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(54) Title: COMPOUNDS AND DEVICES CONTAINING SUCH COMPOUNDS

(57) Abstract: Disclosed herein are novel compounds. Such compounds may be synthesized using a hexadehydro-Diels- Alder (HDD A) reaction. Also disclosed are organic devices including one or more disclosed compounds. The organic devices can include organic electronic devices, organic photonic devices, or combinations thereof. Specific types of devices can include, for example, organic light-emitting diodes (OLEDs), organic photovoltaic (OPV) devices, organic field-effect transistors (OFETs), or combinations thereof.

COMPOUNDS AND DEVICES CONTAINING SUCH COMPOUNDS

5 GOVERNMENT FUNDING

This invention was made with government support under CA076497 and GM065597 awarded by the National Institutes of Health. The government has certain rights in the invention.

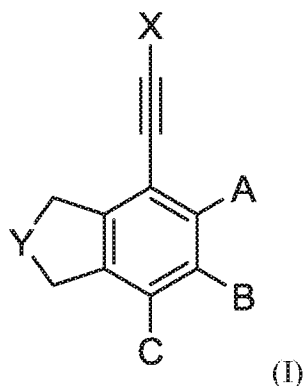
PRIORITY

10 This application claims priority to United States Provisional Application Numbers 62/362,952 filed on July 15, 2016 entitled COMPOUNDS AND DEVICES CONTAINING SUCH COMPOUNDS and 62/362,962 filed on July 15, 2016 entitled COMPOUNDS AND DEVICES CONTAINING SUCH COMPOUNDS, the disclosures of which are incorporated herein by reference thereto in their entirety.

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SUMMARY

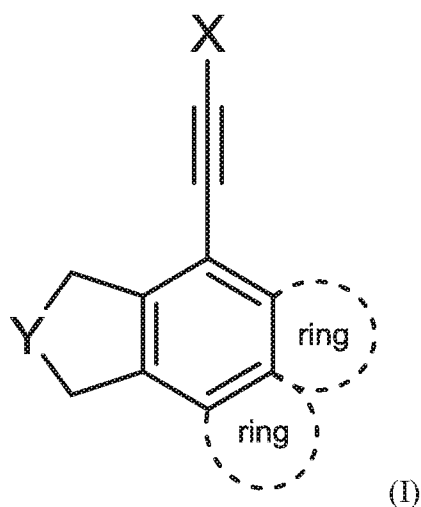
Disclosed are compounds of formula I



where Y can be selected from $(R^1O_2C)_2C$, O, CH_2 , NR^2 with R^2 being SO_2R^3 , aryl, alkyl, $C(=O)R^4$; and R^1 , R^3 and R^4 independently selected from H, substituted or unsubstituted
20 branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof. X can be selected from SiR^5_3 , $C(=O)R^4$, CO_2R^4 , $CONR^4_2$, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted

aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof, where R^4 is as defined above and R^5 is selected from H, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof. A, B, and C are independently selected from H, SiR^5_3 , substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof, $C(=O)R^4$, CO_2R^4 , $CONR^4_2$, $C\equiv CR^2$ where R^2 , R^3 , R^4 and R^5 are independently defined as above.

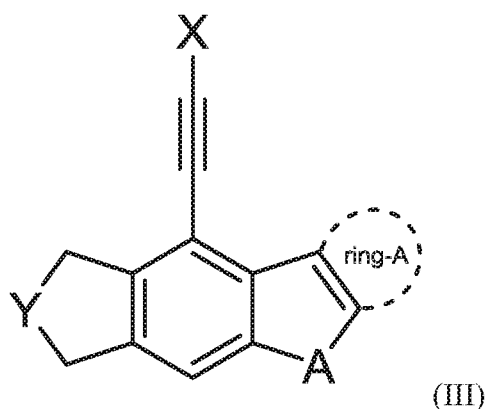
Disclosed herein are compounds of formula II:



where Y can be $(R^1_2O_2C)_2C$, O, CH_2 , NR^3 , where R^2 is SO_2R^3 , aryl, alkyl, $C(=O)R^4$ and R^1 , R^3 and R^4 are independently selected from hydrogen (H) and substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof; X can be selected from SiR^5_3 , $C(=O)R^4$, CO_2R^4 , $CONR^4_2$, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof, where R^4 is as defined above and R^5 is selected from H, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof; and ring is selected from benzo-, naphtheno-, or anthracenofurano-, -thiofurano-, or

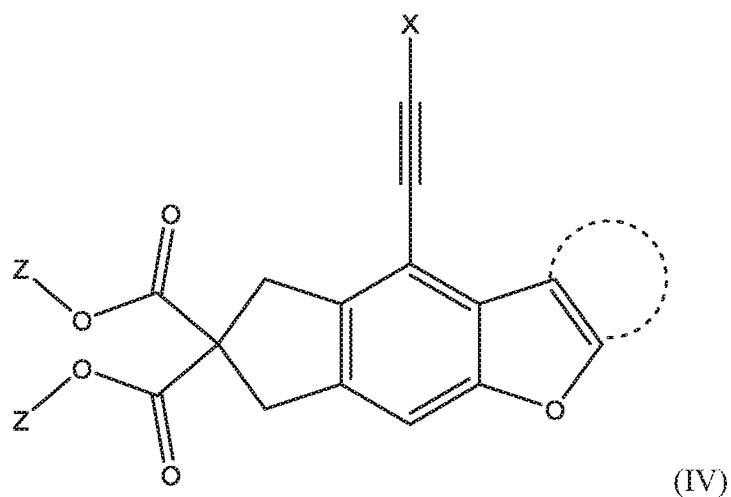
indolo, where the indolo nitrogen can bear R^2 (the ring structure, as indicated by the connection of the general “ring” can connect to two or three of the carbons on the main structure).

Also disclosed herein are compounds of formula III:



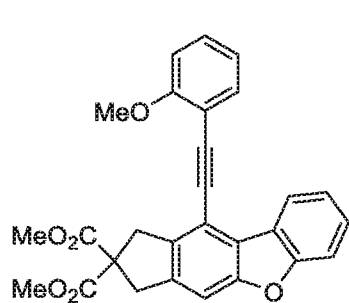
- 5 where Y can be $(R^1_2O_2C)_2C$, O, CH_2 , NR^3 , where R^2 is SO_2R^3 , aryl, alkyl, $C(=O)R^4$ and R^1 , R^3 and R^4 are independently selected from hydrogen (H) and substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof; X can be selected from SiR^5_3 , $C(=O)R^4$, CO_2R^4 , $CONR^4_2$, substituted or unsubstituted
- 10 branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof, where R^4 is as defined above and R^5 is selected from H, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof;
- 15 A can be O, S, or NR^1 where R^1 is as defined above; ring-A can be selected from benzo-1,2-naphtheno-, 2,3-naphtheno-, 1,2-anthraceno-, 2,3-anthraceno-, 9,10-phenanthreno- as well as any substituted derivatives thereof.

Also disclosed herein are compounds of formula IV:

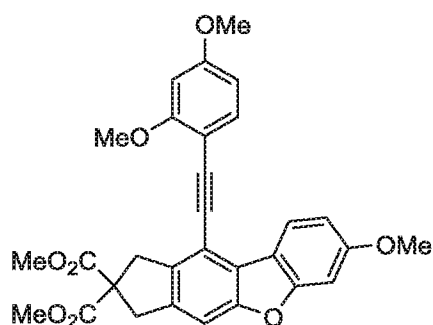


where X can be selected from hydrogen (H), substituted or unsubstituted alkyl groups, fluoroalkyl groups, substituted or unsubstituted aryl groups, esters, halides, alkoxy groups, aryloxy groups, or combinations thereof; Z can independently be selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted heteroaryls, or combinations thereof.

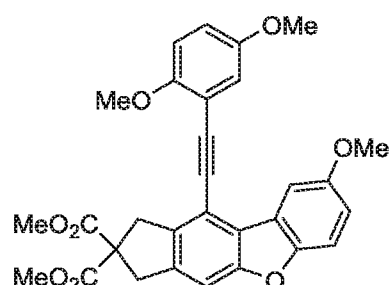
Specific illustrative examples of compounds of formula I, II, III and/or IV can include compounds **100** to **110** and **2000** to **2004**, and **2006** to **2007** below.



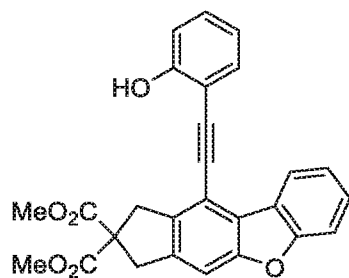
100



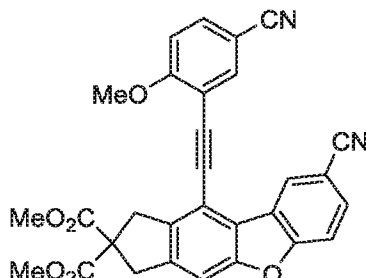
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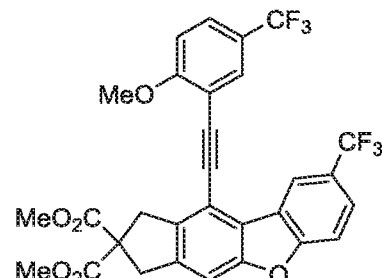
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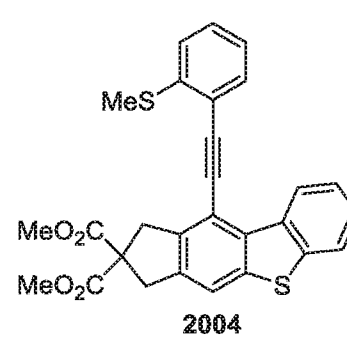
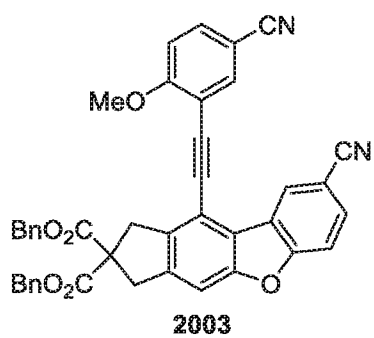
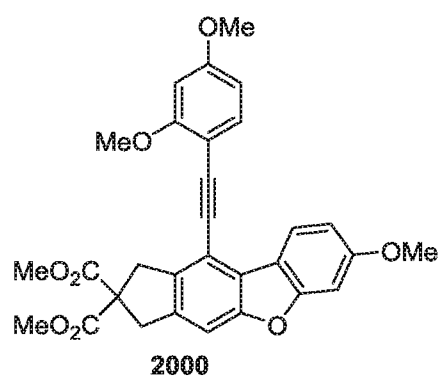
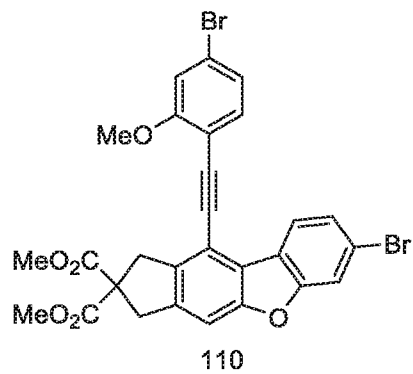
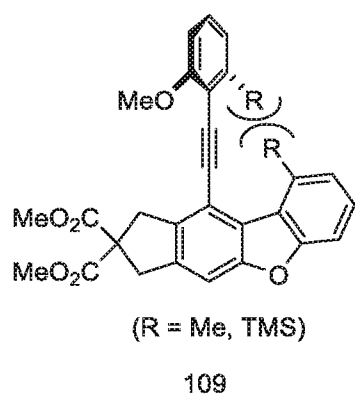
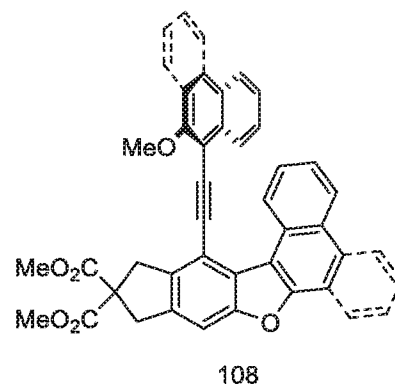
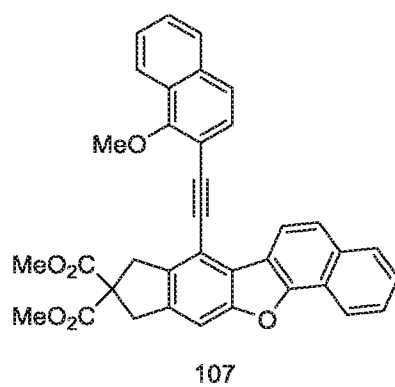
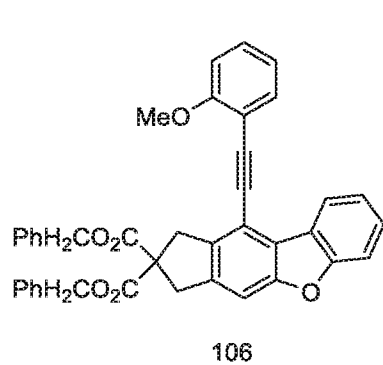
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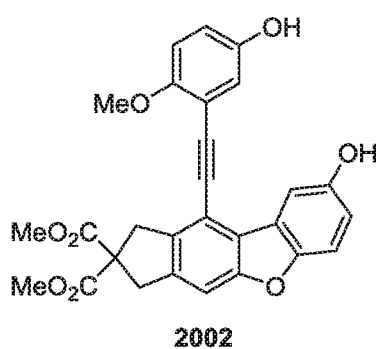
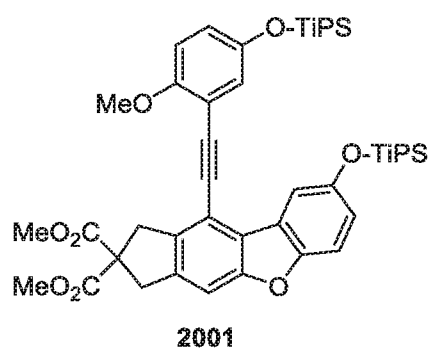
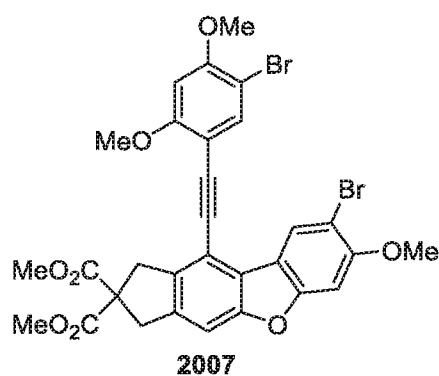
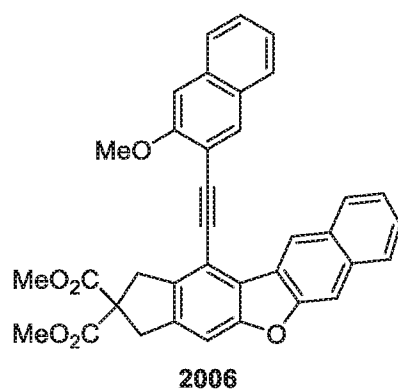


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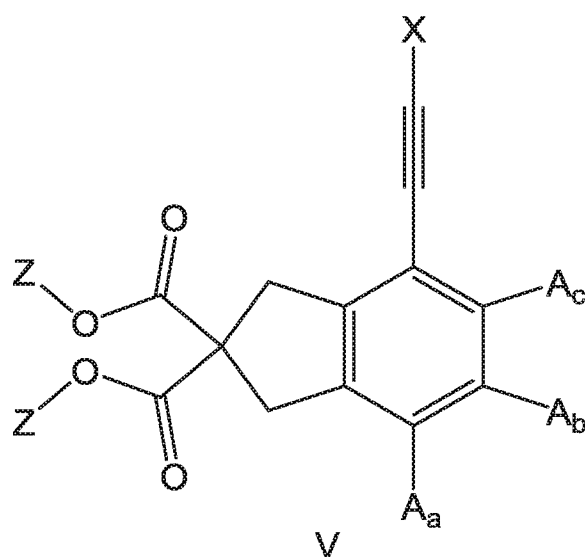


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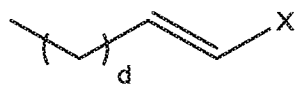
Also disclosed are compounds of formula V:



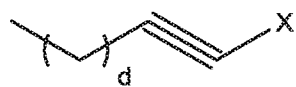
5

where X can be selected from hydrogen, substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, esters, amides, ketones, sulfates, sulfonyls, phosphates, phosphonates, or combinations thereof; Z can independently be selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted heterocyclic

aromatic groups; A can be independently selected from



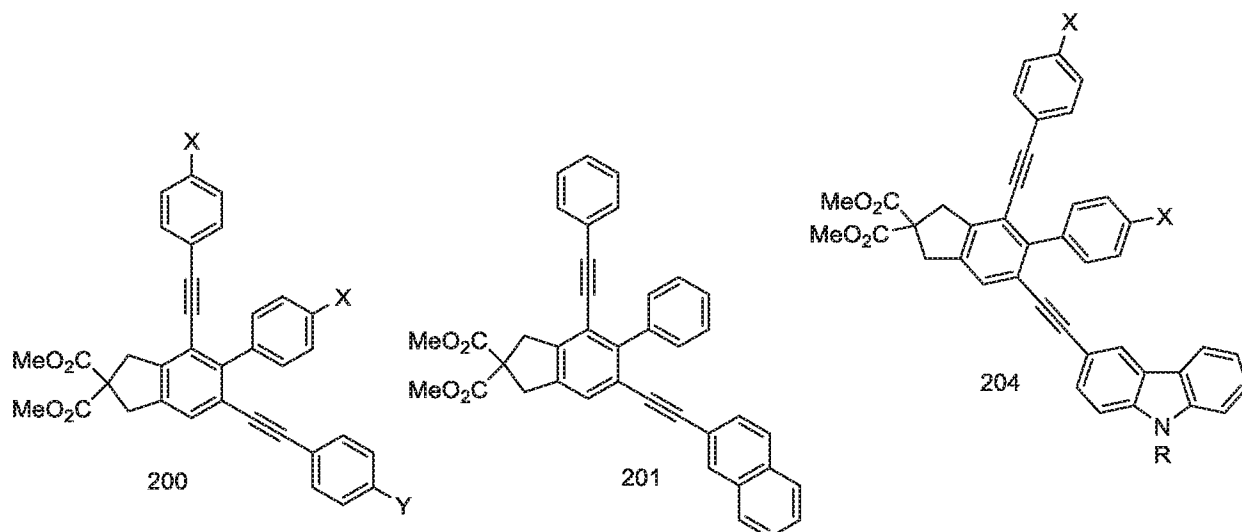
, and

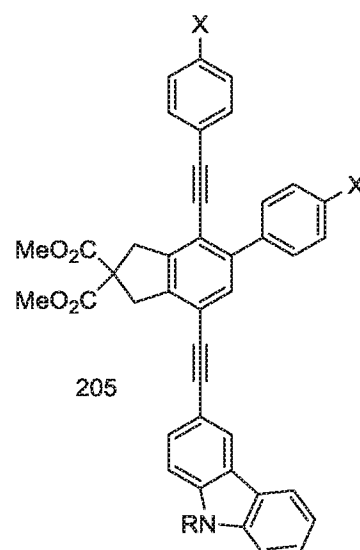
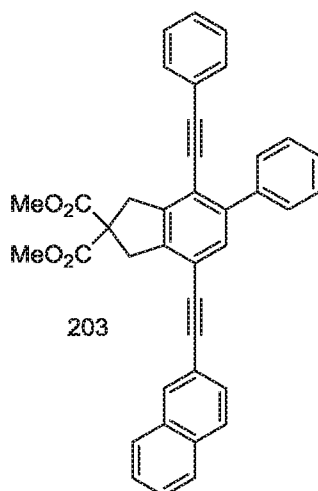
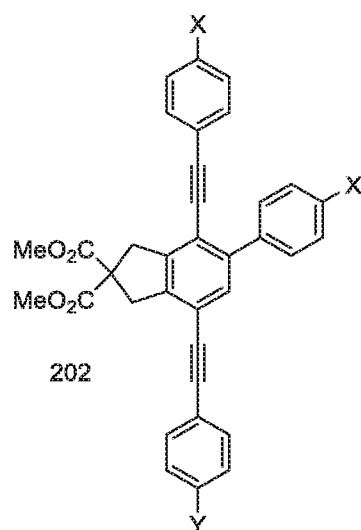


, where X is as indicated above and d is an integer from 0 to 6; and a, b and c are 0 or 1 with the caveat that only 1 of a and b can be, but need not be 1.

Specific illustrative examples of compounds of formula V can include compounds **200** to

205 below.



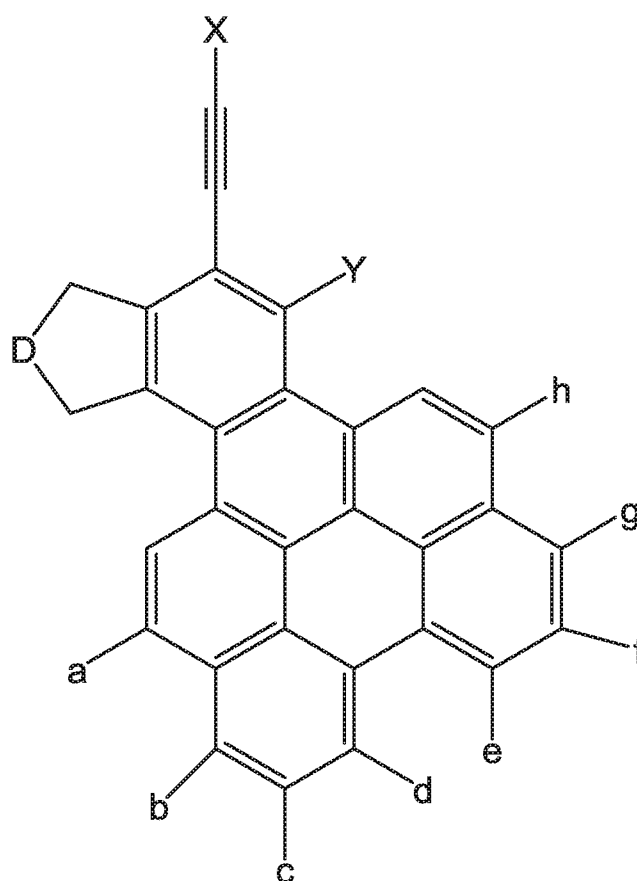


In compounds 200 to 205, the following substituents can include the following:

X=Y= H;	
X=Y=OMe;	X=CO ₂ Me;
X=Y=CO ₂ Me;	Y=NPh ₂
X=Y=CN	

In Compound 205, R can be an alkyl, aryl, sulfonyl or carbonyl-containing functional group.

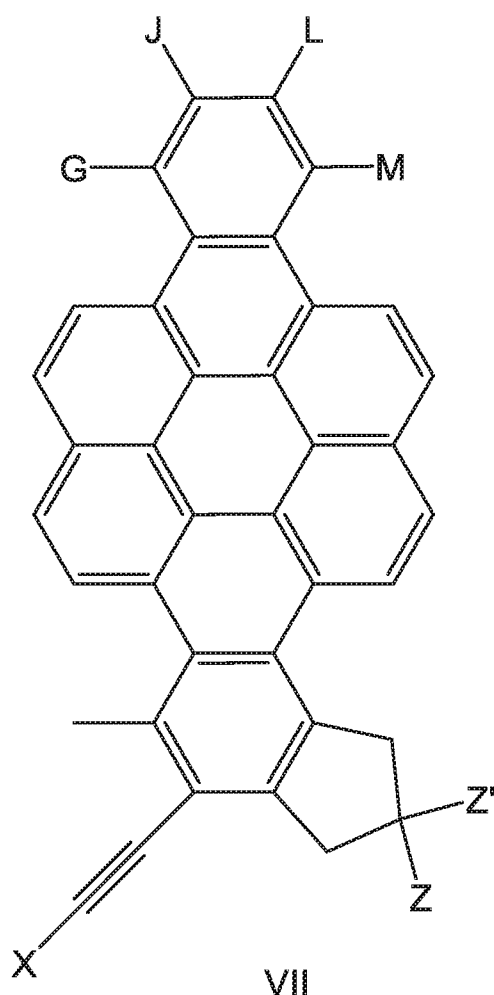
Also disclosed are compounds of formula VI:



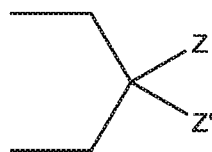
VI

where X and Y can independently be selected from hydrogen, substituted or unsubstituted alkyl groups, aryl groups, esters, halides, alkoxy groups, aryloxy groups, or combinations thereof; D is selected from N-alkyl, N-sulfonyl, N-acyl, N-protecting group, O, $C(CO_2Z)_2$ where Z can independently be selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted heterocyclic aromatic groups; a, b, c, d, e, f, g and h are independently H or $C(O_2)alkyl$, or a and b, g and h, or both a and b and g and h together are embedded in a common, five- or six-membered ring, imide ring (e.g., $—CO—NR—CO—$, where R can be H or an alkyl, cycloalkyl, or aryl substituent).

Also disclosed are compounds of formula VII:



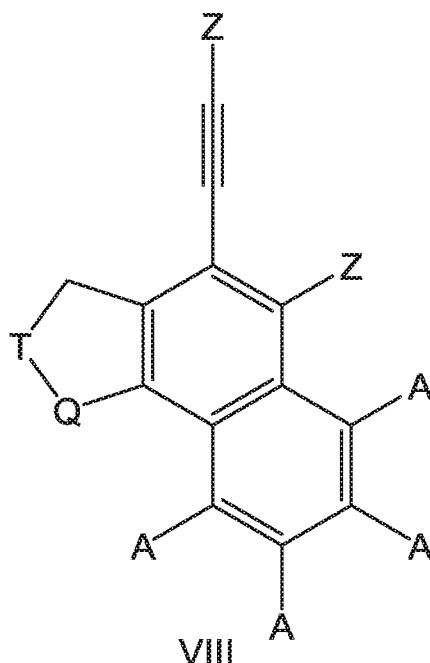
where X can be selected from hydrogen, substituted or unsubstituted alkyl groups, aryl groups, esters, esters, halides, alkoxy groups, aryloxy groups, or combinations thereof; Z and Z' can independently be selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted alkoxy groups, substituted or unsubstituted ester groups, substituted or unsubstituted heterocyclic aromatic groups; G and M are independently selected from hydrogen, substituted or unsubstituted alkyl groups, aryl groups, esters, or combinations thereof; J and L are $\text{---}\equiv\text{---X}$, where X is as defined above, or G together with J, L together with M, or both G together with J and L together with M forms



, where Z and Z' can be independently selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted

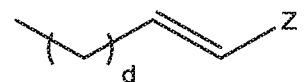
alkoxy groups, substituted or unsubstituted ester groups, substituted or unsubstituted heterocyclic aromatic groups.

