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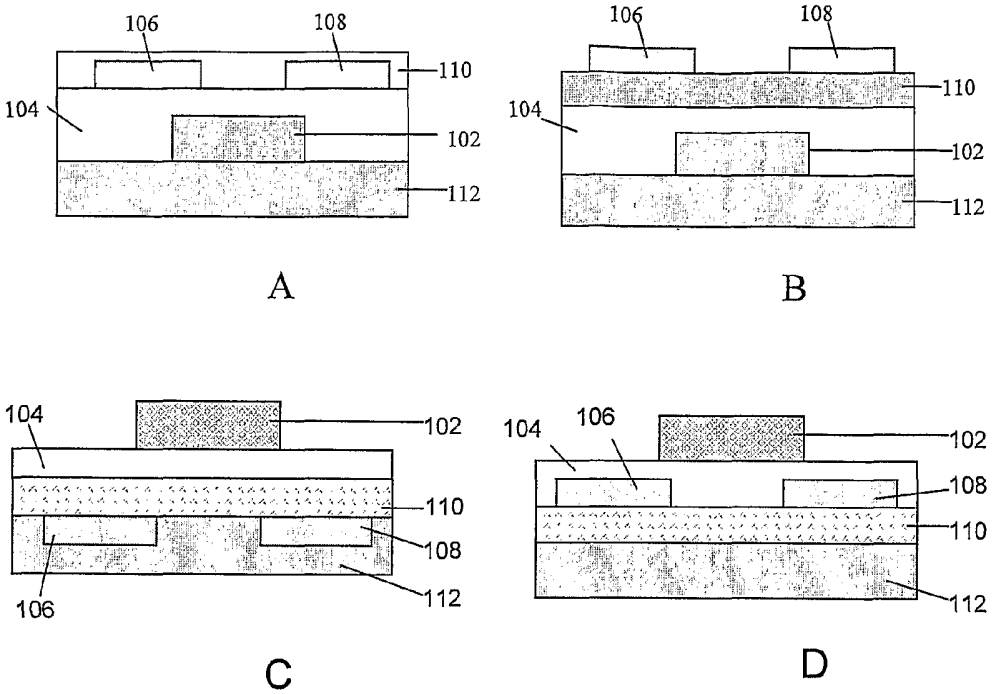
(54) Title: ARYL-ETHYLENE SUBSTITUTED AROMATIC COMPOUNDS AND THEIR USE AS ORGANIC SEMICONDUCTORS



(57) Abstract: There are disclosed aryl-ethylene aromatic compounds and their use as organic semiconductors. The compounds can be used in electronic devices such as organic thin film transistors (OTFTs), display devices, light-emitting diodes, photovoltaic cells, photo-detectors, and memory cells. Methods for manufacturing these aryl-ethylene aromatic compounds are also disclosed.

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ARYL-ETHYLENE SUBSTITUTED AROMATIC COMPOUNDS AND THEIR USE AS ORGANIC SEMICONDUCTORS

BACKGROUND INFORMATION

Field of the Disclosure

The disclosure relates to a new class of aryl-ethylene substituted aromatic compounds. The disclosure also relates to the use of these compounds in electronic devices and a method of manufacturing these devices.

Description of the Related Art

Organic materials have been widely used in electronic devices such as organic thin film transistors (OTFTs), organic light emitting diodes (OLEDs), photovoltaic diodes, and liquid crystal displays. OTFTs are of special interest for use in low-cost integrated circuit (IC) technology suitable for applications such as smart cards, electronic tags, displays, and memory devices. In OTFTs, the semiconductor layer consists of organic semiconductor materials including conjugated polymers and oligomers. Many organic materials possessing the required electronic properties for the electronic device applications have been synthesized.

Organic compounds that have been investigated for use as semiconductors include conjugated polymers such as regioregular poly(3-alkylthiophene)s; copolymers of polyfluorene-bithiophene; polyaromatic amine and polythiophene derivatives; fused aromatic compounds such as pentacene, tetracene and their derivatives; and conj ugated oligomers such as oligothiophenes, fluorene-thiophene oligomers, and phenyl-thiophene oligomers.

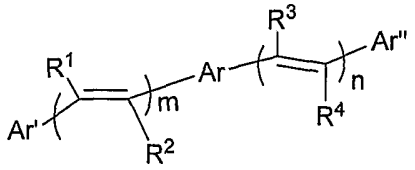
Unfortunately, the performance of most of the above organic semiconductors compounds suffers from either low charge mobility (ca. ~0.1 cm^2/Vs) or instability. For example, although pentacene possesses high mobility (about 0.1 to 2 cm^2/Vs), it also has a relatively low band gap (2.2 eV) and a high HOMO (highest occupied molecular orbital) energy level and is easily oxidized. Moreover, pentacene compounds often show high oxygen and humidity sensitivity, and therefore high on/off ratios can

only be obtained in an inert atmosphere. These characteristics result in poor device stability and make pentacene compounds unsuitable for practical electronic circuit applications. On the other hand, compounds such as oligofluorenes, oligofluorene-thiophenes, phenylene-thiophene, and conjugated polyfluorene-thiophene polymers show improved stability, but their low mobility limits their applications in high efficiency electronic devices. Therefore, there still exists a need for a class of organic compounds that have high mobility and high on/off ratio, and that are stable to heat, light, and air.

There is also a need for organic compounds that can be readily incorporated into electronic devices, such as OLEDs, using commercially viable fabrication methods. In another aspect of OLEDs, the short life time of the devices is still a deficiency for commercial applications. Organic triarylamine compounds such as NPD and its derivatives are widely used as hole transport materials. It is believed that the low charge mobility of these triarylamine compounds and the low glass transition temperatures of these hole transport materials may limit the stability of OLEDs. It is for this reason that new materials with high hole charge mobility and thermal stability are needed for OLEDs.

SUMMARY

There are provided compounds represented by Formula 1:



Formula 1

wherein

Ar is an arylene group;

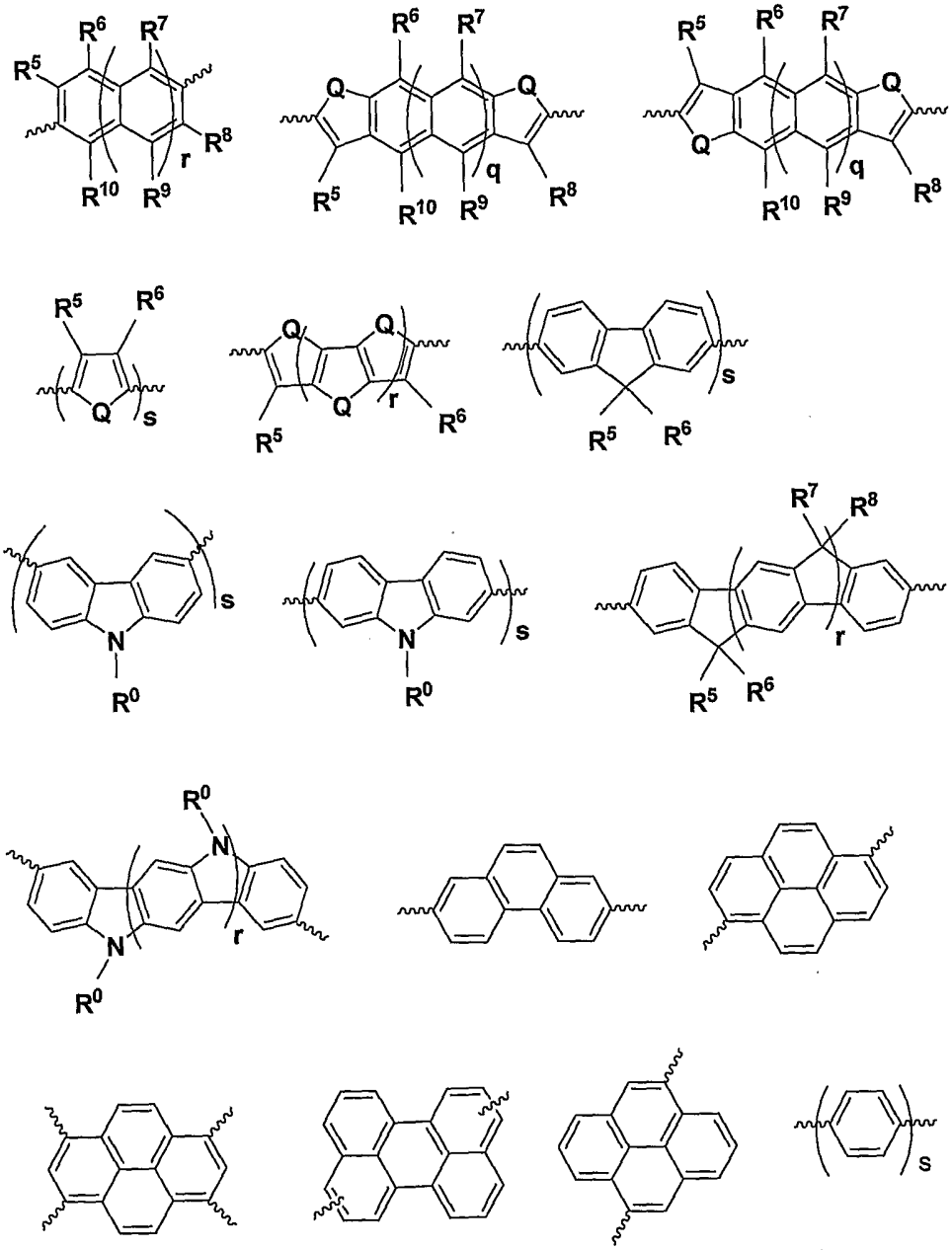
Ar', and Ar" are selected independently from aryl groups;

R^1 through R^4 are selected independently from the group consisting of hydrogen, alkyl, aryl, halogen, hydroxyl, aryloxy, alkoxy, alkenyl, alkyny, amino, alkylthio, phosphino, silyl, -COR, -COOR, -PO_3R_2, -OPO_3R_2, and CN;

R is selected from the group consisting of hydrogen, alkyl, aryl, alkenyl, alkynyl, and amino; and

m and n are integers each independently having a value of from 0 to 5, where $m + n \neq 0$.

In one embodiment, Ar is selected from the group consisting of



and combinations thereof,

wherein:

Q is selected from the group consisting of S, Se, Te, O, and NR^0

q and r are independently integers having a value of from 0 to 5;

s is an integer having a value of from 1 to 5;

R^0 is selected independently from the group consisting of hydrogen, alkyl, and aryl;

R^5 through R^{10} are selected independently from the group consisting of hydrogen, alkyl, aryl, halogen, hydroxyl, aryloxy, alkoxy, alkenyl, alkyny, amino, alkylthio, phosphino, silyl, -COR, -COOR, $-PO_3R_2$, $-OPO_3R_2$, and CN;

R is as defined above; and

wherein any two adjacent groups R^5 through R^{10} can be taken together to form a ring.

There is also provided a synthetic method for the production of the compounds of Formula 1.

There are also provided hole transport compounds represented by Formula 1 and hole transport layers comprised of these compounds.

There are also provided electron transport compounds represented by Formula 1 and electron transport layers comprised of these compounds.

There are also provided buffer layers comprised of these compounds.

There are also provided electronic devices that comprise organic thin film transistors (OTFTs) that comprise the compounds represented by Formula 1. There is also provided a method for manufacturing these electronic devices.

There are also provided display devices comprising the compounds represented by Formula 1.

There are also provided organic light-emitting diodes, photo conductors, memory cells, current limiters, field-effect diodes, Schottky diodes, photovoltaic cells, photo-detectors, rectifiers, transistors, thermistors and p-n junctions comprising the compounds represented by Formula 1.

BRIEF DESCRIPTION OF THE DRAWINGS

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

Figure 1A is a schematic representation of an organic thin film transistor (OTFT) in bottom contact mode.

Figure 1B is a schematic representation of an OTFT in a top contact mode.

Figure 1C is a schematic representation of another embodiment of an OTFT.

Figure 1D is a schematic representation of another embodiment of an OTFT.

Figure 2 is a schematic representation of a display 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

There are provided a new class of substituted aryl ethylene aromatic compounds and a method for synthesizing these compounds. The use of these and other substituted aryl ethylene aromatic compounds in organic semiconductor devices is disclosed.

Many aspects and embodiments have been described above and are merely 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 Aryl-Ethylene Aromatic Compounds, General Preparation, Semiconductor Devices, and finally Examples.

1. Definitions and Clarification of Terms

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

The term "aromatic" as used herein refers to an unsaturated cyclic organic compound or group having continuous conjugation with delocalized π-electrons. The aromatic group may have one or more rings, each having $2n + 2$ π-electrons. The term includes groups having one or more heteroatoms having π-electrons in the ring. In one embodiment, the heteroatom is selected from the group consisting of N, O, and S.

The term "acene" as used herein refers to a hydrocarbon parent component that contains two or more *ortho*-fused benzene rings in a straight linear arrangement. "Acenes" include naphthalene (two *ortho*-fused benzene rings) and anthracene (three *ortho*-fused benzene rings). Systems of four or more fused benzene rings are named from the numerical prefix denoting the number of benzene rings followed by the ending "-acene".

The term "alkyl", whether as part of another term or used independently, denotes a saturated hydrocarbon radical. Examples of alkyl groups include n-butyl, n-pentyl, n-heptyl, iso-butyl, t-butyl, and iso-pentyl. The term includes heteroalkyls. In one embodiment, the alkyl group has from 1-20 carbon atoms. In one embodiment, the alkyl group is a fluoroalkyl group.

The term "alkyl ether" refers to an alkyl group having one or more carbon atoms replaced with O, and attached via the oxygen.

The term "ether alkyl" refers to an alkyl group having one or more carbon atoms replaced with O, and attached via a carbon.

The term "alkenyl", whether as part of another term or used independently, denotes hydrocarbon radicals having one or more double bonds between neighboring carbon atoms of the radical. Examples of alkenyl groups include vinyl, allyl, butenyl, pentenyl, and heptenyl. The term includes heteroalkyenyl groups. In one embodiment, the alkenyl group has from 1-20 carbon atoms.

The term "alkynyl", whether as part of another term or used independently, denotes hydrocarbon radicals having one or more triple bonds between neighboring carbon atoms of the radical. Examples of alkynyl groups include ethynyl, propynyl, butynyl, hexynyl and heptynyl. The term includes heteroalkyl groups. In one embodiment, the alkynyl group has from 1-20 carbon atoms.

The term "aryl", whether as part of another term or used independently, refers to an aromatic group having one point of attachment. The term "arylene" refers to an aromatic group having two points of attachment. In one embodiment, the aryl group has from 4-30 carbon atoms.

The term "silyl", whether as part of another term or used independently, refers to the group $-SiR_3$, where R is selected from the group consisting of hydrogen, alkyl, aryl, alkenyl, alkynyl, and amino.

The term "thioalkyl", whether as part of another term or used independently, refers to the group –SR, where R is selected from the group consisting of hydrogen, alkyl, aryl, alkenyl, and alkynyl.

The prefix "hetero" indicates that one or more carbons has been replaced with a different atom. In one embodiment, the heteroatom is selected from the group consisting of N, O, and S.

The prefix "fluoro" indicates that one or more hydrogens has been replaced with fluorine. The term includes partially and fully fluorinated materials.

Any of the above groups may be a straight-chain or branched-chain. Examples of straight-chain alkyls, alkenyls, and alkynyls include n-butyl, n-pentyl, n-heptyl, n-octyl, n-butenyl, n-pentenyl, n-heptenyl, and n-heptynyl. Examples of branched-chain alkyls, alkenyls, and alkynyls include iso-butyl, t-butyl, iso-pentyl, neo-pentyl, isopentenyl, and neo-pentenyl.

Any of the above groups may be substituted or unsubstituted. The term "substituted" denotes a group that is mono- or poly-substituted with the same or different substituent groups. Suitable substituent groups include cyano groups, nitro groups, ester groups, ether groups, halogen,

hydroxy, alkyl groups, aryl groups, and alkoxy groups. In one embodiment, substituents include ether groups and fluorine substituents.

As used herein, 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. "Electron transport" refers to negative charge transport, and "hole transport" refers to positive charge transport.

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.

Group numbers corresponding to columns within the Periodic Table of the elements use the "New Notation" convention as seen in the *CRC Handbook of Chemistry and Physics*, 81st Edition (2000-2001).

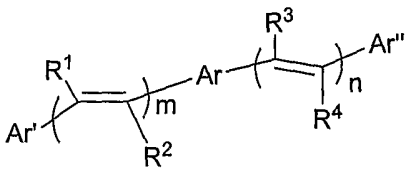
Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments 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, unless a particular passage is cited. 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.

To the extent not described herein, many details regarding specific materials, processing acts, and circuits are conventional and may be found in textbooks and other sources within the organic light-emitting diode display, photodetector, photovoltaic, and semiconductive member arts.

2. Aryl-Ethylene Aromatic Compounds

There are provided compounds represented by Formula 1:



Formula 1

wherein

Ar is an arylene group;

Ar', and Ar" are selected independently from aryl groups;

R^1 through R^4 are selected independently from the group consisting of hydrogen, alkyl, aryl, halogen, hydroxyl, aryloxy, alkoxy, alkenyl, alkyny, amino, alkylthio, phosphino, silyl, -COR, -COOR, -PO_3R_2, -OPO_3R_2, and CN;

R is selected from the group consisting of hydrogen, alkyl, aryl, alkenyl, alkynyl, and amino; and

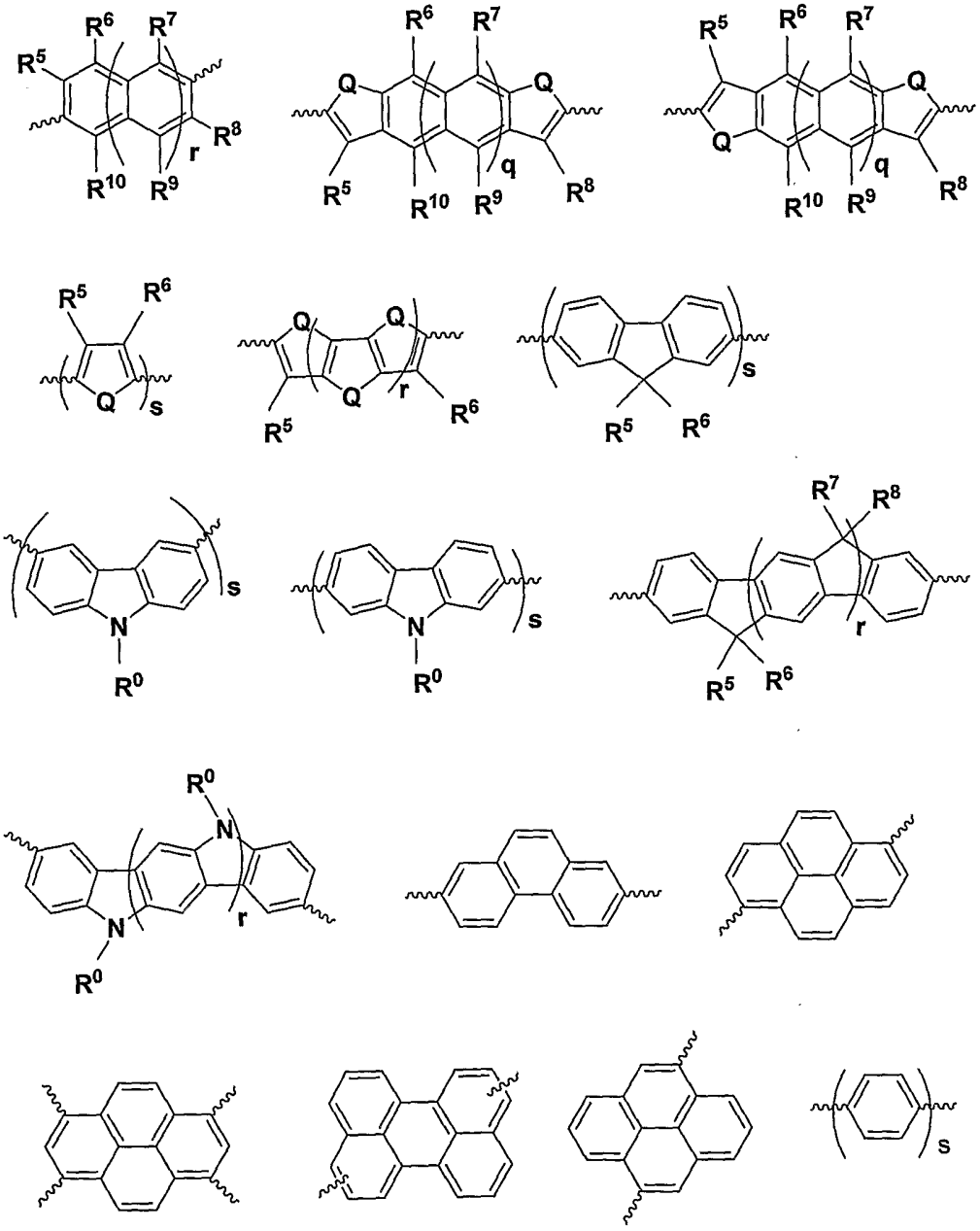
m and n are integers each independently having a value of from 0 to 5, where $m + n \neq 0$.

In one embodiment, at least one of Ar, Ar', and Ar" is selected from the group consisting of aromatic groups having at least two fused rings and aromatic groups having at least two rings joined by a single bond. In one embodiment, Ar is selected from the group consisting of aromatic groups

having at least two fused rings and aromatic groups having at least two rings joined by a single bond. In one embodiment, Ar is an acene group.

In one embodiment, R^1 through R^4 are H. In one embodiment, both m and n are non-zero. In one embodiment, m = n = 1.

In one embodiment, Ar is selected from the group consisting of



and combinations thereof,

wherein:

Q is selected from the group consisting of S, Se, Te, O, or NR^0;

q and r are integers each independently having a value of from 0 to 5;

s is an integer having a value of from 1 to 5;

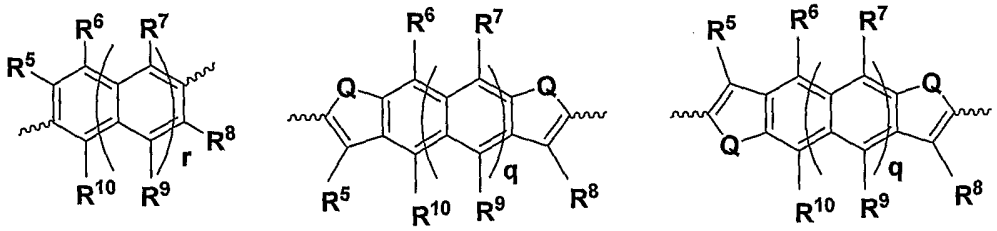
R^0 is selected from the group consisting of hydrogen, alkyl, and aryl;

R^5 through R^{10} are selected independently from the group consisting of hydrogen, alkyl, aryl, halogen, hydroxyl, aryloxy, alkoxy, alkenyl, alkyny, amino, alkylthio, phosphino, silyl, -COR, -COOR, $-PO_3R_2$, $-OPO_3R_2$, and CN; and

R is selected from the group consisting of hydrogen, alkyl, aryl, alkenyl, alkynyl, and amino;

wherein any two adjacent groups, R^5 through R^{10} can be taken together to form a ring.

In one embodiment, Ar is selected from the group consisting of:



where:

Q, q, r, s, R^0, R^5 and R^6 are as defined above.

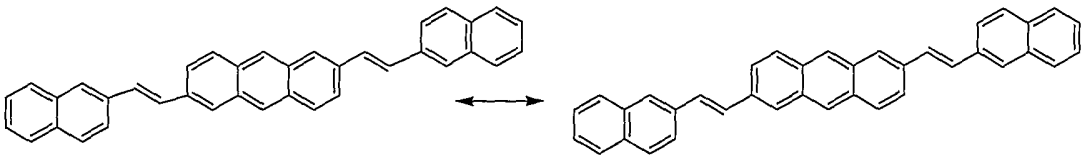
In one embodiment, for any of the above Ar groups, r is at least 1 and s is at least 2. In one embodiment, q is 0, 1, 2, or 3; r is 1, 2, or 3; s is 2 or 3. In one embodiment Ar is selected from tetracene and pentacene.

In one embodiment, Ar has at least one group selected from the group consisting of 2,6-naphthalene, substituted 2,6-naphthalene, 2,6-anthracene, substituted 2,6-anthracene, 2,7-fluorene, substituted 2,7-fluorene, 3,6-carbazole, substituted 3,6-carbazole, and combinations thereof, with the proviso that there are no diaryl amino substituents. In one embodiment, the substituents are independently selected from the group consisting of alkyl, alkoxy, alkylether, etheralkyl, thioalkyl, silyl, and combinations thereof. As used herein, the numbers indicate the points of

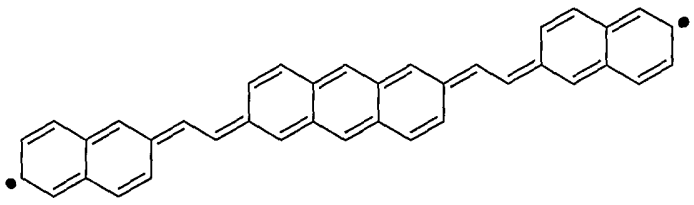
attachment of the groups and follow the convention as seen in the *CRC Handbook of Chemistry and Physics*, 81st Edition (2000-2001).

In one embodiment, Ar' and Ar" are selected independently from substituted aryl groups, with the proviso that there are no diarylamino substituent groups. In one embodiment, there are no amino substituent. In one embodiment, Ar' and Ar" are selected independently from substituted aryl groups, and the substituents are selected independently from the group consisting of alkyl, aryl, alkylaryl, alkoxy, alkylether, etheralkyl, fluoro, thioalkyl, silyl, and combinations thereof.

Although not wanting to be bound by theory, it is believed that certain geometric characteristics of these compounds correlate with their performance in electronic devices. In one embodiment, compounds of Formula 1 that possess a flat, symmetrical chemical structure have utility for use in OTFTs. Such configurations can form extended conjugated systems with multiple possible resonance structures, as illustrated below for two resonance structures of 2,6-bis-(2-naphthalen-2-yl-vinyl)-anthracene:



It is also believed that resonance structures of the aryl-ethylene acenes can be converted to the quinoid state when exposed to an electric field, as illustrated herein for of 2,6-bis-(2-naphthalen-2-yl-vinyl)-naphthalene:



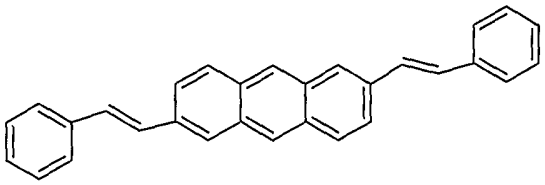
This is expected to result in high mobility. In fact, mobilities over 1 cm^2/ Vs have been achieved using compounds of Formula 1 as the active

semiconductor in OTFTs. Since the band gap of these semiconductors are relatively large (ca. ~2.3-3.5 eV), the compounds are also highly stable materials. Such high mobility semiconductors can also be used as charge transport materials or host materials in OLEDs.

