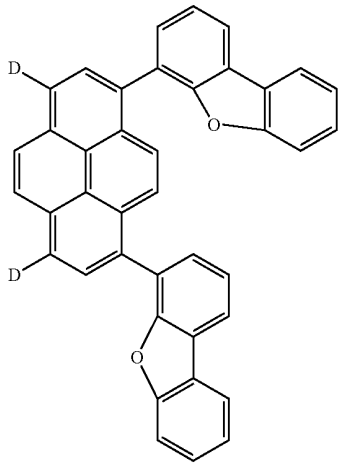

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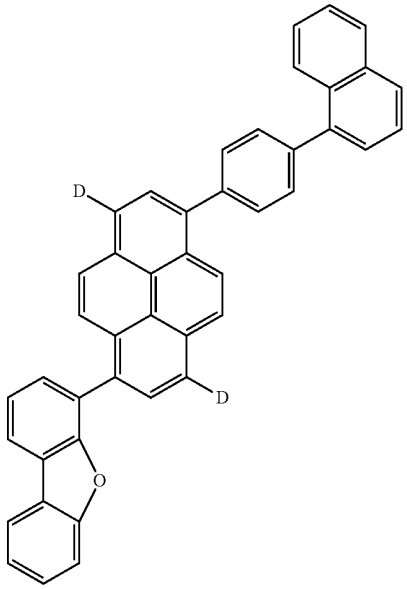

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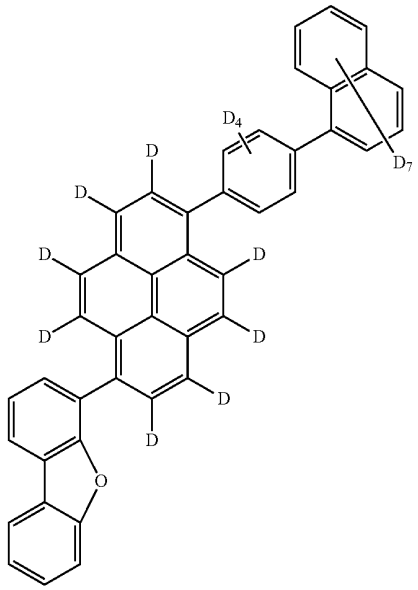

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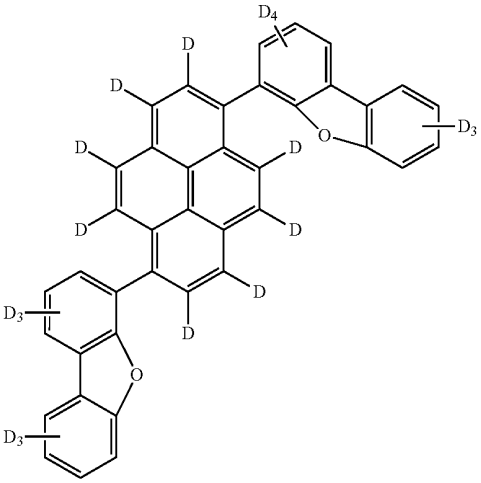

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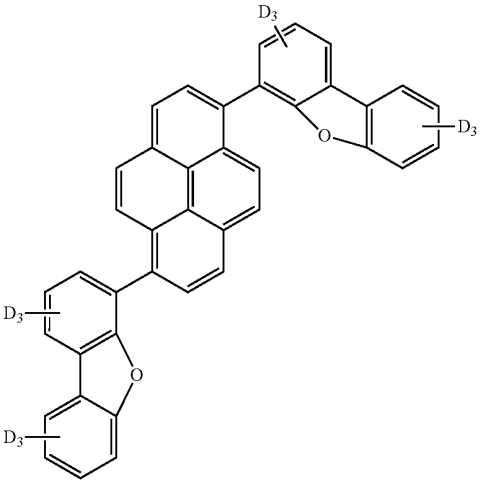