Also disclosed are compounds of formula VIII:



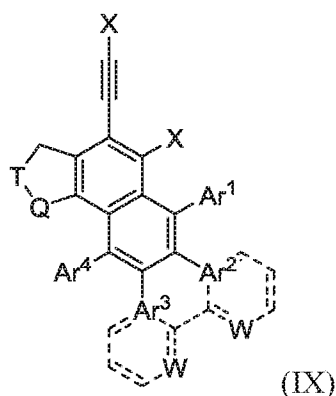
- 5 where Q is a substituted or unsubstituted N or substituted or unsubstituted C; Z can independently be selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted alkoxy groups, substituted or unsubstituted ester groups, substituted or unsubstituted heterocyclic aromatic groups; A can be

independently selected from substituted or unsubstituted aryl groups,



- 10 where Z is as indicated above and d is an integer from 0 to 6, or two adjacent A can together form a conjugated ring structure having at least 3 additional members in the ring; and T is $-\text{C}(\text{CO}_2\text{Z})$, a substituted or unsubstituted N, or a substituted or unsubstituted C.

Also disclosed are compounds of Formula IX:



where T can be $(R^1)_2O_2C$, O, CH_2 , NR^3 , where $R^2 = SO_2^3$, aryl, alkyl, $C(=O)R^4$ and R^1 , R^3 and R^4 are independently selected from hydrogen (H) and substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl

(including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations

thereof and Q can be CH_2 ; or T can be CH_2 and Q can be NR^2 , with R^2 being SO_2^3 , aryl, alkyl, $C(=O)R^4$ and R^1 , R^3 and R^4 are independently selected from hydrogen (H) and substituted or

unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or

combinations thereof. Each X can independently be selected from SiR^5_3 , substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof, $C(=O)R^4$, CO_2R^4 , $CONR^4_2$ where R^4 and R^5 can independently be selected

from H, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof. Ar1, Ar2, Ar3, Ar4 are independently selected from aryl substituents (phenyl, naphthyl, anthracenyl, and phenanthrenyl), including substituted aryls. In some embodiments, Ar2 and Ar3 can be joined to one another and further fused with benzo($W=CH$)- or pyrido($W=N$)- rings.

Any of the above compounds can be synthesized using a hexadehydro-Diels-Alder (HDDA) reaction.

Also disclosed are organic devices including one or more disclosed compounds. The organic devices can include organic electronic devices, organic photonic devices, or combinations thereof. Specific types of devices can include, for example organic light-emitting

diodes (OLEDs), organic photovoltaic (OPV) devices, organic field-effect transistors (OFETs), or combinations thereof.

The above summary of the invention is not intended to describe each disclosed embodiment or every implementation of the invention. The description that follows more particularly exemplifies illustrative embodiments. In several places throughout the application, guidance may be provided through lists of examples, which examples can be used in various combinations. In each instance, the recited list serves only as a representative group and should not be interpreted as an exclusive list.

BRIEF DESCRIPTION OF FIGURES

FIG. 1A shows the architecture of a generic OLED and its functioning is depicted in **FIG. 1B**, while **FIG. 1C** depicts an organic photovoltaic (OPV) device.

FIG. 2A shows the thermal cycloisomerization reaction of triyne substrates like **1** to produce isomeric benzyne derivatives; and the first stage is termed a "hexadehydro-Diels–Alder" (HDDA) reaction, as depicted in **FIG. 2B**.

FIG. 3A shows the preparation of the tetrayne **6** in two steps; results of measuring the absorption and emission spectra of compound **8** (also referred to as compound **100**) both in solution (red and green, respectively) and as a film (yellow and blue, respectively) are seen in **FIG. 3B**; a photograph of the actual devices prepared (four, in the quadrants of this single ITO/glass substrate) for this preliminary set of measurements is shown in **FIG. 3C** (top left), the behavior of each was similar when subjected to a voltage bias and current flow (top right of **FIG. 3C**), the chromaticity diagram is also shown (bottom of **FIG. 3C**); **FIG. 3D** shows results of initial DFT calculations; **FIG. 3E** shows specific illustrative compounds or groups of compounds **9a** to **9e**.

FIG. 4A shows an illustrative synthetic scheme for compounds **12a** and **12b**; **FIG. 4B** shows an illustrative synthetic scheme for compound **14**; **FIG. 4C** shows an illustrative synthetic scheme for compound **16a** and **b**, and **17a** and **b** and the solid state and solution emission of compound **16a**; **FIG. 4D** an illustrative synthetic scheme for compounds **19a**, **19b** and **20** and **FIG. 4E** shows specific illustrative compounds or groups of compounds **21**.

FIG. 5A shows an illustrative synthetic scheme for compound **24**; and **FIG. 5B** shows specific illustrative compounds or groups of compounds **25**.

FIG. 6A illustrates a HDDA + perylene cascade; **FIG. 6B** shows typical characterization data (UV, PL, CV, DFT) of illustrative compounds illustrated in **FIG. 6A**; **FIG. 6C** illustrates Larock Pd-promoted benzannulation of arynes; **FIG. 6D** illustrates the benzannulation of HDDA benzyne to dibenzocarbazoles (**1010**), fluoranthenes (**1011**), or dinaphthoperylenes (**1013**).

FIG. 7A shows an illustrative synthetic scheme for compound or groups of compounds **28a/b** and solution emission of two illustrative compounds with X=H and X=NPh₂; **FIG. 7B** shows specific illustrative compounds or groups of compounds **29a, 29b, 29c, 30, 31, and 32**; **FIG. 7C** shows an illustrative synthetic scheme for various compounds; **FIG. 7D** shows an illustrative synthetic scheme for various compounds; and **FIG. 7E** shows an illustrative synthetic scheme for various compounds.

FIG. 8A shows tetraphenylcyclopentadienone (TPCPD) (**1014**) trapping efficiently to give strongly fluorescent solids **15**; **FIG. 8B** shows conceptually related chemistry proposed for accessing more highly elaborated polycyclics (e.g., **1016**).

FIG. 9A shows symmetrical and unsymmetrical A-B-C structures (**33**) that can be used in the derived fused benzyne shown in **FIG. 9B** to **9E**; **FIG. 9B** shows an illustrative synthetic scheme for compound or groups of compounds **34** to **36**; **FIG. 9C** shows an illustrative synthetic scheme for compound or groups of compounds **39**; **FIG. 9D** shows an illustrative synthetic scheme for compound or groups of compounds **40**; **FIG. 9E** shows an illustrative synthetic scheme for compound or groups of compounds **41, 42 43 and 44**; **FIG. 9F** shows an illustrative synthetic scheme for compound or groups of compounds **46, 47 and 48**.

FIG. 10A shows an illustrative synthetic scheme for compound or groups of compounds **50**; **FIG. 10B** shows an illustrative synthetic scheme for compound or groups of compounds **52, 53 and 54**; **FIG. 10C** shows specific illustrative compounds or groups of compounds **55 and 56**; **FIG. 10D** shows an illustrative synthetic scheme for compound or groups of compounds **57**; **FIG. 10E** shows an illustrative synthetic scheme for compound or groups of compounds **58**; and **FIG. 10F** shows specific illustrative compounds or groups of compounds.

FIG. 11A shows Pd(0)-Catalyzed benzyne trimerization; **FIG. 11B** shows unexpected, one-pot Cu-catalysis of both the HDDA cycloisomerization and a hydroalkynylation trapping reaction; **FIG. 11C** shows the regioselective hydroalkynylation of a (unsymmetrical) triyne; **FIG. 11D** shows post-HDDA alkyne/arene cyclization; **FIG. 11E** shows double

hydroalkynylation and subsequent cyclization; and **FIG. 11F** shows dimers via alkyne self-cross-metathesis or Glaser homo-coupling.

FIG. 12A illustrates trapping with *p*-diaminobenzene (**1042**); **FIG. 12B** illustrates a bidirectional, bis-benzyne precursor (**1044**) to push-pull bis-indanone (**1045**) strategy; **FIG. 12C** illustrates oligomer formation via capture of a bis-benzyne precursor by a diamine; **FIG. 12D** shows the first deep blue emitting HDDA products (arylalkynyldibenzofurans) produced; oligomers containing these chromophores as the repeat units; **FIG. 12E** illustrates push-pull highly fused bis indanones; and **FIG. 12F** shows indacenes and spirobifluorenes moieties readily derived from indanones.

FIG. 13A shows the domino-HDDA reaction: **1056a-c** to **1057a-c**; **FIG. 13B** shows an inside-out motif; and **FIG. 13C** shows benzo analogs improve solubility and support a benzyne-to-naphthyne-to-anthracene-to-tetracyne cascade.

FIGs. 14A and **14B** illustrate a mid-chain Glaser coupling (and convergent) strategy for synthesis of polydiyne substrates **1065**; **FIG. 14C** illustrates a statistical Glaser coupling strategy for 2-step synthesis of oligomeric domino-HDDA substrates **1067**; **FIG. 14D** shows iterative exponential growth strategy for synthesis of monodisperse poly-yne substrates **1070** and acenes **1071**.

FIGs. 15A and **15B** are a thermal gravimetric analysis scan (**FIG. 15A**) and a differential scanning calorimetry scan (**FIG. 15B**) for compound **1015a**.

FIGs. 16A – 16C are a thermal gravimetric analysis scan (**FIG. 16A**); a differential scanning calorimetry scan (**FIG. 16B**) for compound **1015b**; and a x-ray crystallographic structure for **1015b** (**FIG. 16C**).

FIGs. 17A and **17B** are a thermal gravimetric analysis scan (**FIG. 17A**) and a differential scanning calorimetry scan (**FIG. 17B**) for compound **1015c**.

FIGs. 18A, 18B and **18C** show the photoluminescence efficiency (solution quantum yield) for compounds **1015a** (**FIG. 18A**), **1015b** (**FIG. 18B**) and **1015c** (**FIG. 18C**) in THF/water mixtures.

FIGs. 19A, 19B and **19C** show electroluminescence for all nine devices including compound **1015a** (**FIG. 19A**), **1015b** (**FIG. 19B**) and **1015c** (**FIG. 19C**) taken at 2 mA/cm².

FIGs. 20A – 22C show current-voltage and brightness-voltage data for compounds **1015a** in 4%, 20% and 100% UGH2 (**FIG. 20A, 20B** and **20C** respectively); **1015b** in 4%, 20%

and 100% UGH2 (**FIG. 21A, 21B and 21C** respectively); and **1015c** in 4%, 20% and 100% UGH2 (**FIG. 22A, 22B and 22C** respectively).

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

5 The words “preferred” and “preferably” refer to embodiments of the invention that may afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful, and is not intended to exclude other embodiments from the scope of the invention.

10 The terms “comprises” and variations thereof do not have a limiting meaning where these terms appear in the description and claims.

 Unless otherwise specified, “a,” “an,” “the,” and “at least one” are used interchangeably and mean one or more than one. Reference to “a carboxylic acid compound”, for example, refers to a single carboxylic acid compound, multiple compounds of the same carboxylic acid
15 compound, more than one specific carboxylic acid compound, multiple types of carboxylic acid compounds, mixtures of carboxylic acid compounds, or any combination thereof.

 As used herein, “alkyl” is an unsubstituted or substituted saturated hydrocarbon chain radical having from 1 to about 12 carbon atoms; from 1 to about 10 carbon atoms; or from 1 to about 6 carbon atoms. Illustrative, non-limiting examples of alkyl groups include, for example,
20 methyl, ethyl, propyl, iso-propyl, and butyl. A C₂ to C₄ substituted or unsubstituted alkyl radical, for example refers to a C₂ to C₄ linear alkyl chain that may be unsubstituted or substituted. If the C₂ to C₄ linear alkyl chain is substituted with an alkyl radical, the carbon number of the alkyl radical increases as a function of the number of carbons in the alkyl substituent.

 As used herein “cycloalkyl” refers to a saturated hydrocarbon containing one ring having
25 a specified number of carbon atoms. Examples of cycloalkyl include cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl.

 As used herein, “aryl” means a monocyclic, bicyclic, or tricyclic monovalent aromatic radical, such as phenyl, biphenyl, naphthyl, or anthracenyl, which can be optionally substituted with up to five substituents which may be selected from C1- C6 alkyl, C1-C6 alkenyl, C1-C6
30 alkynyl, aryl, heteroaryl, hydroxy, C1-C3 hydroxyalkyl, C1-C3 alkoxy, C1-C3 haloalkoxy, amino, and C1-C3 mono alkylamino for example.

As used herein, "alkoxy" alone or in combination, includes an alkyl group connected to the oxy connecting atom. The term "alkoxy" also includes alkyl ether groups, where the term 'alkyl' is defined above, and 'ether' means two alkyl groups with an oxygen atom between them. Examples of suitable alkoxy groups include methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, s-
5 butoxy, t-butoxy, methoxymethyl, and methoxyethyl.

As used herein, "cyano group" or "cyano" refers to a $-\text{CN}$ group.

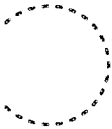
As used herein, "ester" refers to a substituent group of formula $-\text{CO}_2\text{Alkyl}$ (or $\text{C}(=\text{O})\text{O}-\text{Alkyl}$ to be even more specific).

As used herein, "halogen" or "halide" refers to fluoride, chloride, bromide, or iodide. The
10 terms "fluoro", "chloro", "bromo", and "iodo" may also be used when referring to halogenated substituents, for example, "trifluoromethyl."

As used herein, "heteroaryl" refers to aromatic moieties containing one or more heteroatoms (e.g., N, O, S, or the like) as part of the ring structure. "Substituted heteroaryl" refers to heteroaryl groups further bearing one or more substituents as set forth above. The term
15 "heteroaryl", as used herein except may represent a stable 5- to 7-membered monocyclic- or stable 9- to 14-membered fused bicyclic heterocyclic ring system that contains an aromatic ring, any ring of which may be saturated, such as pyridinyl, partially saturated, or unsaturated, or piperidinyl, and which consists of carbon atoms and from one to four heteroatoms selected from the group consisting of N, O, and S, and wherein the nitrogen and sulfur heteroatoms may
20 optionally be oxidized, and the nitrogen heteroatom may optionally be quaternized, and including any bicyclic group in which any of the above-defined heterocyclic rings is fused to a benzene ring. The heterocyclic ring may be attached at any heteroatom or carbon atom which results in the creation of a stable structure. Examples of such heteroaryl groups include, but are not limited to, benzimidazole, benzisotbiazole, benzisoxazole, benzofuran, benzothiazole,
25 benzothiophene, benzotriazole, benzoxazole, carboline, cinnoline, furan, furazan, imidazole, indazole, indole, indolmne, isoquinoline, isothiazole, isoxazole, naphthyridine, oxadiazole, oxazole, phthalazme, pteridine, purine, pyran, pyrazine, pyrazole, pyridazine, pyridine, pyrimidine, pyrrole, quinazoline, quinoline, quinoxaline, tetrazole, thiadiazole, thiazole, thiophene, triazine, triazole, and N-oxides thereof.

30 As used herein, "hydroxyl group" refers to a substituent group of formula $-\text{OH}$.

As used herein, a structure referred to as a “ring” or represented in a formula as one or

more structures similar to:  indicates the presence of a cyclic moiety. The cyclic moiety can include all aryl moieties heteroaryl moieties, cyclic moieties, heterocyclic moieties, and combinations thereof. The cyclic moieties can also be substituted or unsubstituted. The number of rings, the number of connections to the main formula, or both will be understood by one of skill in the art based on the nature of the particular cyclic moiety. Additionally, more ring structures can be indicated on a formula than can exist in order to show all possible connection points. For example, in Formula II, it is understood that only one of the two rings shown can be present at one time; the two rings are shown to indicate the two possible connection points of the ring to the main structure.

Unless otherwise stated, as employed herein, when a moiety (e.g., alkyl, or alkenyl) is described as “substituted” it is meant that the group optionally has from one to four, from one to three, or one or two, non-hydrogen substituents. Suitable substituents include, without limitation, halo, hydroxy, oxo (e.g., an annular -CH- substituted with oxo is -C(O)-), nitro, halohydrocarbyl, hydrocarbyl, aryl, aralkyl, alkoxy, aryloxy, amino, acylamino, alkylcarbamoyl, arylcarbamoyl, aminoalkyl, acyl, carboxy, hydroxyalkyl, alkanesulfonyl, arenesulfonyl, alkanesulfonamido, arenesulfonamido, aralkylsulfonamido, alkylcarbonyl, acyloxy, cyano, and ureido groups.

In all chemical structures, any carbon without four bonds thereto should be understood as having additional hydrogens thereon as necessary.

Also herein, the recitations of numerical ranges by endpoints include all numbers subsumed within that range (e.g., 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, 5, etc.).

For any method disclosed herein that includes discrete steps, the steps may be conducted in any feasible order, unless context indicates otherwise. And, as appropriate, any combination of two or more steps may be conducted simultaneously.

All headings are for the convenience of the reader and should not be used to limit the meaning of the text that follows the heading, unless so specified.

Disclosed herein are novel compounds and groups of compounds. The disclosed compounds can be useful, for example in organic devices.

Organic Devices

Organic devices as described herein can include both organic electronic devices and organic photonic devices. The field of organic electronic and photonic materials dates from the discovery of photoconduction in anthracene reported in 1906. Nonetheless, it is burgeoning today at an amazing pace. There is tremendous potential for practical advantage in the use of organic compounds as the essential components for driving the conversion of light to current [as in solar and related types of photovoltaic (PV) cells] or vice-versa [as in light-emitting diodes (LEDs)] and in field-effect transistors (FETs). Among these features are lower cost, more rapid response rates, higher power conversion efficiency, thinner films, more environmentally friendly, flexible substrates, greater versatility, and improved longevity. A brief introduction to the organic (O) versions of these types of devices and applications—OPVs, OLEDs, and OFETs—is given below.

Organic electronic and photonic materials already find application in many electronic devices and displays. Organic light-emitting diodes (OLEDs) are now found in many smaller hand-held electronic displays; notably, Samsung Galaxy smartphones and tablets, starting with the Note in 2011, use OLED technology. Even OLED big-screen televisions have recently made their way onto the market (Samsung and LG). It should be emphasized that robust, deep blue-emitting (shorter λ end of the visible spectrum) organic LEDs remain an arena in need of considerable improvement. Creating emitters of highly saturated blue light has always been challenging. The 2014 Nobel Prize in physics was awarded "for the invention of efficient blue light-emitting diodes, which has enabled bright and energy-saving white light sources." Manifold lighting applications for OLEDs are on the horizon. Solar energy panels based on organic photovoltaics represent the Holy Grail with the greatest potential.

The architecture of a generic OLED is depicted in FIG. 1A and its functioning in FIG. 1B. A metal cathode (aluminum is common) and optically transparent anode [indium tin oxide (ITO) is common], the latter initially deposited on a glass substrate, are separated by thin layers comprised of several components having complementary functions. This particular device contains a green (a) electron transporter layer that assists in injecting electrons from the Al cathode into unoccupied orbitals (UMOs), most easily the LUMO, of molecules of the blue (b) active (emissive) layer. The yellow (c) hole-transporter component assists in injecting holes from the anodic ITO into the active layer (b). This can also be viewed as removal of an electron from a

filled orbital (OMO), most easily the HOMO, and then using the traditional curly arrow in the conventional and unidirectional way, always moving electrons in one direction throughout the circuit as the current flows. As these radical anions and radical cations cross paths, they often intersect to form an exciton on the same active layer molecule—the electronically excited state.

5 These can be of either the singlet or triplet spin state; spin statistics typically result in formation of a ca. 1:3 ratio of S_1 and T_1 , respectively. Photon emission can ensue through fluorescence from S_1 or phosphorescence from T_1 if spin-orbit coupling can be harnessed to overcome the forbiddenness of emission from the triplet. Although more sophisticated OLED architectures certainly have been developed, the basic concepts captured here are typical of those used to
10 guide OLED prototype construction at the exploratory level. FIG. 1D offers further explanation related to the function of an OLED.

An organic photovoltaic (OPV) device is, in the simplest sense, an inverse OLED (FIG. 1C). A photon enters, an exciton is created, and an electron-hole pair is formed following charge separation. It is desirable to use molecules whose excited states can undergo ready exciton
15 dissociation, a requirement for charge extraction. Absorption properties that overlap well with large portions of the solar spectrum are also desirable (Small molecule organic semiconductors on the move: Promises for future solar energy technology. Mishra M.; Bäuerle, P. *Angew. Chem. Int. Ed.* **2012**, *51*, 2020–2067).

Organic field-effect transistors (OFETs) comprise a major subset of what are known as
20 thin-film transistors (TFTs). In simple terms (FIG. 1D), the organic semiconductor in an OFET allows current to flow between source and drain in its open state, but the current can be throttled by adjustment of the gate voltage. Good OFET semiconductor compounds often have small HOMO/LUMO band gaps (e.g., through extended π -conjugation) and planar structures (Semiconductors for organic transistors. Facchetti, A. *Materials Today* 2007, *10*, 28–37).

25 Crystalline small molecules or highly ordered conducting polymers are most typically used as the semiconductor layer. The crystal lattice properties of these compounds are often critical to the success in OFET applications. More specifically, "the molecules should be preferentially oriented with the long axes approximately parallel to the FET substrate normal since the most efficient charge transport occurs along the direction of intermolecular π - π -stacking"
30 (Semiconductors for organic transistors. Facchetti, A. *Materials Today* 2007, *10*, 28–37).

Architectures that use films of conducting and/or emitting polymers may be produced by sequential solvent casting processes. It is easy to imagine how a host of device-building strategies can be engineered to alter the outcome and performance of, e.g., OLEDs and OFETs.

5 Hexadehydro-Diels-Alder (HDDA) Reactions

The thermal cycloisomerization reaction of triyne substrates like **1** to produce isomeric benzyne derivatives **2** (FIG. 2A) is an extraordinarily general reaction (The hexadehydro-Diels–Alder reaction. Hoyer, T. R.; Baire, B.; Niu, D.; Willoughby, P. H.; Woods, B. P. *Nature* 2012, 490, 208–212). Both known and new *in situ* trapping reactions of arynes then convert **2** into a
10 multitude of adducts **3** by engaging both tethered (intramolecular) moieties as well as external (bimolecular) trapping agents. This two-stage cascade process is a remarkably powerful overall transformation. We termed the first stage the "hexadehydro-Diels–Alder" (HDDA) reaction (FIG. 2B) because the oxidation states of the substrates (1,3-diyne and diynophile) and product (benzyne) are higher—by the absence of three molecules of dihydrogen—than for the case of
15 classical DA reactions between 1,3-dienes and dienophiles (The hexadehydro-Diels–Alder reaction. Hoyer, T. R.; Baire, B.; Niu, D.; Willoughby, P. H.; Woods, B. P. *Nature* 2012, 490, 208–212; and Synthesis of complex benzenoids via the intermediate generation of *o*-benzynes through the hexadehydro-Diels-Alder reaction. Baire, B.; Niu, D.; Willoughby, P. H.; Woods, B. P.; Hoyer, T. R. *Nature Protocols* 2013, 8, 501–508).