The compounds of Formula 1 exhibit high mobilities and high on/off ratios and are suitable for use in the fabrication of semiconductor devices. These compounds have high thermal stability and are unaffected by light or air so that semiconductor devices do not need to be fabricated in an inert atmosphere. The use of these compounds also allows the manufacture of electronic devices at a low substrate temperature. In addition, these compounds have good film-forming abilities.

In one embodiment, R^1 - R^4 are, independently, H, F or CN for aryl-ethylene compounds used in OTFTs. It is also preferable that aryl ethylene acene compounds used in OTFTs have a *trans* configuration for all double C=C bonds, maximizing the conjugation of the unsaturated system.

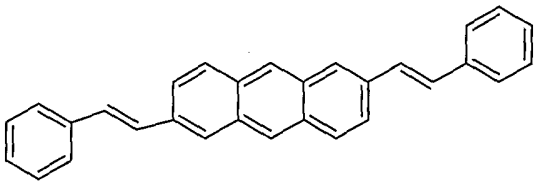
In one embodiment, the aryl ethylene acene compounds intended for use in OTFTs also have flat, symmetrical molecular structures. By "flat" is meant that the twist angles between the middle ring and the trans- C=C double bond-linked segments are between 0 ° and 10 °, preferably 0 °. "Twisted" molecular structures have twist angles greater than 10 °. The twisting of the acene group is largely controlled by the steric interactions of the substituents on the acene ring. Compounds with adjacent groups, R^6 - R^{10}, that are relatively bulky tend to be more twisted than compounds in which all R^6 - R^{10} are H, F or CN. In "symmetrical" molecules, the aryl-ethylene substituents are identical, i.e., Ar' = Ar", $R^1 = R^4$ and $R^2 = R^3$. Compound A is a suitable material for use as a semiconductor in an OTFT.



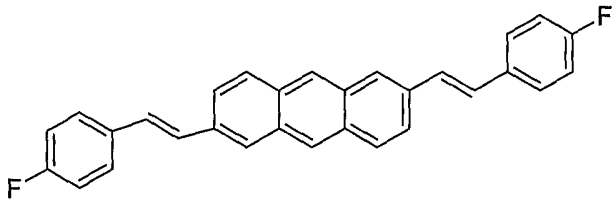
Compound A

Flat and symmetric
Suitable for OTFT semiconductor

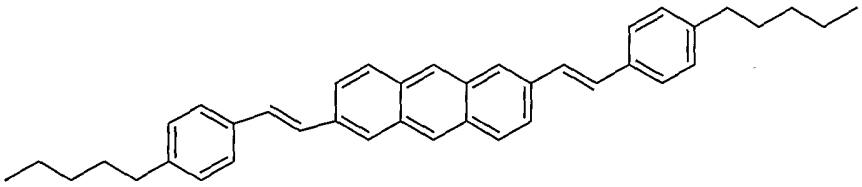
Examples of compounds represented by Formula 1 include:



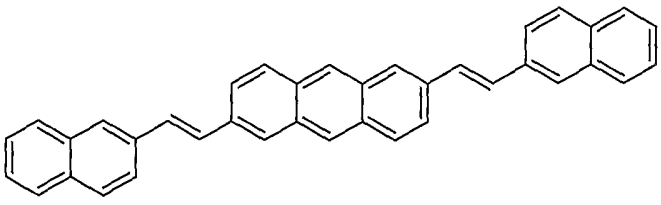
Compound 1



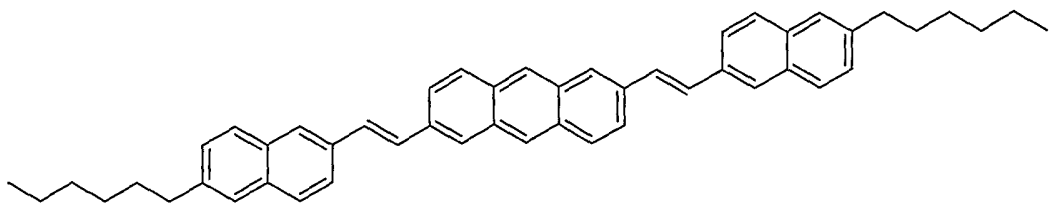
Compound 2



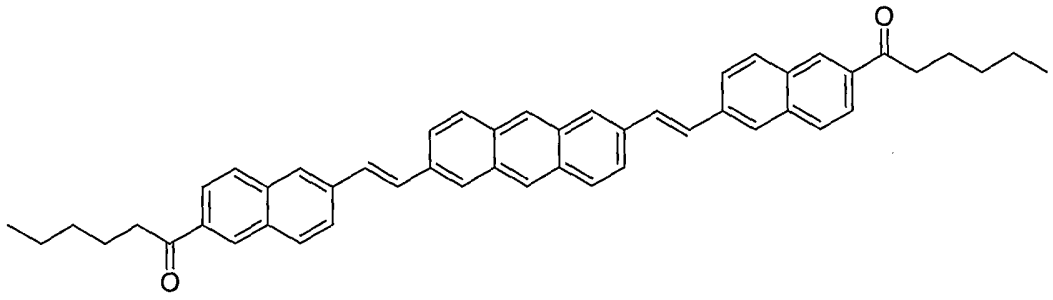
Compound 3



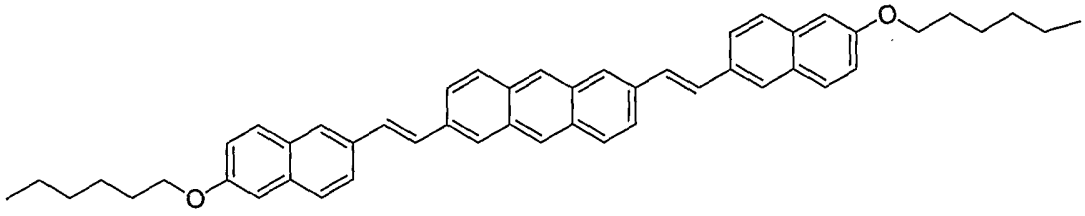
Compound 4



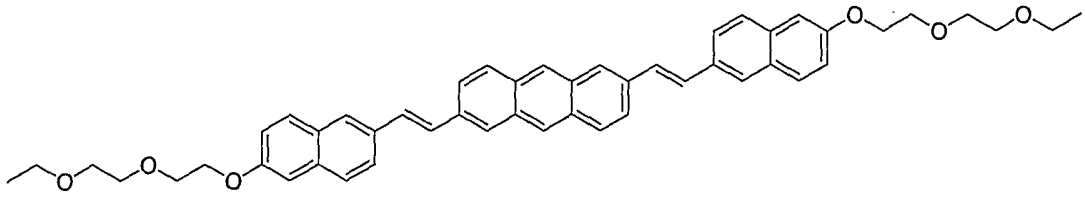
Compound 5



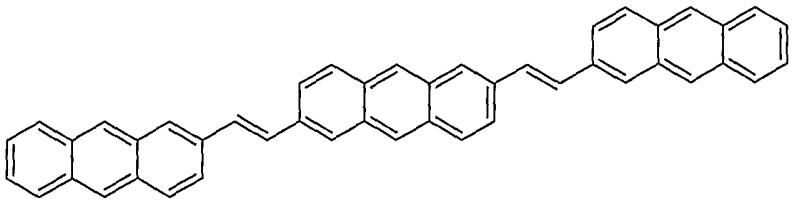
Compound 6



Compound 7



Compound 8



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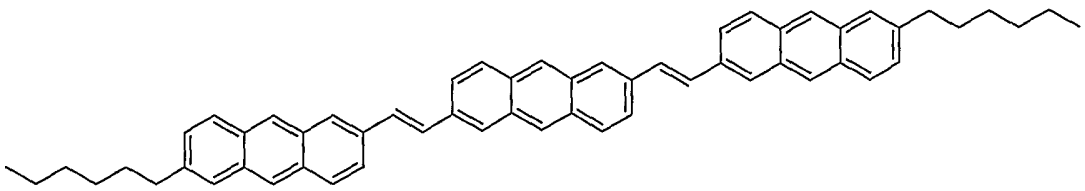

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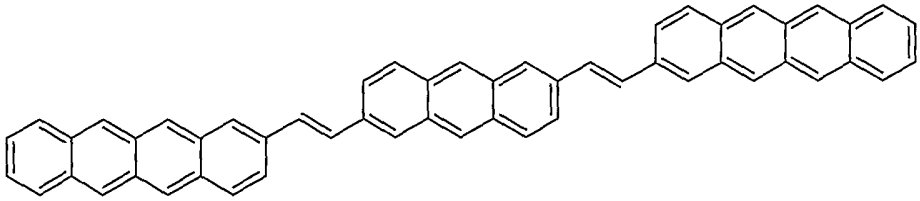

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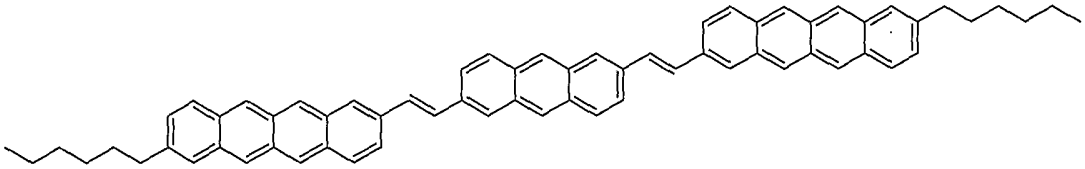

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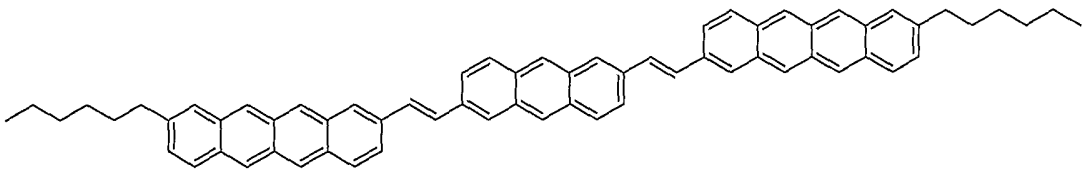

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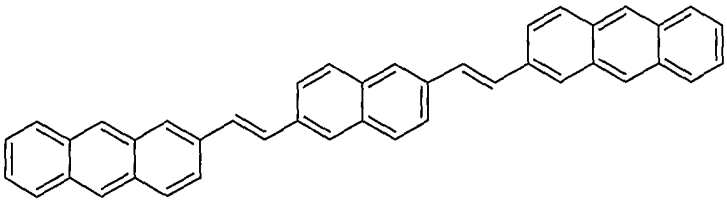

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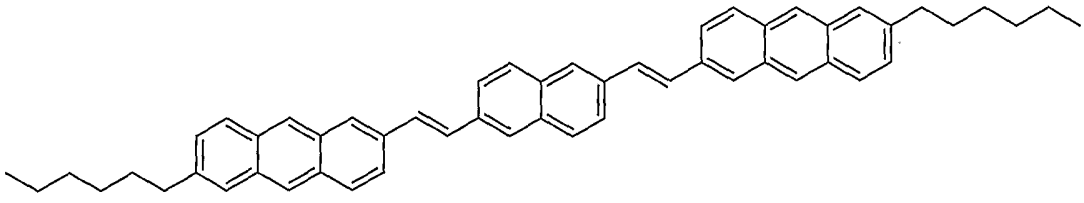

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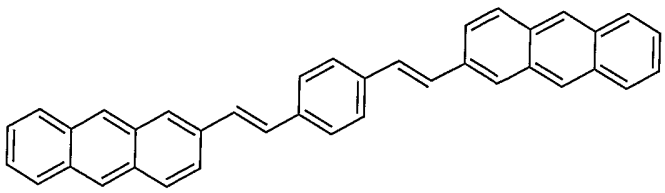

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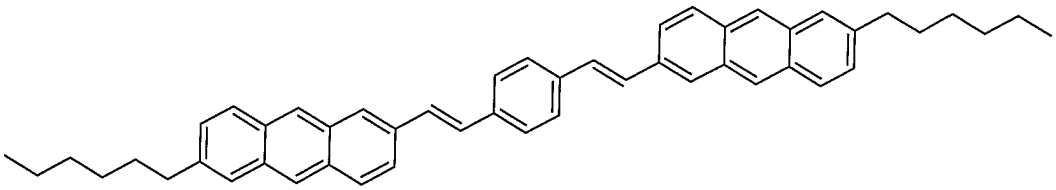

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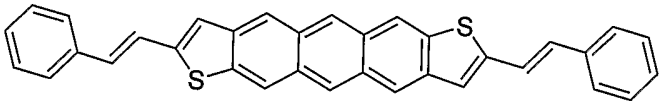

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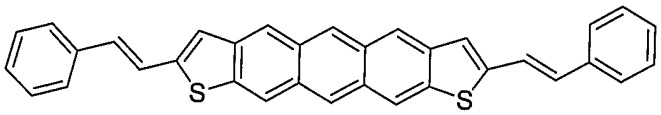

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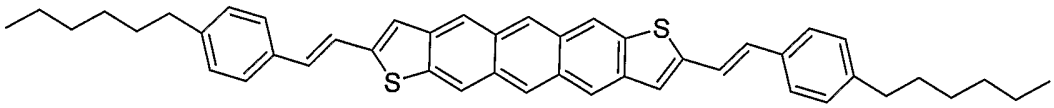

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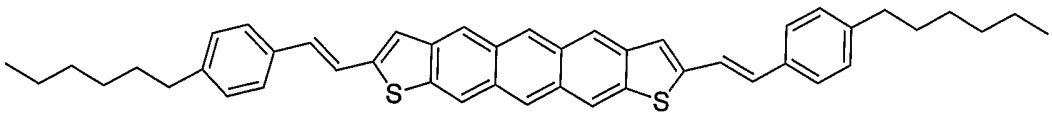

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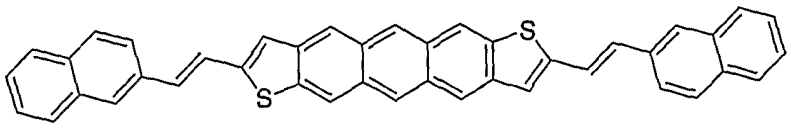

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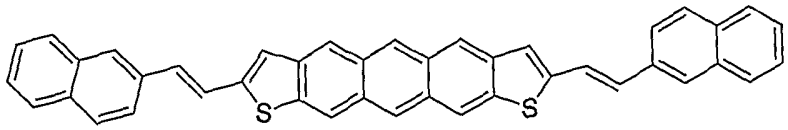

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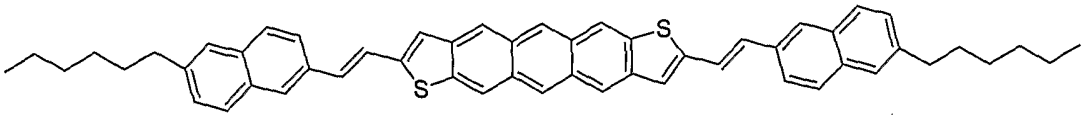

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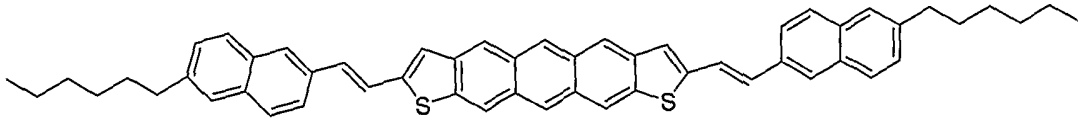

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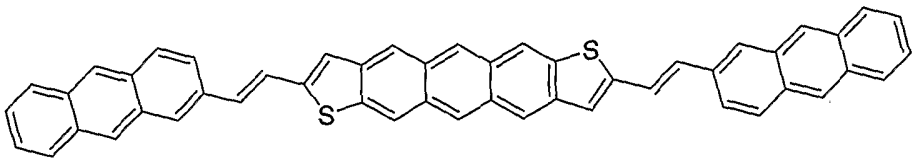

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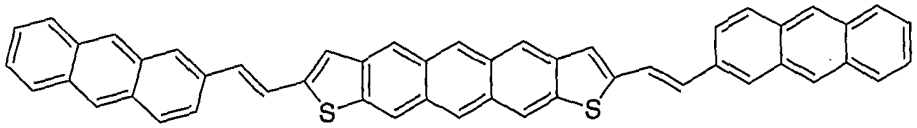

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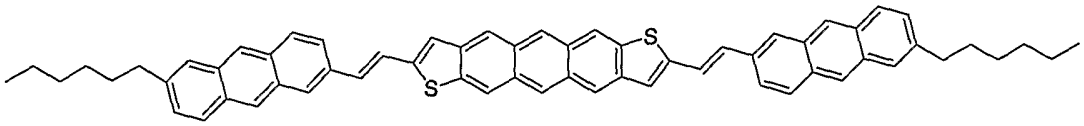

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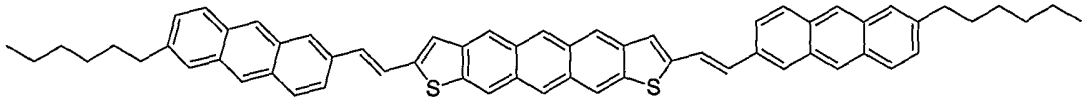

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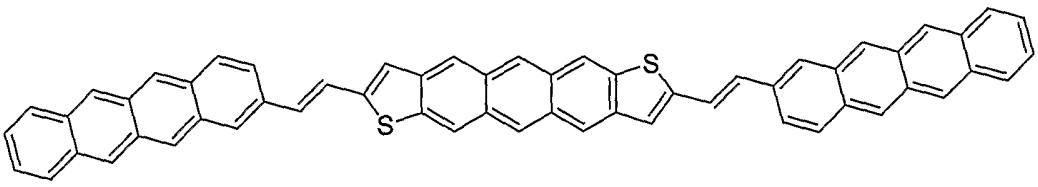

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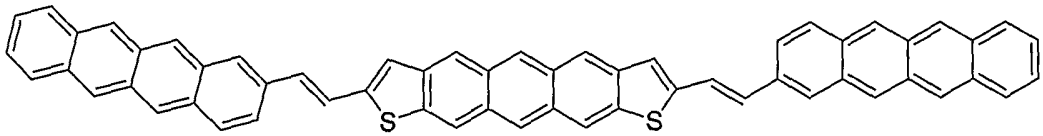

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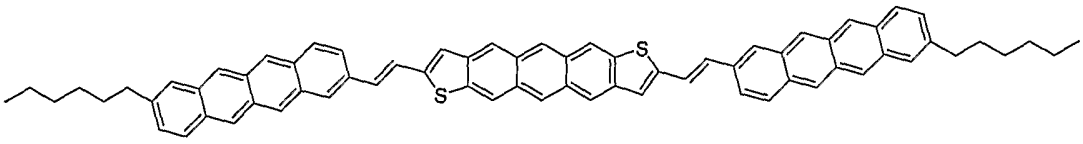

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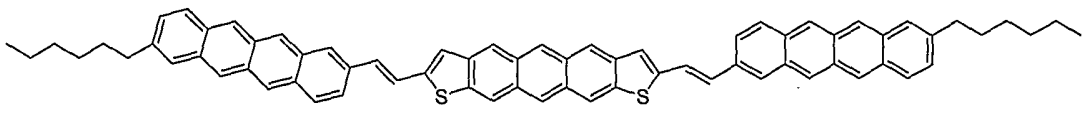

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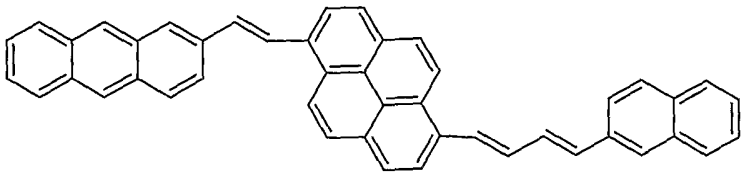

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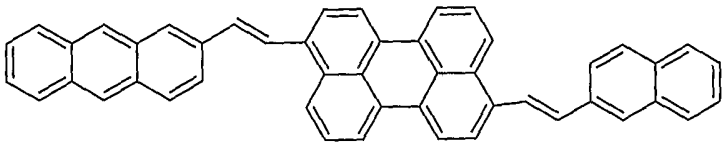

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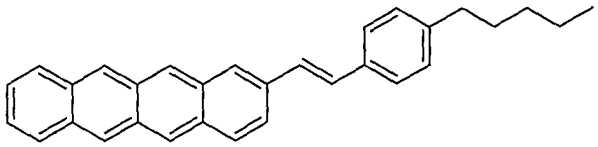

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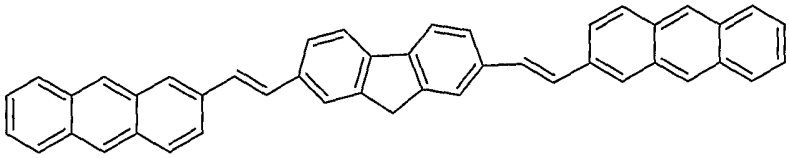

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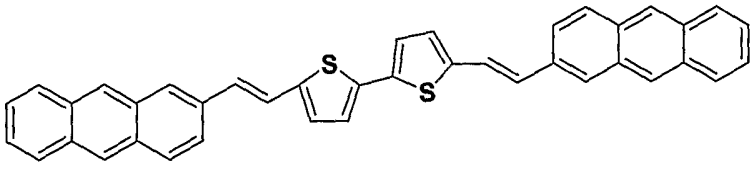

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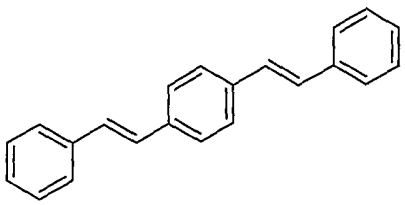

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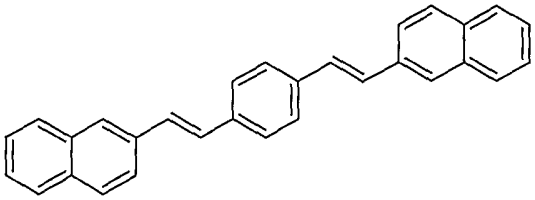

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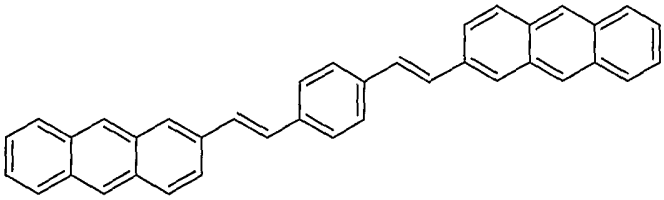

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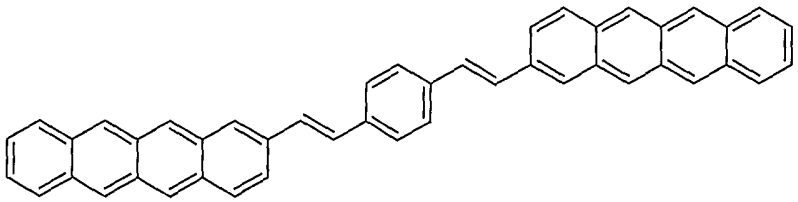

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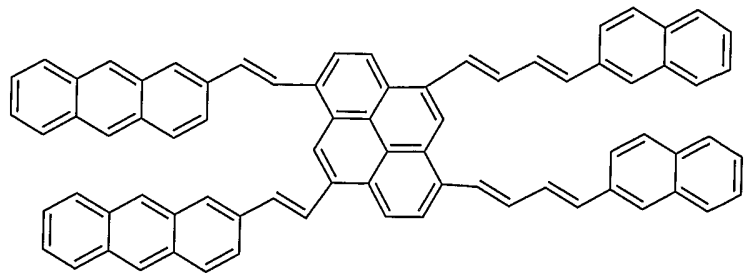

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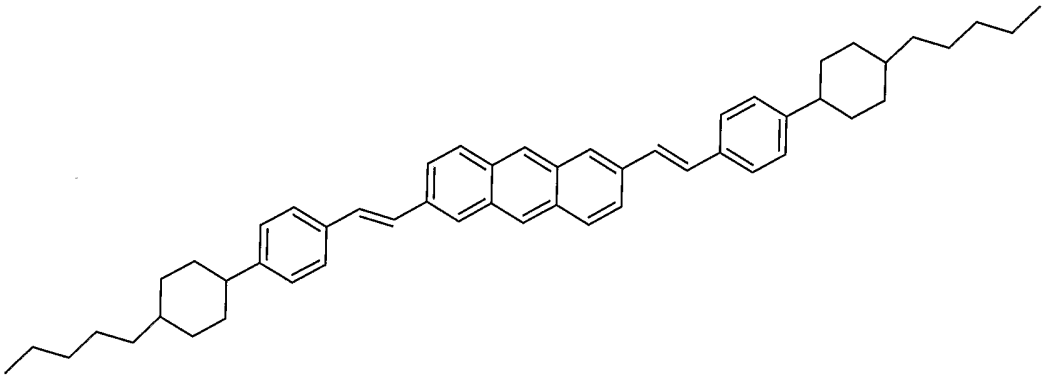

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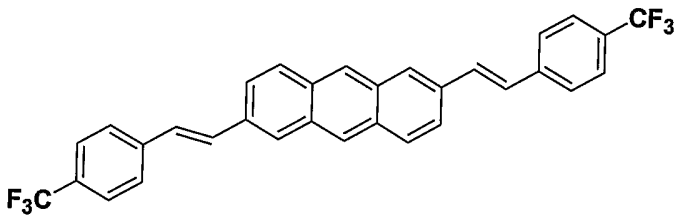

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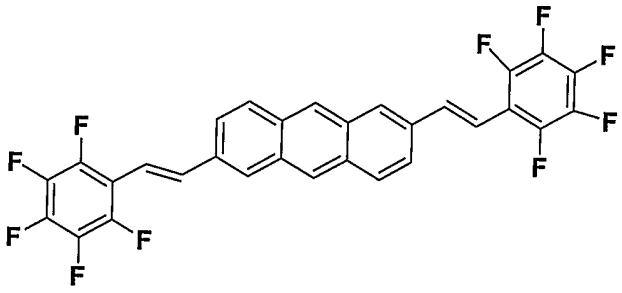