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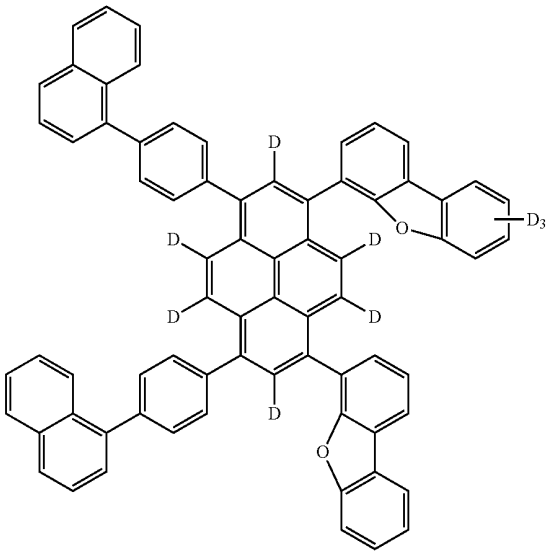

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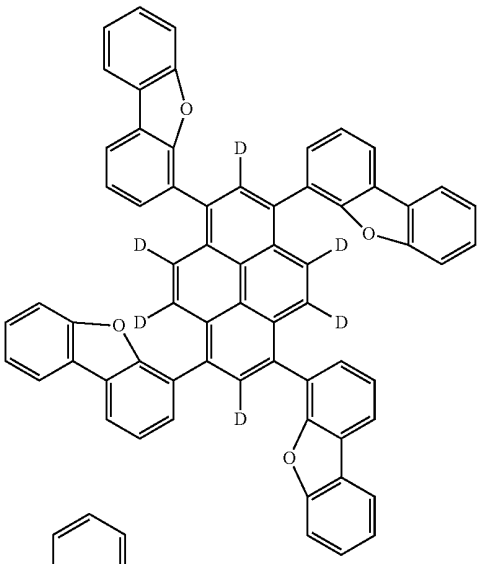

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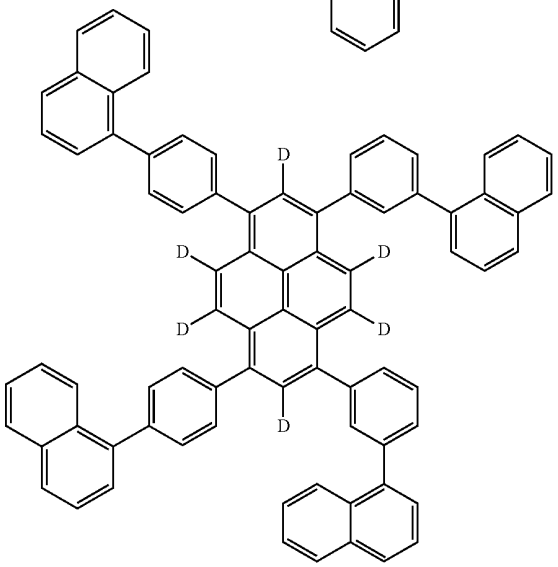

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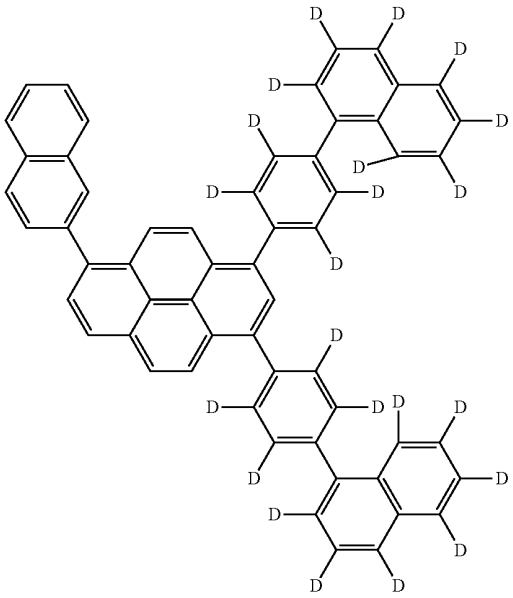