20 Although the cycloisomerization of 1,3,*n*-triyne substrates to benzyne intermediates was not without precedent in several isolated settings (Thermolysis of 1,3,8-nonatriyne: evidence for intramolecular [2+4] cycloaromatization to a benzyne intermediate. Bradley, A. Z.; Johnson, R. P. *J. Am. Chem. Soc.* 1997, 119, 9917–9918; Cycloaromatization of a non-conjugated polyenyne system: Synthesis of 5H-benzo[d]fluoreno[3,2-*b*]pyrans via diradicals generated from 1-[2-{4-(2-alkoxymethylphenyl)butan-1,3-diynyl}]phenylpentan-2,4-diyn-1-ols and trapping evidence for
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30 thermal reaction of non-conjugated aromatic enetetraynes and DNA strand cleavage. Ueda, I.; Sakurai, Y.; Kawano, T.; Wada, Y.; Futai, M. *Tetrahedron Lett.* 1999, 40, 319–322; Domino

thermal radical cycloaromatization of non-conjugated aromatic hexa- and heptynes: synthesis of fluoranthene and benzo[a]rubicene skeletons. Miyawaki, K.; Kawano, T.; Ueda, I. *Tetrahedron Lett.* **2000**, *41*, 1447–1451; Synthesis of indeno[1,2-*b*]phenanthrene-type heterocycles by cycloaromatization of acyclic non-conjugated benzotetraynes. Miyawaki, K.; Ueno, F.; Ueda, I. *Heterocycles* **2001**, *54*, 887–900; Synthesis of indenothiophenone derivatives by cycloaromatization of non-conjugated thienyl tetraynes. Kawano, T.; Inai, H.; Miyawaki, K.; Ueda, I. *Tetrahedron Lett.* **2005**, *46*, 1233–1236; Effect of water molecules on cycloaromatization of non-conjugated aromatic tetraynes. Kawano, T.; Inai, H.; Miyawaki, K.; Ueda, I. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 944–949; Synthesis and DNA cleavage activity of water-soluble non-conjugated thienyl tetraynes. Torikai, K.; Otsuka, Y.; Nishimura, M.; Sumida, M.; Kawai, T.; Sekiguchi, K.; Ueda, I. *Bioorg. Med. Chem.* **2008**, *16*, 5441–5451; A metal-templated 4 + 2 cycloaddition reaction of an alkyne and a diyne to form a 1,2-aryne. Tsui, J. A.; Sterenberg, B. T. *Organometallics* **2009**, *28*, 4906–4908) our major advance was to demonstrate the hitherto unrecognized broad generality and scope of the reaction. This innovation has opened the door for researchers both elsewhere (Alkane C–H insertion by aryne intermediates with a silver catalyst. Yun, S. Y.; Wang, K.; Lee, N.; Mamidipalli, P.; Lee, D. *J. Am. Chem. Soc.* **2013**, *135*, 4668–4671; Alder-Ene reactions of arynes. Karmakar, R.; Mamidipalli, P.; Yun, S. Y.; Lee, D. *Org. Lett.* **2013**, *15*, 1938–1941; Silver-mediated fluorination, trifluoromethylation, and trifluoromethylthiolation of arynes. Wang, K.; Yun, S. Y.; Mamidipalli, P.; Lee, D. *Chem. Sci.* **2013**, *4*, 3205–3211; Formal hydrogenation of arynes with silyl C–H bonds as an active hydride source. Mamidipalli, P.; Yun, S. Y.; Wang, K.; Zhou, T.; Xia, Y.; Lee, D. *Chem. Sci.* **2014**, *5*, 2362–2367; Hydroarylation of arynes catalyzed by silver for biaryl synthesis. Lee, N.; Yun, S. Y.; Mamidipalli, P.; Salzman, R. M.; Lee, D.; Zhou, T.; Xia, Y. *J. Am. Chem. Soc.* **2014**, *136*, 4363–4368; Regioselectivity in the nucleophile trapping of arynes: the electronic and steric effects of nucleophiles and substituents. Karmakar, R.; Yun, S. Y.; Wang, K.; Lee, D. *Org. Lett.* **2014**, *16*, 6–9; Benzannulation of triynes to generate functionalized arenes by spontaneous incorporation of nucleophiles. Karmakar, R.; Yun, S. Y.; Chen, J.; Xia, Y.; Lee, D. *Angew. Chem. Int. Ed.* **2015**, *54*, 6582–6586; Synthesis of phenolic compounds by trapping arynes with a hydroxy surrogate. Karmakar, K.; Ghorai, S.; Xia, Y.; Lee, D. *Molecules* **2015**, *20*, 15862–15880; A new approach for fused isoindolines via hexadehydro-Diels–Alder reaction (HDDA) by Fe(0) catalysis. Vandavasi, J. K.; Hu, W.; Hsiao, C.; Senadia, G. C.; Wang, J. J. *RSC Adv.*

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5 J.; Hoye, T. R.; Kuwata, K. T. *J. Org. Chem.* 2015, 80, 11744–11754; The pentadehydro-Diels–Alder reaction. Wang, T.; Naredla, R. R.; Thompson, S. K.; Hoye, T. R. *Nature* 2016, 532, 484–

488; Reactions of HDDA-derived benzyne with sulfides: Mechanism, modes, and three-component reactions. Chen, J.; Palani, V.; Hoye, T. R. *J. Am. Chem. Soc.* 2016, 138, 4318–

4321; The hexadehydro-Diels–Alder (HDDA) cycloisomerization reaction proceeds by a

10 stepwise mechanism. Wang, T.; Niu, D.; Hoye, T. R. *J. Am. Chem. Soc.* 138, 7832–7835)) a) to

discover entirely new types of benzyne reactivity and b) to understand more intimately the

mechanistic details for certain types of benzyne trapping reactions. A major feature of the

HDDA cascade distinguishes it from classical benzyne chemistry. Namely, HDDA-generated

benzyne are formed thermally (and, now, photochemically) and, as a consequence, in the

15 absence of the reagents and byproducts that necessarily accompany all classical methods of

aryne synthesis (Synthetic methods for the generation and preparative application of benzyne.

Kitamura, T. *Aust. J. Chem.* 2010, 63, 987–1001; Arynes and cyclohexyne in natural product

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comprehensive history of arynes in natural product total synthesis. Tadross, P. M.; Stoltz, B. M.

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carbon-heteroatom bond-forming reactions using arynes. Bhunia, A.; Yetra, S. R.; Biju, A. T.

Chem. Soc. Rev. 2012, 41, 3140–3152). Other hallmarks of the HDDA cascade distinguish it vis-

à-vis traditional benzyne chemistry. Of particular relevance are that i) much more highly

substituted benzyne can be routinely accessed; ii) much more structurally complex, polycyclic

25 and highly conjugated benzenoid products arise, often via efficient convergent or

multicomponent trapping reactions; iii) the synthetic sequences are not only efficient, but often

very short in step-count; and iv) the modular nature of substrate and/or trapping agents lends

itself to rapid and reliable synthesis of series of structurally related compounds, often from

common precursors.

30 HDDA products have shown excellent thermal, oxidative, and photochemical robustness.

The power of the HDDA cascade provides the ability to promptly deliver multiply substituted

(including alkynyl), π -rich aromatic core structures composing unique chemical space in a single step. The HDDA reaction allows access to far more structurally complex benzyne with far greater ease of synthesis than classical aryne chemistries. The modular nature of the substrate tri- or tetraynes lends itself to easy modification for preparation of series of structurally related
5 analogs with which to establish structure-property-performance relationships. Disclosed herein are new chemistries that will define new classes of structures that can be easily accessed.

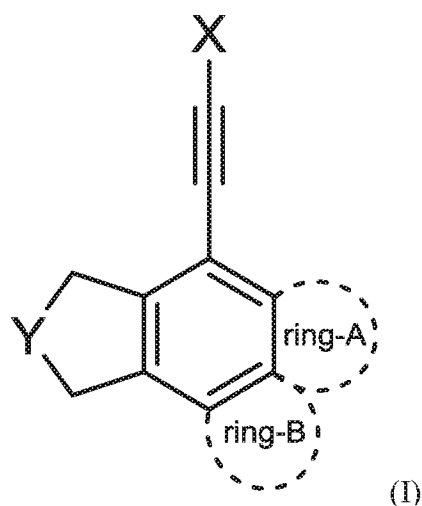
Further information related to HDDA and compounds that may be produced thereby can be found, for example in United States Patent Application Publication Number US
2013/0197241, entitled CYCLIZATION METHODS, filed on January 31, 2013, the disclosure
10 of which is incorporated herein by reference thereto.

Disclosed Compounds

There are relatively few classes of compounds that have found favor for having attractive photophysical and/or redox properties to serve as the active emissive materials in actual product applications. Such structures are typically either polymeric/oligomeric in nature [for example,
15 poly(paraphenylene), poly(phenylenevinylene) (PPV), poly(9,9'-dioctylfluorene), poly(9-vinylcarbazole)] or discrete small molecules [for example, 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl, tris-(8-hydroxyquinoline)aluminum, 2-(4-*tert*-butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole, or rubrene (5,6,11,12-tetraphenyltetracene)], acting either alone or in admixture with a dopant whose function can be, for example, to harvest both the singlet and triplet exciton spin states and
20 then subsequently phosphoresce [e.g., tris(2-phenylpyridinato- C^2,N)iridium(III)].

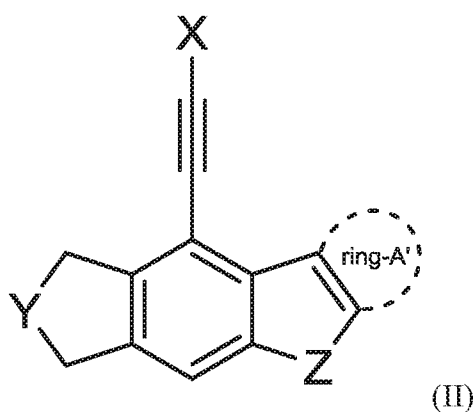
Disclosed herein are novel compounds, which may have chromophoric properties, the structures of which can be systematically modified and synthesized.

Some disclosed embodiments of compounds can include those having a structure of formula I:



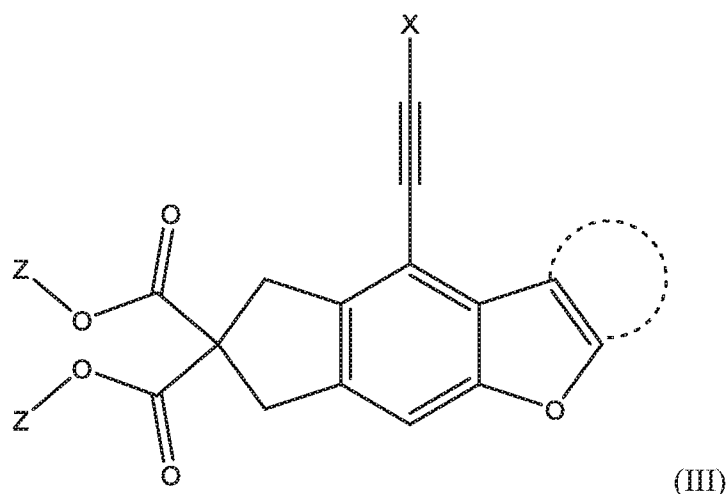
In formula I, Y can be $(R^1)_2O_2C)_2C$, O, CH_2 , NR^3 , where $R^2 = SO_2^3$, aryl, alkyl, $C(=O)R^4$ and R^1 , R^3 and R^4 are independently selected from hydrogen (H) and substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof. X can be selected from SiR^5_3 , $C(=O)R^4$, CO_2R^4 , $CONR^4_2$, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof, where R^4 and R^5 are independently selected from H, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof. ring-A and ring-B can be independently selected from benzo-, naphtheno-, or anthracenofurano, -thiofurano, or indolo, where the indolo nitrogen can bear R^2 .

Some disclosed embodiments of compounds can include those having a structure of formula II:



In formula II, Y can be $(R^1)_2O_2C)_2C$, O, CH_2 , NR^3 , where $R^2 = SO_2^3$, aryl, alkyl, $C(=O)R^4$ and R^1 , R^3 and R^4 are independently selected from hydrogen (H) and substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof. X can be selected from SiR^5_3 , $C(=O)R^4$, CO_2R^4 , $CONR^4_2$, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof, where R^4 and R^5 are independently selected from H, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof. Z can be O, S, or NR^1 where R^1 is as indicated above. ring-A can be selected from benzo- 1,2-naphtheno-, 2,3-naphtheno-, 1,2-anthraceno-, 2,3-anthraceno-, 9,10-phenanthreno- as well as any substituted derivatives thereof.

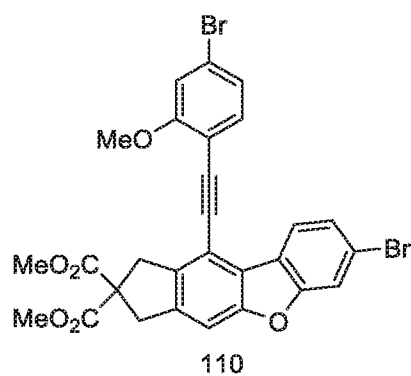
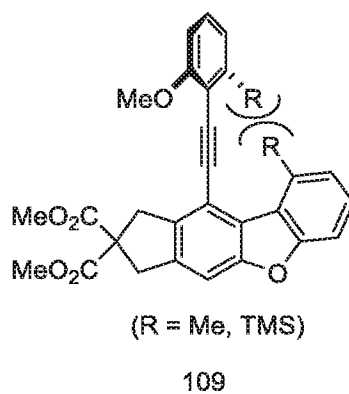
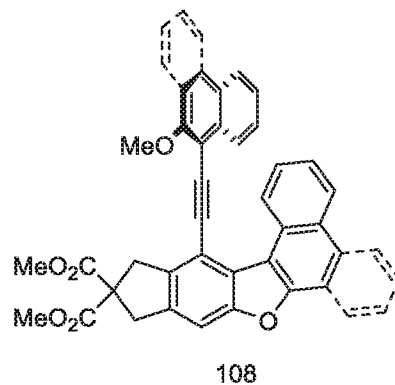
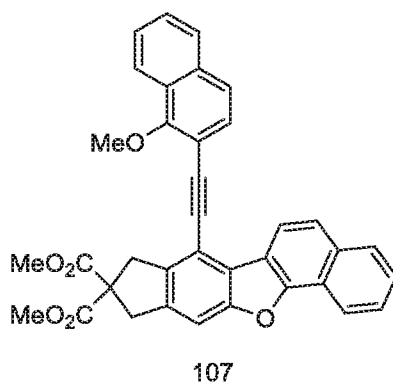
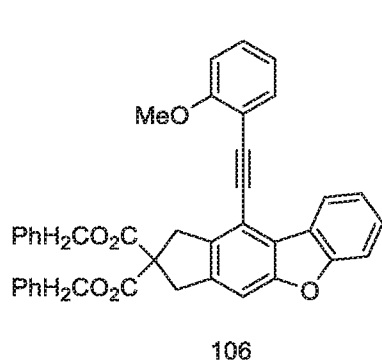
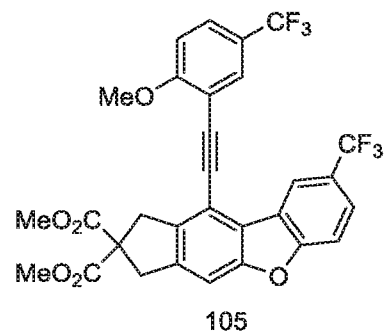
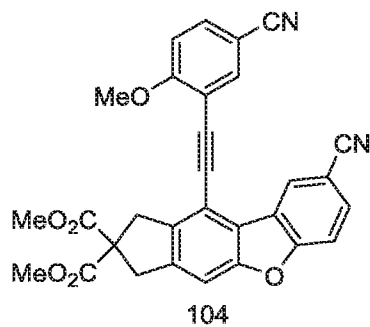
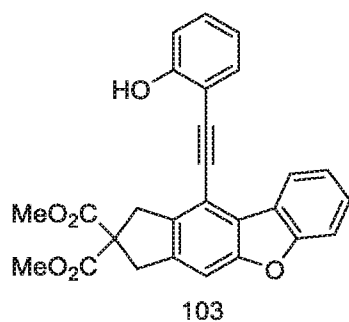
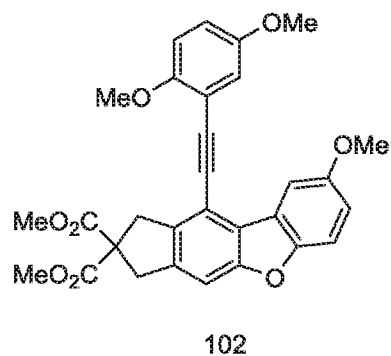
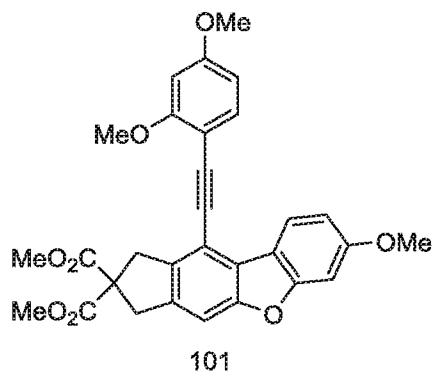
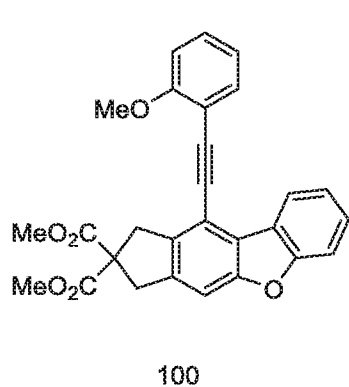
Some disclosed embodiments of compounds can include those having a structure of formula III:

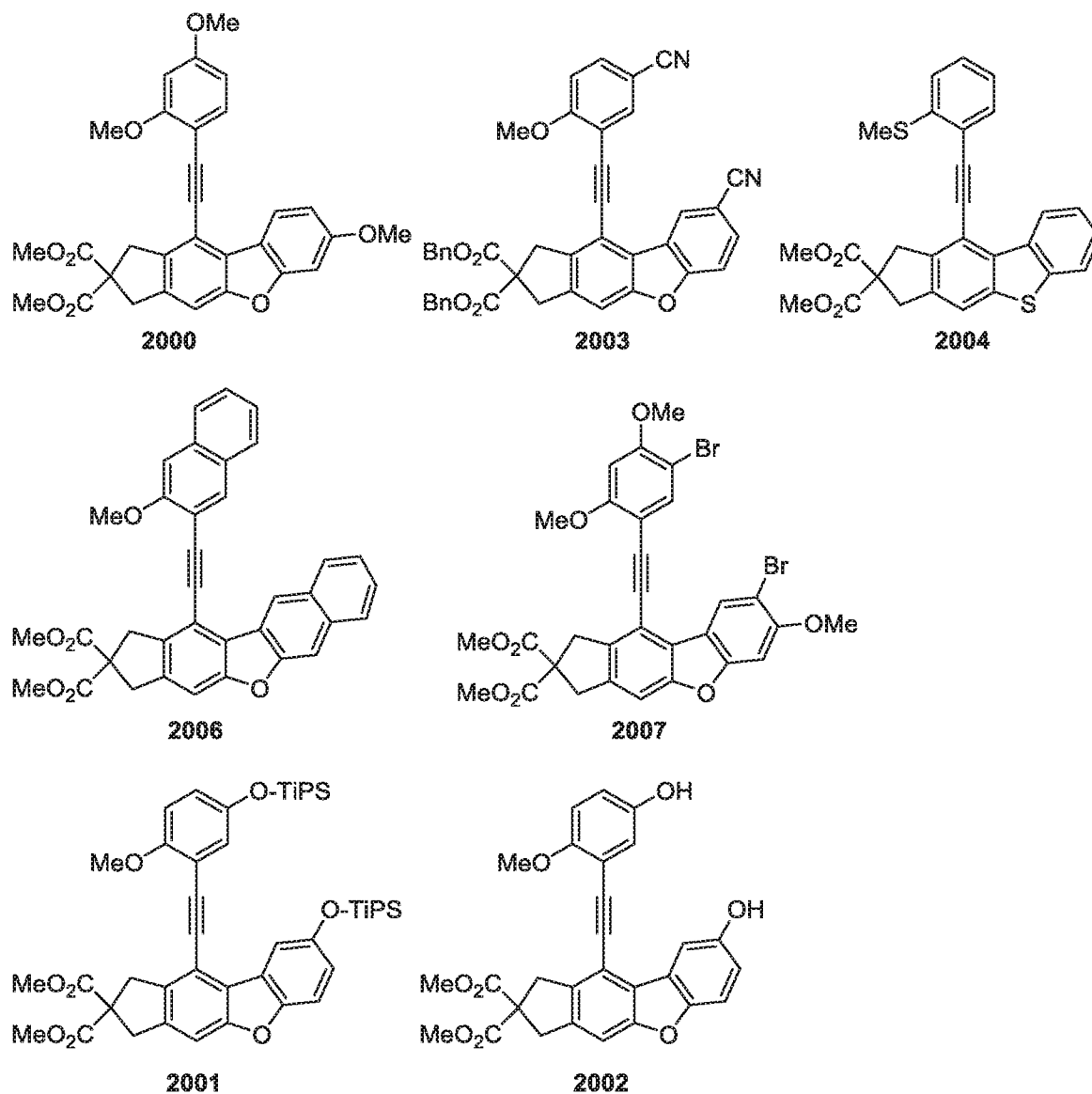


X can be selected from hydrogen (H), substituted or unsubstituted alkyl groups, fluoroalkyl groups, substituted or unsubstituted aryl groups, esters, halides, alkoxy groups, aryloxy groups, or combinations thereof; Z can independently be selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted heteroaryls, or combinations thereof. In some illustrative embodiments, X and Y can independently be selected from substituted or unsubstituted aryl groups such as phenyl, naphthyl, phenanthryl, carbazyl, or combinations thereof; and the dashed ring represents a substituted or unsubstituted fused aromatic or heteroaromatic ring. In some illustrative embodiments

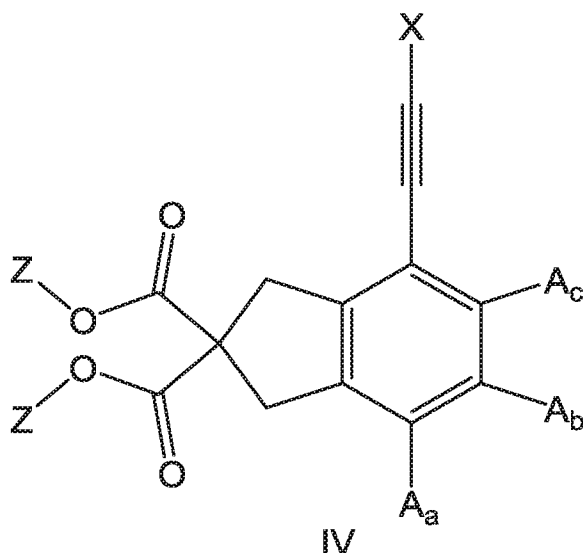
substituents for X can include alkoxyl groups, hydroxyl groups, cyano groups, haloalkyl groups, alkyl groups, halides, protecting groups, or any combinations thereof. In some illustrative embodiments Z can independently be selected from substituted or unsubstituted cycloalkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted alkyls, or combinations thereof. In some illustrative embodiments Z can independently be selected from substituted or unsubstituted C₁ to C₆ alkyl groups, or substituted aryl groups. In some illustrative embodiments Z can independently be selected from substituted or unsubstituted benzyl groups. In some illustrative embodiments, W can be oxygen (O). In some embodiments, the dashed ring can be a fused aromatic ring such as benzo or naphtho for example. In some embodiments, the dashed ring can be a heteroaromatic ring such as pyrido, quinolone, isoquinoline, furano, or thiopheno, for example. The fused aromatic or heteroaromatic ring can be substituted with, for example 1-3, alkoxy, aryloxy, halo, alkyl, amino, fluoroalkyl, trialkylsilyl, or combinations thereof.

Specific illustrative examples of compounds of formula I, II, or III can include compounds **100** to **110**, **2000** to **2004**, and **2006** to **2007** below.



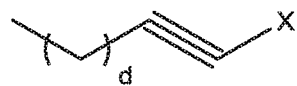
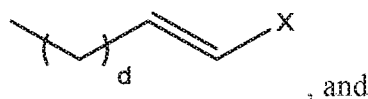


5 Some disclosed embodiments of compounds can include those having a structure of formula IV:



where X can be selected from hydrogen, substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, esters, amides, ketones, sulfates, sulfonyls, phosphates, phosphonates, or combinations thereof; Z can independently be selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted heterocyclic

aromatic groups; A can be independently selected from

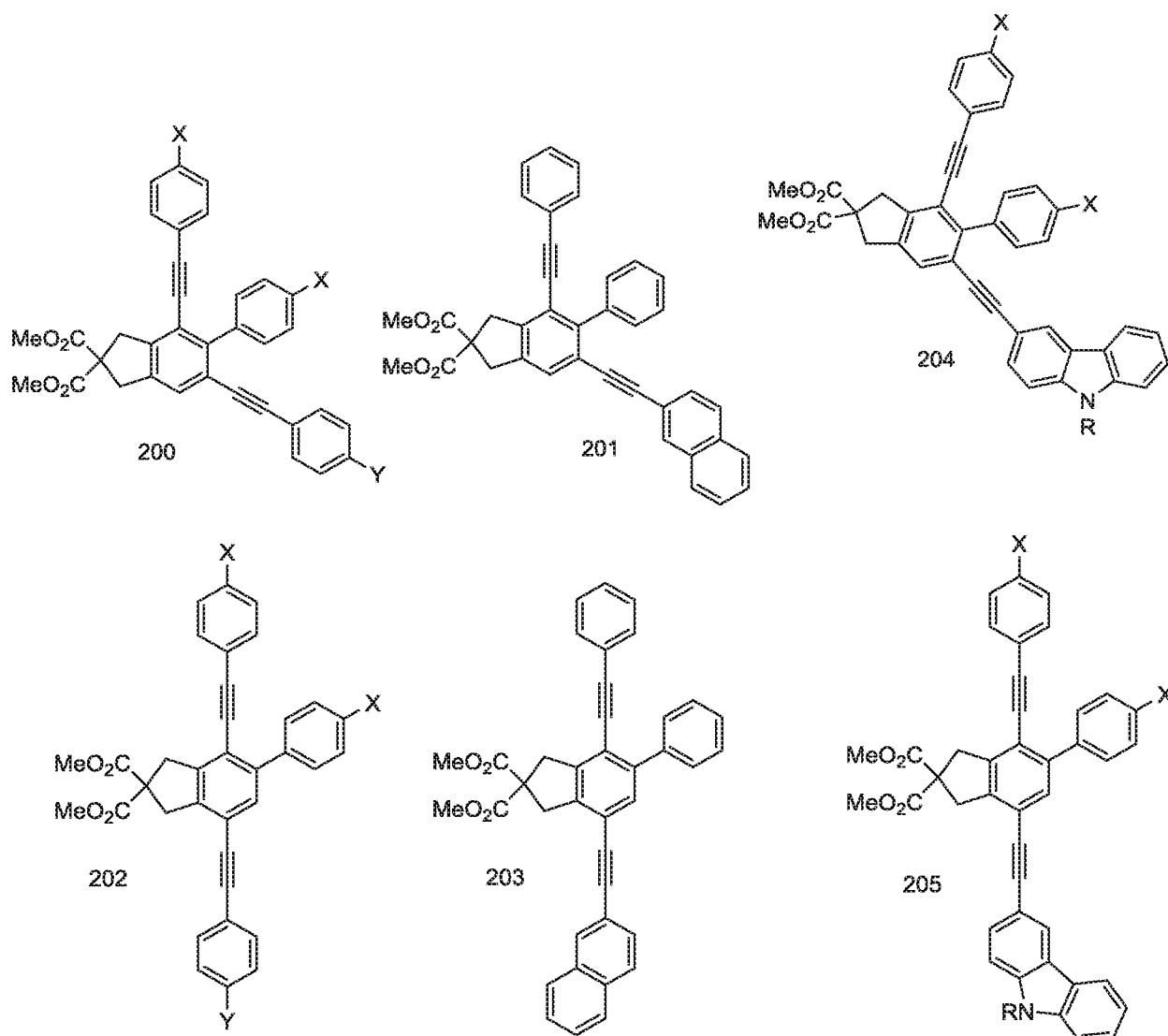


, where X is as indicated above and d is an integer from 0 to 6; and a, b and c are 0 or 1 with the caveat that only 1 of a and b can be, but need not be 1.