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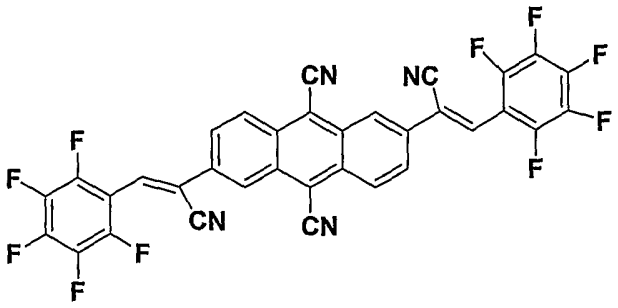

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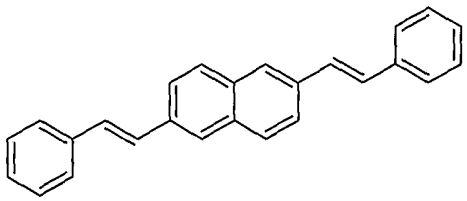

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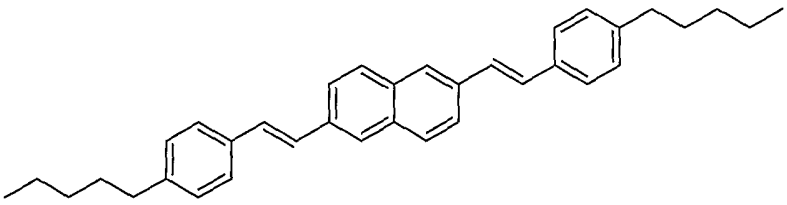

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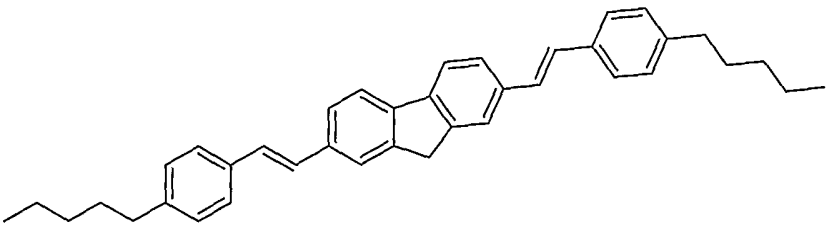

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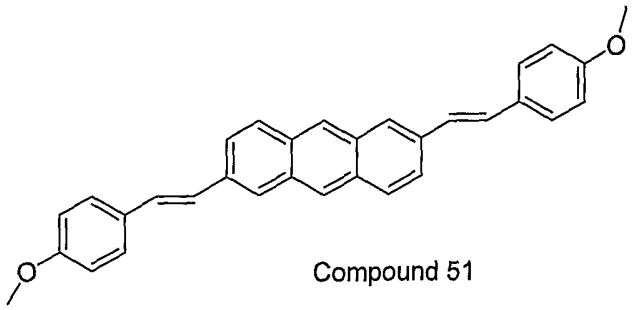

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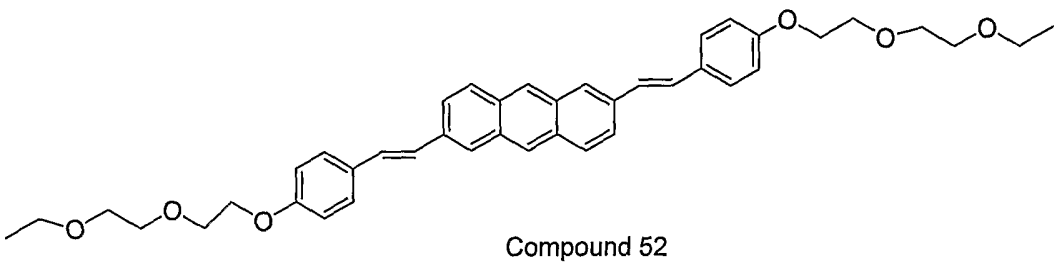

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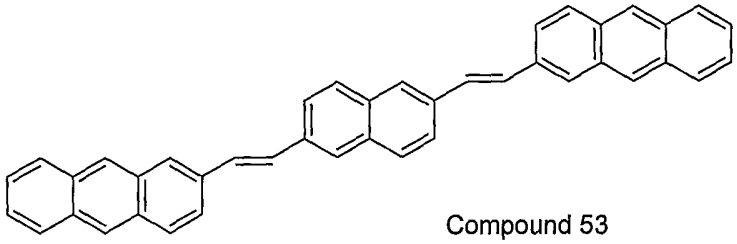

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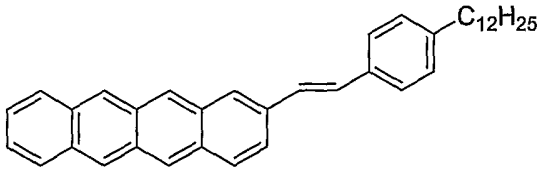

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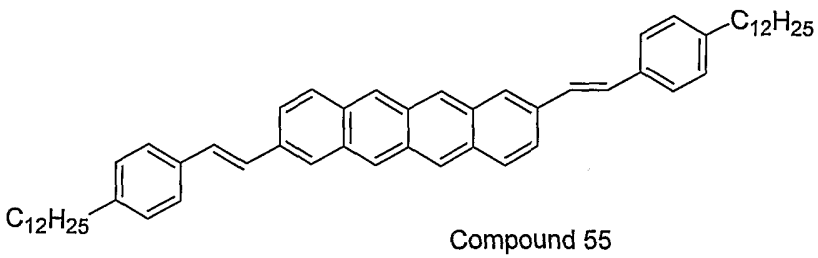

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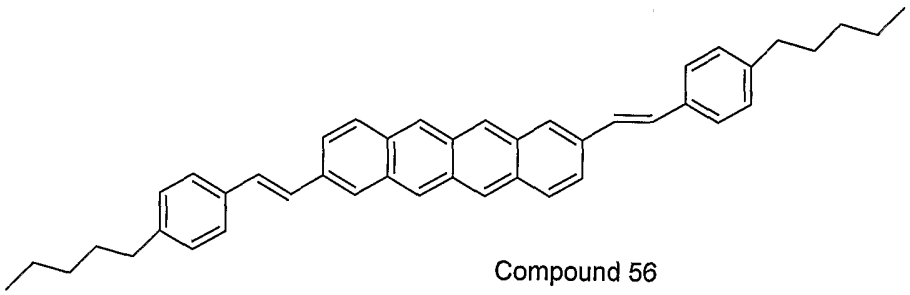

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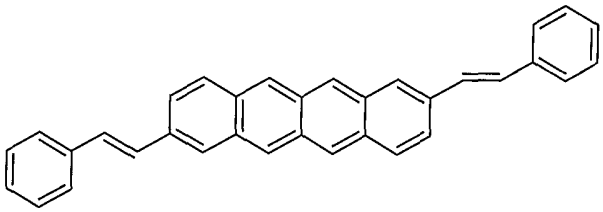

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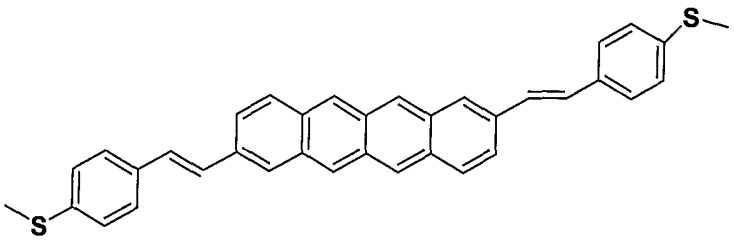

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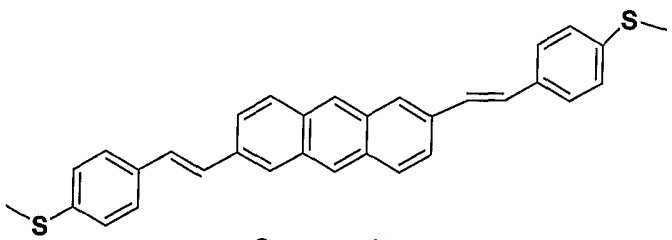

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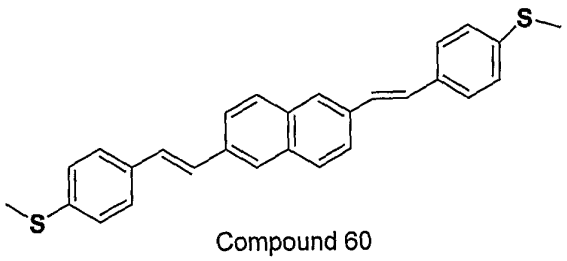

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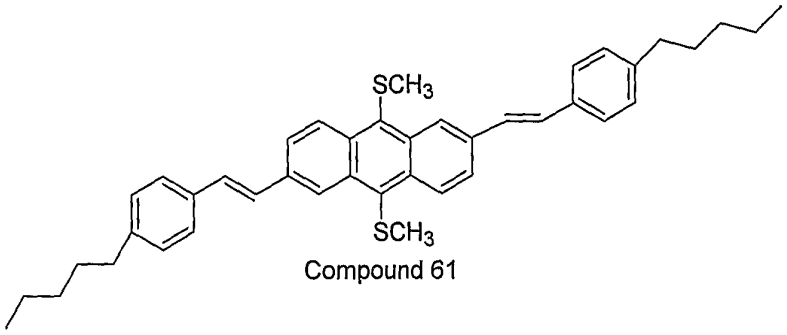

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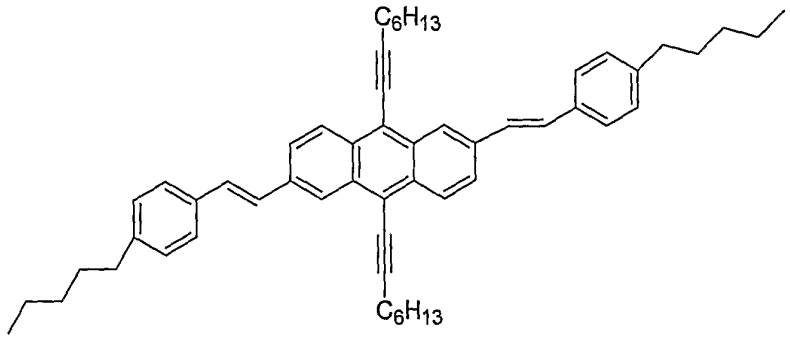

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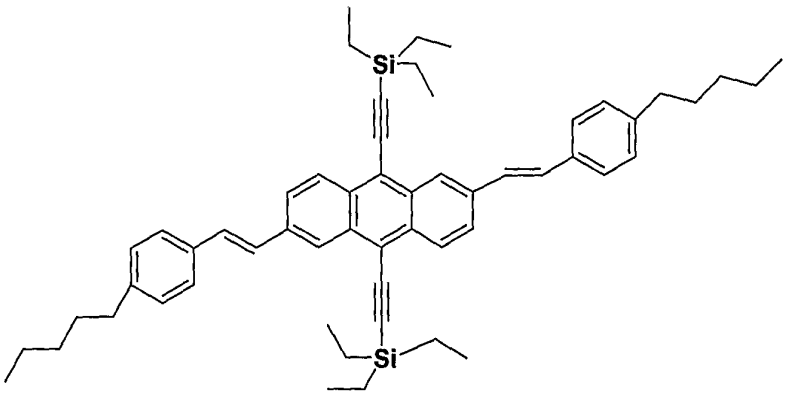

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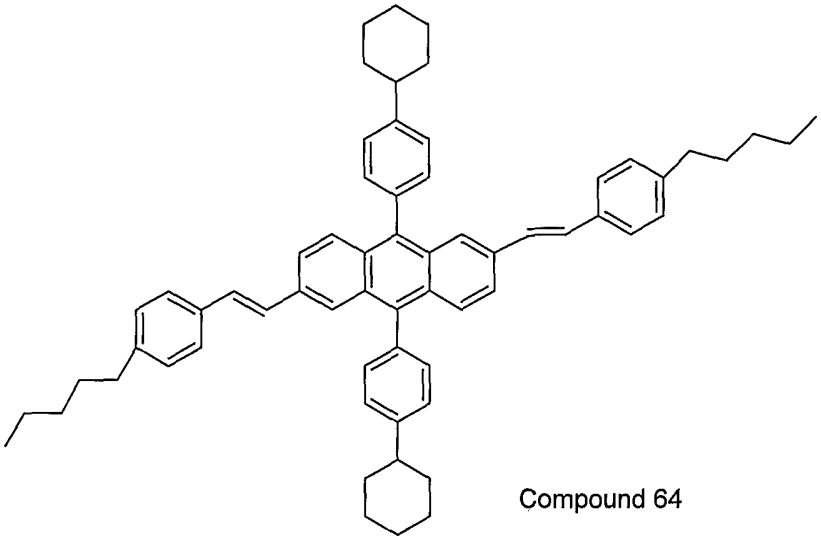
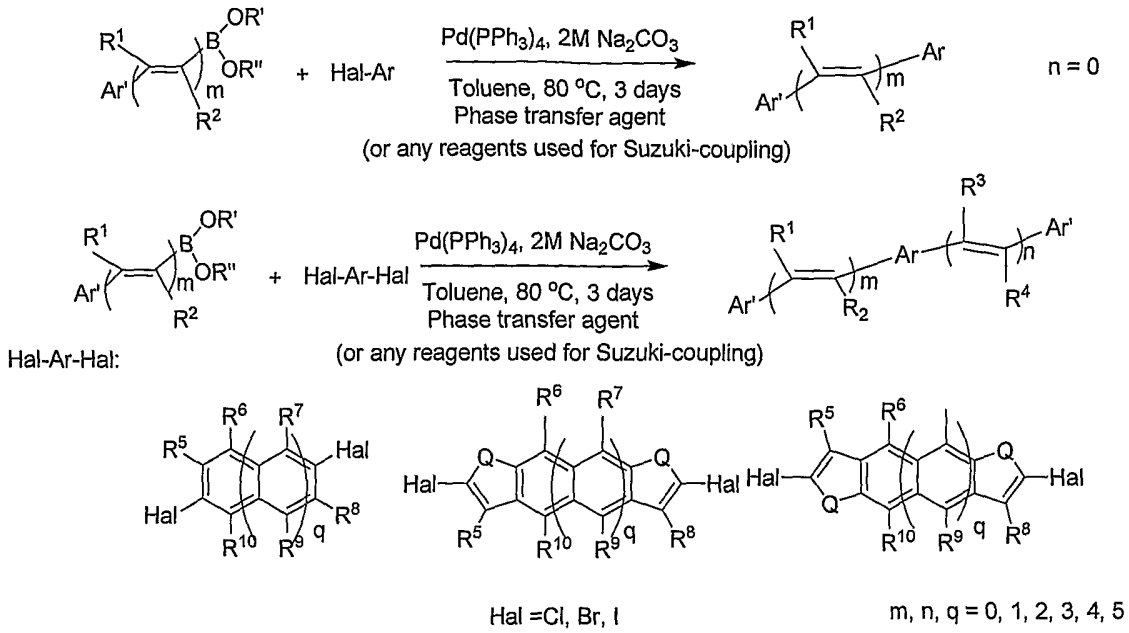


Compound 64

In one embodiment, the compounds having Formula 1 may be polymerized to form longer oligomers or polymers. In one embodiment, the compounds having Formula 1 may be copolymerized with one or more different compounds having Formula 1, and/or with one or more different monomers that do not have Formula 1. In one embodiment, the compounds having Formula 1 may have cross-linkable groups. These compounds may be applied to form a layer and then cross-linked to improve durability and solvent-resistance.

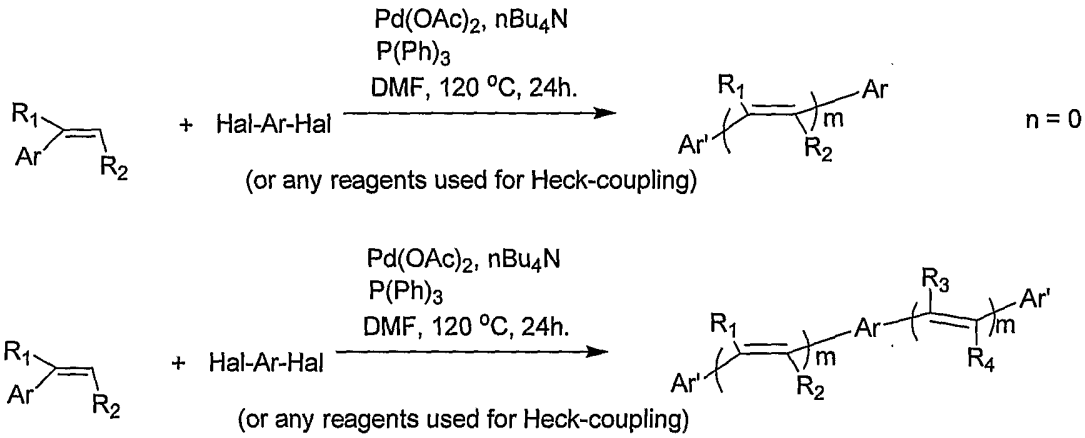
3. General Preparation of the Compounds having Formula 1

The compounds represented by Formula 1 can be prepared by the conjugated cross-coupling reaction of a substituted boronic acid (or ester) with a dihaloarylene compound. Such reactions are commonly referred to as "Suzuki couplings" and are illustrated in Scheme 1.



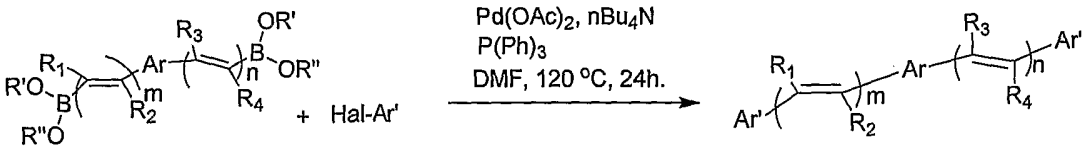
Scheme 1

"Heck coupling reactions" can also be used, in which a substituted aryl-ethylene is reacted with a dihaloarylene compound in the presence of a Pd(II) catalyst and a phosphine, as illustrated in Scheme 2. Hal-Ar-Hal is as defined above in Scheme 1.

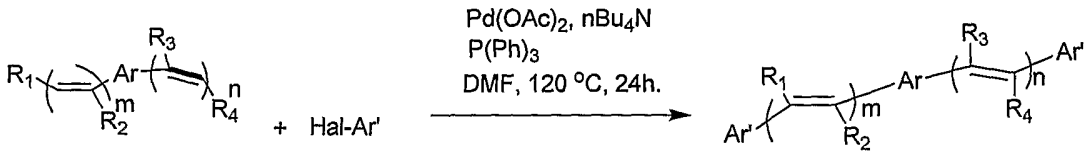


Scheme 2

Variations on these synthetic approaches can also be used, as illustrated in Schemes 3 and 4.



Scheme 3

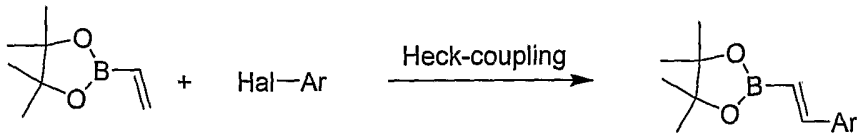


Scheme 4

In Schemes 3 and 4, Ar' is defined as above.

Suzuki coupling reactions are well known in organic chemistry and have been described in the literature (Miyaura, N.; Suzuki, A., Chem. Rev. (1995), 95(7), 2457-83).

The boronic acid or ester reagents can be synthesized according to literature methods (see Scheme 5 and Lightfoot, A. P.; Maw, G.; Thirsk, C.; Twiddle, S. J. R.; Whiting, A., Tetrahedron Lett. (2003), 44(41), 7645-7648.)



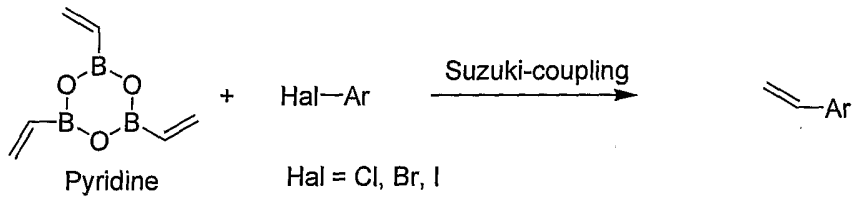
Scheme 5

The reagents are not restricted to the above substituted boronic acids or esters. Any Suzuki-coupling reagents used as organoboronic coupling reagents can be used, such as potassium trifluoro(organo)borates. (Darses, S.; Genet, J.P., Eur. J. of Org. Chem. (2003), (22), 4313-4327.). The reaction conditions, catalysts, solvents, phase transfer agents, and reaction media can also be varied. (Herrmann, W. A.; Reisinger, C. P.; Haerter, P.,

"C-C coupling reactions (Heck, Stille, Suzuki, etc.). Aqueous-Phase Organometallic Catalysis" (2nd Edition) (2004), 511-523.)

Heck coupling reactions are also well-established in organic chemistry and have been described in the literature (Huo, S.; Negishi, E. Palladium-catalyzed alkenyl-aryl, aryl-alkenyl, and alkenyl-alkenyl coupling reactions. Handbook of Organopalladium Chemistry for Organic Synthesis (2002), 1, 335-408. Littke, A. F.; Fu, G.C. Angew. Chem. Int. Ed. (2002), 41(22), 4176-4211. Farina, V., Adv. Synthesis & Catalysis (2004), 346(13-15), 1553-1582. Braese, S.; De Meijere, A. Double and multiple Heck reactions. Handbook of Organopalladium Chemistry for Organic Synthesis (2002), 1: 1179-1208. Itami, K.; Ushiogi, Y.; Nokami, T.; Ohashi, Y.; Yoshida, J., Org. Lett. (2004), 6(21), 3695-3698. Reetz, M. T.; de Vries, J. G., Chem. Commun. (2004), (14) 1559-1563.)

The aryl-ethylene or substituted styrene reagents can be synthesized according to literature methods (see Scheme 6 and Kerins, F.:, O'Shea, D. F. J. Org. Chem. 2002, 67, 4968-4971.)



Scheme 6

4. Semiconductor Devices

Semiconductor devices have been described by S. M. Sze in Physics of Semiconductor Devices, 2nd edition, John Wiley and Sons, New York (1981). Such devices include rectifiers, transistors (of which there are many types, including p-n-p, n-p-n, and thin-film transistors), current limiters, thermistors, p-n junctions, field-effect diodes, Schottky diodes, and so forth. Semiconductor devices can be prepared or manufactured by known methods (Peter Van Zant, Microchip Fabrication, Fourth Edition, McGraw-Hill, New York (2000)). In each semiconductor device, the semiconductor material is combined with one or more metals

or insulators to form the device. Common to all semiconductor devices is the presence of one or more semiconductor materials. The compounds represented by Formula 1 can be used as the semiconductor material in semiconductor devices.

In one embodiment, the semiconductor devices comprise at least one charge transport layer comprising the compounds represented by Formula 1.

(i) Thin-Film Transistors

A particularly useful type of transistor device, the thin-film transistor (TFT), generally includes a gate electrode, a gate dielectric on the gate electrode, a source electrode and a drain electrode adjacent to the gate dielectric, and a semiconductor layer adjacent to the gate dielectric and adjacent to the source and drain electrodes (see, for example, S. M. Sze, *supra*, page 492). These components can be assembled in a variety of configurations. More specifically, an organic thin-film transistor (OTFT) has an organic semiconductor layer.

Typically, a substrate supports the OTFT during manufacturing, testing, and/or use. Optionally, the substrate can provide an electrical function for the OTFT. Useful substrate materials include organic and inorganic materials. For example, the substrate can comprise inorganic glasses, ceramic foils, polymeric materials (e.g., acrylics; epoxies; polyamides; polycarbonates; polyimides; polyketones; poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene), sometimes referred to as poly(ether ether ketone) or PEEK; polynorbornenes; polyphenyleneoxides; poly(ethylene naphthalenedicarboxylate) (PEN); poly(ethylene terephthalate) (PET); poly(phenylene sulfide) (PPS)). The substrate can also comprise filled polymeric materials (for example, fiber-reinforced plastics (FRP)), or coated metallic foils.

The gate electrode can be any useful conductive material. For example, the gate electrode can comprise doped silicon or a metal (e.g., aluminum, chromium, gold, silver, nickel, palladium, platinum, tantalum, or titanium). Conductive polymers also can be used, for example polyaniline or poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate)

(PEDOT:PSS). In addition, alloys, combinations, and multilayers of these materials can be used. In some OTFTs, a single material can function as the gate electrode function and the substrate. For example, doped silicon can function as the gate electrode and also support the OTFT.

The gate dielectric generally covers the gate electrode. The gate dielectric electrically insulates the gate electrode from the balance of the OTFT device. Useful materials for the gate dielectric can comprise any inorganic electrically insulating material (e.g., strontiates, tantalates, titanates, zirconates, aluminum oxides, silicon oxides, tantalum oxides, titanium oxides, silicon nitrides, barium titanate, barium strontium titanate, barium zirconate titanate, zinc selenide, or zinc sulfide). In addition, alloys, combinations, and multilayers of these materials can be used for the gate dielectric.

The source and drain electrodes are separated from the gate electrode by the gate dielectric, while the organic semiconductor layer can be over or under the source and drain electrodes. The source and drain electrodes can be any sufficiently conductive material (e.g., metals such as aluminum, barium, calcium, chromium, gold, silver, nickel, palladium, platinum, titanium, or alloys thereof). Conductive polymers such as polyaniline, PEDOT:PSS, as well as combinations and multilayers thereof can also be used a source and drain electrodes. Some of these materials are appropriate for use with n-type semiconductor materials and others are appropriate for use with p-type semiconductor materials, as is known in the art.

The thin film electrodes (i.e., the gate, source, and drain electrodes) can be provided by any of several means, including physical vapor deposition (e.g., thermal evaporation or sputtering) and ink jet printing. The patterning of these electrodes can be accomplished by known methods such as shadow masking, additive photolithography, subtractive photolithography, printing, microcontact printing, or pattern coating.

Figures 1A and 1B are schematic diagrams of the bottom contact mode and top contact mode, respectively, of an OTFT. An OTFT typically comprises a substrate, e.g., an n-type silicon wafer 102.

The wafer functions as the gate electrode for the TFT device. A dielectric layer 104 of silicon dioxide is typically thermally grown on the gate electrode.

For the bottom-contact mode OTFT (Figure 1A), electrodes 106 and 108, which form channels for the source and drain, respectively, can be created on the silicon dioxide layer using a photolithographic process. A semiconductor layer 110 is then deposited over the surface of electrodes 106 and 108 and layer 104.

For the top-contact mode OTFT (Figure 1B), layer 110 is deposited on layer 104 before the fabrication of electrodes 106 and 108. is a schematic diagram of an OTFT showing the relative positions of the active layers of such a device in top contact mode.