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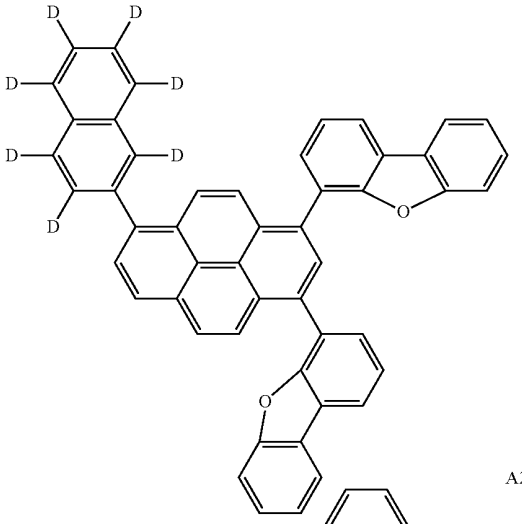

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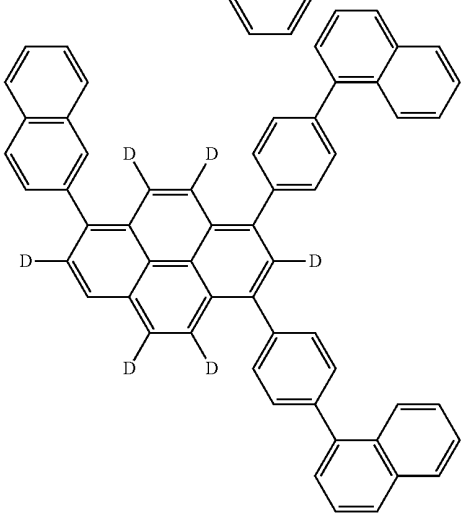

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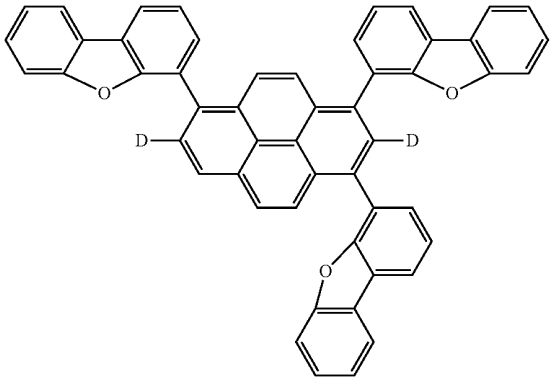

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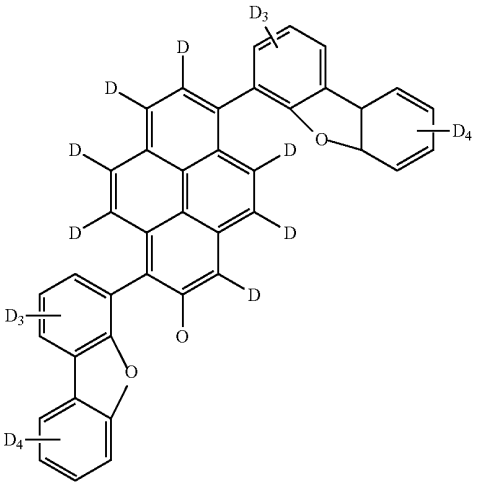

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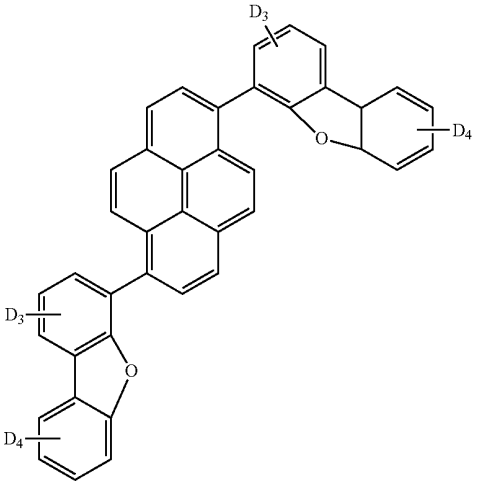