In some illustrative embodiments, X can independently be selected from hydrogen, substituted or unsubstituted aryl groups such as phenyl, naphthyl, phenanthryl, carbazyl, or combinations thereof. In some illustrative embodiments substituents for X can be substituted with alkoxy groups, hydroxyl groups, cyano groups, haloalkyl groups, alkyl groups, halogens, protecting groups, or any combinations thereof. In some illustrative embodiments Z can independently be selected from substituted or unsubstituted cycloalkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted alkyls, or combinations thereof. In some illustrative embodiments Z can independently be selected from substituted or unsubstituted C₁ to C₆ alkyl groups, or substituted aryl groups. In some illustrative embodiments Z can independently be selected from substituted or unsubstituted benzyl groups. In some illustrative

embodiments, X, at any point of formula II can be substituted. In some illustrative embodiments, substituents of X can include methoxy, methanoate, N-phenyl, phenyl, naphthyl, carbazyl (e.g., substituted at the nitrogen).

Specific illustrative examples of compounds of formula IV can include compounds **200** to **205** below.



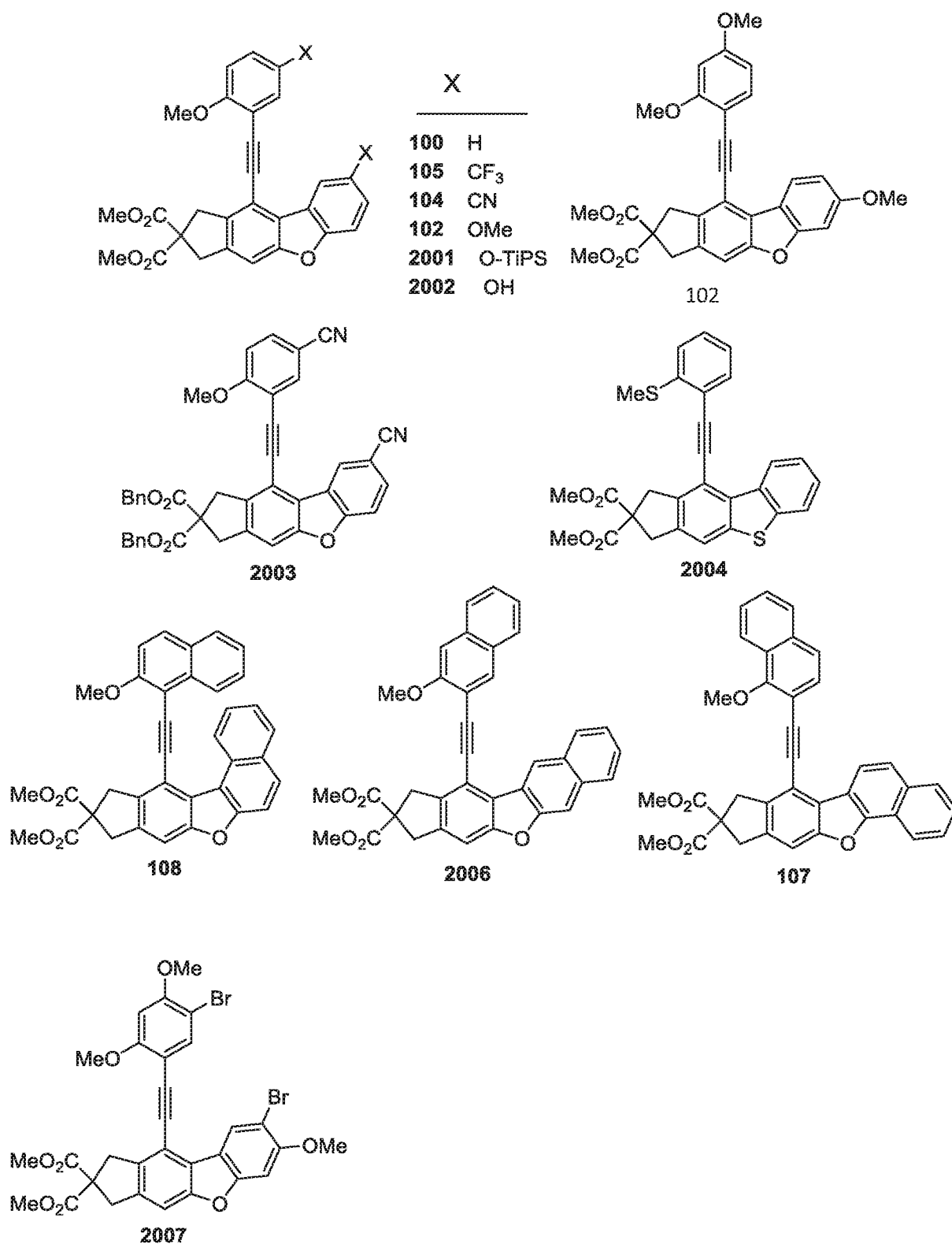
In compounds **200** to **205**, the following substituents can include the following:

X=Y=H;	X=Y=OMe;	X=CO ₂ Me;
X=Y=CO ₂ Me;	Y=NPh ₂	
X=Y=CN		

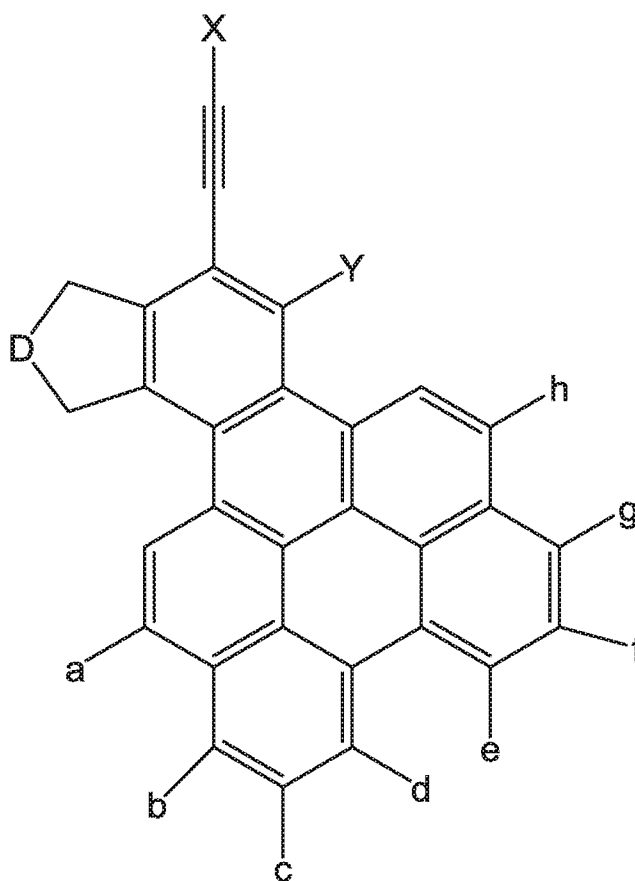
In Compound **205**, R can be an alkyl group.

Some illustrative embodiments include compounds **200** to **203**, for example.

Structural similarities of compounds **100**, **102**, **104**, **105**, **107**, **108**, **2001**, **2002**, **2003**, **2004**, **2006** and **2007** are shown below.



Some disclosed embodiments of compounds can include those having a structure of formula VI:

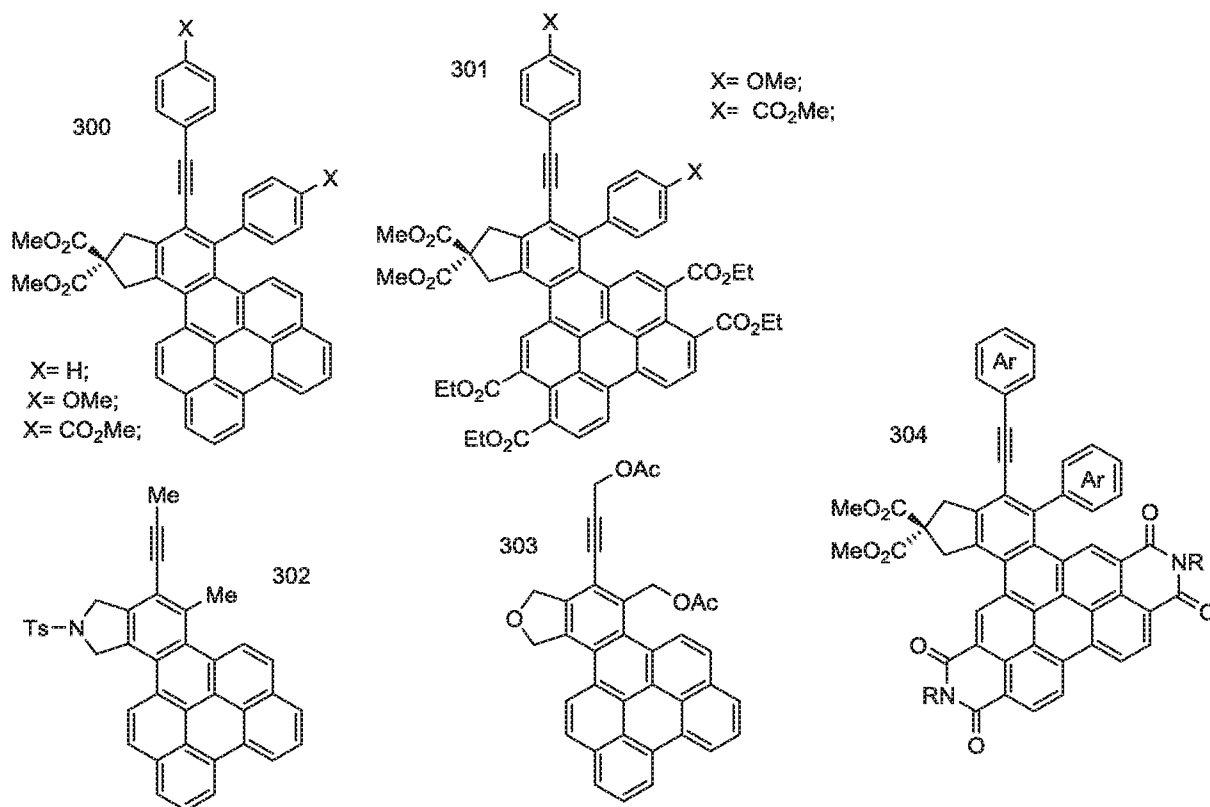


VI

where X and Y can independently be selected from hydrogen, substituted or unsubstituted alkyl groups, aryl groups, esters, halides, alkoxy groups, aryloxy groups, or combinations thereof; D is
 5 selected from N-alkyl, N-sulfonyl, N-acyl, N-protecting group, O, C(CO₂Z)₂, where Z can independently be selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted heterocyclic aromatic groups; a, b, c, d, e, f, g and h are independently H or C(O₂)alkyl, or a and b, g and h, or both a and b and g and h
 10 together are embedded in a common, five- or six-membered ring, imide ring (i.e., —CO—NR—CO—, where R can be H or an alkyl, cycloalkyl, or aryl substituent). In some illustrative embodiments, X and Y can be independently selected from hydrogen, alkoxy, esters, or combinations thereof. In some illustrative embodiments, only four of a to h are CO₂alkyl. In

some embodiments, CO₂alkyl can be CO₂CH₂CH₃. In some embodiments, a and b, g and h, or both a and b and g and h together form a piperidine-2,6-dione group.

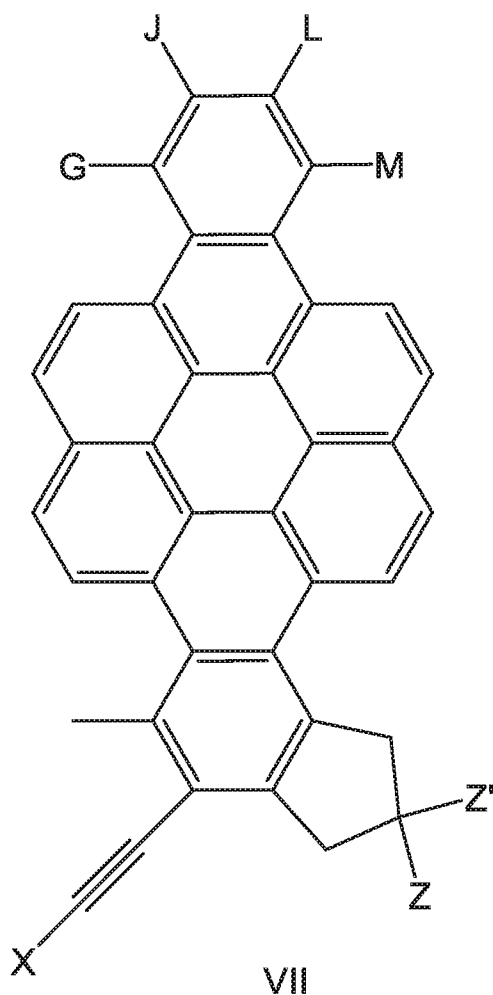
Specific illustrative examples of compounds of formula III can include compounds **300** to **304** below.



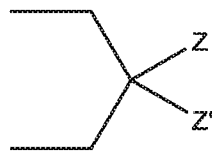
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Some illustrative embodiments include compounds **300** to **303**, for example.

Some disclosed embodiments of compounds can include those having a structure of formula VII:



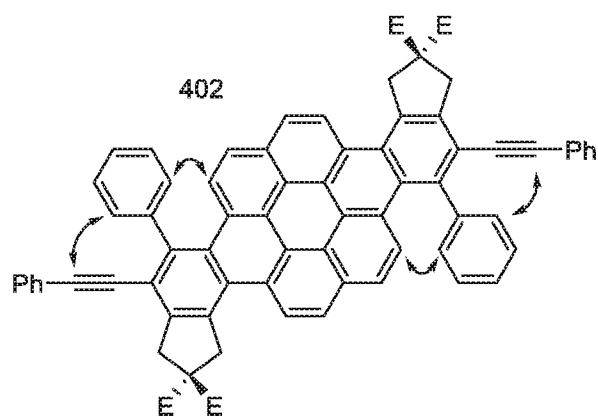
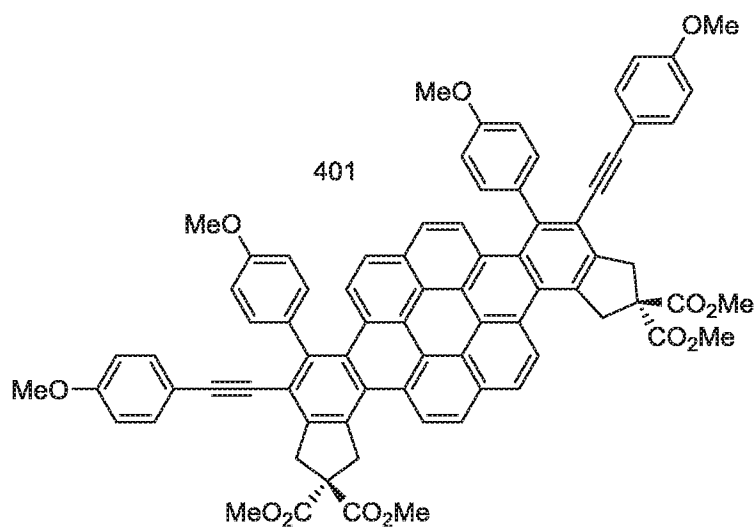
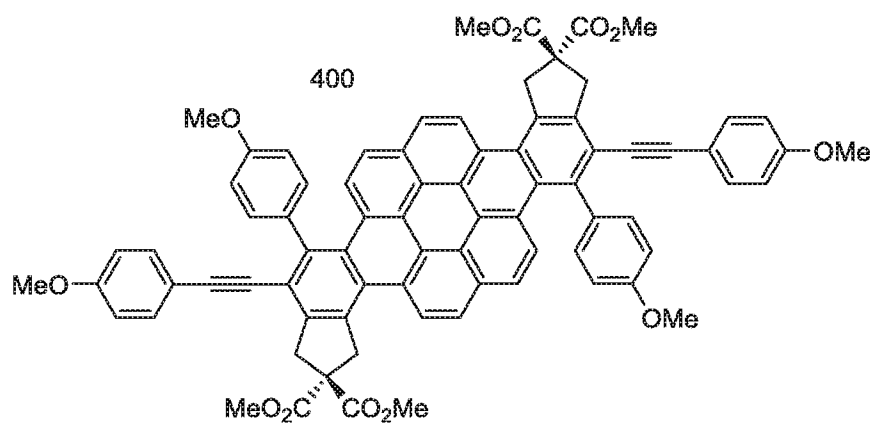
where X can be selected from hydrogen, substituted or unsubstituted alkyl groups, aryl groups, esters, esters, halides, alkoxy groups, aryloxy groups, or combinations thereof; Z and Z' can independently be selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted alkoxy groups, substituted or unsubstituted ester groups, substituted or unsubstituted heterocyclic aromatic groups; G and M are independently selected from hydrogen, substituted or unsubstituted alkyl groups, aryl groups, esters, or combinations thereof; J and L are $\text{---}\equiv\text{---X}$, where X is as defined above, or G together with J, L together with M, or both G together with J and L together with M forms



, where Z and Z' can be independently selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted

alkoxy groups, substituted or unsubstituted ester groups, substituted or unsubstituted heterocyclic aromatic groups.

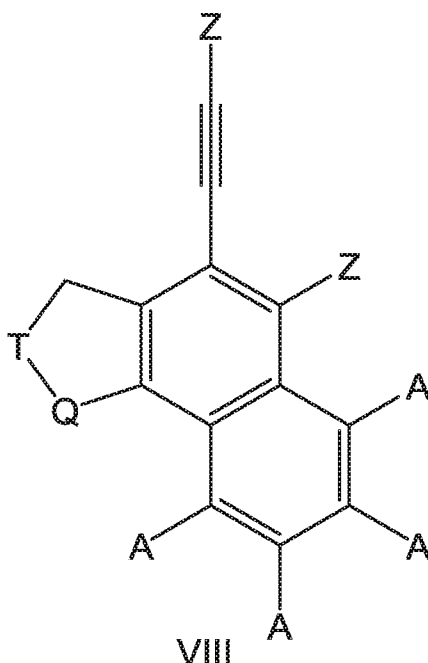
Specific illustrative examples of compounds of formula VII can include compounds **400** to **402**, for example.



(where E is an ester group).

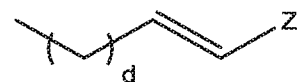
Some illustrative embodiments include compounds **400** and **401**, for example.

Some disclosed embodiments of compounds can include those having a structure of formula VIII:



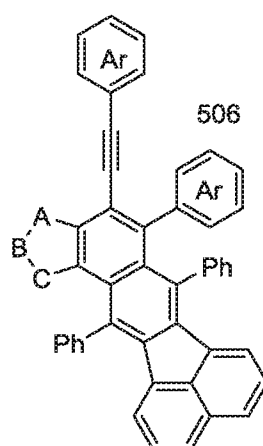
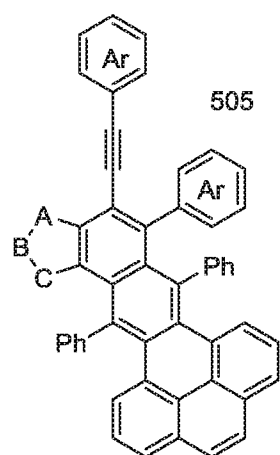
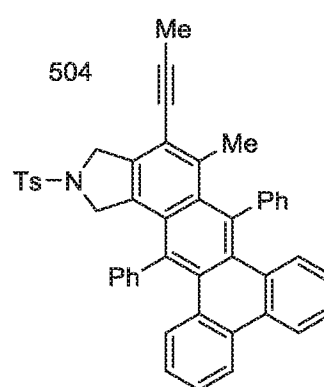
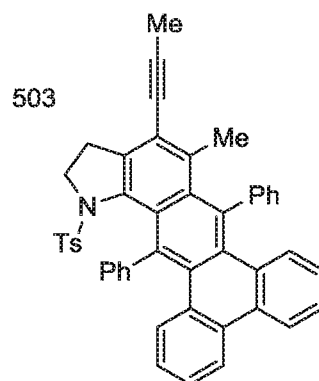
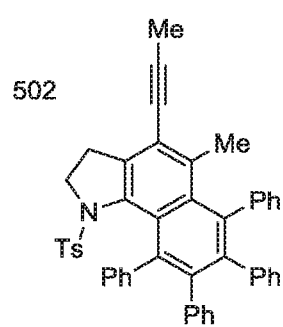
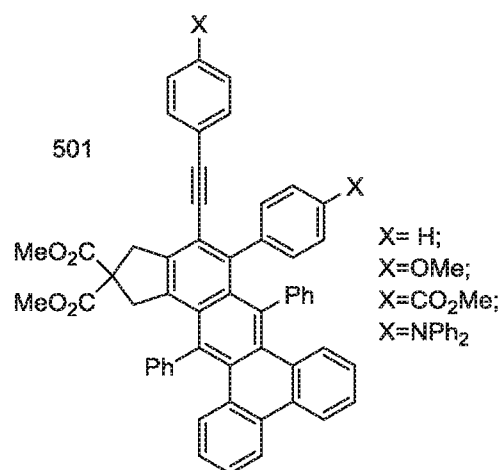
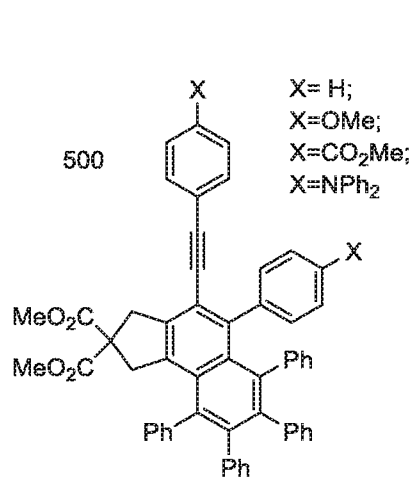
- 5 where Q is a substituted or unsubstituted N or substituted or unsubstituted C; Z can independently be selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted alkoxy groups, substituted or unsubstituted ester groups, substituted or unsubstituted heterocyclic aromatic groups; A can be

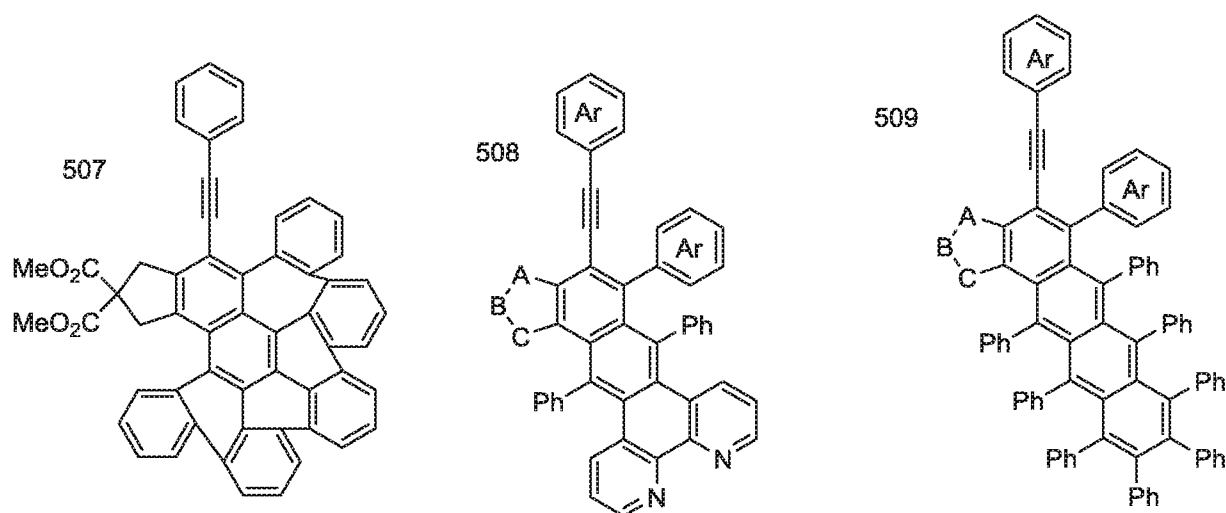
independently selected from substituted or unsubstituted aryl groups,



- 10 where Z is as indicated above and d is an integer from 0 to 6, or two adjacent A can together form a conjugated ring structure having at least 3 additional members in the ring; and T is $-\text{C}(\text{CO}_2\text{Z})$, a substituted or unsubstituted N, or a substituted or unsubstituted C.

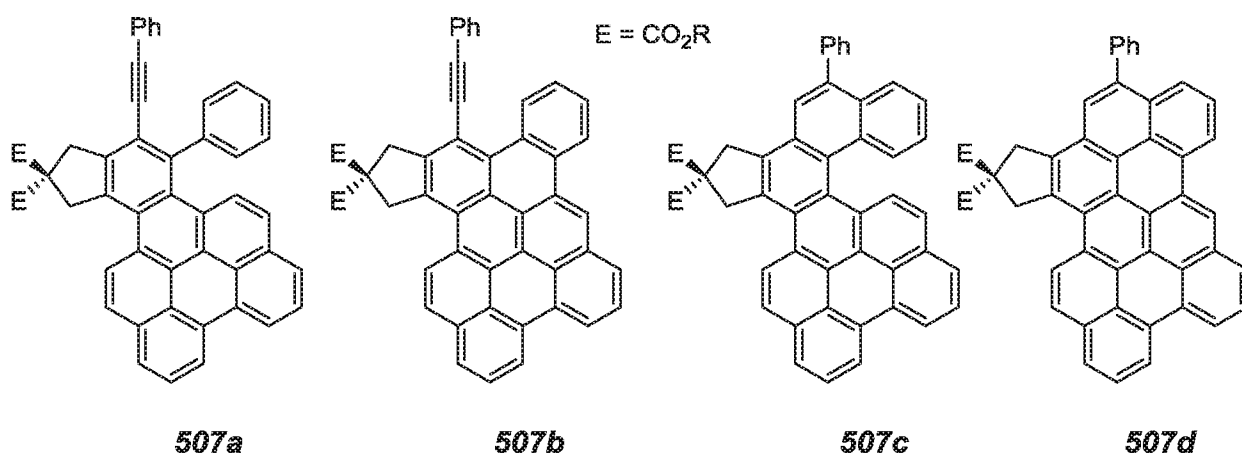
Specific illustrative examples of compounds of formula VIII can include compounds **500** to **509**, for example.