Figure 1C is a schematic diagram of an OTFT showing the relative positions of the active layers of such a device in bottom contact mode with the gate at the top.

Figure 1D is a schematic diagram of an OTFT showing the relative positions of the active layers of such a device in bottom contact mode with the gate at the top.

Semiconductor layer 110 can comprise one or more compounds represented by Formula 1. Layer 110 may be deposited by various techniques known in the art, such as thermal evaporation, chemical vapor deposition, thermal transfer, ink-jet printing, and screen-printing. Useful dispersion thin film coating techniques for deposition include spin coating, doctor blade coating, and drop casting.

For the top-contact mode OTFT (Figure 1B), layer 110 is deposited on layer 104 before the fabrication of electrodes 106 and 108.

The semiconductor compounds described herein can also be used in other OTFT device configurations, e.g., gate-top device configurations. US 6,621,098 describes such device structures.

In some cases the substrate 100 can be a plastic polymer material, inorganic insulator or metal substrate. The gate electrode 102 can be coated onto the substrate by various coating methods such as

spin coating, bar coating, and doctor blade coating, or printing methods such as thermal laser printing, inkjet printing, and screen printing.

Characterization of OTFT devices provided herein, can be performed as follows:

Linear regime ($V_g <= V_{sd}$) mobility is calculated according to the equation:

$$\mu_{lin} = (L/WC_iV_{sd})(dI_d/dV_g) \quad \text{Equation 1}$$

where I_d is the drain current, V_g is gate voltage, V_{sd} is source-drain voltage, L is channel length, W is channel width, and C_i is capacitance per unit area of the gate dielectric. C_i is in units F/cm^2 and is calculated according to the following formula:

$$C_i = (\varepsilon_o\varepsilon/t)(10^{-4}) \quad \text{Equation 2}$$

where ε_o is the permittivity constant, ε is the dielectric constant, and t is the dielectric thickness.

Saturation regime ($V_g >= V_{sd}$) mobility is calculated according to the equation:

$$\mu_{sat} = (2L(d\sqrt{I_d}/dV_g)^2)/(WC_i) \quad \text{Equation 3}$$

Threshold voltage, V_t, is measured in the saturation regime. The square root of I_d is plotted versus V_g. Extrapolation of a line from the steepest portion of the curve to the x-axis provides V_t.

The on/off ratio is the ratio of the current I_{DS} at the highest V_{GS} to the current I_{DS} at the lowest V_{GS} under the highest applied drain voltage V_{DS}.

b. Display Devices

Figure 2 is a schematic representation of a display device 200. An anode 202 and a cathode 204 are electrically connected to an electric power supply 206. Electric power supply 206 is preferably a current source. A buffer layer 208 is present in contact with anode 202. Buffer layer 208 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. A hole-transporting layer 210 is present in contact with buffer layer 208 from one side and an organic semiconductor layer 212 on the other side. Hole-transporting layer 210 facilitates the passage of holes from hole-injecting layer 208 to organic semiconductor layer 212.

Similarly, an electron-injecting layer 214 is present in contact with cathode 204. Electron-injecting layer 214 facilitates the injection of electrons from cathode 204 into display device 200. An electron-transporting layer 216 is present in contact with hole-injecting layer 214 from one side and organic semiconductor layer 212 on the other side. Electron-transporting layer 216 facilitates the passage of electrons from electron-injecting layer 214 to organic semiconductor layer 212. In one embodiment, the organic semiconductor layer comprises photoactive material. The term "photoactive" refers to a material that emits light when activated by an applied voltage (such as in a light emitting diode or chemical cell) or responds to radiant energy and generates a signal with or without an applied bias voltage (such as in a photodetector).

In some embodiments, one of the hole-injecting layer 208 and the hole-transporting layer 210 is omitted. In some embodiments, one of the electron-injecting layer 214 and the electron-transporting layer 216 is omitted.

When electric current is applied to anode 202 and cathode 204, electrons and holes are injected into device 200. These electrons and holes combine in organic semiconductor layer 212 and emit light photons due to the electroluminescent properties of the compounds present in organic semiconductor layer 212. Layer 212 is also called the "light-emitting layer".

In one embodiment, the light-emitting layer 212 comprises one or more compounds having Formula 1. In one embodiment, a compound having Formula 1 is present in layer 212 as a host for a photoactive material. In one embodiment, the compounds having Formula 1 in layer 212 have no amino substituents.

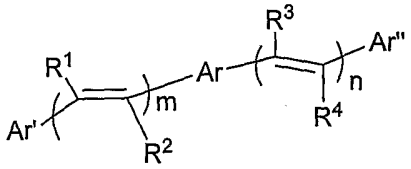
In one embodiment, the electron transporting layer 214 comprises one or more compounds having Formula 1. In one embodiment, the electron transporting layer 214 comprises one or more compounds having Formula 1 in combination with other known charge transport materials (such as Alq3 derivatives). The term "electron transport or electron-transporting" does not include light-emitting or light-sensing layers, materials, members, or structures, even though such layers, materials, members or structures may have electron transporting properties as well.

In one embodiment, the hole transporting layer 210 comprises one or more compounds having Formula 1. In one embodiment, a compound having Formula 1 is present in a host hole transporting material in layer 210. Examples of host materials include, but are not limited to, polythiophenes, polypyrroles, polyanilines, and polyvinylcarbazoles. In one embodiment, the hole transporting layer 210 comprises one or more compounds having Formula 1 in combination with other known charge transport materials (such as NPD derivatives). The term "hole transport or hole-transporting" does not include light-emitting or light-sensing layers, materials, members, or structures, even though such layers, materials, members or structures may have hole transporting properties as well.

In one embodiment, the buffer layer 208 comprises one or more compounds having Formula 1. In one embodiment, the compounds having Formula 1 in buffer layer 208 have no amino substituents.

In one embodiment, the hole-transporting layer 210 comprises one or more compounds having Formula 1 having no amino substituents.

In one embodiment, the hole-transporting layer 210 comprises one or more compound having Formula 1,



Formula 1

wherein Ar is selected from

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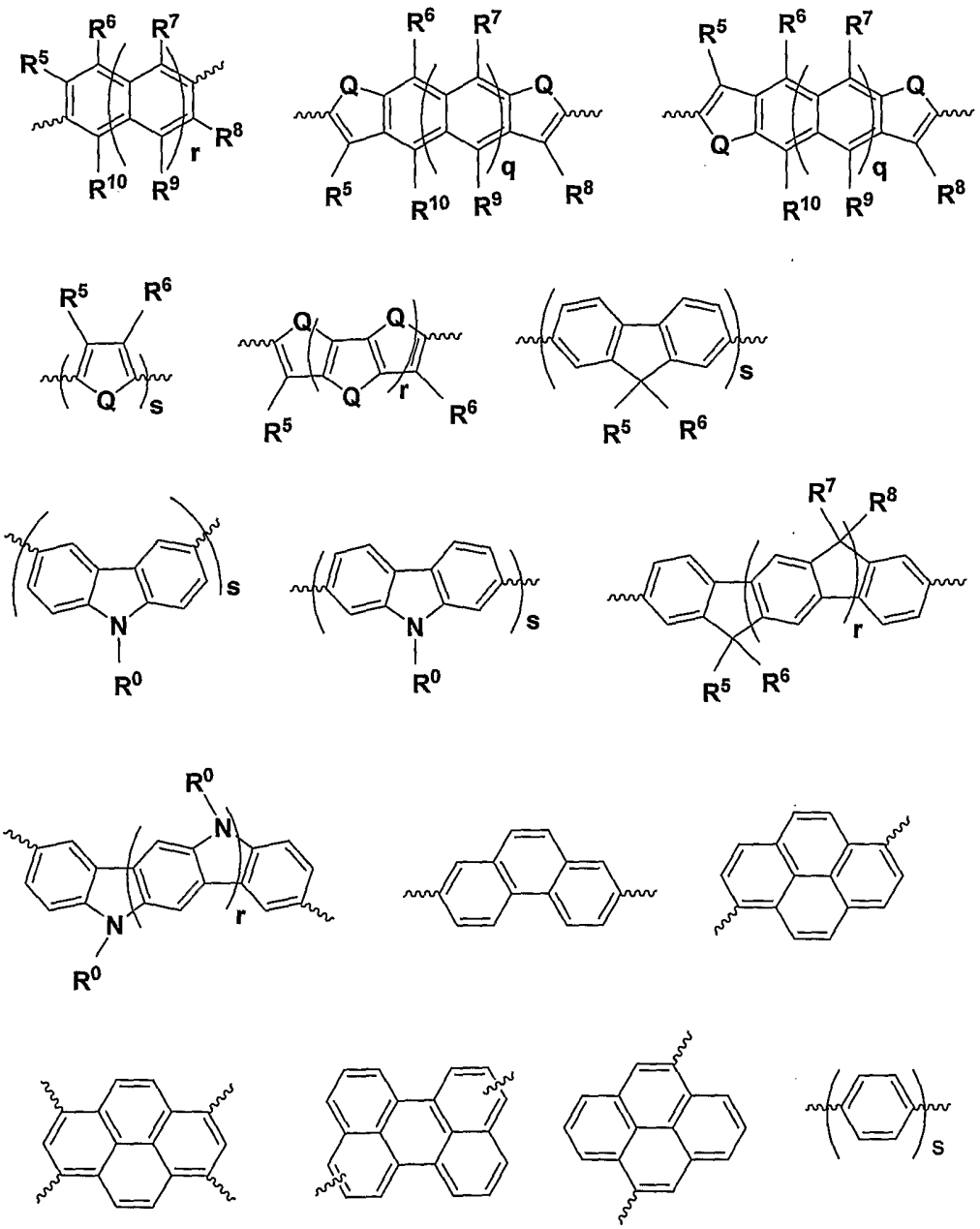


and combinations thereof;

wherein:

Q is selected from the group consisting of S, Se, Te, O, and NR^0;

q, and r are integers each independently having a value of from 0 to 5;

s is an integer having a value of from 1 to 5;

R^0 is selected from the group consisting of hydrogen, alkyl, and aryl;

R^5 through R^{10} are selected independently from the group consisting of hydrogen, alkyl, aryl, halogen, hydroxyl, aryloxy, alkoxy, alkenyl, alkyny, amino, alkylthio, phosphino, silyl, -COR, -COOR, $-PO_3R_2$, $-OPO_3R_2$, and CN; and

R is selected from the group consisting of hydrogen, alkyl, aryl, alkenyl, and alkynyl;

wherein any two adjacent groups, R^5 through R^{10} can be taken together to form a ring;

and further wherein there are no diarylamino groups.

In one embodiment, the substituents on substituted R and R^1 through R^{10} are selected independently from the group consisting of alkyl, aryl, thioalkyl, silyl, alkylaryl, alkoxy, alkylether, etheralkyl, fluorine, and combinations thereof.

In one embodiment, m = n = 1 and all R^1 through R^{10} are selected from the group consisting of hydrogen, fluorine, linear alkyl groups, aryl groups, and aryl groups substituted with linear alkyl groups. In one embodiment, the alkyl groups have from 1 to 10 carbon atoms. In one embodiment, Ar is an acene group.

In one embodiment, the hole-transporting layer 210 comprises one or more compounds selected from the group consisting of Compound 1, Compound 3, Compound 48, Compound 49, and Compound 50.

Other layers in the device can be made of any materials which are known to be useful in such layers upon consideration of the function to be served by such layers.

The anode 202 can be made of, for example, materials containing or comprising metal, mixed metals, alloy, metal oxides or mixed-metal oxide. The anode may comprise a conducting polymer, polymer blend or polymer mixtures. Suitable metals include the Group 11 metals, the

metals in Groups 4, 5, and 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 may also comprise an organic material, especially a conducting polymer such as polyaniline, including exemplary materials as described in "Flexible light-emitting diodes made from soluble conducting polymer," Nature vol. 357, pp 477 479 (11 June 1992). At least one of the anode and cathode should be at least partially transparent to allow the generated light to be observed.

The buffer layer may comprise hole transport materials such as those summarized, for example, in Kirk Othmer Encyclopedia of Chemical Technology, Fourth Edition, Vol. 18, p. 837 860, 1996, by Y. Wang. Both hole transporting "small" molecules as well as oligomers and polymers may be used. Hole transporting molecules include, but are not limited to: 4,4',4"-tris(N,N-diphenyl-amino)-triphenylamine (TDATA); 4,4',4"-tris(N-3-methylphenyl-N-phenyl-amino)-triphenylamine (MTDATA); 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); α-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 (α-NPB); 4;4'-*N,N'*-dicarbazolyl-biphenyl (CBP); and porphyrinic compounds, such as copper phthalocyanine. Useful hole transporting polymers include, but are not limited to, polyvinylcarbazole, (phenylmethyl)polysilane, poythiophene, polypyrrole, and polyaniline. The hole transporting polymer can be a complex of a conducting polymer and a colloid-forming polymeric acid, as disclosed in, published US applications US 2004/0254297 and US

2004/029133. Conducting polymers are useful as a class. It is also possible to obtain hole transporting polymers by doping hole transporting moieties, such as those mentioned above, into polymers such as polystyrenes and polycarbonates.

Any organic electroluminescent ("EL") material can be used as a photoactive material in light-emitting layer 212. Such materials include, but are not limited to, fluorescent dyes, small molecule organic fluorescent compounds, fluorescent and phosphorescent metal complexes, conjugated polymers, and mixtures thereof. Examples of fluorescent dyes include, but are not limited to, pyrene, perylene, rubrene, derivatives thereof, and mixtures thereof. Examples of metal complexes include, but are not limited to, metal chelated oxinoid compounds, such as tris(8-hydroxyquinolato)aluminum (Alq3); cyclometalated iridium and platinum electroluminescent compounds, such as complexes of Iridium with phenylpyridine, phenylquinoline, or phenylpyrimidine ligands as disclosed in Petrov et al., Published PCT Application WO 02/02714, and organometallic complexes described in, for example, published applications US 2001/0019782, EP 1191612, WO 02/15645, and EP 1191614; and mixtures thereof. Electroluminescent emissive layers comprising a charge carrying host material and a metal complex have been described by Thompson et al., in U.S. Patent 6,303,238, and by Burrows and Thompson in published PCT applications WO 00/70655 and WO 01/41512. Examples of conjugated polymers include, but are not limited to poly(phenylenevinylenes), polyfluorenes, poly(spirobifluorenes), polythiophenes, poly(p-phenylenes), copolymers thereof, and mixtures thereof.

In one embodiment of the device, photoactive material can be an organometallic complex. In another embodiment, the photoactive material is a cyclometalated complex of iridium or platinum. Other useful photoactive materials may be employed as well. Complexes of iridium with phenylpyridine, phenylquinoline, or phenylpyrimidine ligands have been disclosed as electroluminescent compounds in Petrov et al., Published PCT Application WO 02/02714. Other organometallic

complexes have been described in, for example, published applications US 2001/0019782, EP 1191612, WO 02/15645, and EP 1191614. Electroluminescent devices with an active layer of polyvinyl carbazole (PVK) doped with metallic complexes of iridium have been described by Burrows and Thompson in published PCT applications WO 00/70655 and WO 01/41512. Electroluminescent emissive layers comprising a charge carrying host material and a phosphorescent platinum complex have been described by Thompson et al., in U.S. Patent 6,303,238, Bradley et al., in Synth. Met. (2001), 116 (1-3), 379-383, and Campbell et al., in Phys. Rev. B, Vol. 65 085210.

Examples of electron-transporting materials for layer 218 include, but are not limited to, metal chelated oxinoid compounds, such as bis(2-methyl-8-quinolinolato)(para-phenyl-phenolato)aluminum(III) (BAlQ) and tris(8-hydroxyquinolato)aluminum (Alq_3); azole compounds such as 2-(4-biphenylyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole (PBD), 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 cathode layer 204 may be deposited as lines or as a film. The cathode can be any metal or nonmetal having a lower work function than the anode. Exemplary materials for the cathode can include alkali metals of Group 1, especially lithium, 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-containing and other compounds, such as LiF and Li_2O, may also be deposited as an electron-injection layer 214 between an organic layer and the cathode layer to lower the operating voltage of the system.

Though not depicted, it is understood that the device 200 may comprise additional layers. Other layers that are known in the art or otherwise may be used. In addition, any of the above-described layers

may comprise two or more sub-layers or may form a laminar structure. Alternatively, some or all of anode layer 202, the hole transport layer 210, the electron transport layer 218, the electron injection layer 214, cathode layer 204, and other layers may be treated, especially surface treated, to increase charge carrier transport efficiency or other physical properties of the devices. The choice of materials for each of the component layers is preferably determined by balancing the goals of providing a device with high device efficiency with device operational lifetime considerations, fabrication time and complexity factors and other considerations appreciated by persons skilled in the art. It will be appreciated that determining optimal components, component configurations, and compositional identities would be routine to those of ordinary skill of in the art.

In one embodiment, the different layers have the following range of thicknesses: anode 202, 500-5000 Å, in one embodiment 1000-2000Å; buffer layer 208 and hole-transporting layer 210, each 50-2000 Å, in one embodiment 200-1000 Å; photoactive layer 212, 10-2000 Å, in one embodiment 100-1000 Å; layers 216 and 214, 50-2000 Å, in one embodiment 100-1000 Å; cathode 204, 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. Thus the thickness of the electron-transport layer should be chosen so that the electron-hole recombination zone is in the light-emitting layer. The desired ratio of layer thicknesses will depend on the exact nature of the materials used. The different layers can be formed by any known deposition method, including liquid deposition, vapor deposition, and thermal transfer. In one embodiment, the device is fabricated by liquid deposition of the buffer layer, the hole transport layer, and the photoactive layer, and by vapor deposition of the electron transport layer, the electron injection layer, and the cathode.

While detailed embodiments of the invention have been illustrated and described, it will be clear that the disclosure is not limited to these embodiments only. Numerous modifications, changes, variations,

substitutions, and equivalents will be apparent to those skilled in the art without departing from the spirit and scope of the invention as described in the claims.

EXAMPLES

The present invention is further illustrated in the following Examples. It should be understood that these Examples, while indicating preferred embodiments of the invention, are given by way of illustration only.

General

Thermo-gravimetric analysis (TGA) was carried out on a TA Instruments Q550 TGA system™ at a heating rate of 10 °C/minutes and at a nitrogen flow rate of 60 cm^3/min.

Cyclic voltammetry (CV) was performed on an EG&G Parc Model 273A™ potentiostat / galvanostat system with a three-electrode cell in a solution of Bu_4NBF_4 (0.1 M) in acetonitrile at a scan rate of 50 mV/s.

The semiconductor films were coated on a disc Pt electrode (0.050 cm^2) by vacuum sublimation. A Pt wire was used as the counter electrode and an $Ag/AgNO_3$ (0.01M) electrode was used as the reference electrode. Prior to each series of measurements, the cell was deoxygenated with argon. Organic semiconductor was added to the electrolyte solution (0.2 mg/mL). A Pt wire was used as the counter electrode and an Ag wire electrode was used as the reference electrode. The electrode's potential was calibrated with the saturated calomel electrode (SCE) by measuring the ferrocene/ferrocenium couple in this system (0.15 V versus SCE). The band gaps were derived from the difference between onset potentials.

The synthetic results were confirmed by mass spectrometry, nmr analysis, and/or x-ray crystal structure.

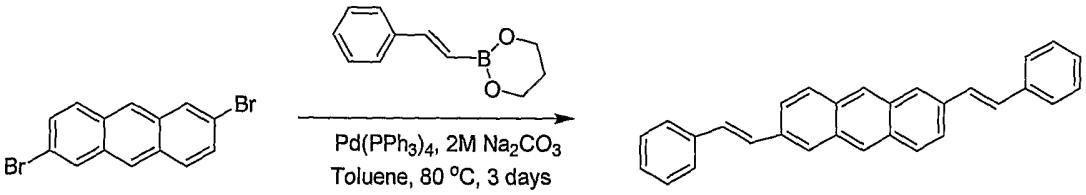
X-ray data were taken on a CAD-4 diffractometer with copper Kα radiation, and the structure was solved using the NRCVAX™ suite of programs.

Nuclear magnetic resonance (NMR) spectra were taken on a Bruker™ 500 MHz spectrometer. All chemical shifts were reported relative to tetramethylsilane (TMS) at 0.0 ppm, unless otherwise stated. 2,6-Dibromoanthracene was synthesized according to the method of Hodge, P.; Power, G. A.; Rabjohns, M. A. *Chem. Commun.* **1997**, 73.

Unless stated, other reagents were purchased from Aldrich and were used without any purification.

EXAMPLE 1

Synthesis of 2,6-distyryl-anthracene (Compound 1)

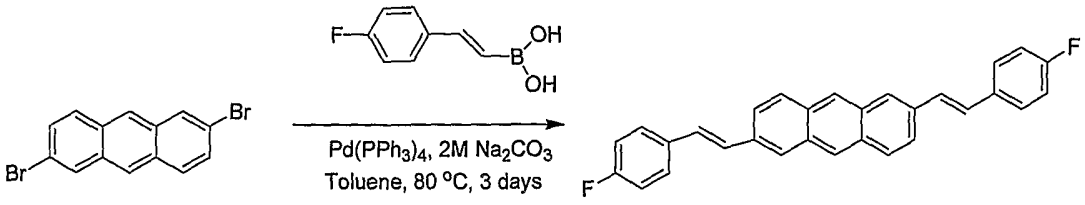


Compound 1

To a mixture of 2,6-dibromoanthracene (5.20 g, 15.48 mmol) and 2-styryl-[1,3,2]-dioxaborinane (8.73 g, 46.43 mmol, Sigma-Aldrich Chemical Co., Milwaukee, WI) in toluene (200 ml) was added 2M sodium carbonate (8.20 g, 77.36 mmol) dissolved in water (38.7 ml), followed by the addition of phase-transfer agent Aliquat® 336 (3.10 g, 7.74 mmol, Sigma-Aldrich Chemical Co.). The mixture was bubbled with nitrogen for 15 min, followed by addition of tetrakis(triphenylphosphine)palladium(0) (358.5 mg, 2 % mol, Sigma-Aldrich Chemical Co.). The mixture was heated to 90 °C for three days under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol (600 ml). The precipitate was filtered off, washed with water, dilute acid (5 % HCl), water, methanol, then with acetone three times to remove the starting material as well as the mono-substituted by-product. The crude product was purified by sublimation (twice) in a 3-zone furnace to give 2.71 g (46 %) of a yellow solid.

EXAMPLE 2

Synthesis of 2,6-bis-[2-4-pentyl-phenyl)-vinyl]-anthracene (Compound 2)

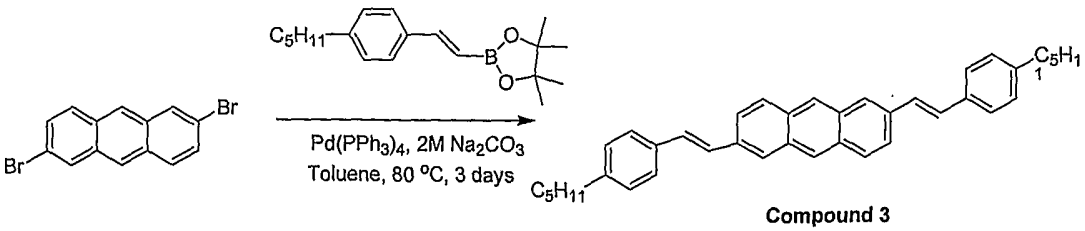


Compound 2

To a mixture of 2,6-dibromoanthracene (2.688 g, 8.0 mmol) and *trans*-2-(4-fluoro-phenyl)vinyl-boronic acid (3.983 g, 24.0 mmol, Sigma-Aldrich Chemical Co.) in toluene (120 ml) was added 2M Na_2CO_3 sodium carbonate (4.24 g, 40 mmol) dissolved in water (20 ml), followed by the addition of phase-transfer agent Aliquat® 336 (1.6 g, 4 mmol, Sigma-Aldrich Chemical Co.). The mixture was bubbled with nitrogen for 15 min, followed by addition of tetrakis(triphenylphosphine)palladium(0) (185.3 mg, 2 % mol, Sigma-Aldrich Chemical Co.). The mixture was heated to 90 °C for three days under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol (300 ml). The yellow precipitate was filtered off, washed with water, dilute acid (5 % HCl), water, methanol, then with acetone three times to remove the starting material as well as the mono-substituted by-product. The crude product was purified by sublimation in a 3-zone furnace and a bright yellow solid was obtained.

EXAMPLE 3

Synthesis of 2,6-bis-[2-4-pentyl-phenyl)-vinyl]-anthracene (Compound 3)

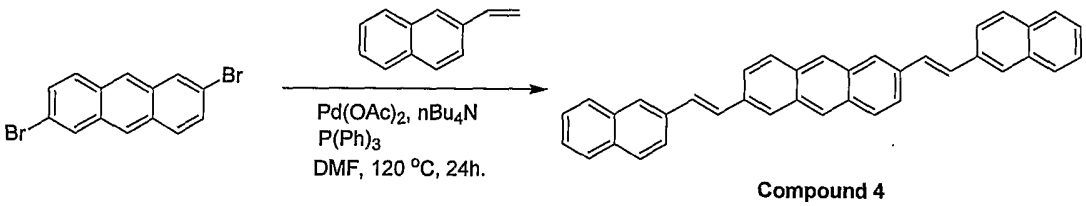


Compound 3

To a mixture of 2,6-dibromoanthracene (5.20 g, 15.48 mmol) and 2-[2-(4-pentylphenyl)vinyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14.67 g, 46.42 mmol, Sigma-Aldrich Chemical Co.) in toluene (200 ml) was added 2M sodium carbonate (8.20 g, 77.36 mmol) dissolved in water (38.7 ml) followed by the addition of phase-transfer agent Aliquat® 336 (3.10 g, 7.74 mmol, Sigma-Aldrich Chemical Co.). The mixture was bubbled with nitrogen for 15 min, followed by addition of tetrakis(triphenylphosphine)-palladium(0) (358.5 mg, 2 % mol, Sigma-Aldrich Chemical Co.). The mixture was heated to 90 °C for three days under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol (600 ml). The precipitate was filtered off, washed with water, dilute acid (5 % HCl), water, methanol, then with acetone three times to remove the starting material as well as the mono-substituted by-product. The crude product was purified by sublimation in a 3-zone furnace twice to give 2.00 g (25 %) of bright yellow solid.