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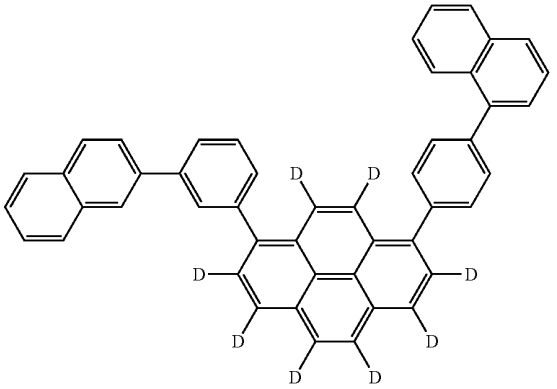

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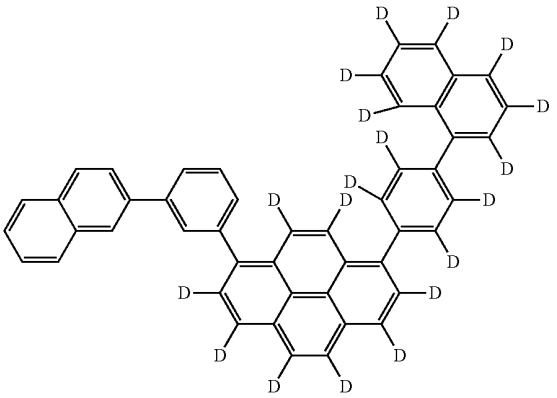

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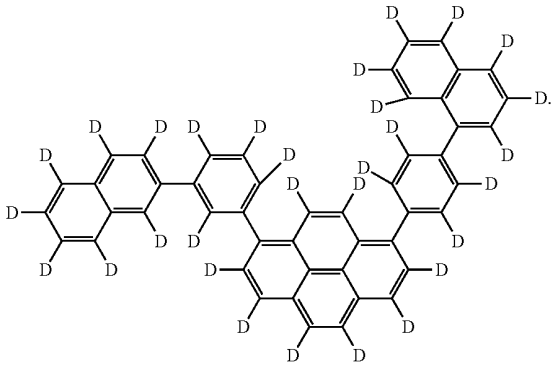

2. An organic electronic device comprising a first electrical contact layer, a second electrical contact layer, and at least one active layer therebetween, wherein the active layer comprises the compound of claim **1**.

3. The device of claim **2**, wherein the active layer is an electroactive layer and further comprises an electroluminescent dopant material.

4. The device of claim **3**, wherein the electroactive layer is a light-emitting layer.

* * * * *

专利名称(译)	用于发光应用的氘代化合物		
公开(公告)号	US8431245	公开(公告)日	2013-04-30
申请号	US12/643567	申请日	2009-12-21
[标]申请(专利权)人(译)	纳幕尔杜邦公司		
申请(专利权)人(译)	E·I·杜邦和公司		
当前申请(专利权)人(译)	E·I·杜邦和公司		
[标]发明人	MENG HONG SHEN YULONG		
发明人	MENG, HONG SHEN, YULONG		
IPC分类号	H01L51/54 C07D407/10 C07D307/91 C07C15/20 C07D407/14		
CPC分类号	C09K11/06 H01L51/0054 H01L51/0058 H05B33/14 C09K2211/1007 C09K2211/1011 C09K2211/1014 H01L51/5012		
优先权	61/246563 2009-09-29 US		
其他公开文献	US20110095273A1		
外部链接	Espacenet USPTO		

摘要(译)

本发明涉及可用于电致发光应用的氘代化合物。它还涉及其中活性层包括这种氘代化合物的电子器件。