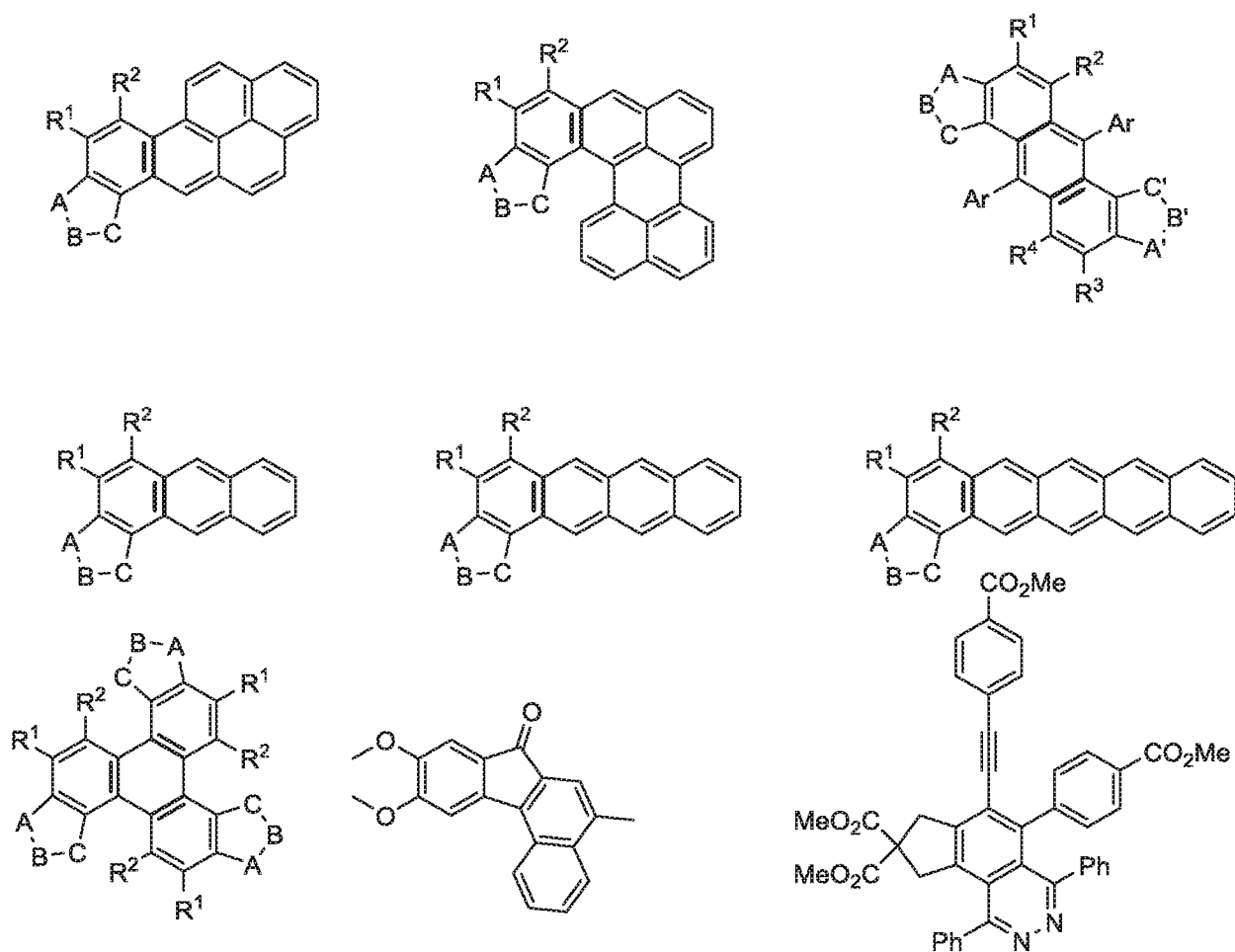
Some illustrative embodiments include compounds **500** to **504**, for example.

Compound **507** above can also be described by the four compounds (**507a** to **507d**) below that explains different fusions that may be encompassed by compound **507** above.

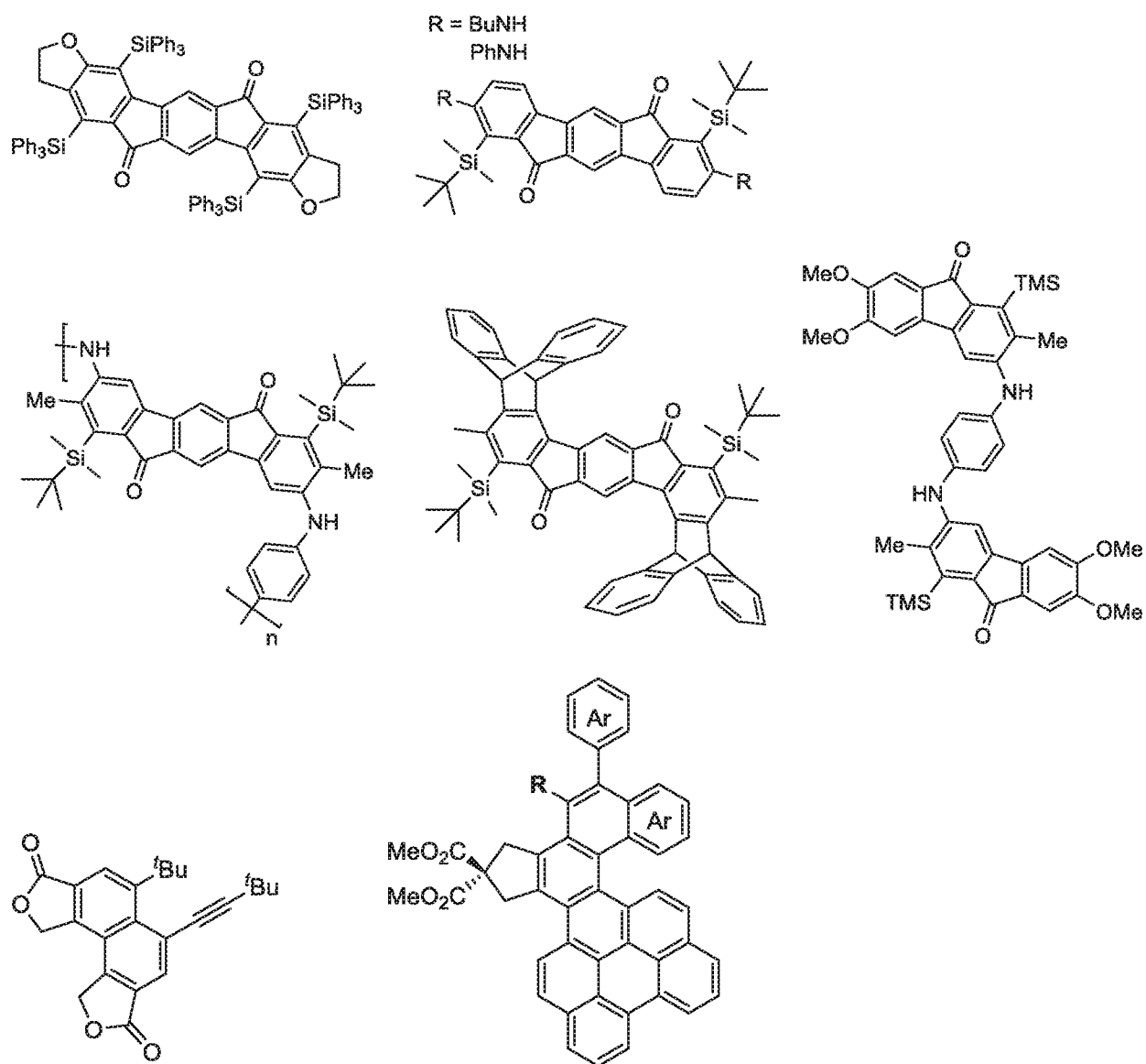


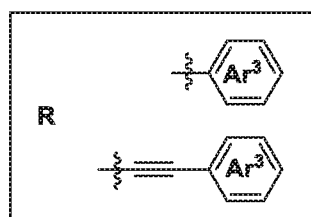
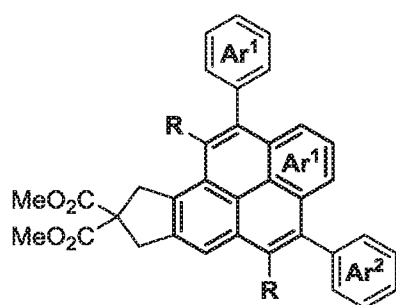
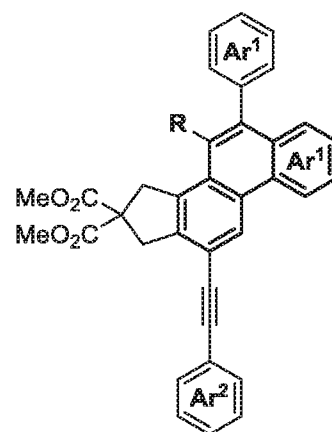
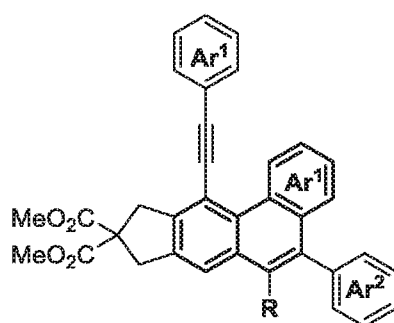
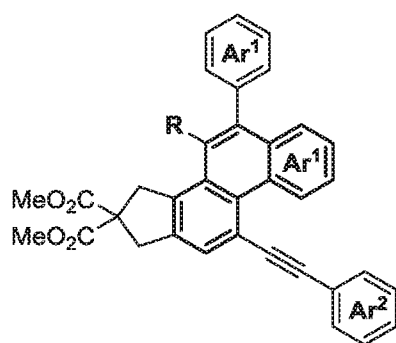
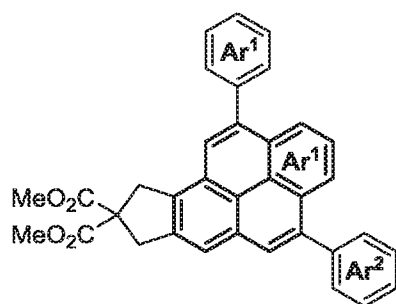
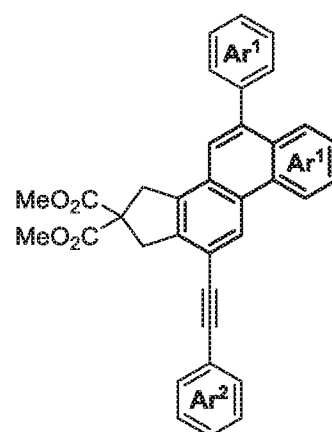
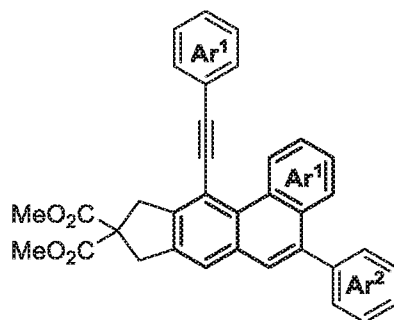
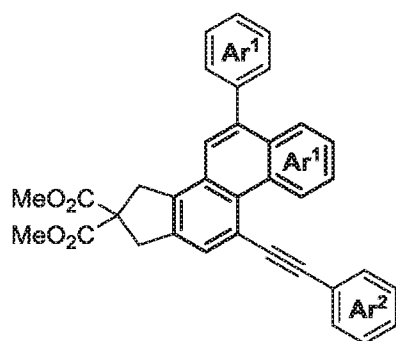
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Specific other illustrative compounds can include the following compounds. It should also be noted that derivatives of the below compounds, for example as could be determined based on the general classes of compounds above, are also considered as disclosed herein.



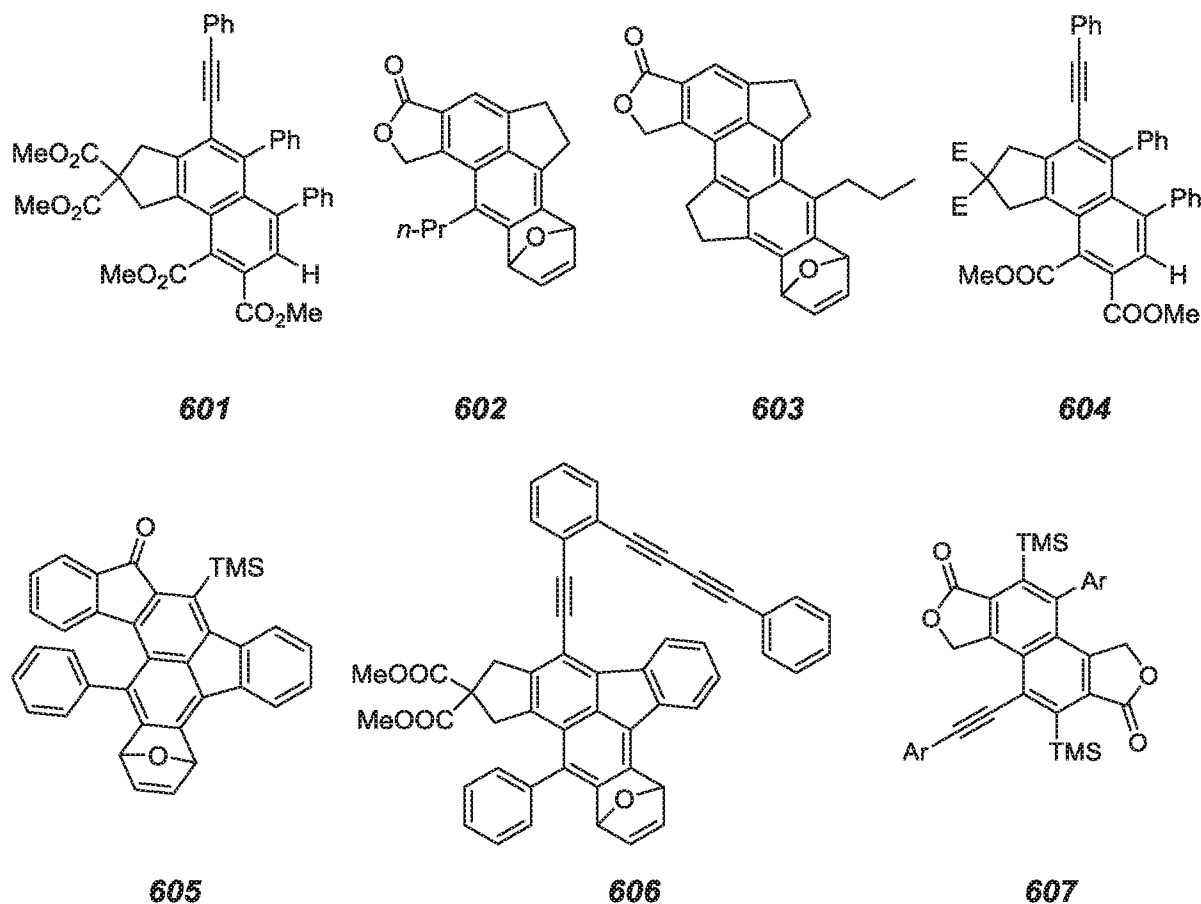
Where applicable above, the A-B-C component can be described as seen in FIG. 9A and R^1 , R^2 , etc. can generally refer to substituted or unsubstituted alkyls.





Where applicable above, Ar, Ar¹, Ar², Ar³ can independently be selected from substituted or unsubstituted aryl groups, including for example heteroaryl groups.

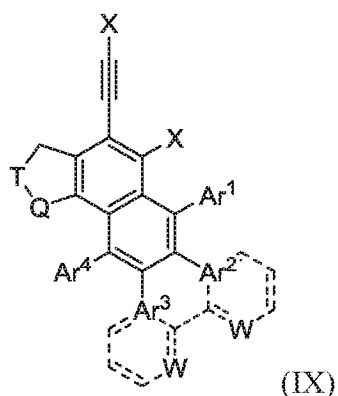
Another group of compounds includes compounds **601** to **607**.



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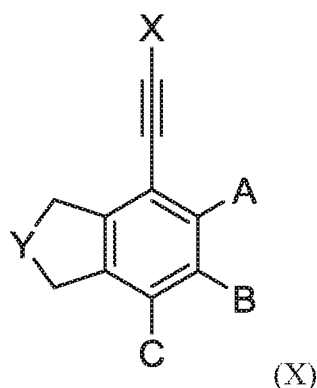
Compounds other than those specifically disclosed above can also be made using disclosed synthesis methods, for example.

Formula IX also represents illustrative compounds according to some disclosed embodiments:



In Formula IX, T can be $(R^1)_2O_2C$, O, CH_2 , NR^3 , where $R^2 = SO_2^3$, aryl, alkyl, $C(=O)R^4$ and R^1 , R^3 and R^4 are independently selected from hydrogen (H) and substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof and Q can be CH_2 ; or T can be CH_2 and Q can be NR^2 , with R^2 being SO_2^3 , aryl, alkyl, $C(=O)R^4$ and R^1 , R^3 and R^4 are independently selected from hydrogen (H) and substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof. Each X can independently be selected from SiR^5_3 , substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof, $C(=O)R^4$, CO_2R^4 , $CONR^4_2$ where R^4 and R^5 can independently be selected from H, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof. Ar1, Ar2, Ar3, Ar4 are independently selected from aryl substituents (phenyl, naphthyl, anthracenyl, and phenanthrenyl), including substituted aryls. In some embodiments, Ar2 and Ar3 can be joined to one another and further fused with benzo($W=CH$)- or pyrido($W=N$)- rings.

Formula X also represents illustrative compounds according to some disclosed embodiments:



In formula X, Y can be selected from $(R^1)_2O_2C)_2C$, O, CH_2 , NR^2 with $R^2 = SO_2^{3+}$, aryl, alkyl, $C(=O)R^4$ and R^1 , R^3 , R^4 can be independently selected from H, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof. A, B, and C are independently selected from H, SiR^5_3 , substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof, $C(=O)R^4$, CO_2R^4 , $CONR^4_2$, $C\equiv CR^2$ where R^2 is selected from SO_2^{3+} , aryl, alkyl, $C(=O)R^4$ and R^1 , R^3 , R^4 can be independently selected from H, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof where R^4 and R^5 are independently selected from H, SO_2^{3+} , aryl, alkyl, $C(=O)R^4$ and R^1 , R^3 , R^4 can be independently selected from H, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof.

In some embodiments, A and B are joined into a benzo-, naphtheno-, or anthracenofurano-, -thiofurano-, or indolo ring, where the indolo nitrogen can bear R^2 and C is selected from those above. In some embodiments, B and C are joined into a benzo- or triphenyleno- ring and may contain additional aryl substituents.

The present disclosure is illustrated by the following examples. It is to be understood that the particular examples, assumptions, modeling, and procedures are to be interpreted broadly in accordance with the scope and spirit of the disclosure as set forth herein.

Detailed Description of Illustrative Compounds and Synthesis Thereof

Referring to FIG. 3A the tetrayne **6** was prepared in two steps (bromination of **4** to **5** and Cadiot-Chodkiewicz coupling with 2-methoxyphenylacetylene) and the rate of its HDDA cyclization was studied (FIG. 3A). When heated in CDCl₃, it proceeded to give the alkynyldibenzofuran **8** in an extremely clean transformation (>90% yield of chromatographed material). Adventitious water in the medium was likely responsible for removal of the methyl group from an intermediate oxonium ion derived from the electrophilic benzyne **7** (An unprecedented arylcarbene formation in thermal reaction of non-conjugated aromatic enetetraynes and DNA strand cleavage. Ueda, I.; Sakurai, Y.; Kawano, T.; Wada, Y.; Futai, M. *Tetrahedron Lett.* **1999**, *40*, 319–322; The cleavage of ethers by benzyne. Richmond, G.; Spendel, W. *Tetrahedron Lett.* **1973**, 4557–4560; Novel tandem reaction of benzyne with cyclic ethers and active methines: Synthesis of ω -trichloroalkyl phenyl ethers. Okuma, K.; Fukuzaki, Y.; Nojima, A.; Shioji, K.; Yokomori, Y. *Tetrahedron Lett.* **2008**, *49*, 3063–3066) methanol was readily identified in the ¹H NMR spectrum of the reaction/product mixture. The isolated product **8** showed strong emission both in solution and the solid-state and it was intensely blue. It should be noted that this compound was prepared in excellent yield from commercially available materials using just three reactions. It should also be noted that many examples point to the fact that compounds possessing an alkynyl substituted aromatic core structural motif are often intensely fluorescent (Modulation of the electronic and mesomorphic properties of alkynyl-spirobifluorene compounds as a function of the substitution pattern. Thiery, S.; Heinrich, B.; Donnio, B.; Poriol, C.; Camerel, F. *J. Phys. Chem. C* **2015**, *119*, 10564–10575).

The absorption and emission spectra of **8** were measured (FIG. 3B) both in solution (red and green, respectively) and as a film (yellow and blue, respectively). Moreover, the alkynyldibenzofuran **8** proved to be very robust, showing virtually no sign of thermal degradation during laboratory sublimation or even following heating in air at 200 °C. An OLED device was built from the compound using standard procedures. The device emitted blue light (λ_{max} 440 nm) with an external quantum efficiency (EQE, the number of photons out of the glass substrate vs. the number of electrons in) of 0.9%. To put this value into context, blue OLEDs rarely show fluorescence EQEs as high as 5%. Charge-transfer between nearby emissive molecules often lowers photoluminescence (PL) efficiency. Because of inherent loss in the

optics, the theoretical maximum EQE for an ITO-based device capable of capturing essentially all of the fluorescence and phosphorescence potential is only about 20%. The initial fabrication was based on a commonly used architecture comprising 30 nm layer each of TCTA [tris(4-carbazoyl-9-ylphenyl)amine] and TPBi [1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene] as the hole and electron transporter layers, respectively. These encased a 23 nm thick active layer of **8**. These layers correspond to the yellow, blue, and green layers depicted in FIG. 2A.

A photograph of the actual devices prepared (four, in the quadrants of this single ITO/glass substrate) for this preliminary set of measurements is shown in FIG. 3C (top left). The four aluminum cathodes are evident as the silver-colored, L-shaped areas on the top surface of the glass. Each of the four devices has a 5 mm x 5 mm area of overlap between its Al and ITO electrodes. Each behaved similarly when subjected to a voltage bias and current flow (onset voltage ca. 2.6 V – blue light seen in top right of FIG. 3C). The chromaticity diagram (bottom of FIG. 3C) gives a more precise characterization of the emission; it is a deep blue (cf. yellow dot), quite near the ideal color saturation point for HDTV application.

The oxidation potential of **8** has also be measured (by cyclic voltammetry in acetonitrile) to be 1.27 V (vs. Fc/Fc^+). From the solution absorption spectra the HOMO/LUMO gap it is calculated to be 3.4 eV. The values for the energies of HOMO and LUMO is one of the parameters that can be used to guide the choice and design of additional materials for the electron and hole transporting materials.

A number of factors may contribute to performance. Some may relate to the device architecture itself and others to the structural features of the compound comprising the active emissive layer. This disclosure focuses on the latter. Preliminary assessments of each new compound were accomplished by measuring its absorption and emission in solution and film, thermal stability and sublimability, and a cyclic voltammogram from the compound.

There are a number of options for structural modification that can be introduced to tailor electro-optical properties and performance. These are discussed here for the case of **8**, but are not limited to that compound. Rather, they are representative of the type(s) of molecular modifications that allow for tuning of the photophysical properties. The degree of planarity in **8** (also referred to as compound **100**) will influence its spectroscopic properties. Initial DFT calculations indicated that compound **8** (also referred to as compound **100**) prefers a nearly planar relationship between the remote 2-methoxyphenyl and dibenzofuran subunits.

Calculations also suggested that the dimethylated analog **9a** (R = Me) may prefer a slightly twisted geometry and that the bis-TMS analog will have its arenes essentially orthogonal (FIG. 3D). This could increase the band gap and, perhaps, move the emission color even deeper into the blue/violet region. As various families of related compounds are assembled, the absorption and emission behavior can be studied computationally to see if a functional and level of theory can be identified that adequately accounts for the experimental spectral data for each given class of chromophores. Time-dependent DFT calculations were recently reported to do an excellent job of correlating key spectral properties in a study designed to capitalize on reverse intersystem crossing (Efficient blue organic light-emitting diodes employing thermally activated delayed fluorescence. Zhang, Q.; Li, B.; Huang, S.; Nomura, H.; Tanaka, H.; Adachi, C. *Nature Photonics* **2014**, 8, 326–332).