EXAMPLE 4

Synthesis of 2,6-bis-(2-naphthalen-2-yl-vinyl)-anthracene (Compound 4)



Compound 4

To a mixture of 2,6-dibromoanthracene (3.36 g, 10.0 mmol) and 2-vinylnaphthalene (4.63 g, 30.0 mmol, Sigma-Aldrich Chemical Co.) in anhydrous DMF (150 ml) was added triphenylphosphine (0.13 g, 0.50 mmol, Sigma-Aldrich Chemical Co.) and tributylamine (11.9 ml, 50.0 mmol, Sigma-Aldrich Chemical Co.). The mixture was bubbled with nitrogen for 15 min. Then palladium acetate (112.0 mg, 0.5 mmol, Sigma-Aldrich Chemical Co.) was added. The mixture was heated to 130 °C for 18 hrs under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol (500 ml). The precipitate was filtered off, washed with methanol, acetone and then with chloroform. The

crude product was purified by sublimation in a 3-zone furnace twice to give a yellow solid.

EXAMPLE 5

Characterization of OTFT devices

This Example summarizes results obtained for the characterization of OTFT devices that had a W/L ratio of 10, where W is the channel width and L is the channel length.

The OTFT devices were fabricated in a similar manner as described in conjunction with Figure 1B. Thereafter, the performance of each OTFT device was characterized using an Agilent 4155C™ Semiconductor Parameter Analyzer interfaced with a probe station.

In Example 5e, a conducting polymer layer of polyaniline (PANI) and dispersed carbon nanotube (PANI/NT) was applied as patterned gate electrodes, which were thermal transfer printed using a CREO-Trendsetter TML printer using a polyaniline-carbon nanotube (PANI/NT) composition as donor and a Mylar® RS 8 receiver sheet. A dielectric layer of latex RS35 was then laminated or thermal printed over the patterned gate. The source and drain patterns were then printed using a CREO-Trendsetter TML printers by using a polyaniline-carbon nanotube (PANI/NT) composition as donor and a Mylar® RS 8 receiver sheet. Semiconductor of Composition 1 was then thermally evaporated on top of the source and drain electrodes through a shadow mask.

Measurements were made under ambient conditions, with no special precautions taken to control temperature, or to exclude light or air.

The results were obtained from the characterization of the OTFT devices are summarized in the Table. These results show that OTFT devices comprising compounds of Formula 1 have high mobilities and high on/off ratios.

Yet, in another device fabrication, the organic thin film field effect transistor (OTFT) device was fabricated on a heavily doped *n*-type Si wafer with 200 nm thermal oxide on the top surface, which acts as a dielectric layer with a capacitance per unit area of 1.73×10^{-8} F/cm^2 and an etched heavily doped *n*-type Si as a back contact (gate electrode). The

wafers were cleaned through subsequent washing with acetone, isopropanol, and deionized water, blown dry with N_2 gas, and cleaned in an oxygen plasma for 6 min. Then the wafer SiO_2 surface was treated with a self-assembling monolayer (SAM) of octyltrichlorosilane (OcTS) by immersing the cleaned wafer substrate in 0.1 M solution of OcTS in toluene at 60 °C for 15 min. After rinsing with toluene and blowing dry with N_2 gas, the substrate was annealed at 150 °C for 5 min to crosslink the SAM layers (the contact angle of OcTS treated surface is about 88° ~ 91°). The semiconductor layer was deposited over the treated dielectric surface through shadow masks (40 shadows each with an area of *ca.* 1000 × 1000 μm to define the active layers). The organic semiconductors were deposited at a rate of 1-2 Å/s under a pressure of ~2.0×10^{-6} Torr to a final thickness of 400 Å determined by a quartz crystal monitor. The film thicknesses were corrected with a stylus profilometer. The substrate temperature during deposition was controlled by heating or cooling the copper block where the substrate was mounted. Gold electrodes were deposited after semiconductor deposition by using shadow masks with *W/L* of ca. 10/1. The mask defined eight sets of source-drain pairs, each with channel widths of *W* 400, 600, 800, 1000 μm, respectively and their corresponding eight different channel lengths *L* 40, 60, 80, and 100 μm, respectively. The electrical characteristics were obtained at room temperature in air using an Agilent 4155C semiconductor parameter analyzer. The mobility and threshold voltages were extracted from the standard TFT analysis. The on/off ratio was determined from the current I_{DS} at V_{GS} = -40 V to the current I_{DS} at V_{GS} = +10 V. All the data in Table 1 were obtained by randomly measuring 8 individual TFTs and determining an average value. Standard deviations were in the range of 5-10 %.

Table 1: OTFT Device Characteristics

SC Material	Substrate Temperature (Example)	Device Characteristics			
		μ^{sat} / μ^{lin} (cm^2/Vs)	On/Off^{sat} / On/Off^{lin}	$V_t{}^{sat}$ / $V_t{}^{lin}$ (V)	SubThrSW^{sat} / SubThrSW^{lin} (V/decade)
Comp 1	22 °C (5a)	0.14±0.037 / 0.11±0.042	8.10×10^5 / 1.50×10^6	-24.3 / -30.0	2.50 / NA
	40 °C (5b)	0.18±0.027 / 0.13±0.014	9.55×10^7 / 5.27×10^6	-20.2 / -25.1	2.25 / NA
	60 °C (5c)	0.99±0.126 / 0.71±0.091	6.14×10^7 / 4.84×10^7	-18.1 / -20.0	1.48 / NA
	120 °C (5d)	0.72±0.155 / 0.54±0.109	4.41×10^6 / 3.15×10^6	-23.9 / -26.9	2.03 / NA
	*22 °C (5e)	0.03±0.021 / 0.02±0.029	5.30×10^5 / 4.50×10^5	-12.5 / -10.7	3.11 / NA
Comp 3	22 °C (5f)	0.53±0.022 / 0.46±0.019	2.65×10^7 / 5.52×10^5	-20.9 / -23.8	2.00 / NA
	60 °C (5g)	1.18±0.096 / 0.97±0.025	1.63×10^8 / 2.14×10^7	-15.4 / -17.6	2.06 / NA
	100 °C (5h)	0.75±0.179 / 0.62±0.027	2.42×10^8 / 5.52×10^6	-17.1 / -20.7	2.00 / NA
	120 °C (5i)	0.70±0.047 / 0.48±0.027	5.55×10^7 / 1.80×10^6	-15.6 / -17.7	1.91 / NA

Comp 48	60 °C (5j)	0.178± 0.068 0.074± 0.043	1.88×10^7 3.17×10^5	-15.1 -26.8	2.78
	80 °C (5k)	0.012± 0.007 0.009± 0.005	3.49×10^6 1.04×10^6	-4.00 -19.7	2.35
Comp 49	20 °C (5l)	0.095± 0.096 0.073± 0.005	5.22×10^7 4.31×10^6	-5.90 -10.5	2.10
	60 °C (5m)	0.349± 0.052 0.214± 0.016	2.44×10^8 1.08×10^7	-9.50 -18.1	2.12
	80 °C (5n)	0.526± 0.021 0.263± 0.014	6.51×10^7 8.00×10^6	-11.3 -18.5	2.52
	100 °C (5o)	0.443± 0.026 0.258± 0.017	2.18×10^8 7.54×10^6	-9.10 -15.8	2.38
Comp 50	20 °C (5p)	0.057± 0.013 0.027± 0.005	1.44×10^7 7.15×10^5	-8.90 -20.8	2.56
	80 °C (5q)	0.075± 0.022 0.029± 0.008	2.31×10^7 2.93×10^5	-13.9 -19.0	2.74
Comp 36	20 °C (5r)	0.056± 0.017 0.045± 0.008	4.11×10^6 2.60×10^6	-2.40 -10.3	3.32
	40 °C (5s)	0.076± 0.012 0.058± 0.002	1.33×10^6 1.85×10^6	-1.60 -6.70	4.51
	60 °C (5t)	0.343± 0.091 0.186± 0.041	1.83×10^7 7.02×10^6	-0.40 -0.80	2.87
	80 °C (5u)	0.770± 0.107 0.502± 0.046	2.80×10^7 1.71×10^7	+10.0 +5.80	2.30
	100 °C (5v)	1.55± 0.142 0.904± 0.054	3.57×10^8 1.85×10^7	+4.80 +4.70	2.10
	110 °C (5w)	2.00± 0.161 1.27± 0.086	8.15×10^7 3.84×10^8	+6.00 +6.20	1.72
	120 °C (5x)	1.23± 0.091 0.813± 0.071	5.07×10^8 4.78×10^7	+4.80 +3.60	1.82
	140 °C (5y)	0.362± 0.043 0.163± 0.024	1.69×10^7 1.03×10^6	22.9 20.0	3.93
Comp 54	20 °C (5z)	0.844± 0.086 0.524± 0.050	8.59×10^7 4.09×10^7	+5.60 +7.00	1.92
	60 °C (5aa)	0.877± 0.090 0.735± 0.002	3.59×10^6 2.02×10^7	+15.4 +16.1	2.80
	80 °C (5bb)	1.090± 0.120 0.643± 0.096	3.51×10^7 2.85×10^7	+7.00 +10.6	2.02
	100 °C (5cc)	0.603± 0.045 0.320± 0.044	2.52×10^6 1.43×10^6	+20.8 +24.6	2.62
	120 °C (5dd)	0.455± 0.134 0.324± 0.106	1.41×10^6 1.85×10^7	+25.8 +22.7	2.64

*Bottom contact device as depicted in Figure 1A. The devices were fabricated with Mylar® substrate, a laminated latex layer as the gate dielectric material, and the source/drain and gate electrodes using printed

conductive PANI with NT as described in the text on page 51, lines 16-26. The semiconductor was thermal evaporated.

μ^{sat}: Saturated mobility; μ^{lin}: Linear mobility; On/Off^{sat}: On (when grain-source voltage is –60V) and Off (when drain-source voltage is 0) current ratio of drain-source current in saturated region when the maximum gate voltage applied (-60 V). On/Off^{lin}: On (when grain-source voltage is –60V) and Off (when drain-source voltage is 0) current ratio of drain-source current in linear region when the maximum gate voltage applied (-5 V). V_t ^{sat}: Threshhold voltage in saturated region; V_t ^{lin}: Threshold voltage in linear region; SubThrSW^{sat}: Subthreshold swing in saturated region; SubThrSW^{lin}: Subthreshhold swing in linear region;
NA = Not Available

EXAMPLE 6

Stability Test for an OTFT Fabricated Using Compound 1, Compound 36

The device was tested according to procedure as described above, and the data analyzed as described by Ficker et al., J. Appl. Phys. 94, 2638 (2003). The device using compound 36 (5n) was subjected to continuous operation under a constant drain-source voltage of –40 V and an alternating gate-source voltage between +40 V and –40 V. It was found that the semiconductor material was stable in the device and the device performance was the same as the initial testing result. The device was in continuous operation for at least 24 hr during the test. In contrast, a device fabricated using pentacene as a semiconductor layer and tested under the similar conditions showed a dramatic loss in the charge mobility (from 0.4 cm^2/Vs down to 0.1 cm^2/Vs) and on/off ratio (from initial I 6.5 x 10^4 down to ~10^1) after only 2 hours of continuous running.

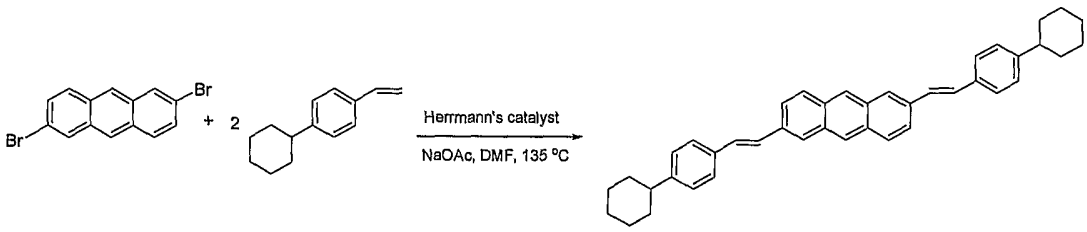
In another test, the devices (5c) were constructed as described above using Compound 1 in the semiconductor layer and the mobility and on/off ratios were measured periodically over a span of 10 months. The performance was essentially stable over that timeframe. The mobility

varied from 0.85 to 1.09 cm^2/Volt-sec. The on/off ratio varied from 1.7x 10^6 to 8.6x10^6. Mobilities were calculated by the method described in U.S. 6,452,207 (col. 9, lines 55-63). In all cases, devices exhibited on/off ratios in excess of 10^6 and mobility stead constantly during the storage for Compound 1 devices, demonstrating high stabilities of these devices in air.

Under similar control conditions, however, pentacene devices exposed to air showed a dramatic drop in charge mobility. The charge mobility dropped from an initial value of 0.4 cm^2/Vs to 0.1 cm^2/Vs after two months storage, and it continued dropping to 0.03 cm^2/Vs after another two months storage. The on/off ratios decreased by an order of magnitude in the first two months and another one order of magnitude after that, confirming the oxidative instability of this benchmark semiconductor material.

EXAMPLE 7

Synthesis of 2,7-Bis-[2-(4-cyclohexyl-phenyl)-vinyl]-anthracene (Compound 44)



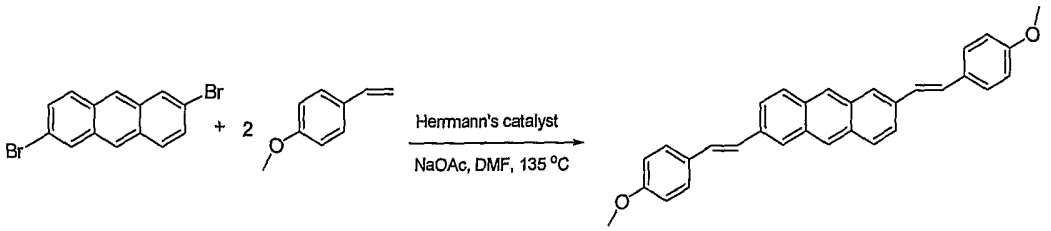
Compound 44

To a mixture of 2,6-dibromoanthracene (3.36 g, 10.00 mmol) and 4-cyclohexylstyrene (7.45 g, 40.00 mmol) in DMF (200 ml, anhydrous) was added sodium acetate (3.73 g, 45.00 mmol). The mixture was bubbled with nitrogen for 15 min. Then trans-di-m-acetatobis[2-(di-o-tolylphosphino)benzyl]dipalladium(II) (19.1 mg, 0.2 mol%) was added. The mixture was heated at 135 °C (oil bath) for 2 days under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol. The precipitate was filtered off, washed with

methanol and acetone. The crude product was purified by sublimation in a 3-zone furnace to give 0.3 g (5.5 %) of a yellow solid.

EXAMPLE 8

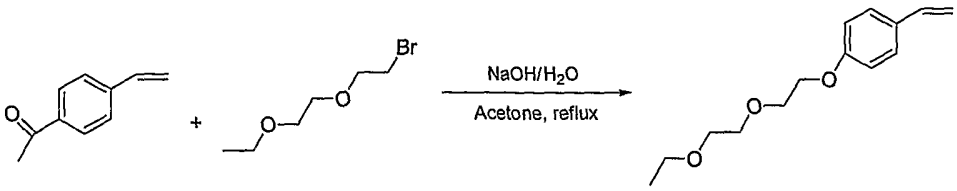
Synthesis of 2,7-Bis-[2-(4-methoxyl-phenyl)-vinyl]-anthracene (Compound 51)

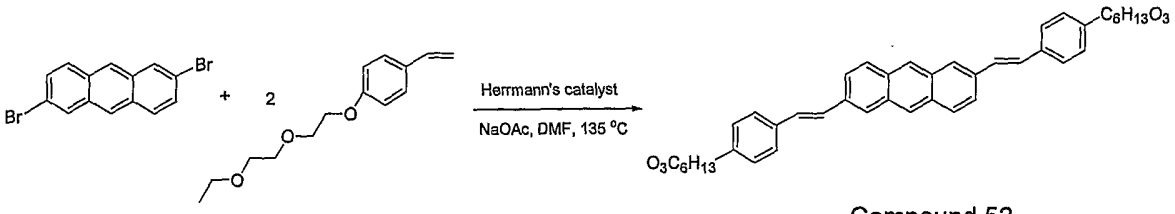


Compound 51

To a mixture of 2,6-dibromoanthracene (2.45 g, 7.29 mmol) and 4-vinylanisole (4.03 g, 29.14 mmol) in DMF (90 ml, anhydrous) was added sodium acetate (2.69 g, 32.79 mmol). The mixture was bubbled with nitrogen for 15 min. Then trans-di-m-acetatobis[2-(di-o-tolylphosphino)benzyl]dipalladium(II) (13.9 mg, 0.2 mol%) was added. The mixture was heated at 135 °C (oil bath) for 2 days under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol. The precipitate was filtered off, washed with methanol and acetone. The crude product was purified by sublimation in a 3-zone furnace to give 0.66 g (20 %) of a yellow solid.

EXAMPLE 9





Compound 52

a. Synthesis of 4-(2-(2-ethoxyethoxy)ethoxystyrene

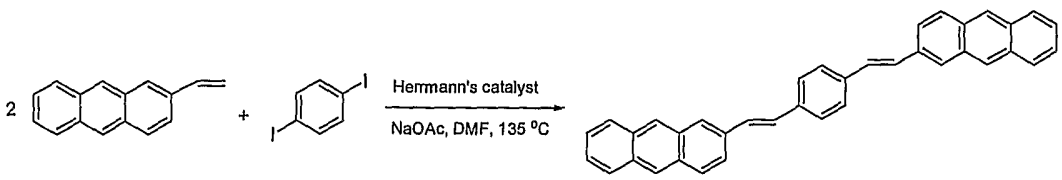
To a solution of 4-acetoxystyrene monomer (22.54 g, 0.14 mol), 2-(2-ethoxyethoxy)-ethylbromide (27.39 g, 0.14 mol) in 200 ml of acetone was added NaOH (16.68 g, 0.42 mol) and water (10 ml). The mixture was refluxed for 2 days. After cooling, the reaction mixture was extracted with ethyl ether. The organic layer was dried over $MgSO_4$, filtered and concentrated. Column purification (hexane/ethyl ether: 8/1 to 2/1) gave 21.82g (66%) of product.

b. 2,7-Bis-[2-(4-(2-(2-ethoxyethoxy)ethoxy)-phenyl)-vinyl]-anthracene (Compound 52)

To a mixture of 2,6-dibromoanthracene (2.79 g, 8.30 mmol) and 4-(2-(2-ethoxyethoxy)ethoxystyrene (7.86 g, 33.26 mmol) in DMF (100 ml, anhydrous) was added sodium acetate (3.07 g, 37.42 mmol). The mixture was bubbled with nitrogen for 15 min. Then trans-di-m-acetatobis[2-(di-o-tolylphosphino)benzyl]dipalladium(II) (15.9 mg, 0.2 mol%) was added. The mixture was heated at 135 °C (oil bath) for 2 days under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol. The precipitate was filtered off, washed with methanol and acetone. The crude product was purified by sublimation in a 3-zone furnace to give a yellow solid.

EXAMPLE 10

Synthesis of Compound 16

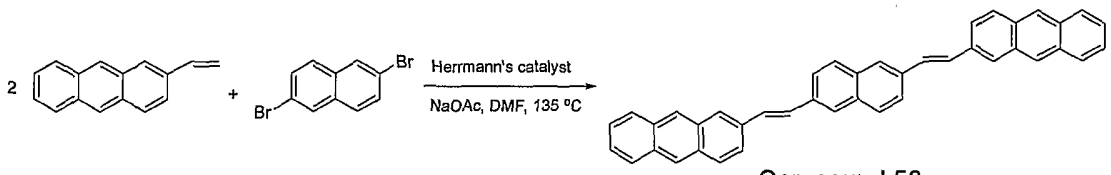


Compound 16

To a mixture of 2-vinylanthracene (4.68 g, 22.91 mmol) and 1,4-diiodobenzene (2.55 g, 7.64 mmol) in DMF (100 ml, anhydrous) was added sodium acetate (2.82 g, 34.37 mmol). The mixture was bubbled with nitrogen for 15 min. Then trans-di-m-acetatobis[2-(di-o-tolylphosphino)benzyl]dipalladium(II) (14.6 mg, 0.2 mol%) was added. The mixture was heated at 135 °C (oil bath) for 2 days under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol. The precipitate was filtered off, washed with water, methanol and acetone. The crude product was purified by sublimation in a 3-zone furnace to give 1.28 g (35 %) of an orange solid.

EXAMPLE 11

Synthesis of Compound 53

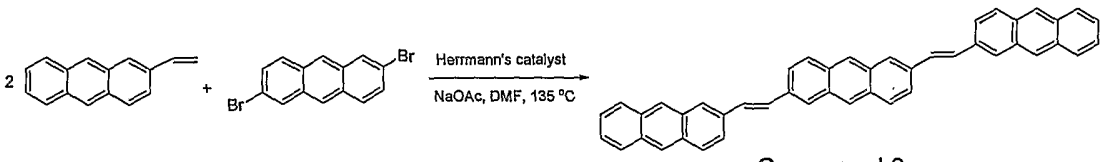


Compound 53

To a mixture of 2-vinylanthracene (4.68 g, 22.91 mmol) and 2,6-dibromonaphthalene (2.21 g, 7.64 mmol) in DMF (100 ml, anhydrous) was added sodium acetate (2.82 g, 34.37 mmol). The mixture was bubbled with nitrogen for 15 min. Then trans-di-m-acetatobis[2-(di-o-tolylphosphino)benzyl]dipalladium(II) (14.6 mg, 0.2 mol%) was added. The mixture was heated at 135 °C (oil bath) for 2 days under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol. The precipitate was filtered off, washed with water, methanol and acetone. The crude product was purified by sublimation in a 3-zone furnace to give 0.086 g (2 %) of an orange solid.

EXAMPLE 12

Synthesis of Compound 9

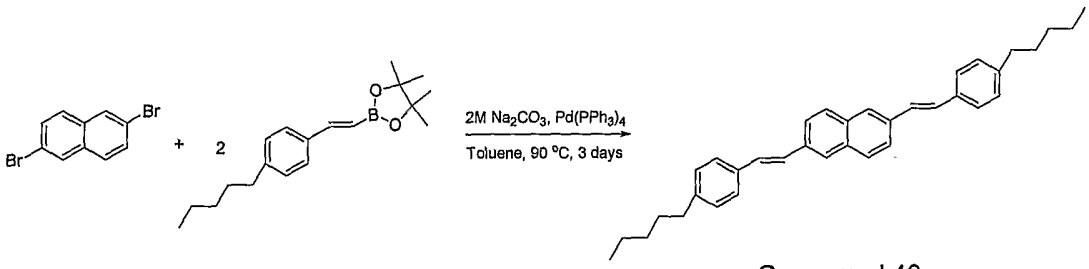


Compound 9

To a mixture of 2-vinylanthracene (4.48 g, 21.93 mmol) and 2,6-dibromoanthracene (2.57 g, 7.64 mmol) in DMF (100 ml, anhydrous) was added sodium acetate (2.82 g, 34.37 mmol). The mixture was bubbled with nitrogen for 15 min. Then trans-di-m-acetatobis[2-(di-o-tolylphosphino)benzyl]dipalladium(II) (14.6 mg, 0.2 mol%) was added. The mixture was heated at 135 °C (oil bath) for 2 days under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol. The precipitate was filtered off, washed with water, methanol and acetone. The crude product was purified by sublimation in a 3-zone furnace to give an orange solid.

EXAMPLE 13

Synthesis of 2,6-Bis-[2-(4-pentylphenyl)-vinyl]-naphthalene (Compound 49)



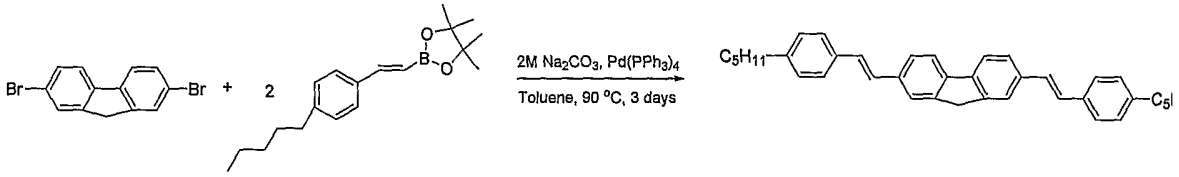
Compound 49

To a mixture of 2,6-dibromonaphthalene (2.29 g, 8.00 mmol) and 2-[2-(4-pentylphenyl)vinyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7.59 g, 24.00 mmol) in toluene (120 ml) was added 2M sodium carbonate (4.24 g dissolved in 20.0 ml of water, 40.00 mmol) followed by the addition of phase-transfer agent Aliquat®336 (1.60 g, 4.00 mmol). The mixture was bubbled with nitrogen for 15 min. Then tetrakis(triphenylphosphine)palladium(0) (185.3 mg, 2 mol%) was added.

The mixture was heated at 90 °C (oil bath) for three days under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol (300 ml). The yellow precipitate was filtered off, washed with dilute acid (5 % HCl), water, methanol, then with acetone. The crude product was purified by sublimation in a 3-zone furnace to give 2.55 g (67 %) of a pale yellow solid.

EXAMPLE 14

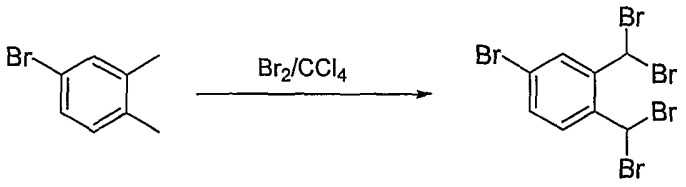
Synthesis of 2,7-Bis-[2-(4-pentyl-phenyl)-vinyl]-9*H*-fluorene (Compound 50)



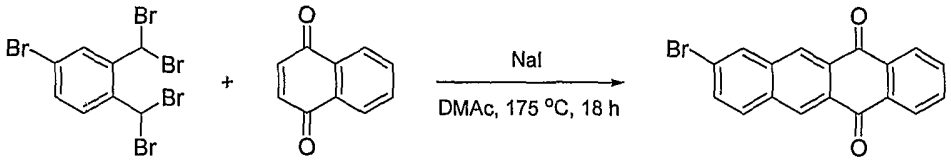
Compound 50

To a mixture of 2,7-dibromofluorene (2.67 g, 8.00 mmol) and 2-[2-(4-pentylphenyl)vinyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7.59 g, 24.00 mmol) in toluene (120 ml) was added 2M sodium carbonate (4.24 g dissolved in 20.0 ml of water, 40.00 mmol) followed by the addition of phase-transfer agent Aliquat®336 (1.60 g, 4.00 mmol). The mixture was bubbled with nitrogen for 15 min. Then tetrakis(triphenylphosphine)palladium(0) (185.3 mg, 2 mol%) was added. The mixture was heated at 90 °C (oil bath) for three days under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol (300 ml). The yellow precipitate was filtered off, washed with dilute acid (5 % HCl), water, methanol, then with acetone. The crude product was purified by sublimation in a 3-zone furnace to give 2.59 g (63 %) of a yellow solid.