The analog **9a**, as well as each of **9b-e** (FIG. 3E) will be relatively straightforward to prepare; a simple change in the alkyne (or malonate ester) moiety provides the tetrayne substrates, each an analog of **6**. The bulk of substituents orthogonal to the plane of the chromophores influences the nature of aggregation, albeit in a largely empirical and unpredictable manner. Analogs of **9b** containing more bulky ester alkyl groups (e.g., bis-benzyl or bis-trichloroethyl to avoid ester pyrolysis issues) as well as the analog lacking the carbomethoxy groups altogether (not shown) can be made, this last from 1,6-heptadiyne as the starting material. The electronic substituent effects can also be studied to learn the extent to which they modify the fluorescence properties (1-alkynyl- and 1-alkenyl-3-arylimidazo[1,5-a]pyridines: Synthesis, photophysical properties, and observation of a linear correlation between the fluorescent wavelength and Hammett substituent constants. Yamaguchi, E.; Shibahara, F.; Murai, T. *J. Org. Chem.* **2011**, 76, 6146–6158.). Compounds **9c** in which X is diphenylamino (Structure-photophysics correlations in a series of 4-(dialkylamino) stilbenes: Intramolecular charge transfer in the excited state as related to the twist around the single bonds. Létard, J. F.; Lapouyade, R.; Rettig, W. *J. Am. Chem. Soc.* **1993**, 115, 2441-2447; Fluorescence enhancement of trans-4-aminostilbene by *N*-phenyl substitutions: The “amino conjugation effect”. Yang, J.; Chiou, S.; Liao, K. *J. Am. Chem. Soc.* **2002**, 124, 2518–2527; Achieving high-efficiency non-doped blue organic light-emitting diodes: Charge-balance control of bipolar blue fluorescent materials with reduced hole-mobility. Chi, C.; Chiang, C.; Liu, S.; Yueh, H.; Chen, C.; Chen, C. *J. Mater. Chem.* **2009**, 19, 5561–5571; Highly efficient blue organic light-emitting diodes based

on 2-(diphenylamino) fluoren-7-ylvinylarene derivatives that bear a *tert*-butyl group. Lee, K. H.; Kwon, Y. S.; Lee, J. Y.; Kang, S.; Yook, K. S.; Jeon, S. O.; Lee, J. Y.; Yoon, S. S. *Chem. Eur. J.* **2011**, *17*, 12994–13006; High efficiency thermally activated delayed fluorescence based on 1,3,5-tris(4-(diphenylamino)phenyl)-2,4,6-tricyanobenzene. Taneda, M.; Shizu, K.; Tanaka, H.; Adachi, C. *Chem. Commun.* **2015**, *51*, 5028–5031), cyano, methoxy, phenyl, or halo in the 4-(or 6-, if planarity disruption proves to be important) position can be considered. Inclusion of iodo substituents has the potential of turning on phosphorescence via spin-orbit coupling. The naphtho (and anthraceno) analogs **9d-e** are also intriguing. The chromophore is extended and the planarity maintained (in **9d**) or not (**9e**). The synthesis of new classes of π -rich compounds are also disclosed herein. For those that show initially promising photophysical, electrochemical, and thermal stability properties, development similar to that depicted and discussed with respect to FIG. 3 can also be undertaken.

Diynyl Benzenes

HDDA benzynes have also been considered and it has been found that they (cf. **11**, FIG. 4A) can be captured, in excellent yield, by net addition of a terminal alkyne when a substrate such as the tetrayne **10** and the alkyne are heated in the presence of a catalytic amount of cuprous chloride (Copper-catalyzed three-component coupling of arynes, terminal alkynes and activated alkenes. Bhuvaneswari, S.; Jegannathan, M.; Cheng, C.-H. *Chem. Commun.* **2008**, 5013–5015; Aryne polymerization enabling straightforward synthesis of elusive poly(ortho-arylene)s. Mizukoshi, Y.; Mikami, K.; Uchiyama, M. *J. Am. Chem. Soc.* **2015**, *137*, 74–77). Although the rather abbreviated size of the chromophore in the products **12** (and **14** from **13**, FIG. 4B) may result in compounds having weak emission of visible light.

The HDDA reaction has also been used in the pursuit of another new class of chromophores (FIG. 4C). For example, upon attempted Cadiot–Chodkiewicz coupling of the bis-bromo alkyne **5** (cf. FIG. 3A) with 4-cyanophenylacetylene at <25 °C, the 3:1 adducts **16a/b** were isolated directly in a combined yield of 54%. Presumably, these arise from capture of the benzyne **15**, formed now in an HDDA reaction that has occurred at room temperature (or below). It is thought, but not relied upon, that affinity of the cyano group(s) for Cu(I) in the tetrayne intermediate (not shown) leads to catalysis of this particular cycloisomerization. This can be studied in greater detail by preparing that tetrayne by alternative synthesis, in the absence of

Cu(I). It is also exciting that each of the 1,3- and 1,4-di(arylethynyl)benzene products **16a/b** shows strong emission, again of blue light (cf. photos of pure **16a** in FIG. 4C). Compounds **16** arise by two reactions from commercially available precursors. In related chemistry, the analogs **17a/b** have also been synthesized in over 90% isolated yield. Their emission, particularly in the solid state, appears to be exceptionally strong (far right photo in FIG. 4C).

Several analogs **18** bearing electronically biasing substituents (FIG. 4D) were also synthesized.

Known cycloaromatization reactions that very efficiently convert 1-alkynyl-2-arylbenzene derivatives to anthracenes and 1,3-dialkynyl-2-arylbenzenes to pyrenes with, e.g., Au(I) triflimidate (Synthesis of pyrenes by twofold hydroarylation of 2,6-dialkynylbiphenyls. Matsuda, T.; Moriya, T.; Goya, T.; Murakami, M. *Chem. Lett.* **2011**, 40, 40–41), ferric triflate (Cationic iron-catalyzed intramolecular alkyne-hydroarylation with electron-deficient arenes. Komeyama, K.; Igawa, R.; Takaki, K. *Chem. Commun.* **2010**, 46, 1748-1750) or, simply, trifluoroacetic acid (Directed electrophilic cyclizations: Efficient methodology for the synthesis of fused polycyclic aromatics. Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, 119, 4579–4593; Exploiting the versatility of organometallic cross-coupling reactions for entry into extended aromatic systems. Tovar, J. D.; Swager, T. M. *J. Organomet. Chem.* **2002**, 653, 215–222) catalysis can also be taken advantage of. These cyclizations of **18** can provide the polycyclic aromatic hydrocarbon (PAH) derivatives **19** and **20**, having anthracenes (blue) or pyrenes (red), respectively, as their core structures.

As seen in FIG. 4E trapping of a diaryl tetrayne analog of **13** with, e.g., 1,4-diethynylbenzene can produce a bis-carbazole containing structure like **21**. The route is six steps in length. Double-barreled (note the definition of "Ar" in **21**) cycloaromatization to pyrenes here will produce highly conjugated core structures, which opens the opportunity for OPV applications. Potential solubility issues can be mitigated through judicious choice of the R and R' substituents.

Perylene-derived Polycyclics

FIG. 5A indicates the feasibility of trapping an HDDA benzyne with perylene (**23**). Tetrayne **22** was heated and the resulting benzyne trapped to provide **24** as the major product. Although the solubility is marginal in hexanes/EtOAc chromatography eluents, the substance

dissolves readily in CDCl_3 . As we expected (Mechanistic insight into the dehydro-Diels–Alder reaction of styrene–ynes. Kocsis, L. S.; Kagalwala, H. N.; Mutto, S.; Godugu, B.; Bernhard, S.; Tantillo, D. J.; Brummond, K. M. *J. Org. Chem. ASAP* (DOI: 10.1021/acs.joc.5b00200)) dihydrogen has been lost. The R groups in the malonate esters and/or on the phenyl rings can be adjusted to address the solubility issues.

The cycloaromatization of the alkyne (red arrow) and oxidative cyclization of the proximal arene carbons (Scholl reaction (Comparison of oxidative aromatic coupling and the Scholl reaction. Grzybowski, M.; Skonieczny, K.; Butenschön, H.; Gryko, D. T. *Angew. Chem. Int. Ed.* **2013**, 52, 9900–9930)) can also be considered. In principle these can be done in either order, although the Scholl reaction may be hard to avoid, given its facile nature in a similar setting (Domino Diels–Alder cycloadditions of arynes: New approach to elusive perylene derivatives. Criado, A.; Peña, D.; Cobas, A.; Guitián, E. *Chem. Eur. J.* **2010**, 16, 9736–9740). Compound **24** is yellow (and emits orange). The products described in this section may be increasingly visibly colored. This suggests applications in OPV and OFET settings, where smaller HOMO/LUMO gaps are desirable. This often correlates with enhanced carrier mobility. A high degree of crystallinity is also often desirable for use in OFET devices.

Adducts like **25** (FIG. 5B) in which two benzyne molecules have been incorporated onto a single perylene scaffold, one to each of its two bay regions, can also be formed. Explicitly shown is the symmetrical 2:1 adduct, but it is noted that by working with isolated **24**, it may be possible to prepare mixed adducts in which two different benzyne compounds, each with an attendant unique chromophore, could be incorporated into analogous adducts. Cyclization to yet higher PAH subunits would then follow.

It should also be noted that there is a large body of chemistry that uses classically generated benzyne to produce larger PAHs. This is captured in two recent reviews, each containing well over 100 citations (Aryne cycloaddition reactions in the synthesis of large polycyclic aromatic compounds. Pérez, D.; Peña, D.; Guitián, E. *Eur. J. Org. Chem.* **2013**, 5981–6013; Arynes in the synthesis of polycyclic aromatic hydrocarbons. Wu, D.; Ge, H.; Liu, S. H.; Yin, J. *RSC Adv.* **2013**, 3, 22727–22738). The benzyne used in these studies are, necessarily, either relatively simple in structure or come with a fairly hefty price tag in the way of burdensome synthesis prior to their use in these conjunctive reactions. Again, HDDA-produced benzyne will prove advantageous in these applications.

Additional polycyclics can be seen in FIG. 5C.

Various symmetrical tetraynes **1103**, when warmed to generate **1103^{Benz}** in the presence of perylene (**1104a**) or its tetraethyl ester (**1104b**), gave an array of adducts **1105** in good yield (FIG. 6A). The "X" group in the linker as well as the aromatic substituents R¹/R² were varied.

5 The absorption (UV/Vis) and emission (photoluminescence, PL) spectra and cyclic voltammograms (CVs) were recorded (FIG. 6B). DFT calculations were used to evaluate the orbital distribution maps for the HOMO and LUMO and time-dependent DFT (TDDFT) was used to calculate the HOMO-LUMO energy gaps. These features can be valuable, for example, in judging the stability of compounds toward photooxidation (a factor in some applications of organic electronic or photonic materials). Such properties can also guide the design of new structural analogs that may have different or improved photophysical properties or that have substituents that impact aggregation (solution as well as crystalline or amorphous solids). In FIG. 6B, the CVs of compounds **1105a** vs. **1105b** show that there is a strong response in this alkynynaphthoperylene family to the aromatic substituents on both the oxidation and reduction half-wave potentials. In addition, although the absorption spectra for **1105b** and **1105c** are very similar, the PL spectra show a marked red-shift for the latter compound. This is consistent with the differences in the HOMO/LUMO maps for (a simplified model of) **1105c**, which suggests a substantial amount of charge-transfer character in the excited state; in contrast the maps for the FMOs for the **1105b** model (not shown) are very similar.

20 The synthesis of **1105** (X = C(CO₂Me)₂, R¹ = CO₂Me = E, R² = H) has also been completed using photochemical conditions. This can be referred to as a "photo-HDDA" (hv-HDDA) reaction. It can be generally utilized (i) with many diaryltetraynes **1105**, (ii) is compatible with a wide variety of trapping agents, and (iii) can even be effected cleanly at very low temperature (J. Am. Chem. Soc. 2017 139,8400-8403)

25 In the reactions leading to mono-adduct **1105c** (and, to an even lesser extent, many of the other variants of **1105**), a minor amount (5%) of a coeluting mixture of the isomeric 2:1 adducts **1106-syn** and **1106-anti** was formed. Solutions of this red compound fluoresced yellow in ambient lab light and markedly so when exposed to a 365 nm black light. However, the production of this tantalizing double-DA adduct was never efficient, even when an excess of **1103** was used. As a solution, the powerful Larock Pd(0)-mediated annulation of benzyne (FIG. 6C) could be utilized to efficiently synthesize, initially, **1013-anti**. This is representative of a

significantly broader class of highly conjugated dialkynyldinaphthoperylenes that will be equally accessible using other HDDA benzyne. In that annulation simple *o*-benzyne (e.g, **1108**), generated by the Kobayashi method are trapped with aryl halides (red) that contain, at a minimum, an *o*-halobiphenyl subunit (**1107**, FIG. 6C), giving elaborated triphenylenes **1109**. Net carbopalladation of **108**, followed by cyclization via electrophilic palladation and reductive elimination to the arene atom labeled blue in **1109**, finishes the overall [4+2] annulation. Notably, the Pd species on this cycle tolerate the high temperature used to produce **1108**, which provides a high confidence that HDDA-benzyne will function well in this impressively efficient and versatile process. One initial target was the dibenzocarbazole **1010** (FIG. 6D); carbazoles are privileged structures among light-emitting organics. The top portion comes from 3-(2-iodophenyl)-N-methylindole; the bottom from **1103** (X = O, R¹ = E). The green dashed line in the product cuts the two bonds formed in the HDDA reaction; the blue those produced by the Pd-annulation.

If the arylhalide lacks an ortho arene substituent and the benzyne precursor bears a suitably disposed trapping group, it is proposed that the annulation will proceed by back-biting into that group. E.g., the fluoranthene derivative **1012** could arise from tetrayne **1011** (FIG. 6E). C8 in the naphthyl ring (blue) is envisioned to capture the initial adduct of ArPdI with **1011**^{Benz}. Fluoranthene derivatives have been explored as emitters in blue OLEDs. The sense and extent of regioselectivity of the reactions of **1103**^{Benz} or **1011**^{Benz} with ArPdX await to be defined, but we note that potential modifiers include ligands on the Pd and use of a different benzyne from among the >dozen currently in the palette (see FIG. 6B). Again it is emphasized that **1012** would be available in only three reactions (alkyne bromination, Cadiot-Chodkiewicz cross-coupling, and HDDA cascade) if this chemistry can be reduced to practice.

Finally, returning to the 2:1 adduct motif present in **1106-syn/1106-anti**, we will exploit the double benzyne annulation developed by the Müllen group. They used a 1,7-dibromoperylenediimide derivative and Pd(dba)₂ to forge a bis-naphthoperylene by incorporating two molecules of benzyne (**1108**). Use of **1103**^{Benz} could be utilized to achieve the yet more elaborate bis-arylalkynyl analogs **13-anti** (FIG. 6F).

Tetraphenylcyclone-derived Compounds

Trapping of the HDDA-generated benzyne from the tetraynes **26a** and **26b** with tetraphenylcyclopentadienone (**27**, tetraphenylcyclone) gives adducts **28a/b** in extremely clean reactions. (FIG. 7A). These alkynylpentaarylnaphthalenes are also strongly, indeed brilliantly, emissive in the solid state. Importantly, the emission spectra are noticeably different, suggesting that further modification of X in **28** can be used to tailor the color of emitted light. Heavy atoms, such as halogens (e.g, Br and I) can be utilized to possibly turn on phosphorescence in the molecules.

Three-atom linker structures in the starting tetrayne (cf. the linker structures shown in FIG. 7B) can be utilized to provide analogs **29a**, which still possess the tetraphenyl-naphthalene subunit. Contrasting characteristics arising from adducts derived from the cyclone analogs **30** (Pyrene-based fluorescent nitric oxide cheletropic traps (FNOCTs) for the detection of nitric oxide in cell cultures and tissues. D ppe, P. M.; Talbierski, P. M.; Hornig, P. S.; Rauen, U.; Korth, H.-G.; Wille, T.; Boese, R.; Omlor, T.; de Groot, H.; Sustmann, R. *Chem. Eur. J.* **2010**, *16*, 11121–11132; Synthesis and structure of longitudinally twisted polycyclic aromatic hydrocarbons. Pascal, Jr., R. A.; McMillan, W. D.; Van Engen, D.; Eason, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4660–4665; Synthesis and properties of diamino-substituted dipyrido[3,2-1:2',3'-c]phenazine. Yamada, M.; Tanaka, Y.; Yoshimoto, Y.; Kuroda, S.; Shima, I. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1006–1011), each of which has planarity locked into the fused ring portion of its "back" rings, can also be considered. This may change the electronic character and nature of the chromophore in analogs **29b**. It is noted that phenanthroline ligands (cf. X = N) have been used to bind heavy metal atoms such as europium (Lanthanide-based luminescent hybrid materials. Binnemans, K. *Chem. Rev.* **2009**, *109*, 4283–4374) in order to dope emissive layers and enhance phosphorescence. By analogy, the impact of the use of the known cyclone analogs **31** (Novel perylene chromophores obtained by a facile oxidative cyclodehydrogenation route. Wehmeier, M.; Wagner, M.; M llen, K. *Chem. Eur. J.* **2001**, *7*, 2197–2205) and **32** (Versuche zur Darstellung von aromatischen Monocarbonyl- und o-Dicarbonyl-Verbindungen, II. Darstellung aromatischer Monocarbonyl- und o-Dicarbonyl-Verbindungen durch Diensynthesen. Ried, W.; Bonnighausen, K. H. *Liebigs Ann. Chem.* **1961**, *639*, 61–67) have on the properties of adducts analogous to **29b** (structures not shown) has also been considered. Benzyne adducts of hexaphenylisobenzofuran (**32**) have been deoxygenated/reduced (e.g., Zn⁰/AcOH (The most

stable and fully characterized functionalized heptacene. Chun, D.; Cheng, Y.; Wudl, F. *Angew. Chem. Int. Ed.* **2008**, *47*, 8380–8385)) to the corresponding anthracene adducts (Octaphenylnaphthalene and decaphenylanthracene. Qiao, X.; Padula, M. A.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, Jr., R. A. *J. Am. Chem. Soc.* **1996**, *118*, 741-745).

5 FIGs. 7C, 7D and 7E illustrate further illustrative compounds.

Trapping of HDDA benzyne with the classic benzyne trap TPCPD (**1014**) has proven to be extremely clean chemistry (FIG. 8A), even using a nearly 1:1 stoichiometric ratio. Each compound in the initial set of adducts, **1015a–d**, was isolated in >90% yield after simple chromatographic purification. Each was strongly, indeed brilliantly, emissive, both in solution
10 and, especially so, in the solid state. Each showed behavior reminiscent of aggregation-induced emission (AIE), which is somewhat surprising in view of the twisted biaryl moieties that picket the naphthalene core. However, other molecules having similar topological features have shown AIE and/or promise as blue emitters in OLEDs. The color of the emission of **1015d** is decidedly more green than **1015a–c**, which all showed strong blue emission and were further explored as
15 candidates for incorporation into a prototypical OLED. All of these compounds are thermally robust; they can be sublimed with little to no sign of decomposition under a simple mechanical pump vacuum. They gain color only slowly when held in the air at 300 °C. Differential scanning calorimetry (DSC) showed no onset of thermal characteristics below 300 °C and thermal gravimetric analysis (TGA) showed mass loss of 5% only at temperatures ranging from 336–
20 357 °C. Given these promising characteristics, we worked with a researcher in the lab of Russ Holmes to prepare thin films and measured their photoluminescence efficiencies (η_{PL}). We then fabricated OLED devices. Our compounds survived the vapor deposition techniques very well; there was no sign of residue in the heating crucible after deposition. These OLEDs showed impressive deep blue emission; the champion device had an external quantum efficiency (η_{EQE})
25 of 3.0%. Notably, the maximum η_{EQE} expected for an OLED based on a fluorescent emitter fabricated and measured in this fashion (forward emission only) is 5%.

The power of this method to deliver complex polycyclics in a streamlined fashion (again, 3 steps) is further evidenced by preparing compounds like those implied in FIG. 8B. Each of the arylalkynyl-benzotriphenylene **1016a** and -naphthopyrene **1016b** (from 2,5-diphenylphenanthro-
30 and 2,5-diphenylpyrenocyclopentadienone, respectively) has an extended planar chromophore that is sterically protected near its midsection by the two orthogonal phenyl substituents. This feature

is common to each of the analogous products are anticipated to arise starting from **1017**, **1018**, or **1019**. It is relevant that: (i) benzyne adducts of hexaphenylisobenzofuran (**1019**) can be deoxygenated/reduced (e.g., Zn⁰/AcOH) to the corresponding anthracene adducts and (ii) phenanthrolines are ligands for lanthanides and Ir(III). These heavy metals are often used as dopants to the emissive layer, where their promotion of intersystem crossing can turn on phosphorescence by capture of triplet states to dramatically improve η_{EQE} in OLED architectures. Two-to-one HDDA cascade adducts will emerge from use of the readily available 1,4-phenylene-linked bis-cyclopentadienone **1020**. The structural complexity factor of the anticipated products, which contain *p*-phenylene-linked chromophores, doubles with no additional effort.

Tethers, Dimers, and Trimers

Malonate and 2-azatrimethylene linkers/tethers have been used to join the diyne and diynophile moieties in the HDDA substrates used above. However, it is known that tri- and tetrayne substrates having a substantially larger variety of connecting units are similarly productive (cf. A-B-C in the generic structure **33** of the derived fused benzynes, FIG. 9A) (Alkane C–H insertion by aryne intermediates with a silver catalyst. Yun, S. Y.; Wang, K.; Lee, N.; Mamidipalli, P.; Lee D. *J. Am. Chem. Soc.* 2013, *135*, 4668–4671; Alder-Ene reactions of arynes. Karmakar, R.; Mamidipalli, P.; Yun, S. Y.; Lee, D. *Org. Lett.* 2013, *15*, 1938–1941; Silver-mediated fluorination, trifluoromethylation, and trifluoromethylthiolation of arynes. Wang, K.; Yun, S. Y.; Mamidipalli, P.; Lee, D. *Chem. Sci.* 2013, *4*, 3205–3211; Formal hydrogenation of arynes with silyl C π –H bonds as an active hydride source. Mamidipalli, P.; Yun, S. Y.; Wang, K.; Zhou, T.; Xia, Y.; Lee, D. *Chem. Sci.* 2014, *5*, 2362–2367; Hydroarylation of arynes catalyzed by silver for biaryl synthesis. Lee, N.; Yun, S. Y.; Mamidipalli, P.; Salzman, R. M. Lee, D.; Zhou, T.; Xia, Y. *J. Am. Chem. Soc.* 2014, *136*, 4363–4368; Regioselectivity in the nucleophile trapping of arynes: the electronic and steric effects of nucleophiles and substituents. Karmakar, R.; Yun, S. Y.; Wang, K.; Lee, D. *Org. Lett.* 2014, *16*, 6–9; Benzannulation of triynes to generate functionalized arenes by spontaneous incorporation of nucleophiles. Karmakar, R.; Yun, S. Y.; Chen, J.; Xia, Y.; Lee, D. *Angew. Chem. Int. Ed.* 2015, *54*, 6582–6586; Synthesis of phenolic compounds by trapping arynes with a hydroxy surrogate. Karmakar, K.; Ghorai, S.; Xia, Y.; Lee, D. *Molecules* 2015, *20*, 15862–15880; A new approach

- for fused isoindolines via hexadehydro-Diels–Alder reaction (HDDA) by Fe(0) catalysis. Vandavasi, J. K.; Hu, W.; Hsiao, C.; Senadia, G. C.; Wang, J. J. *RSC Adv.* **2014**, *4*, 57547–57552; [4.2](2,2')(2,2')-Biphenylophanetriyne: A twisted biphenylophane with a highly distorted diacetylene bridge. Nobusue, S.; Yamane, H.; Miyoshi, H.; Tobe, Y. *Org. Lett.* **2014**, *16*, 1940–1943; Straightforward synthesis of 5-bromopenta-2,4-diynenitrile and its reactivity towards terminal alkynes: A direct access to diene and benzofulvene scaffolds. Kerisit, N.; Toupet, L.; Larini, P.; Perrin, L.; Guillemin, J.; Trolez, Y. *Chem. Eur. J.* **2015**, *21*, 6042–6047; Hydroboration of arynes formed by hexadehydro-Diels–Alder cyclizations with *N*-heterocyclic carbene boranes. Watanabe, T.; Curran, D. P.; Taniguchi, T. *Org. Lett.* **2015**, *17*, 3450–3453; Alkane desaturation by concerted double hydrogen atom transfer to benzyne. Niu, D.; Willoughby, P. H.; Baire, B.; Woods, B. P.; Hoye, T. R. *Nature* **2013**, *501*, 531–534; The aromatic ene reaction. Niu, D.; Hoye, T. R. *Nature Chem.* **2014**, *6*, 34–40; Tactics for probing aryne reactivity: mechanistic studies of silicon–oxygen bond cleavage during the trapping of (HDDA-generated) benzyne by silyl ethers. Hoye, T. R.; Baire, B.; Wang, T. *Chem. Sci.* **2014**, *5*, 545–550; Dichlorination of (HDDA-generated) benzyne and a protocol for interrogating the kinetic order of bimolecular aryne trapping reactions. Niu, D.; Wang, T.; Woods, B. P.; Hoye, T. R. *Org. Lett.* **2014**, *16*, 254–257; Cycloaddition reactions of azide, furan, and pyrrole units with benzyne generated by the hexadehydro-Diels–Alder (HDDA) reaction. Chen, J.; Baire, B.; Hoye, T. R. *Heterocycles* **2014**, *88*, 1191–1200 (invited, V. Snieckus celebratory issue); Rates of hexadehydro-Diels–Alder (HDDA) cyclizations: Impact of the linker structure. Woods, B. P.; Baire, B.; Hoye, T. R. *Org. Lett.* **2014**, *16*, 4578–4581; Mechanism of the reactions of alcohols with *o*-benzyne. Willoughby, P. H.; Niu, D.; Wang, T.; Haj, M. K.; Cramer, C. J.; Hoye, T. R. *J. Am. Chem. Soc.* **2014**, *136*, 13657–13665; Differential scanning calorimetry (DSC) as a tool for probing the reactivity of polyynes relevant to hexadehydro-Diels–Alder (HDDA) cascades. Woods, B. P.; Hoye, T. R. *Org. Lett.* **2014**, *16*, 6370–6373; Intramolecular [4+2] trapping of a hexadehydro-Diels–Alder (HDDA) benzyne by tethered arenes. Pogula, V. D.; Wang, T.; Hoye, T. R. *Org. Lett.* **2015**, *17*, 856–859; Competition between classical and hexadehydro-Diels–Alder (HDDA) reactions of HDDA triynes with furan. Luu Nguyen, Q.; Baire, B.; Hoye, T. R. *Tetrahedron Lett.* **2015**, *56*, 3265–3267 (Memorial Symposium-in-Print for H. H. Wasserman); Mechanism of the intramolecular hexadehydro-Diels–Alder reaction. Marell, D. J.; Furan, L. R.; Woods, B. R.; Lei, X.; Bendel-Smith, A. J.; Cramer, C. J.; Hoye, T. R.; Kuwata, K. T. *J. Org.*

Chem. 2015, 80, 11744–11754; The pentadehydro-Diels–Alder reaction. Wang, T.; Naredla, R. R.; Thompson, S. K.; Hoyer, T. R. *Nature* 2016, 532, 484–488; Reactions of HDDA-derived benzyne with sulfides: Mechanism, modes, and three-component reactions. Chen, J.; Palani, V.; Hoyer, T. R. *J. Am. Chem. Soc.* 2016, 138, 4318–4321; The hexadehydro-Diels–Alder (HDDA) cycloisomerization reaction proceeds by a stepwise mechanism. Wang, T.; Niu, D.; Hoyer, T. R. *J. Am. Chem. Soc.* ASAP (DOI: 10.1021/jacs.6b03786))

The properties of the resulting trapped adducts are influenced at least in part, by the nature of A-B-C. The linkers in the precursors to the benzyne in the top row of FIG. 9A are symmetrical and contain propargylic methylene (and sp^3) carbons. All of the linkers in the bottom row of FIG. 9B have functionality that is conjugated with either the diyne, the diynophile, or both. Thus, the product chromophores can be substantially and easily modified merely by altering the triyne (or tetrayne) substrate and dropping it into virtually any of the reactions already described above or below. It should also be noted that the synthesis of the unsymmetrical substrates may be a bit longer, but virtually every one listed here is available in ≤ 4 -5 total reactions from commercial compounds. Even the tetrayne variants react regioselectively, giving essentially one of the two possible isomeric benzyne.