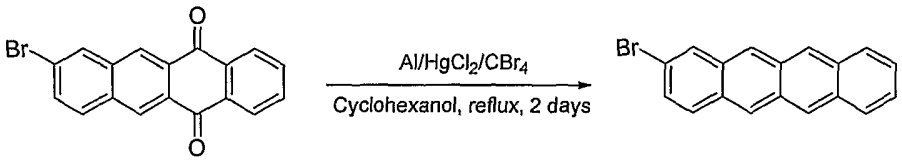
EXAMPLE 15



(a) 4-Bromo-o-xylene (75.00 g, 0.28 mol) was dissolved in 900 ml of CCl_4. Bromine (82.00 ml, 1.60 mol) was added slowly while irradiating with a UV light. After addition the reaction mixture was irradiated for an additional hour. The reaction mixture was then washed with water 2 times, and concentrated in a rotary evaporator. The precipitate was filtered off and washed with hexane, and dried in a vacuum oven (80.59 g, 57%).

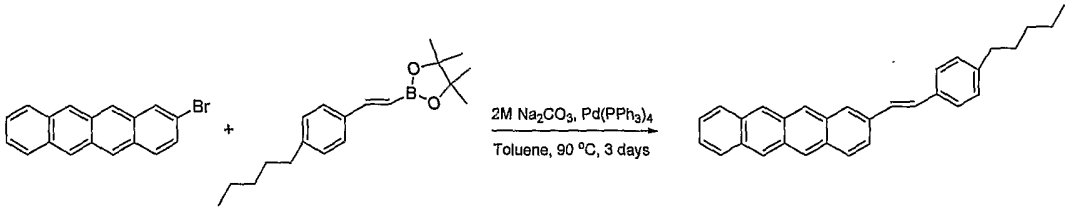


(b) The mixture of 4-bromo-1,2-bis-dibromomethyl-benzene (20.00 g, 0.040 mol), 1,4-naphthoquinone (6.31 g, 0.040 mol) and NaI (68.81 g, 0.46 mol) in 300 ml of DMAc was refluxed for 18 hr. After cooling, the reaction mixture was poured into water. The precipitate was filtered off and washed with MeOH, then purified by sublimation to give a yellow solid product (3.67 g, 27%).



(c) Into a 300 ml of flask was added Al wire (8.67 g, 0.32 mol), $HgCl_2$ (0.17 g, 0.64 mol), cyclohexanol (200 ml) and a catalytic amount of CBr_4 (0.85 g, 0.0026 mol). The mixture was bubbled with nitrogen for 15 min. The reaction was initiated by heating, cooling to slow down the reaction, and

then completed by refluxing for 4 hr. To this solution was added 8-bromo-naphthacene-5,12-dione (12.72 g, 0.032 mol). The mixture was refluxed for 2 days. After cooling down a little bit the reaction mixture was poured into MeOH/H_2O/conc. HCl solution (1/1/1, 800 ml). The precipitate was filtered off, washed with MeOH/H_2O/conc. HCl (1/1/1) and then methanol. The crude product was purified by sublimation in a 3-zone furnace to give pure product (8.97 g, 77%) as an orange solid.



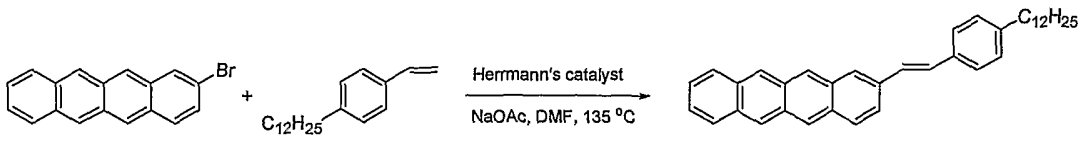
Compound 36

(d) Synthesis of 2-(4-Pentylphenyl)-vinyl]-tetracene (Compound 36)

To a mixture of 2-bromotetracene (3.50 g, 11.39 mmol) and 2-[2-(4-pentylphenyl)vinyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.32 g, 13.67 mmol) in toluene (150 ml) was added 2M sodium carbonate (6.04 g dissolved in 28.5 ml of water, 56.95 mmol) followed by the addition of phase-transfer agent Aliquat®336 (2.28 g, 5.70 mmol). The mixture was bubbled with nitrogen for 15 min. Then tetrakis(triphenylphosphine)palladium(0) (263.0 mg, 2 mol%) was added. The mixture was heated at 90 °C (oil bath) for three days under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol. The precipitate was filtered off, washed with dilute acid (5 % HCl), water, methanol, then with acetone. The crude product was purified by sublimation in a 3-zone furnace to give 2.91 g (64 %) of a red solid.

EXAMPLE 16

Synthesis of 2-(4-Dodecylphenyl)-vinyl]-tetracene (Compound 54)

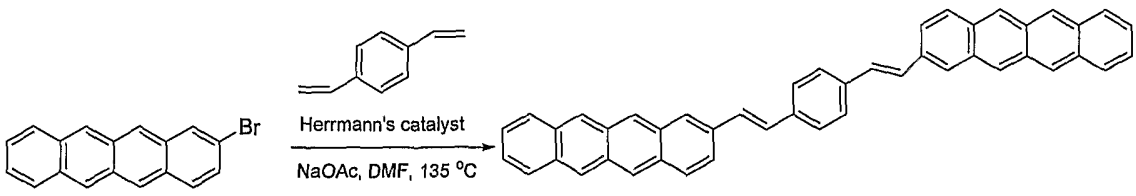


Compound 54

To a mixture of 2-bromotetracene (4.91 g, 15.97 mmol) and 4-dodecylstyrene (5.22 g, 19.00 mmol) in DMF (200 ml, anhydrous) was added sodium acetate (1.97 g, 24.00 mmol). The mixture was bubbled with nitrogen for 15 min. Then trans-di-m-acetatobis[2-(di-o-tolylphosphino)benzyl]dipalladium(II) (15.00 mg, 0.2 mol%) was added. The mixture was heated at 135 °C (oil bath) for 2 days under a nitrogen atmosphere. The reaction mixture was cooled to room temperature. The precipitate was filtered off, washed with water, methanol, chloroform and acetone. The crude product was purified by sublimation in a 1-zone furnace to give 3.60 g (45 %) of a red solid.

EXAMPLE 17

Synthesis of Compound 42



Compound 42

To a mixture of 2-bromotetracene (3.60 g, 11.72 mmol) and p-divinylbenzene (0.51 g, 3.91 mmol) in DMF (80 ml, anhydrous) was added sodium acetate (1.44 g, 17.58 mmol). The mixture was bubbled with nitrogen for 15 min. Then trans-di-m-acetatobis[2-(di-o-tolylphosphino)benzyl]dipalladium(II) (7.5 mg, 0.2 mol%) was added. The

mixture was heated at 135 °C (oil bath) for 2 days under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into methanol. The precipitate was filtered off, washed with water, methanol and acetone. The crude product was purified by sublimation in a 3-zone furnace to give a red solid.

EXAMPLE 18

This example illustrates the fabrication and devices properties of OLEDs made with an aryl-vinylene aromatic compound in the hole transport layer.

ITO was used as the anode on glass substrates. The glass substrate with patterned ITO was cleaned with Oxygen Plasma for 5 minutes. Immediately after cooling, a buffer material (Buffer-1) was spin-coated from an aqueous dispersion over the ITO surface. After drying, the substrates were then transferred into a vacuum deposition chamber and 200 Å of a hole transport material was evaporated. Subsequently a blue light-emitting material and host material were deposited by co-evaporation. An electron transport material was then formed by evaporation. The layer was made of 300 Å of ZrQ or 100 Å of BAlq and 100 Å of ZrQ. A thin, 6 Å film of lithium fluoride was evaporated on top of the ZrQ layer as an electron injection layer. Masks were then changed in vacuo and a 1000 Å layer of Al was deposited by thermal evaporation to form the cathode. The chamber was vented to argon and the devices were encapsulated using a glass lid, dessicant, and UV curable epoxy.

Abbreviations used are as follows:

Buffer-1 refers to an aqueous dispersion of poly(3,4-dioxythiophene) and a polymeric fluorinated sulfonic acid. The material was prepared using a procedure similar to that described in Example 3 of published U.S. patent application no. 2004/0254297.

BAlq refers to the complex bis(2-methyl-8-hydroxyquinolinato)(4-phenylphenolato)aluminum.

ZrQ refers to the complex tetrakis(8-hydroxyquinolinato)zirconium.

NPB, below, refers to N,N'-bis(naphthalen-1-yl)-N,N'-bis-(phenyl)benzidine.

The materials used for the device and the device characteristics are shown in Table 2 below.

Table 2. OLED Device Characteristics

Hole Transport Material	ITO Thick-ness [Å]	Emitter-Host Ratio	Emissive Layer Thickness [Å]	Electron Transport Material	V @ 1000 cd/m^2	Current Efficiency @ 1000 cd/m^2	CIE [x, y] @ 1000 cd/m^2
NPB	1850	1:13	388	ZrQ	6.0	7.2	0.136, 0.135
Compound 3	1850	1:13	388	ZrQ	4.8	1.5	0.153, 0.185
Compound 3	1850	1:4	600	BAlQ / ZrQ	5.7	7.4	0.135, 0.237
Compound 3	1600	1:4	600	BAlQ/ZrQ	5.8	6.7	0.143, 0.181
Compound 1	1850	1:13	540	ZrQ	6.0	2.7	0.148, 0.178
Compound 49	1850	1:4	600	BAlQ/ZrQ	5.3	5.1	0.130, 0.185
Compound 49	1600	1:7	600	BAlQ/ZrQ	5.6	4.0	0.140, 0.154
Compound 50	1850	1:13	450	ZrQ	6.5	6.3	0.136, 0.156

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.

Claims

What is claimed is:

1. An organic thin film transistor comprising:

a substrate

an insulating layer;

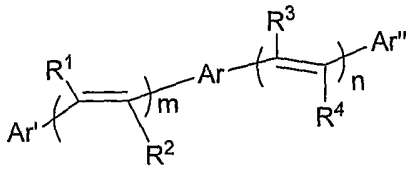
a gate electrode;

an organic semiconductor layer;

a source electrode; and

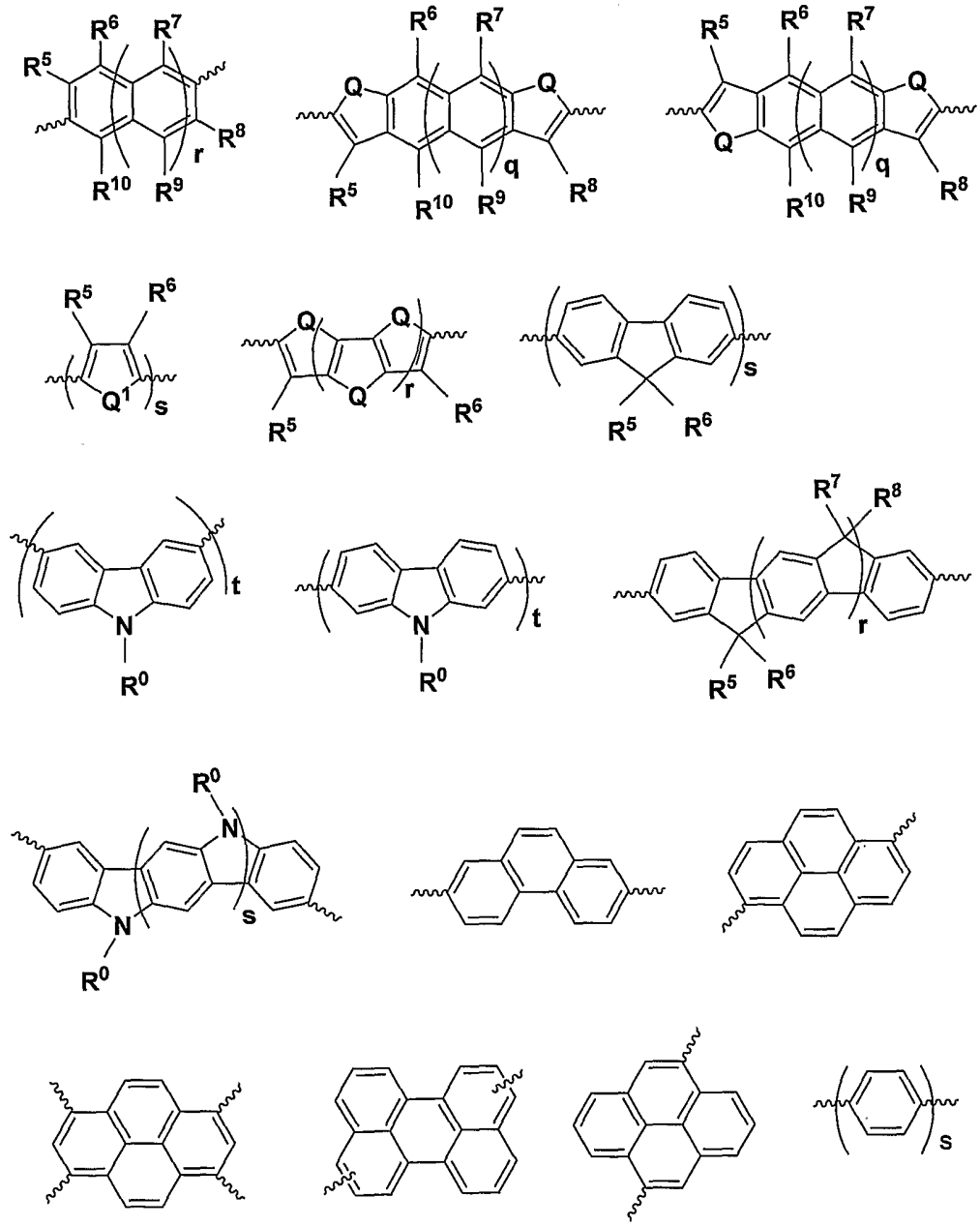
a drain electrode;

wherein the organic semiconductor layer comprises a compound of Formula 1:



Formula 1

wherein Ar is selected from the group consisting of:



and combinations thereof,

wherein:

Ar', and Ar" are selected independently from the group consisting of aryl groups;

m and n are integers each independently having a value of from 0 to 5, where $m + n \neq 0$;

Q is selected from the group consisting of S, Se, Te, O, and NR^0;

Q^1 is selected from the group consisting of Se, Te, O, and NR^0;

q and r are selected independently from the group consisting of 0, 1, 2, 3, 4, and 5;

s is an integer having a value of from 1 to 5;

t is an integer having a value of from 2 to 5;

R^0 is selected from the group consisting of hydrogen, alkyl, and aryl;

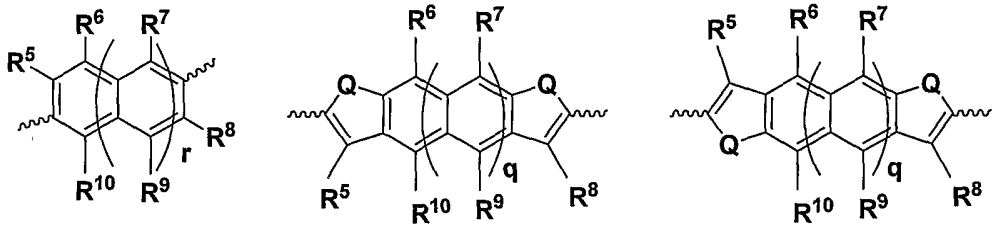
R^1 through R^{10} are selected independently from the group consisting of hydrogen, alkyl, aryl, halogen, hydroxyl, aryloxy, alkoxy, alkenyl, alkyny, amino, alkylthio, phosphino, silyl, -COR, -COOR, $-PO_3R_2$, $-OPO_3R_2$, and CN; and

R is selected from the group consisting of hydrogen, alkyl, aryl, alkenyl, alkynyl, and amino;

wherein any two adjacent groups, R^5 through R^{10} can be taken together to form a ring.

2. The transistor of Claim 1, wherein $r \neq 0$, and $s \neq 0$ or 1.

3. The transistor of Claim 1, wherein Ar is selected from the group consisting of:



and combinations thereof,

wherein $r \neq 0$.

4. The transistor of Claim 1, wherein the insulating layer, the gate electrode, the semiconductor layer, the source electrode and the drain electrode are arranged in any sequence, provided that the gate electrode and the semiconductor layer both contact the insulating layer,

the source electrode and the drain electrode both contact the semiconductor layer, and the electrodes are separated from each other.

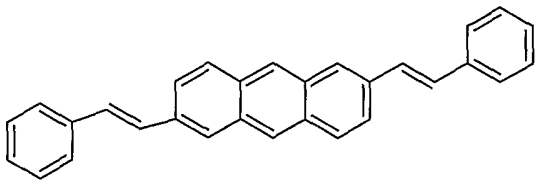
5. The transistor of Claim 1, wherein the substrate comprises one or more inorganic glass, ceramic foil, acrylic, epoxy, polyamide, polycarbonate, polyimide, polyketone, poly(oxy-1, 4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene), polynorbornene, polyphenyleneoxide, poly(ethylene naphthalenedicarboxylate), poly(ethylene terephthalate), poly(phenylene sulfide), fiber-reinforced plastic, or coated metallic foil.

6. The transistor of Claim 1, wherein the gate electrode comprises a doped silicon; aluminum; gold; chromium; indium tin oxide; polystyrene sulfonate-doped poly(3,4-ethylenedioxythiophene) (PSS-PEDOT); carbon black or graphite dispersed in a polymer binder; and a colloidal silver dispersion in a polymer binder.

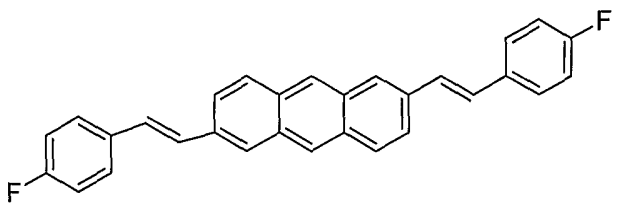
7. The transistor of Claim 1, wherein the source and drain electrodes comprise aluminum, barium, calcium, chromium, gold, silver, nickel, palladium, platinum, titanium, and alloys thereof; carbon nanotubes; polyaniline; poly(3,4-ethylenedioxythiophene)/poly-(styrene sulfonate) (PEDOT:PSS); dispersion of carbon nanotubes in conducting polymers; dispersion of a metal in a conducting polymer; and multilayers thereof.

8. The transistor of Claim 1, wherein the insulating layer comprises one or more aluminum oxide, silicon oxide, tantalum oxide, titanium oxide, silicon nitride, barium titanate, barium strontium titanate, barium zirconate titanate, zinc selenide, zinc sulfide, and alloys, combinations, and multilayers thereof; one or more polyester, polycarbonate, poly(vinyl phenol), polyimide, polystyrene, poly(methacrylate), poly(acrylate), epoxy resin, and blends and multilayers thereof.

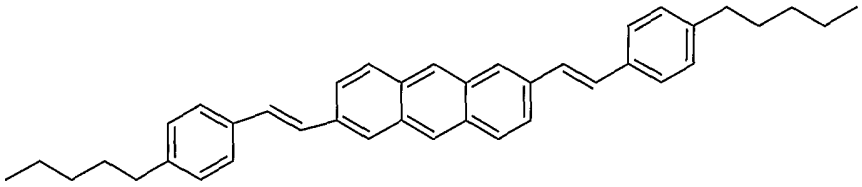
9. The transistor of Claim 1 wherein the semiconductor compound is selected from the group consisting of Compounds 1 - 64:



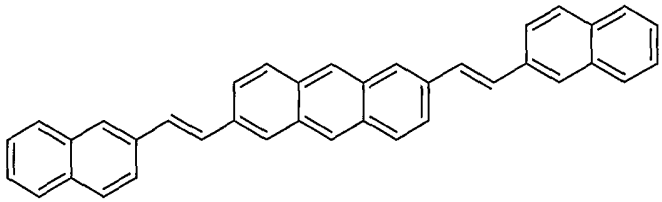
Compound 1



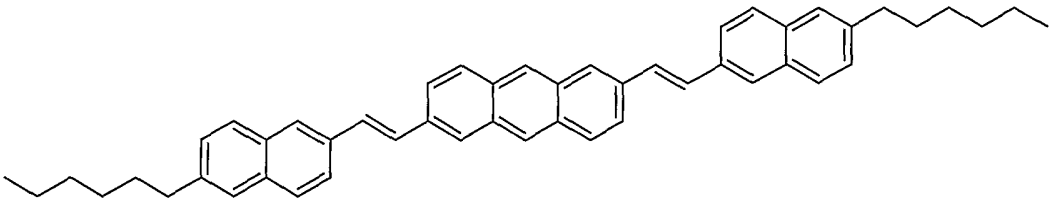
Compound 2



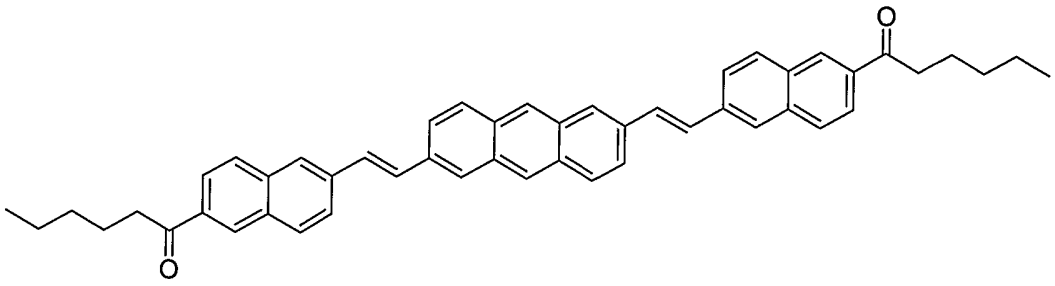
Compound 3



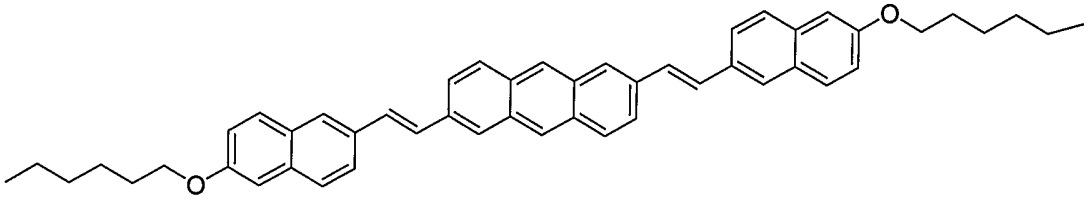
Compound 4



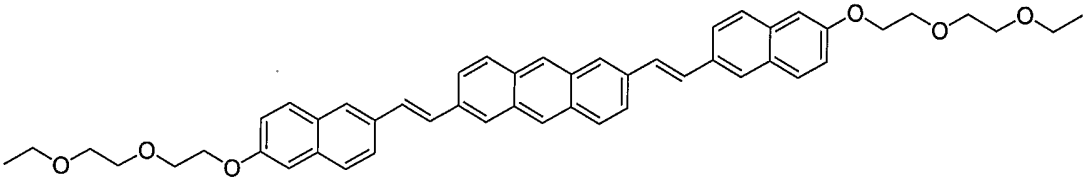
Compound 5



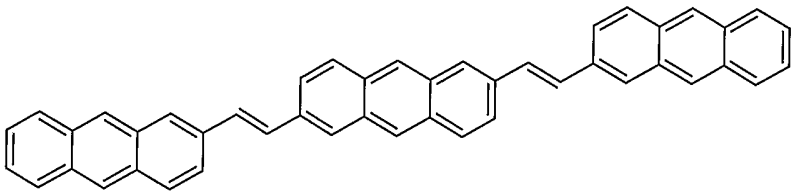
Compound 6



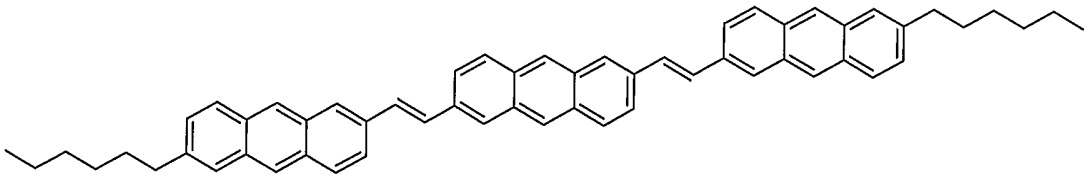
Compound 7



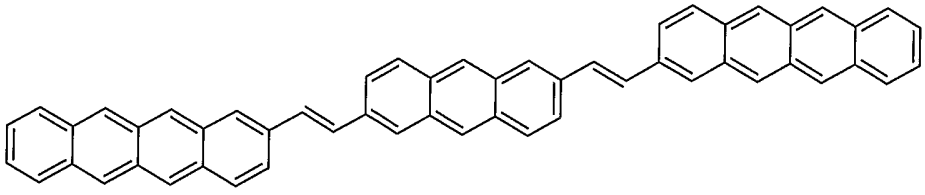
Compound 8



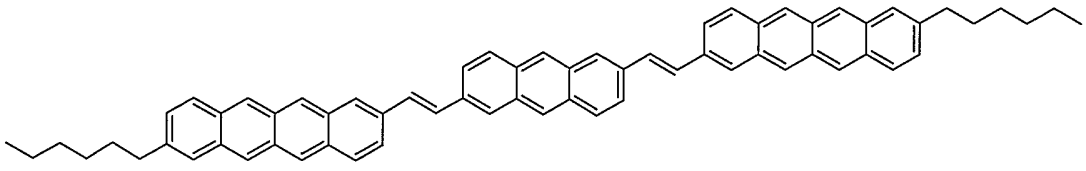
Compound 9



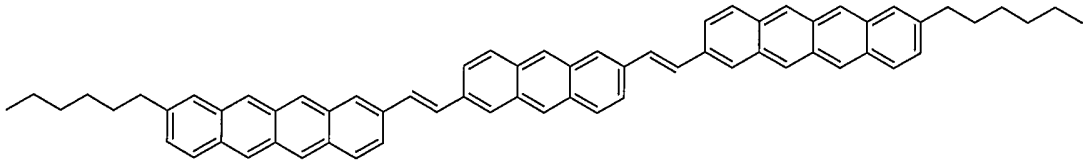
Compound 10



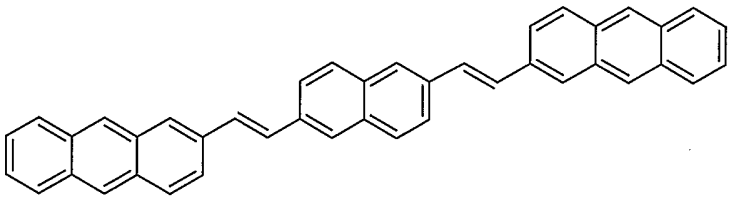
Compound 11



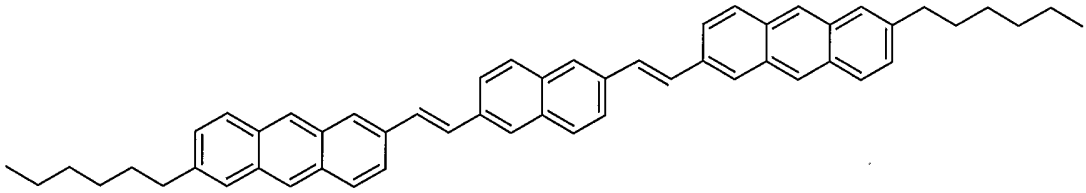
Compound 12



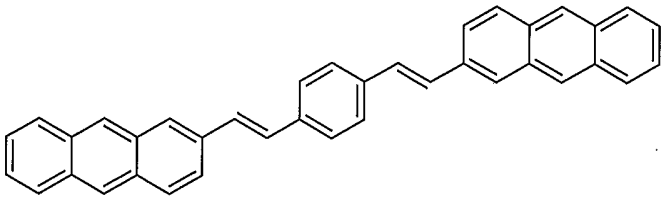
Compound 13



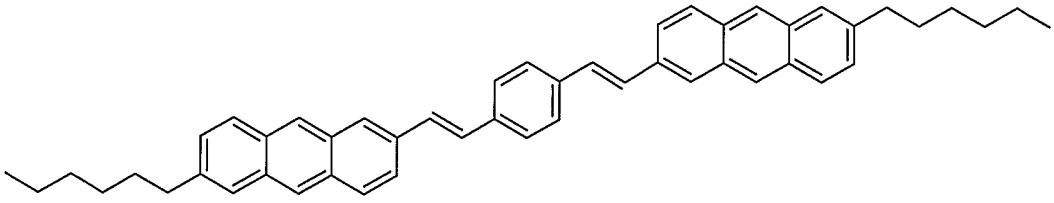
Compound 14



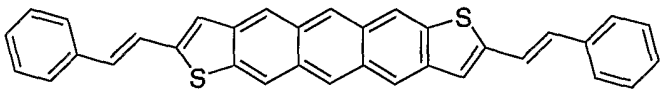
Compound 15



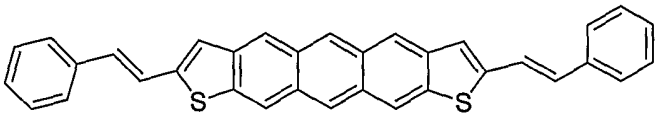
Compound 16



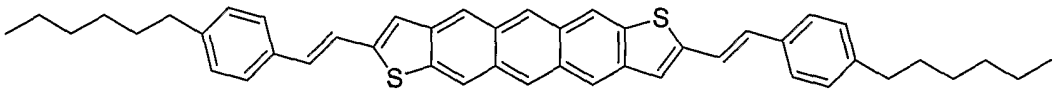
Compound 17



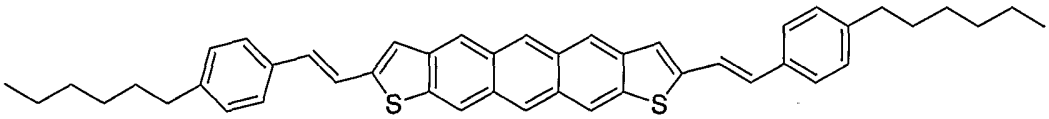
Compound 18



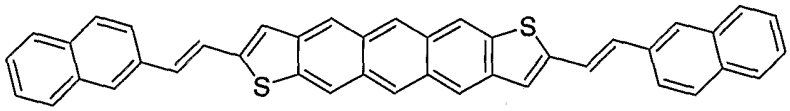
Compound 19



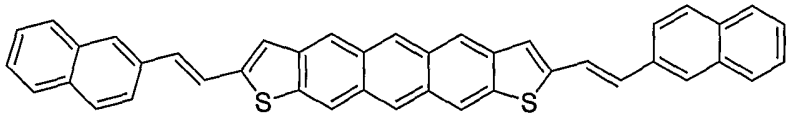
Compound 20



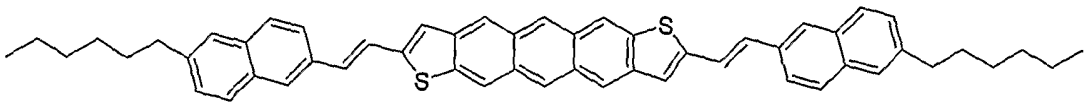
Compound 21



Compound 22



Compound 23



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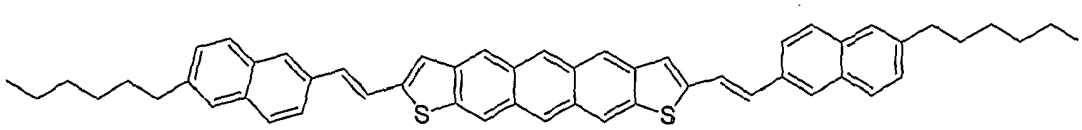

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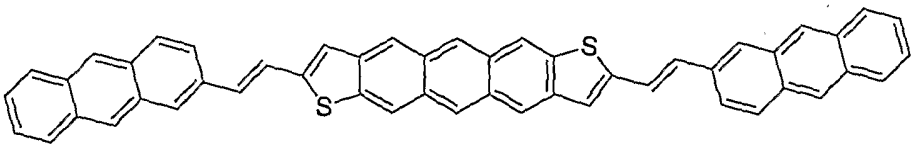

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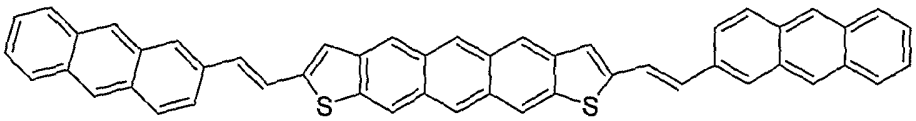

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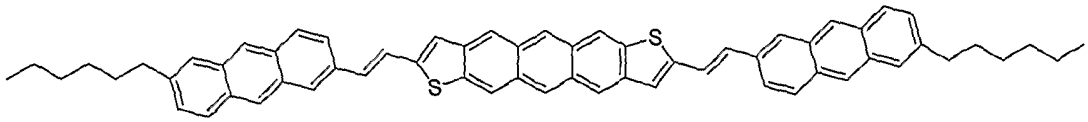

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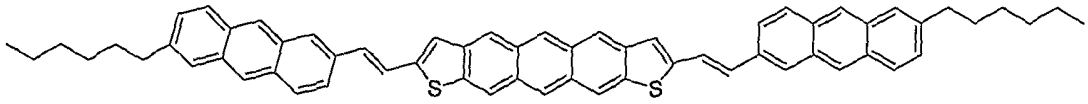

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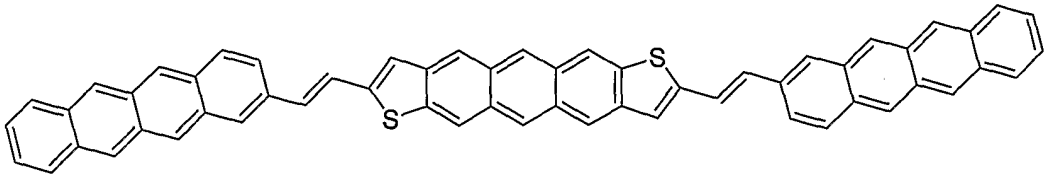

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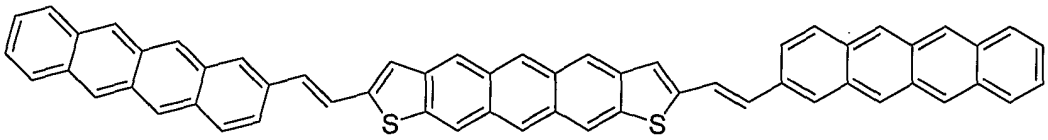

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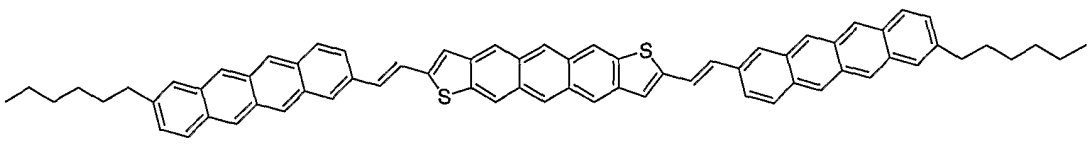

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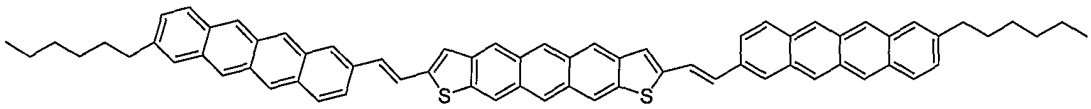

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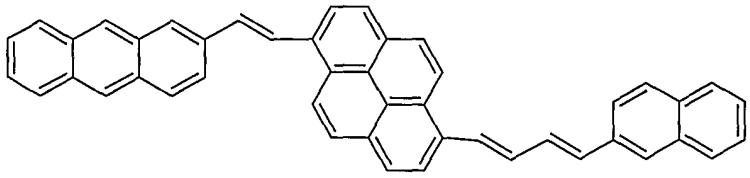

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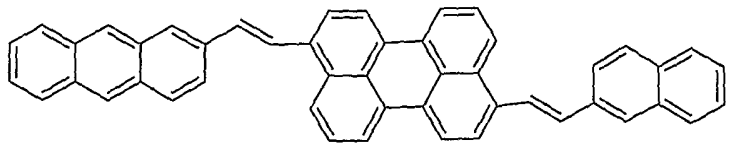

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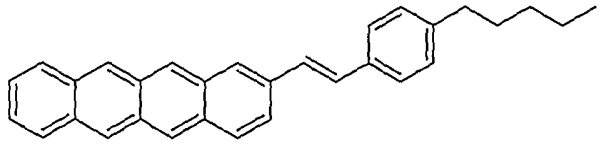

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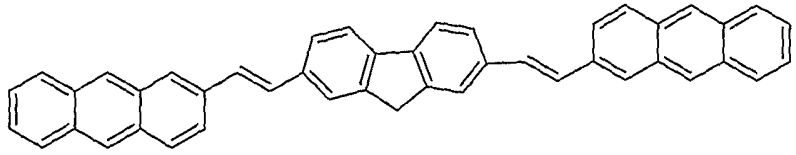

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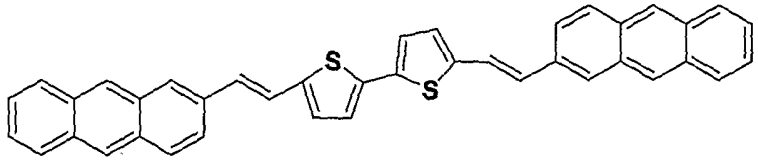

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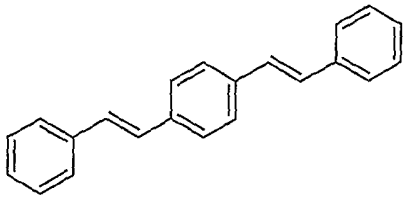

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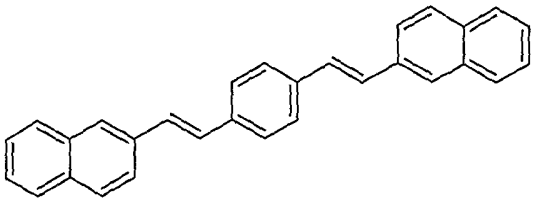

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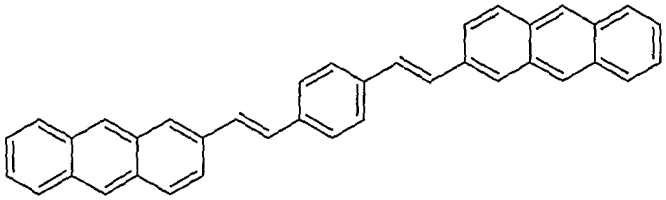

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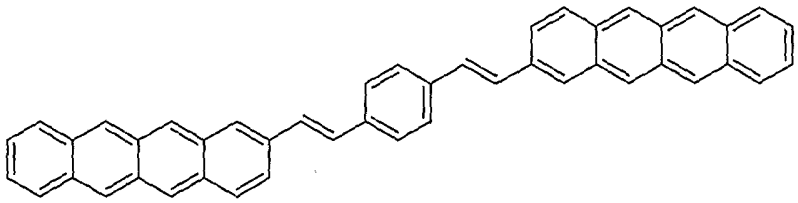

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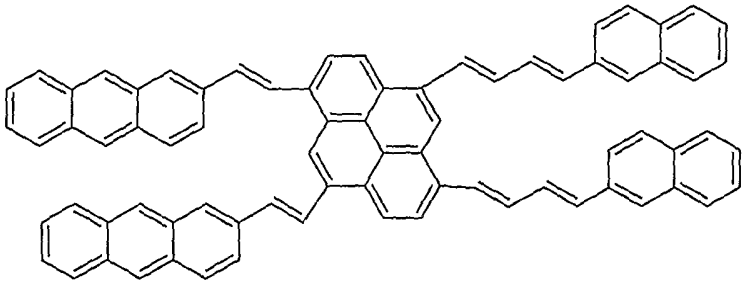

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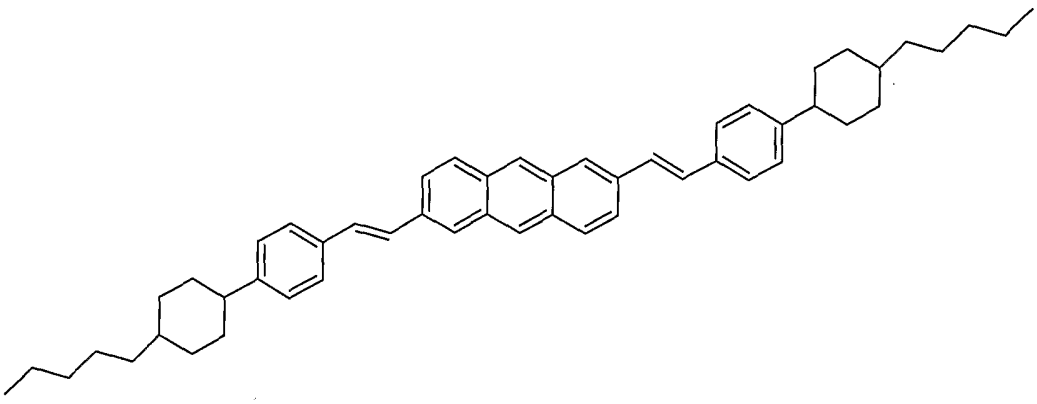

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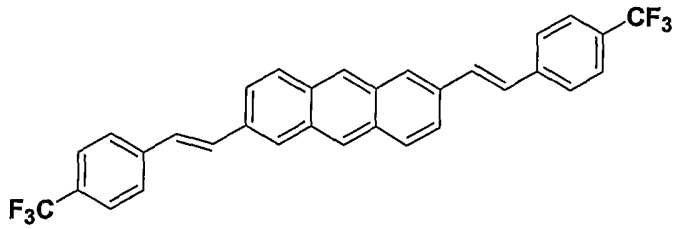

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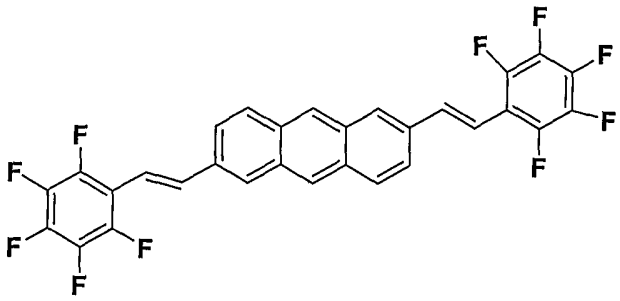

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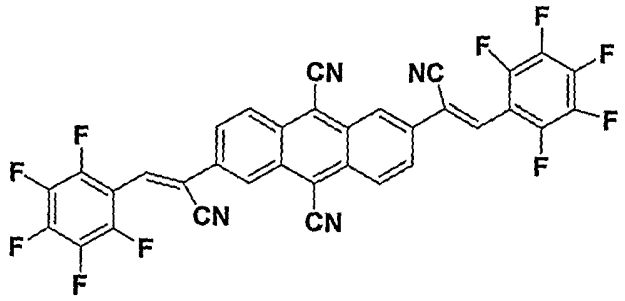

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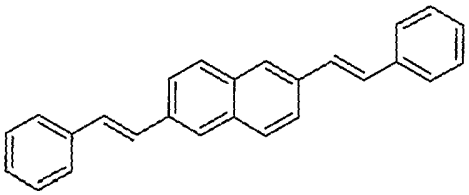

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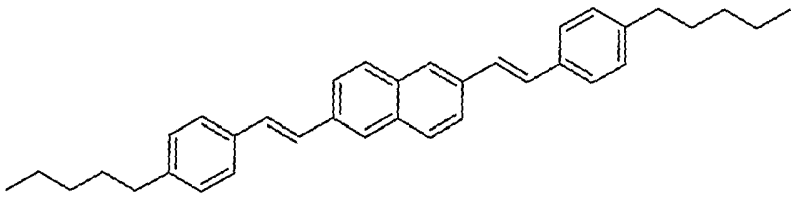

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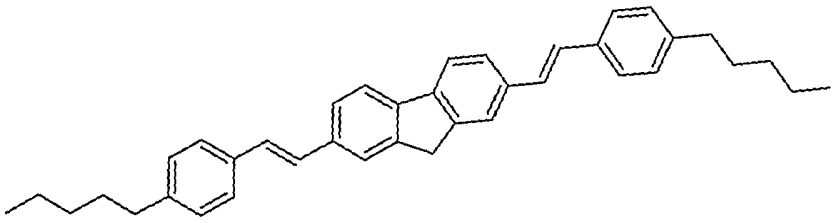

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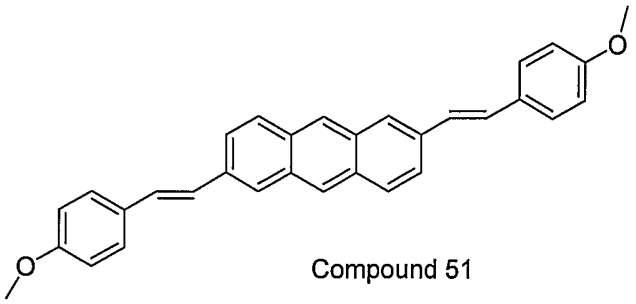

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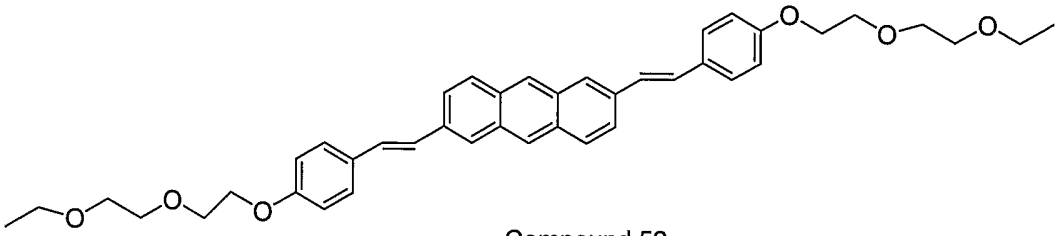

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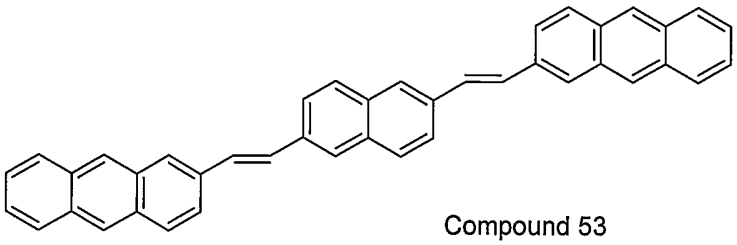

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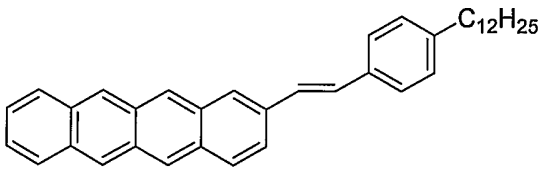

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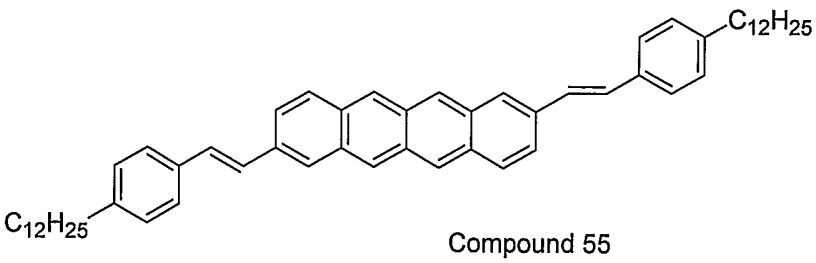

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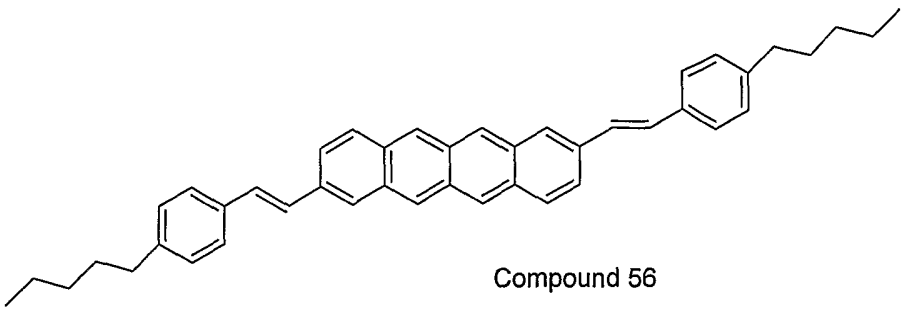

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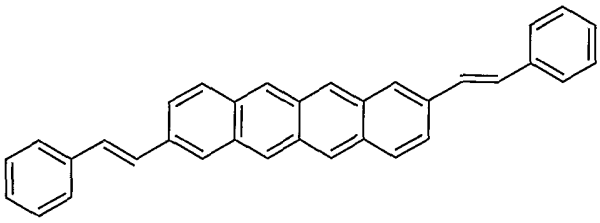

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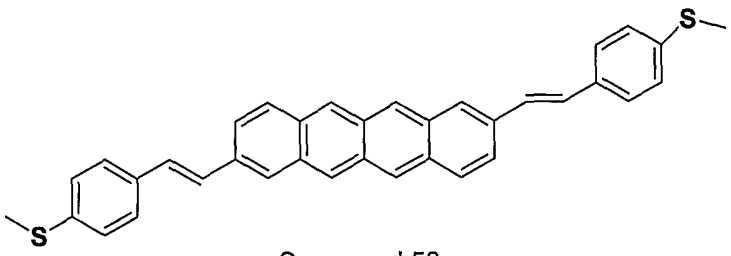

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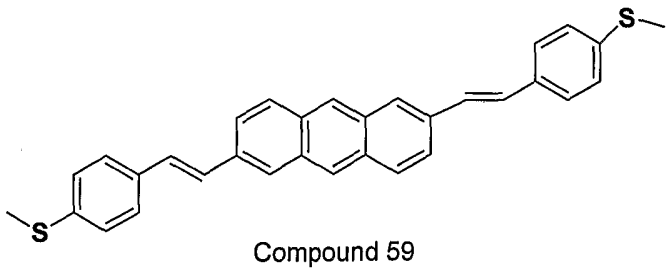

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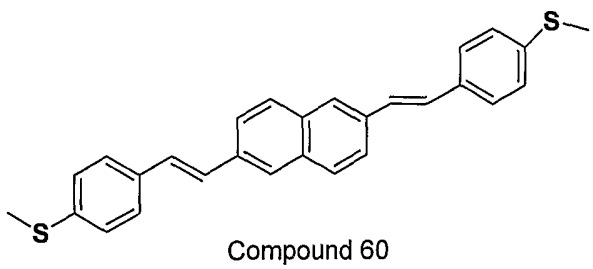

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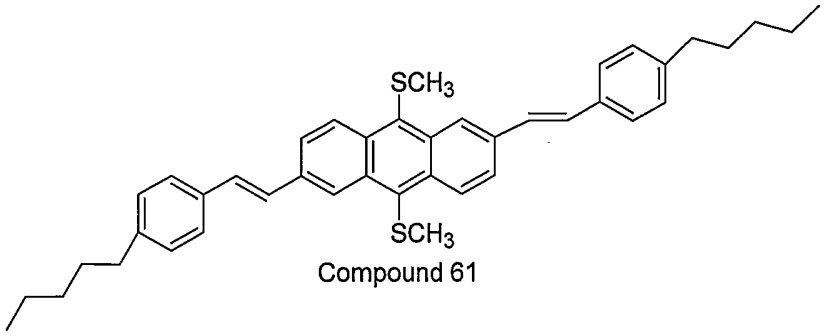