Shown in FIGs. 9B to 9F are a variety of possibilities for quickly accessing various structures that may have interesting electro-optical properties. Alkyne cross-metathesis (FIG. 9B) could prove to be very powerful—and it should be emphasized that "since the catalysts have evolved from the glovebox to the benchtop, there should be little barrier left for a wider use of this reaction in organic synthesis." (Alkyne metathesis on the rise. Fürstner, A. *Angew. Chem. Int. Ed.* 2013, 52, 2794–2819). Homo-metathesis of **34** (R=Me) with concomitant removal of volatile 2-butyne is a powerful method for directly accessing the alkyne-linked dimers **35**, a process applicable to many of tetrayne-derived products described already. A complementary strategy would be to effect cross metathesis between **34** (R = Ar¹) and an excess of Ar²-propyne, in order to escape the symmetry-imposed identity of the R groups in **34**. The impact of electronic complementarity of the Ar¹/Ar² pair in **36** could then efficiently be explored from a penultimate common intermediate.

A strategy for conjoining two benzyne intermediates, **37**, into products containing a new central benzenoid ring (cf. **39**) using the 1,4-diarylated mesoionic pyrimidine **38** is shown in FIG. 9C. The consecutively slower thermal extrusion of each methylisocyanate (Mesoionic six-

membered heterocycles, XVII. Cycloaddition of benzyne to mesoionic pyrimidines. Kappe, T.; Pocivalnik, D. *Heterocycles* 1983, 20, 1367–1371; Synthesis, characterization, and physical properties of a conjugated heteroacene: 2-Methyl-1,4,6,7,8,9-hexaphenylbenz(g)isoquinolin-3(2*H*)-one(BIQ). Zhang, Q.; Xiao, J.; Yin, Z. Y.; Duong, H. M.; Qiao, F.; Boey, F.; Hu, X.; Zhang, H.; Wudl, F. *Chem. Asian J.* **2011**, 6, 856–862; “Clean Reaction” Strategy to Approach a Stable, Green Heptatwistacene Containing a Single Terminal Pyrene Unit. Xiao, J.; Malliakas, C. D.; Liu, Y.; Zhou, F.; Li, G.; Su, H.; Kanatzidis, M. G.; Wudl, F.; Zhang, Q. *Chem. Asian J.* **2012**, 7, 672–675) permits either two of the same or two *different* benzyne (cf. **37a** vs. **37b**) to be incorporated into products **39**.

FIG. 9D also shows the homotrimerization of HDDA benzyne **37a**, a reaction that is well preceded for simple benzyne made by classical methods of elimination (Aryne cycloaddition reactions in the synthesis of large polycyclic aromatic compounds. Pérez, D.; Peña, D.; Guitián, E. *Eur. J. Org. Chem.* **2013**, 5981–6013; Arynes in the synthesis of polycyclic aromatic hydrocarbons. Wu, D.; Ge, H.; Liu, S. H.; Yin, J. *RSC Adv.* **2013**, 3, 22727–22738; Efficient palladium-catalyzed cyclotrimerization of arynes: Synthesis of triphenylenes. Peña, D.; Escudero, S.; Pérez, D.; Guitián, E.; Castedo, L. *Angew. Chem. Int. Ed.* **1998**, 37, 2659–2661) to produce novel adducts **40** having a newly created triphenylene core.

As shown in FIG. 9E, benzyne itself can be trapped by the 1,8-disubstituted naphthalene derivatives **41** (An interesting benzyne-mediated annulation leading to benzo[a]pyrene. Cobas, A.; Guitián, E.; Castedo, L. *J. Org. Chem.* **1997**, 62, 4896–4897) or **43** (Domino Diels–Alder cycloadditions of arynes: New approach to elusive perylene derivatives. Criado, A.; Peña, D.; Cobas, A.; Guitián, E. *Chem. Eur. J.* **2010**, 16, 9736–9740) to produce, either directly or following reductive dehydration, benzo[pqr]tetraphene and benzo[a]perylene. Use of this reaction to capture all manner of HDDA-derived benzyne **37a** should give, by analogy, the PAHs **42** or **44**, respectively (possibly along with their regioisomers). The “l” and “n” in Fig. 9E are misleading. The examiner would want to see them defined. The intent of the highlight in the original graphic was merely to help the reader more easily pair which carbon in the substrate maps onto which in the product. I’d suggest you just remove them to avoid confusion.

FIG. 9F shows a transformation resulting from heating the triynyl ester **46** alone (i.e., in the absence of any trapping agent) (Spontaneity to serendipity: From an enediyne core biosynthetic hypothesis to the hexadehydro-Diels–Alder reaction. Woods, B. P. Ph.D. Thesis,

University of Minnesota, Minneapolis, MN, 2014). This reaction produced the dimeric alkynyl naphthalene derivative **48** in 45% yield following chromatographic purification. This can perhaps be rationalized via cross dimerization of the benzyne **45** with **46** to give a benzocyclobutadiene and subsequent IMDA to the hemi-Dewar naphthalene (cf. **47**). In one experiment the 1-naphthyl (in place of *t*-butyl) analog of **46** has been prepared. Upon heating, an intensely emitting spot was observed (TLC analysis).

Compounds disclosed in and related to FIGs. 9A to 9E may have a greater degree of conjugation than others, and, as such, they may be more likely to be colored and therefore be good candidates for consideration and initial evaluation in OPV and OFET devices.

Double-barreled HDDAs: Oligomeric Substances

Two different types of *difunctional* reactants have been utilized. One (FIG. 10A) involves the use of 1,4-diaminobenzene. With just 0.5 molar equivalents, the benzyne derived from triyne **49** was efficiently trapped to give the orange-red adduct **50**. In a complementary strategy (FIG. 10B), the doubly armed, bis-benzyne precursor **51** was cyclized to deliver the heptacycle **52**, again in a reasonably clean fashion. Bis-indanone adducts like **52** can be exploited by converting them into: (a) the quasi-delocalized *s*-indacene derivatives **53** (*s*-Indacene, a quasi-delocalized molecule with mixed aromatic and anti-aromatic character. Nendela, M.; Goldfussa, M.; Houk, K. N.; Hafner, K. *J. Mol. Struct. (THEOCHEM)* **1999**, *461–462*, 23–28; Electron-accepting 6,12-diethynylindeno[1,2-*b*]fluorenes: Synthesis, crystal structures, and photophysical properties. Chase, D. T.; Fix, A. G.; Rose, B. D.; Weber, C. D.; Nobusue, S.; Stockwell, C. E.; Zakharov, L. N.; Lonergan, M. C.; Haley M. M. *Angew. Chem. Int. Ed.* **2011**, *50*, 11103–11106; Synthesis, crystal structures, and properties of 6,12-diaryl-substituted indeno[1,2-*b*]fluorenes. Nishida, J.; Tsukaguchi, S.; Yamashita, Y. *Chem. Eur. J.* **2012**, *18*, 8964–8970) and (b) the bis-spirocyclic derivatives **54** (New 3 π -2spiro ladder-type phenylene materials: Synthesis, physicochemical properties and applications in OLEDs. Cocherel, N.; Poriel, C.; Rault-Berthelot, J.; Barrière, F.; Audebrand, N.; Slawin, A. M. Z.; Vignau, L. *Chem. Eur. J.* **2008**, *14*, 11328–11342). These motifs have shown promising electro-optical behaviors, albeit for different reasons—the 4n π -electron count of the former brings interesting consequences to the redox and HOMO-LUMO gap properties (Electron-accepting 6,12-diethynylindeno[1,2-*b*]fluorenes: Synthesis, crystal structures, and photophysical properties. Chase, D. T.; Fix, A. G.; Rose, B. D.; Weber, C. D.;

Nobusue, S.; Stockwell, C. E.; Zakharov, L. N.; Lonergan, M. C.; Haley M. M. *Angew. Chem. Int. Ed.* 2011, *50*, 11103–11106: Synthesis, crystal structures, and properties of 6,12-diaryl-substituted indeno[1,2-b]fluorenes. Nishida, J.; Tsukaguchi, S.; Yamashita, Y. *Chem. Eur. J.* **2012**, *18*, 8964–8970) and the orthogonal bulk of the latter (Modulation of the electronic and mesomorphic properties of alkynyl-spirobifluorene compounds as a function of the substitution pattern. Thiery, S.; Heinrich, B.; Donnio, B.; Poriel, C.; Camerel, F. *J. Phys. Chem. C* **2015**, *119*, 10564–1057) is believed to suppress excimer formation in solid films (New 3π -2spiro ladder-type phenylene materials: Synthesis, physicochemical properties and applications in OLEDs. Cocherel, N.; Poriel, C.; Rault-Berthelot, J.; Barrière, F.; Audebrand, N.; Slawin, A. M. Z.; Vignau, L. *Chem. Eur. J.* **2008**, *14*, 11328–11342).

This "double-barreled" approach is applicable to preparation of compounds like **55** and **56** (FIG. 10C). The synthetic sequences for preparation of the hexaynyl precursors (not shown), now bearing aryl substituents in place of the siloxyethyls in **51**, by analogy should include 5 to 6 linear steps.

In certain applications (e.g., large area electronics and solar cells), highly conjugated polymeric materials are quite desirable (Materials and Applications for Large Area Electronics: Solution-Based Approaches. Arias, A. C.; MacKenzie, J. D.; McCulloch, I.; Rivnay, J.; Salleo, A. *Chem Rev.* 2010, *110*, 3–24; Recent advances in bulk heterojunction polymer solar cells. Lu, L.; Zheng, T.; Wu, Q.; Schneider, A. M.; Zhao, D.; Yu, L. *Chem Rev.* **2015**, *115*; Color control in π -conjugated organic polymers for use in electrochromic devices. Beaujuge, P. M.; Reynolds, J. R. *Chem Rev.* **2010**, *110*, 268–320; Parker, T. C.; Marder, S. R. Synthetic methods in organic electronic and photonic materials: A practical guide, Royal Society of Chemistry: Cambridge, UK, 2015). The HDDA chemistry can be readily harnessed to quickly access novel macroscopic materials.

First, and as shown in FIG. 10D, the two types of difunctional substrates described in panels A and B can be joined to produce oligomeric materials like **57**. It is thought, but not relied upon that the extended conjugation may lead to strongly absorbing materials across a broad spectral range in solvent-cast films prepared with these oligomers. Analogs synthesized using aliphatic diamines may provide substances with interrupted conjugation for comparative benchmarking of the effect of the linker aryl groups.

Second, a series of polymeric materials derived directly from the compound described above (FIG. 3) can be synthesized. Namely, compound **99c** where X is a bromide or iodide (FIG. 10E) can be oligomerized through Stille or Suzuki coupling (Parker, T. C.; Marder, S. R. *Synthetic methods in organic electronic and photonic materials: A practical guide*, Royal Society of Chemistry: Cambridge, UK, 2015; Monodisperse conjugated polymer particles by Suzuki–Miyaura dispersion polymerization Kuehne, A. J. C.; Gather, M. C.; Sprakel, J. *Nat. Commun.* **3**:1088 doi:10.1038/ncomms2085 (2012); Conjugated polymers containing diketopyrrolopyrrole units in the main chain. Tieke, B.; Rabindranath, A. B.; Zhang, K.; Zhu, Y. *Beilstein J. Org. Chem.* **2010**, *6*, 830–845; Green chemistry for organic solar cells. Burke, D. J.; Lipomi, D. J. *Energy Environ. Sci.* **2013**, *6*, 2053–2066; Conjugated polymers based on naphthalene diimide for organic electronics. Sommer, M. *J. Mater. Chem. C* **2014**, *2*, 3088–3098) of dimetallated aromatic co-reactants to give **58**. Similar chain extensions with diyne linkers (Conjugated polymers containing diketopyrrolopyrrole units in the main chain. Tieke, B.; Rabindranath, A. B.; Zhang, K.; Zhu, Y. *Beilstein J. Org. Chem.* **2010**, *6*, 830–845; Conjugated polymers based on naphthalene diimide for organic electronics. Sommer, M. *J. Mater. Chem. C* **2014**, *2*, 3088–3098) can also be considered. Finally, the preparation of **99c** should require only three reactions—yet another testament to the power and potential of the HDDA cascade.

Metal-catalyzed reactions of HDDA benzyne have the power (and precedented efficiency) to dramatically increase the complexity of polycyclic products. Experiments that fall into two classes are proposed: ones in which the metal-enabled process is occurring either (i) in situ (i.e., simultaneously with the HDDA reaction; FIG. 11A to 11D) or (ii) subsequent to isolation of an initial HDDA cascade product (FIG. 11E to 11G).

The use of a Pd(0) annulation strategy for accessing the 2:1 adducts **1013** (FIG. 6F). In the absence of an arylhalide trapping agent, Pd(0) catalysts are known to promote efficient cyclotrimerization of classical benzyne to triphenylene derivatives. 3,6-Disubstituted benzyne have also been efficiently trimerized. In the context of an HDDA benzyne, the products take the form of **1021** (FIG. 11A)—once again arising from just three chemical reactions. Recall (FIG. 6B) that the fused-rings represented by A-B-C can include fully conjugated π -systems (e.g., fluorenones and carbazoles). If this trimerization proves workable, the electronic vs. steric factors of the unsymmetrical HDDA benzyne (as well ligand(s) on Pd) influence on the selectivity for h-h-h vs. h-h-t isomer formation will be examined.

A very surprising observation was made (FIG. 11B) when **22** was treated with excess *p*-cyanophenylacetylene at 0 °C under typical Cadiot-Chodkiewicz cross-coupling conditions. The brightly emitting, regioisomeric diynes **25a** and **25b** were formed. The clear implication is that the benzyne **24** is being catalytically hydroalkynylated. Even more remarkably, the HDDA cyclization to **1024** is presumably also being (dramatically) accelerated by Cu. A variety of ethynylbenzene derivatives other than *p*-cyano (e.g., **103a-d** in FIG. 8A) smoothly gave rise to the corresponding tetraynes under the same conditions. The dicyanophenyltetrayne itself was prepared under Cu-free cross-coupling conditions and that Cu-promoted process was studied; it was hypothesized that the cyanoarenes, are unique in their ability to capitalize on this catalysis because of Cu←N≡CR affinity. If true, this would be the first instance of a catalyzed HDDA reaction.

The hydroalkynylation of the benzyne (second step) is also potentially very powerful. Tetrayne **3c** (FIG. 8A) was very efficiently trapped by alkyne **1023b** to give the green emitters **1026a** and **1026b**. When a more regioselective benzyne like **1027^{Benz}** (FIG. 11C) was used, only the single isomer **1028** was obtained, and the process was efficient even when only a slight excess of alkyne was used. The outcome of a competition trapping experiment using both PhC≡CD and TolC≡CH may reveal the intramolecularity (or not) of the process. It has also completely unexpectedly been discovered (FIG. 11D) that triynes **1037**, when heated in the absence of trapping agents, self-dimerize to the (pale yellow in color and strongly blue-emitting) alkynyl naphthalenes **1040**. These presumably arise through the semi-Dewar naphthalenes **1039**, themselves the intramolecular DA adducts of intermediate benzocyclobutadienes **1038**. The [2+2] rather than [4+2] nature of that cyclization is noteworthy; the latter would have produced a naphthyne, an issue revisited in Module V, below. This represents the first instance in which products have been isolated arising from the "back-biting" of an HDDA benzyne into a substrate molecule. This allowed the design of other examples in which benzocyclobutadienes are formed from benzynes, processes that have only been previously observed in very low yield.

A number of these HDDA products contain functionality that can be further capitalized upon. Cyclization of *o*-alkynylbiaryls to phenanthrenes or of 1,3-dialkynyl-2-arylbenzenes to pyrenes can be achieved with, e.g., Au(I) triflimidate, ferric triflate, or, simply, TFA. These cyclizations applied to **1029** will provide the polycyclic aromatics **1030** and/or **1031** (FIG. 11E). Trapping of a diaryl tetrayne like **1032** with, e.g., 1,4-diethynylbenzene would produce the

linked bis-carbazole adduct **1033** (FIG. 11F). Cycloaromatization to pyrenes here would produce extremely highly conjugated core structures, whose potential for OPV application will be explored. Use of 1,3-diethynyl- or 1,3,5-triethynylbenzene will give polycyclics of complementary shapes.

5 Finally, two different dimerization strategies for self-coupling of polycyclic products **1034** (FIG. 11G) will be explored as another avenue for post-HDDA modification to new chromophoric motifs. Each is applicable to many of the previously described tetrayne-derived products, thus doubling down on the opportunities they afford. Alkyne metathesis of **1034** (R = Me) with concomitant removal of volatile 2-butyne leads to **1035**. We note that "since the
10 catalysts have evolved from the glovebox to the benchtop, there should be little barrier left for a wider use of this reaction in organic synthesis." A complementary approach is to effect Glaser/oxidative coupling, a robust process even for ethynes carrying extremely large substituents, of the terminal alkyne revealed by mild desilylation of **1034** (R = TMS). This results in **1036**, the ethynyl homolog of **1035**. It will be interesting to observe the degree to
15 which these two linkages alter the spectroscopic/electronic properties of each relative to one another as well as to the parent **1034**.

Bidirectional HDDAs

 Mutually reactive, *difunctional* HDDA substrates and trapping agents present an
20 intriguing opportunity; one, the other, or both can be used in an HDDA cascade. A relevant preliminary pair of experiments is shown in FIGs. 12A and 12B. In the first, 1,4-diaminobenzene (**1042**) was used as the trap. With just 0.5 molar equivalents, the benzyne **1041**^{Benz} was efficiently captured to give the (orange-red) adduct **1043**. The push-pull character of this product, as well as many in this module, is a common structural feature in compounds that have
25 been explored for OLED applications. In a complementary reaction (FIG. 12B), the doubly armed, bis-benzyne precursor **1044**, which is just as readily prepared as mono-armed triynes like **1041**, was cyclized to deliver the heptacycle **1045**, again in reasonably clean fashion. This result also demonstrated the viability of a triphenylsilyl ether moiety to function as an intramolecular trap. Bulky triarylsilyl groups have often been explored as components of both the emissive and
30 wide band-gap host materials in OLEDs.

In some optoelectronic applications (e.g., large area electronics and solar cells), highly conjugated polymeric materials are desirable. HDDA chemistry can be readily harnessed to quickly access novel macroscopic materials. An intensely colored, oligomeric substance **1046** was prepared (FIG. 12C). Limited solubility of this material has made it difficult to
5 chromatograph, but SEC analysis indicated the presence of oligomers having a number average of ca. 3-mers. *N,N'*-dialkylated derivatives of **1042** will also be explored as well as the use of higher alkyls in place of the methyl groups in **1041** to circumvent this problem. Finally, analogs synthesized using aliphatic diamines will provide substances with interrupted conjugation for comparative benchmarking of the effect of the linker aryl groups in the conjugated oligomers
10 **1046**.

A type of internal trapping reaction is shown in FIG. 12D. It gave the initial, strongly blue fluorescent compounds with which OLED prototypes were prepared. Tetraynes **1047** containing terminal *o*-methoxyphenyl groups cyclize extremely efficiently to dibenzofurans like **1049**. The analogous dibenzothiophenes and carbazoles have also been made from thioether and
15 aniline precursors. Identification of the four methyl-containing byproducts shown beside **1049** provides strong evidence to support the intermediacy of the oxonium ion-containing zwitterion **1048**. Nearly ten analogs of these arylalkynyldibenzofurans having various substituents on the arenes coming from **1047** have been made and substituent perturbation on the absorption and emission spectra are being studied.

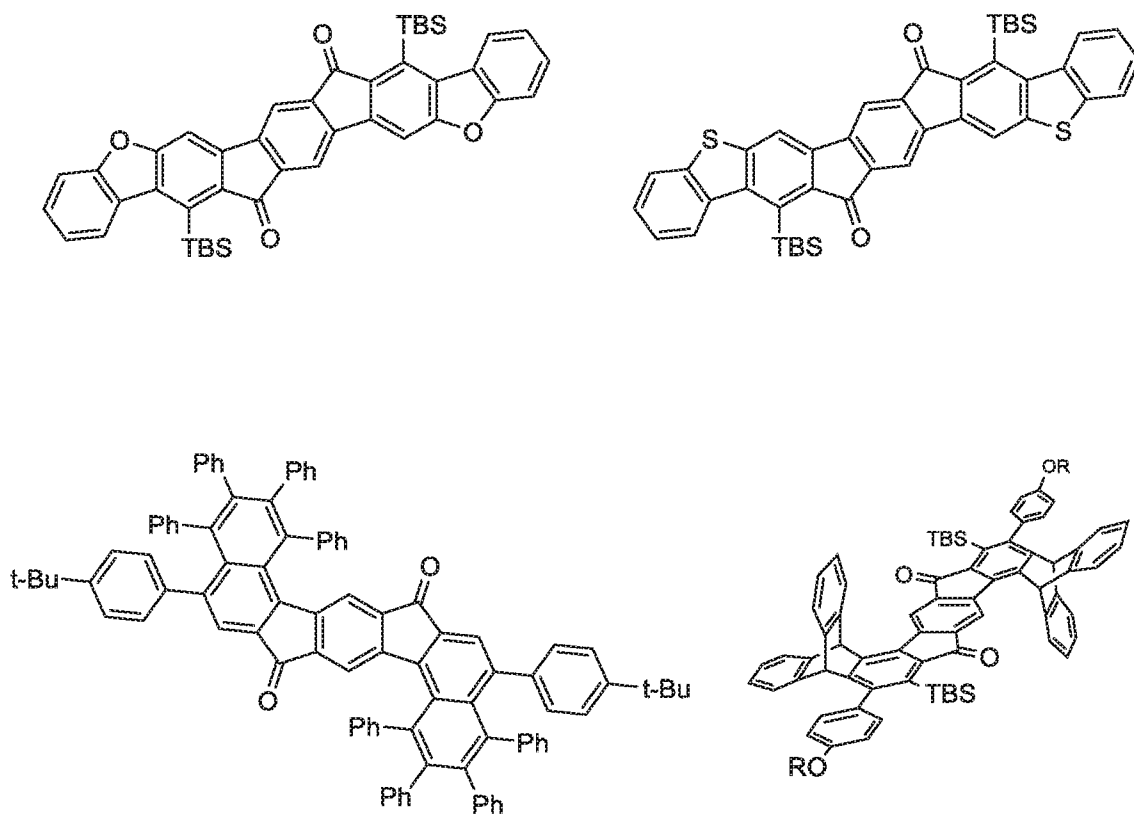
Pd-catalyzed cross couplings (Sonogashira, Suzuki, Stille) are effective for producing
20 novel conjugated oligomers. The use of **1049** (X = Br or I) to prepare oligomers **1050**, containing varying degrees of through-conjugation in the connecting units, depending upon the choice of the difunctional cross-coupling partner (FIG. 12D) will be explored. Notably (again), the co-monomers **1049** can be accessed in three reactions, another testament to the power and potential
25 of the HDDA cascade.

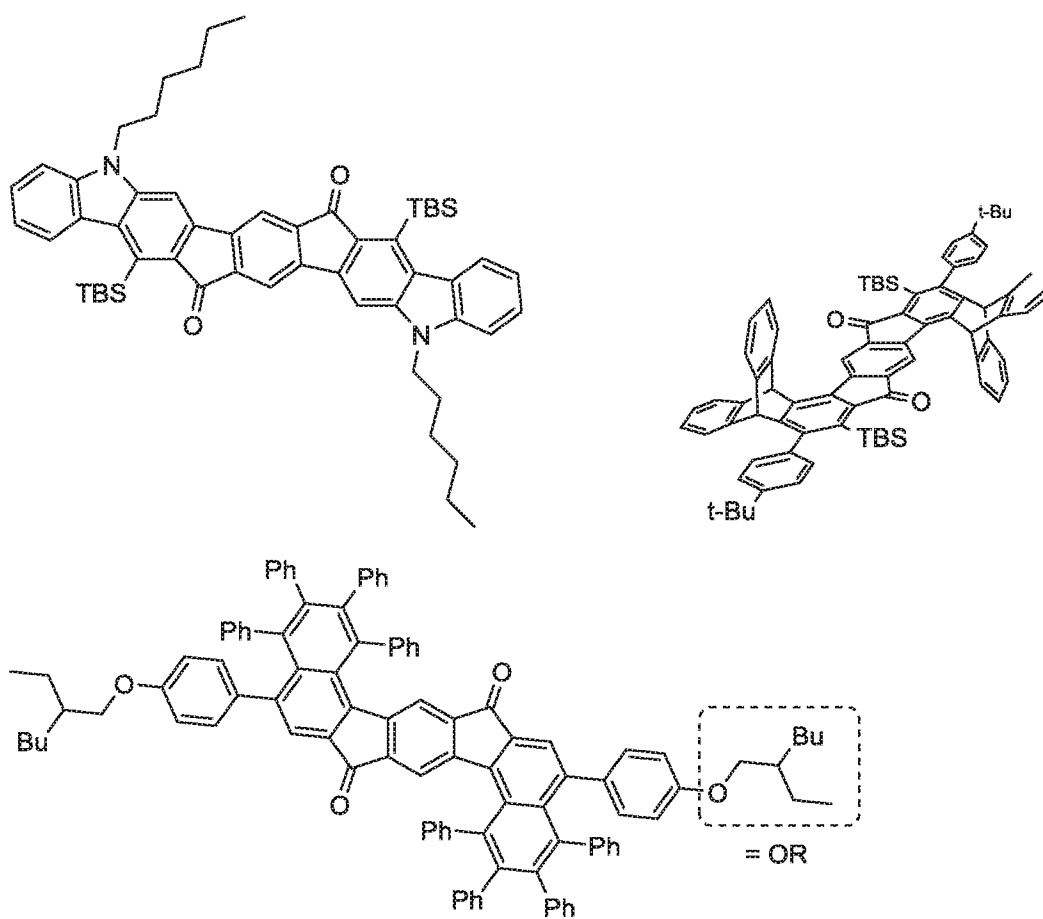
By melding the chemistries in FIG. 12B (bis-benzyne) and FIG. 12D (*o*-methoxyarene trapping), it is thought that there will be no difficulty in synthesizing fused nonacyclic compounds like **1051** or **1052**. The longest linear sequence (LLS) in the planned route for synthesis of the HDDA substrates, analogs of **1044**, is just four or five steps (from 2,5-
30 dibromoterephthalaldehyde or 3,5-dibromoisophthalaldehyde, respectively). Use of a terminal naphthyl or phenanthryl instead of phenyl derivative on the remote terminus of the diyne moiety

will, with no extra effort, provide products **1051** having two or four additional benzo-fused rings (dashed lines).