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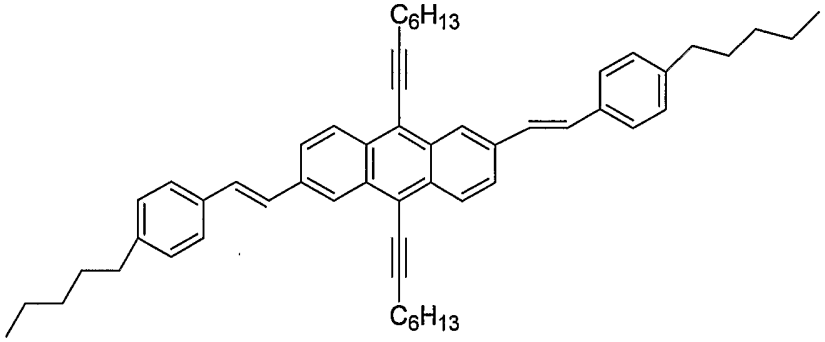
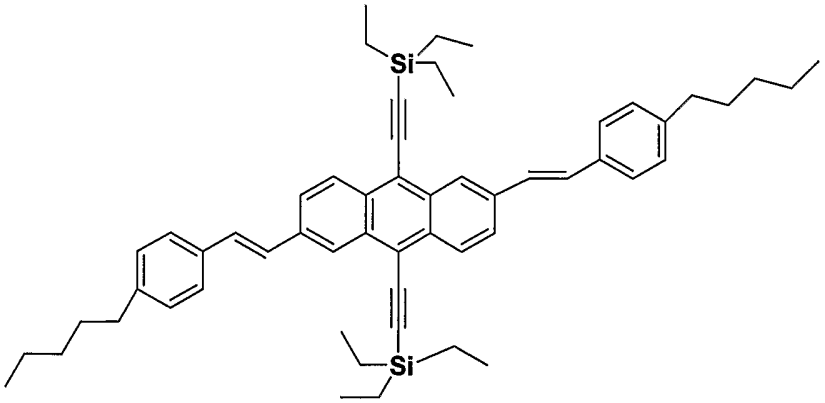
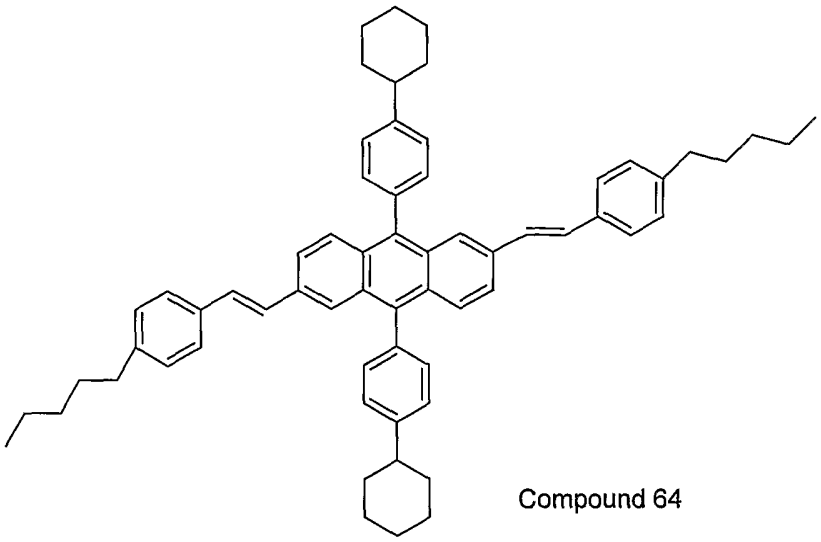


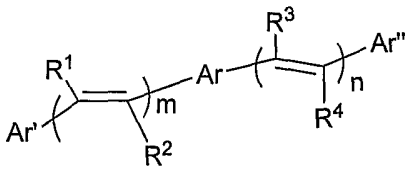
Compound 62



Compound 63



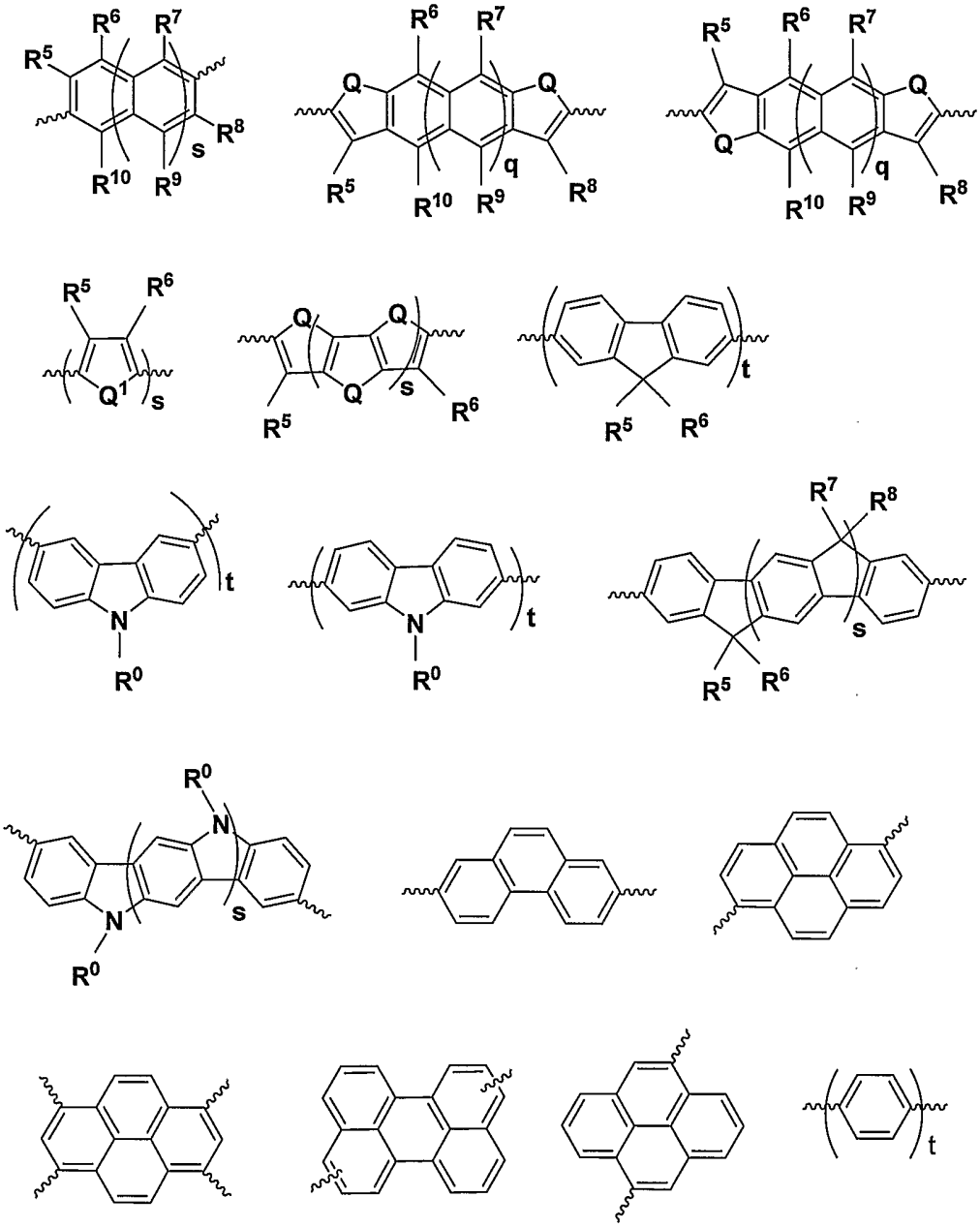
Compound 64



10. A compound represented by Formula 1:

Formula 1

wherein Ar is selected from the group consisting of:



wherein:

Ar', and Ar" are independently selected from the group consisting of aryl groups;

m and n are integers each independently having a value of from 0 to 5, where $m + n \neq 0$;

Q is selected from the group consisting of S, Se, Te, O, and NR^0;

Q^1 is selected from the group consisting of Se, Te, O, and NR^0;

q, and r are integers each independently having a value of from 0 to 5;

s is an integer having a value of from 1 to 5;

t is an integer having a value of from 2 to 5;

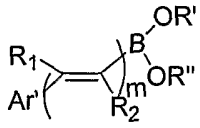
R^0 is selected from the group consisting of hydrogen, alkyl, and aryl;

R^1 through R^{10} are selected independently from the group consisting of hydrogen, alkyl, aryl, halogen, hydroxyl, aryloxy, alkoxy, alkenyl, alkyny, alkylthio, phosphino, silyl, -COR, -COOR, -PO_3R_2, -OPO_3R_2, and CN; and

R is selected from the group consisting of hydrogen, alkyl, aryl, alkenyl, and alkynyl;

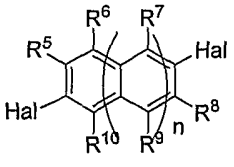
wherein any two adjacent groups, R^5 through R^{10} can be taken together to form a ring.

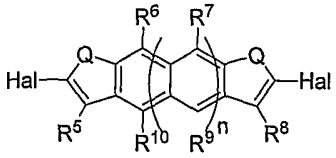
11. A method for preparing an aryl-ethylene acene, comprising reacting a diboronic compound of Formula 2

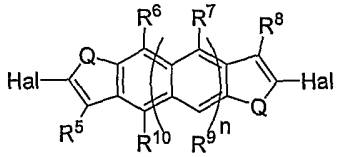


Formula 2

with a dihaloarylene compound selected from the group consisting of







Hal =Cl, Br, I

n = 0, 1, 2, 3

in the presence of a zero-valent Pd complex to form an aryl-ethylene acene compound,

wherein

m and n are integers each independently having a value of from 0 to 3;

R' and R" are independently H or alkyl;

Hal is independently selected from a group consisting of Cl, Br, and I;

Ar' is an aryl group;

Q is selected from the group consisting of S, Se, Te, O, or NR^0;

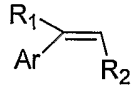
R^1, R^2, and R^5 through R^{10} are selected independently from the group consisting of hydrogen, alkyl, aryl, halogen, hydroxyl, aryloxy, alkoxy, alkenyl, alkyny, amino, alkylthio, phosphino, silyl, -COR, -COOR, $-PO_3R_2$, $-OPO_3R_2$, and CN;

R is selected from the group consisting of hydrogen, alkyl, aryl, alkenyl, alkynyl, and amino; and

R^0 is hydrogen, alkyl, or aryl;

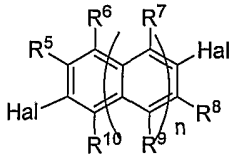
wherein any two adjacent groups, R^5 through R^{10} can be taken together to form a ring.

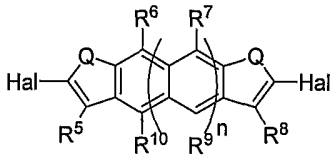
12. A method for preparing an aryl-ethylene acene, comprising reacting an aryl-substituted ethylene compound of Formula 3

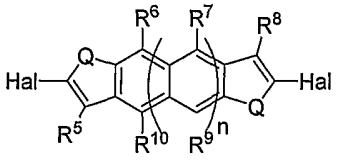


Formula 3

with a dihaloarylene compound selected from the group consisting of







Hal =Cl, Br, I

n = 0, 1, 2, 3

in the presence of a zero-valent Pd complex to form an aryl-ethylene acene compound,

wherein

m and n are integers each independently having a value of from 0 to 3;

R' and R" are independently H or alkyl;

Hal is independently selected from a group consisting of Cl, Br, and I;

Ar' is an aryl group;

Q is selected from the group consisting of S, Se, Te, O, and NR^0;

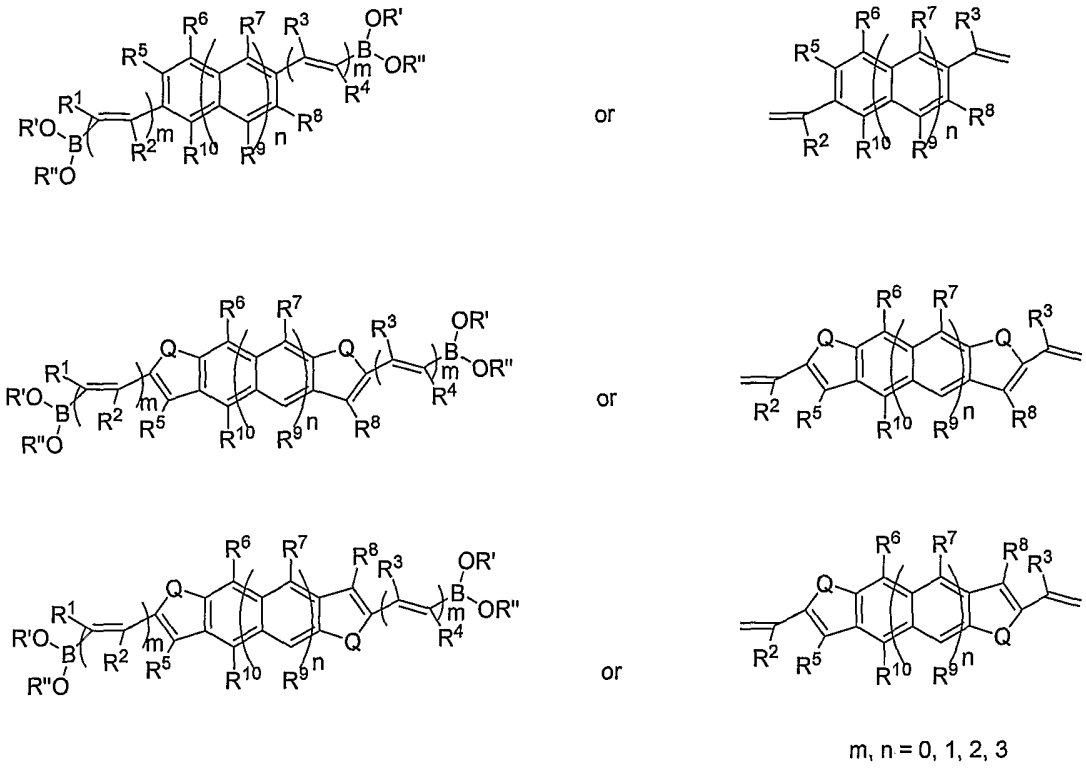
R^1, R^2, and R^5 through R^{10} are selected independently from the group consisting of hydrogen, alkyl, aryl, halogen, hydroxyl, aryloxy, alkoxy, alkenyl, alkyny, amino, alkylthio, phosphino, silyl, -COR, -COOR, $-PO_3R_2$, $-OPO_3R_2$, and CN;

R is selected from the group consisting of hydrogen, alkyl, aryl, alkenyl, alkynyl, and amino; and

R^0 is hydrogen, alkyl, or aryl;

wherein any two adjacent groups, R^5 through R^{10} can be taken together to form a ring.

13. A method for preparing an aryl-ethylene acene, comprising reacting an acene derivative selected from the group consisting of



with a halo-aryl compound, Ar-Hal, in the presence of a zero-valent Pd complex,

wherein

m and n are integers each independently having a value of from 0 to 3;

R' and R" are independently H or alkyl;

Hal is independently selected from the group consisting of Cl, Br, and I;

Ar' is an aryl group;

Q is selected from the group consisting of S, Se, Te, O, and NR^0;

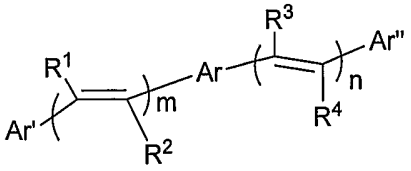
R^1, R^2, and R^5 through R^{10} are selected independently from the group consisting of hydrogen, alkyl, aryl, halogen, hydroxyl, aryloxy, alkoxy, alkenyl, alkyny, amino, alkylthio, phosphino, silyl, -COR, -COOR, $-PO_3R_2$, $-OPO_3R_2$, and CN;

R is selected from the group consisting of hydrogen, alkyl, aryl, alkenyl, alkynyl, and amino; and

R^0 is hydrogen, alkyl, or aryl;

wherein any two adjacent groups, R^5 through R^{10} can be taken together to form a ring.

14. An organic electronic device comprising a charge transport layer comprising at least one compound represented by Formula 1



Formula 1

Ar is an arylene group;

Ar', and Ar" are independently selected from the group consisting of aryl groups;

R^1 through R^4 are selected independently from the group consisting of hydrogen, alkyl, aryl, halogen, hydroxyl, aryloxy, alkoxy, alkenyl, alkyny, amino, alkylthio, phosphino, silyl, -COR, -COOR, -PO_3R_2, -OPO_3R_2, and CN;

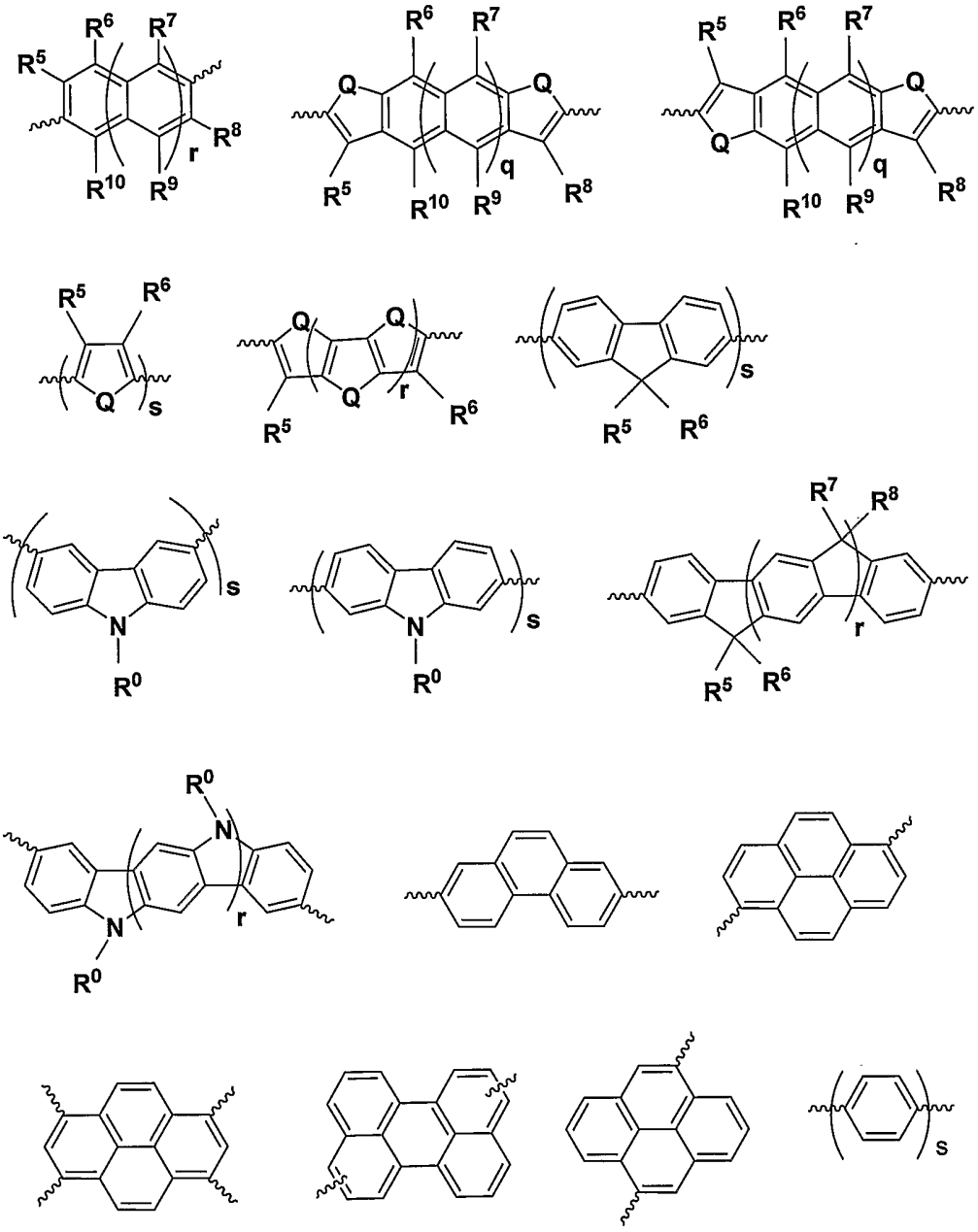
R is selected from the group consisting of hydrogen, alkyl, aryl, alkenyl, alkynyl, and amino; and

m and n are integers each independently having a value of from 0 to 5, where $m + n \neq 0$,

and further wherein there are no diarylamino groups.

15. The device of Claim 14, wherein Ar is selected from the group consisting of fused polycyclic aromatic groups and aromatic groups having at least two rings joined by a single bond.

16. The device of Claim 14, wherein Ar is selected from



and combinations thereof,

wherein:

Q is selected from the group consisting of S, Se, Te, O, or NR^0

q, and r are integers each independently having a value of from 0 to 5;

s is an integer having a value of from 1 to 5;

R^0 is selected independently from the group consisting of hydrogen, alkyl, and aryl;

R^5 through R^{10} are selected independently from the group consisting of hydrogen, alkyl, aryl, halogen, hydroxyl, aryloxy, alkoxy, alkenyl, alkyny, amino, alkylthio, phosphino, silyl, -COR, -COOR, $-PO_3R_2$, $-OPO_3R_2$, and CN; and

R is selected from the group consisting of hydrogen, alkyl, aryl, alkenyl, alkynyl, and amino;

wherein any two adjacent groups, R^5 through R^{10} can be taken together to form a ring.

17. The device of Claim 14, wherein Ar is selected from at least one of the group consisting of 2,6-naphthalene, substituted 2,6-naphthalene, 2,6-anthracene, substituted 2,6-anthracene, 2,6-fluorene, substituted 2,6-fluorene, 2,6-carbazole, substituted 2,6-carbazole, and combinations thereof.

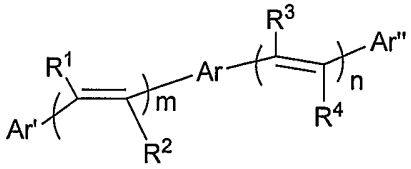
18. The device of Claim 14, wherein Ar' and Ar" are independently selected from unsubstituted aryl groups and substituted aryl groups, and substituents of said aryl groups are independently selected from the group consisting of alkyl, aryl, thioalkyl, silyl, alkylaryl, alkoxy, alkylether, etheralkyl, fluorine, and combinations thereof.

19. The device of Claim 14, further comprising an anode, a cathode, and a photoactive layer positioned therebetween.

20. The device of Claim 19, wherein the charge transport layer is a hole transport layer and is positioned between the photoactive layer and the anode.

21. The device of Claim 19, wherein the charge transport layer is an electron transport layer and is position between the photoactive layer and the cathode.

22. An organic electronic device comprising an anode, a cathode, and a photoactive layer positioned therebetween, wherein the photoactive layer comprises at least one compound represented by Formula 1



Formula 1

wherein:

Ar is an arylene group;

Ar', and Ar" are independently selected from the group consisting of aryl groups;

R^1 through R^4 are selected independently from the group consisting of hydrogen, alkyl, aryl, halogen, hydroxyl, aryloxy, alkoxy, alkenyl, alkyny, amino, alkylthio, phosphino, silyl, -COR, -COOR, -PO_3R_2, -OPO_3R_2, and CN;

R is selected from the group consisting of hydrogen, alkyl, aryl, alkenyl, alkynyl, and amino; and

m and n are integers each independently having a value of from 0 to 5, where $m + n \neq 0$,

and further wherein there are no diarylamino groups.

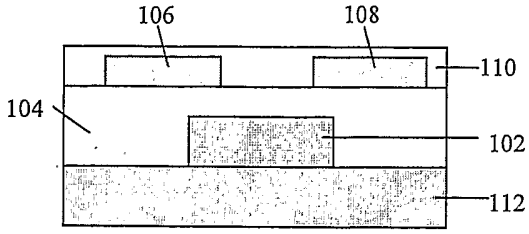


FIG. 1A

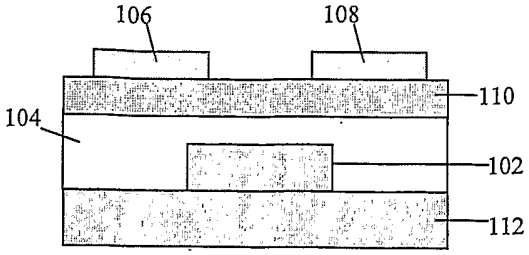


FIG. 1B

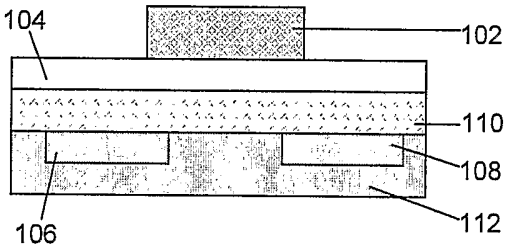


FIG. 1C

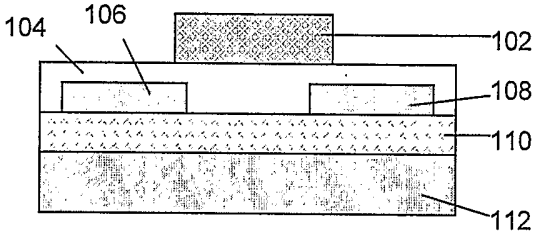


FIG. 1D

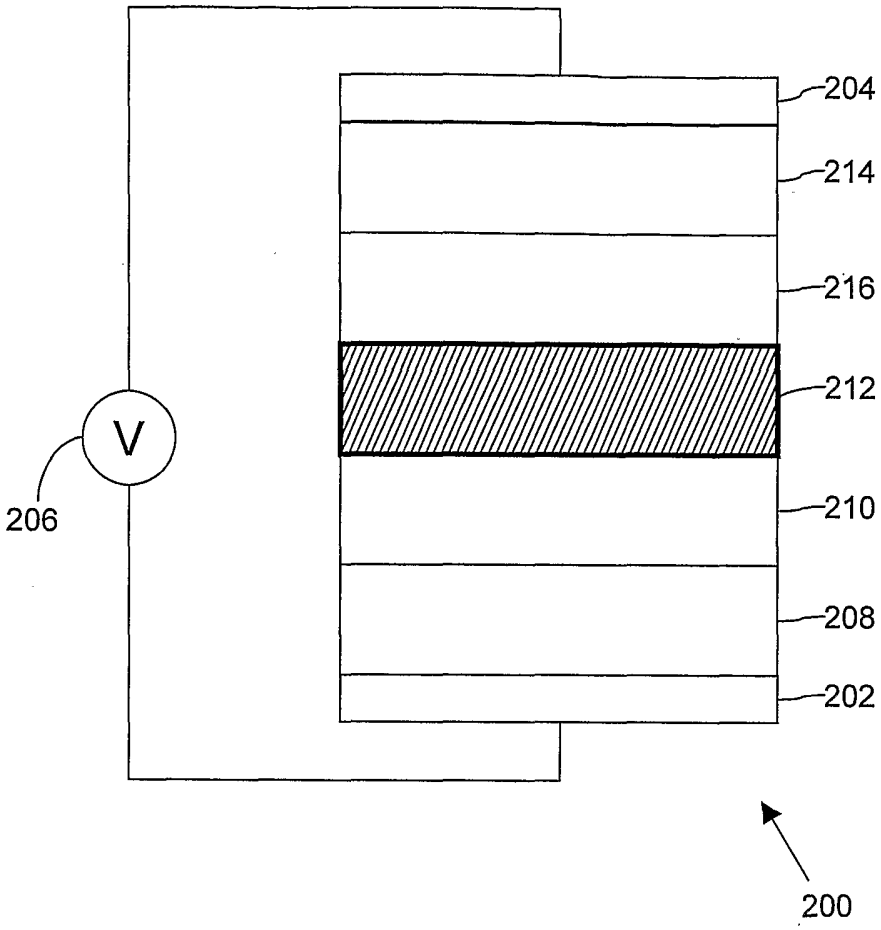


FIG. 2