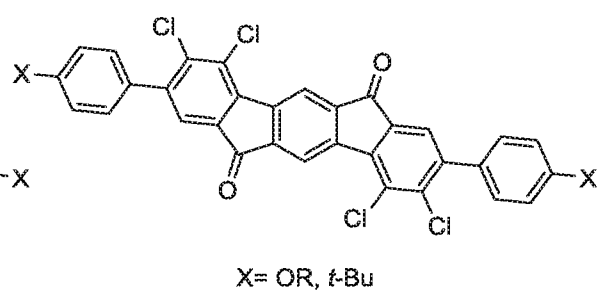
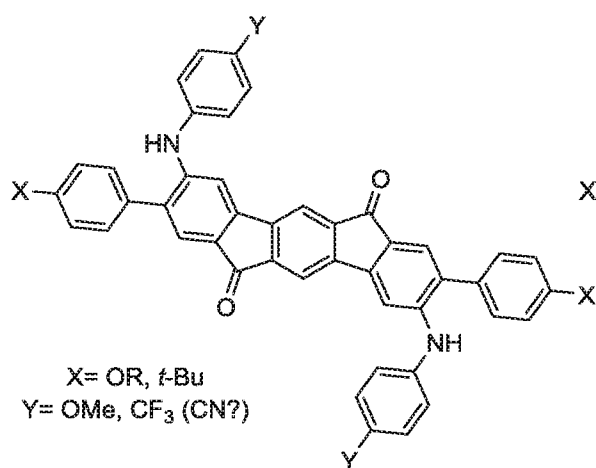
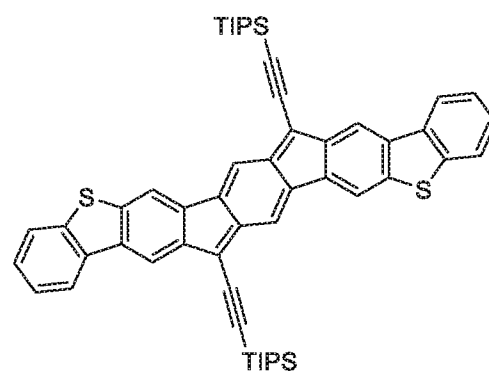
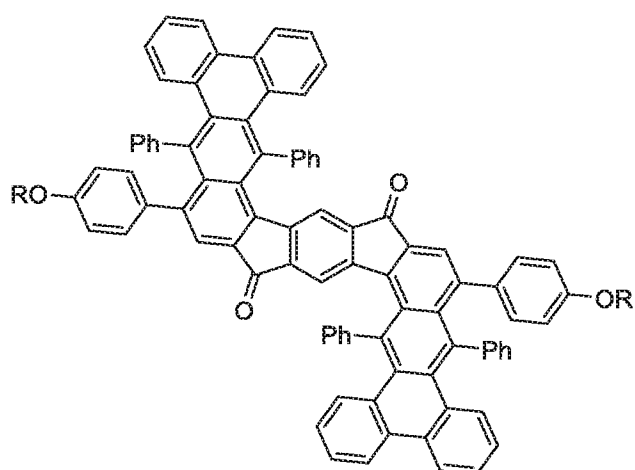
The bis-indanone adducts (FIGs. 12 A-C, E) can also be exploited by converting them into: (i) the quasi-delocalized *s*-indacene derivatives (see **1053** and **1054**) and (ii) bis-spirocyclic derivatives (see **1055**). These motifs have shown useful electro-optical behaviors, albeit for different reasons. The $4n\pi$ electron count of the former brings interesting consequences to the redox and HOMO-LUMO gap properties. The orthogonal bulk of the latter is believed to suppress excimer formation in solid films. Comparison of properties of the *s*- vs. the *as*-indacenes (cf. **1053** vs. **1054**) will also be interesting.

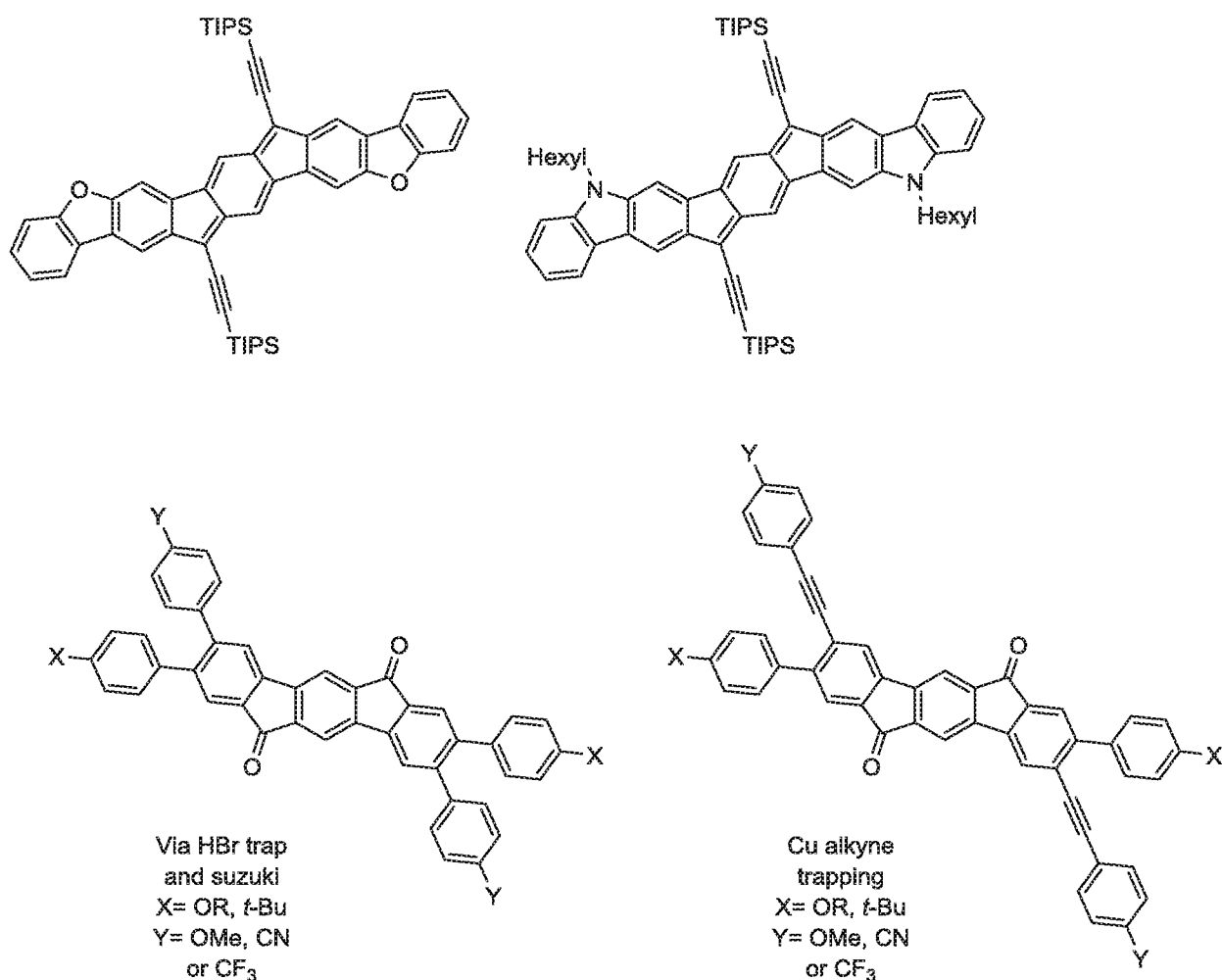
Illustrative compounds that have been made can be seen below.





Illustrative compounds that are planned to be made include the following.





Domino HDDA Reactions

Reactions that proceed through a strained bicyclic [4.2.0] intermediate—the benzocyclobutadiene **1038** have also been utilized. Substrates having only a two-atom linker between the diyne and diynophile typically do not undergo cyclization. Presumably, the resulting benzyne, housed within a benzocyclobutadiene motif, would be simply too strained. We recently hypothesized that we could use this situation to our advantage. A two-atom linker might allow cyclization to materialize, but only *following* initial benzyne formation in a substrate like **1056a** (FIG. 13A). That is, the intermediate benzyne **1056a^{Benz}** now has a nearby diyne whose proximal alkyne carbon is poised five, no longer four, atoms away (red dot and blue diamond in **1056^{Benz}**). An initial experiment showed just that. Thus, the acyclic ester-linked pentayne **1056a** was smoothly converted to the hexacycle **1057a**, in which a final intermediate naphthyne had been trapped (by furan). This represents an exciting new direction for this chemistry. This domino-

HDDA reaction was then extended to the homologous heptyne **1056b**, which proceeds analogously to give **1057b**. The structure of this product surely means that a benzyne-to-naphthylene-to-anthracene sequence had occurred. It was recently observed that the next higher homolog, the nonayne **1056c**, gives the decacyclic **1057c**—almost certainly through a tetracyne.

5 The chromatographed (orange) sample of this compound proved to be sensitive in the solid state, giving rise to a methanol-soluble (red) substance. Higher acenes often react with oxygen and/or are photosensitive. There is still much we need to explore to more fully understand the behavior of **1057c**. Each of the substrates **1056a-c** is available through reaction sequences that are just 3-5 steps in length. Each of these cyclizations has been performed only a single time to date.

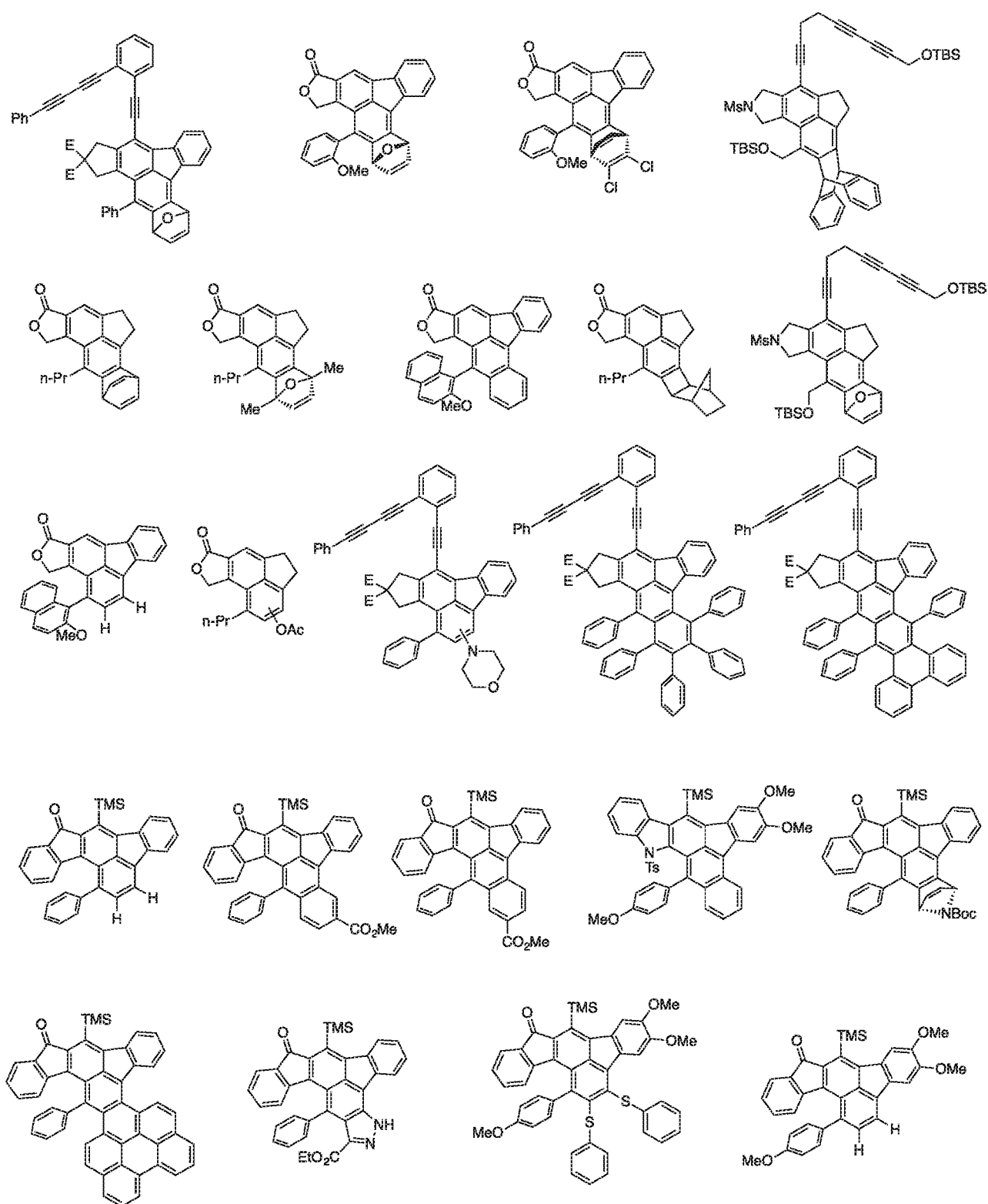
10 The blue bonds in **1057b** outline a structural motif reminiscent of the core structure of rubicene (**1058**), a compound representing a subunit of C₇₀ and of recent interest in OFET applications. This led us to explore some benzo analogs of **1056** as domino-HDDA substrates. The symmetrical octayne **1059** (FIG. 13B), very cleanly gave the blue-emitting arylalkynylfluoranthene derivative **1060**. This is additionally noteworthy in view of the

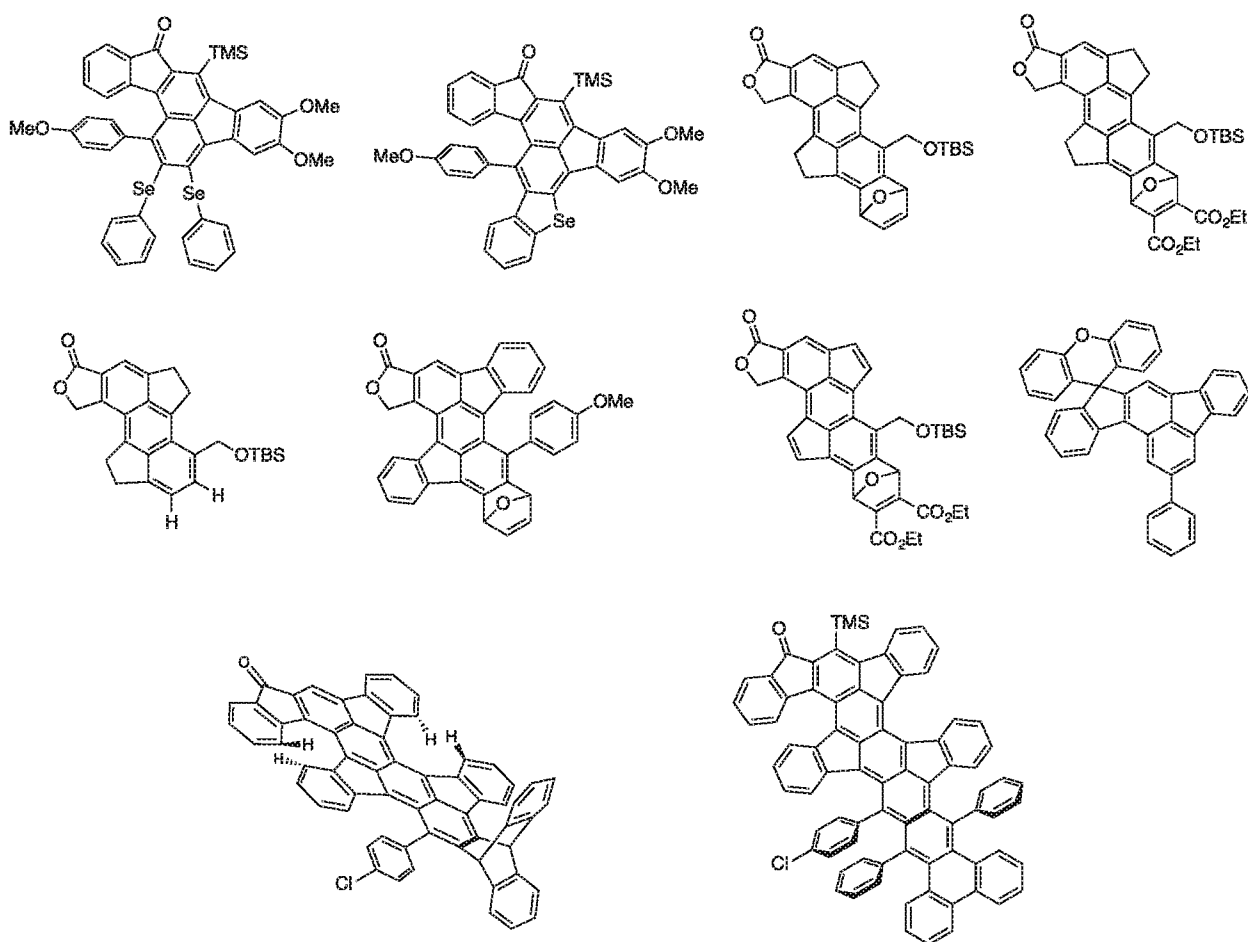
15 stabilizing influence that alkynyl substituents are known to impart on acenes.

Another impressive polycyclization is that of the ynone **1061** (FIG. 13C), which again cascades through a series of intermediate arynes before being trapped by either anthracene to give **1062** or the cyclopentadienone **1063** to provide the dibenzohexacene **1064**. The former, a dark green solid, is non-fluorescent. Thermalization via a low-barrier interconversion of two

20 topological isomers, observable by ¹H NMR spectroscopy and attributable to slippage of the pair of imposing benzo rings flanking the tetracene core in **1062**, could be relevant. Regardless, non-emissive, light-harvesting compounds are of interest for various OPV applications. Finally, it is also worth noting that no evidence of any chemical instability has been found yet, including oxidative or photochemical, with any of these polybenzo, rubicene-like adducts.

25 Specific compounds that have been made using Domino HDDA reactions include those shown below.





Through these early and most encouraging successes the viability of the domino-HDDA has not only been established, but new directions to take these preliminary findings have also been identified.

The bridging oxygen atom in the furan-trapped adducts like **1057** and **1060** may be reductively removed to reveal an additional terminal benzo ring, adding to the acene length. Of course, other traps, as presented earlier in various different contexts, could be used to terminate the final domino acyne.

The length of precursors like **1061** could be extended, but that comes with a labor burden created by the linear nature of the synthetic sequences we have used thus far. One strategy for making that less cumbersome is to use a late-stage, mid-chain Glaser coupling of a long terminal alkyne like **1065** to immediately double the length (FIG. 14A). The head and tail in the product will now be identical, but this introduces no ill consequences. Initiation from either end will be the slow step followed by rapid propagation.

The replacement of the benzo moieties in the domino products by analogs having *o*-dialkynylarene moieties such as those represented by **1066b-g** (FIG. 14B) was also done. Each brings a new feature to the table (tolerance of steric hindrance, extended lateral conjugation, electronic perturbation, etc.). The size of these substrates and products could be limited to the dimers derived from **1065** ($n = 1$) to keep the synthesis routes manageable (all via sequences 3-4 steps long). The products will be planar rubicene analogs. Interesting topological features (cf. **1062**) emerge for the products from **1065** ($n = 2$) having linkers substituted at C3 and C6 of the benzo moiety (i.e., **1066b** or **1066c**). It is noted that thiophene is a relatively poor/slow trap of benzyne and should be compatible with a rapid trapping by furan. This array of compounds should show interesting comparative spectroscopic and CV properties.

Two final strategies for more quickly accessing precursor domino substrate multiynes was also devised (FIGs. 14C and 14D). Statistical Glaser oxidative coupling of an excess of 1,2-diethynylbenzene (**1066a**) with propargyl alcohol will directly produce a family of oligomeric **1067** (FIG. 14C). The number average and distribution of this product array will be a direct function of the molar ratio of the two reactants, relative rates of hetero- vs. homo-coupling, as well as the extent of conversion. We empirically learned how many of the members of this series of doubly end-capped polyynediols could be separated, using a combination of normal and reverse-phase as well as size-exclusion chromatography strategies (we have experience purifying natural products on LH-20 Sephadex®). The statistics require that all of the oligomeric products will be doubly capped with a propargyl alcohol. Following propioloylation, *after merely two synthetic reactions* (and a separation), we will have in hand a set of discrete domino substrates. As with the discrete dimers of **1065**, each of the domino-HDDA substrates **1067** is symmetrical. The homologous series of oligomeric acene products **1068** (as well as their precursors **1067**) differ by having increasing numbers of orange subunits. A large amount of information about the properties of this homologous set of chromophoric structures can be obtained with a relatively small amount of overall effort. The preparation of large quantities of any one member of **1067** for device construction, would be feasible by the mid-chain coupling strategy (FIG. 14A).

Finally, the iterative exponential growth (IEG) strategy recently revealed by the Jamison and Johnson groups was used to prepare the series of monodisperse, domino substrates **1069** (FIG. 14D). The starting material, **1069a** (LLS = 3), contains two orthogonally removable, terminal alkyne protecting groups. A cycle involves deprotection and coupling (LLS = 2): (i)

one-pot brominative deacetonation (KOH, KOB_r), which we have used in other settings, of half of **1069a**, (ii) desilylation (F⁻) of the other half, and (iii) cross-coupling. Each subsequent cycle doubles the length of the precursor. For the finishing operation after each round (2 reactions), which preps the compound for the domino event, we propose conversion to the ynamides **1070**.

5 We have considerable experience with this type of cross-coupling as well as cyclization via carbazolynes (red). We have shown TPCPD as the trapping agent, but many others can be explored once each of **1070** is in hand. We are aware of potential solubility issues and will address these, as needed, by inclusion of side-chain and/or end-group substituents (although, to date, we have seen no limitations in the benzo compounds in FIG. 13). We are eager to learn just
10 how large of a discrete polyacene derivative **1071** we can construct. No one has ever had the opportunity to explore molecular entities of this sort.

EXAMPLES

15 This disclosure is further illustrated by the following examples. It is to be understood that the particular examples, materials, amounts, and procedures are to be interpreted broadly in accordance with the scope and spirit of the disclosure as set forth herein.

I. General Experimental Protocols

¹H and ¹³C NMR spectra were recorded on Bruker Avance 500 and 400 (500 and 400
20 MHz) spectrometers. ¹H NMR chemical shifts in CDCl₃ are referenced to TMS (δ = 0.00 ppm). Non-first order multiplets are identified as "nfom". ¹³C NMR chemical shifts for spectra collected in CDCl₃ are referenced to the carbon in CDCl₃ (δ = 77.16 ppm). ¹³C NMR chemical shifts for spectra recorded in benzene-*d*₆ are referenced to the carbon in C₆D₆ (δ = 128.4 ppm). This format is used to report ¹H resonances: chemical shift in ppm [multiplicity, coupling
25 constant(s) (*J*) in Hz, integration to the nearest whole number of protons, and assignment]. ¹H NMR assignments are indicated by the substructure environment, e.g., OCH_aH_b. Some complex structures are numbered in order to simplify the proton assignment identification. Coupling constant analysis was guided by methods that have been previously reported.

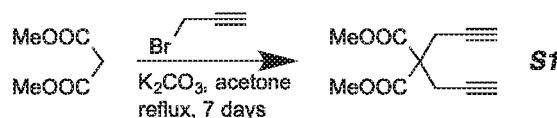
High-resolution mass spectrometry (HRMS) measurements were made on a Bruker
30 BioTOF II (ESI-TOF) instrument in electrospray ionization (ESI) mode. PEG or PPG was used

as an internal standard/calibrant. Samples were introduced as solutions in methanol or, when MeOH-solubility was poor, in methylene chloride.

Infrared spectra were collected on a Midac Corporation Prospect 4000 FT-IR spectrometer. The most diagnostic and/or intense peaks are reported. All spectra were collected in attenuated total reflectance (ATR) mode as neat thin films on a germanium window.

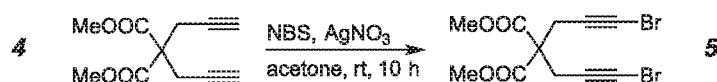
II. Specific Illustrative Synthesis Pathways and Characterization of Molecules Formed Thereby

- 10 **Dimethyl 2,2-di(prop-2-yn-1-yl)malonate S1** (Parsons, P. J.; Jones, D. R.; Padgham, A. C.; Allen, L. A. T.; Penkett, C. S.; Green, R. A.; White, A. J. P. *Chemistry - A European Journal* **2016**, 22, 3981–3984.)



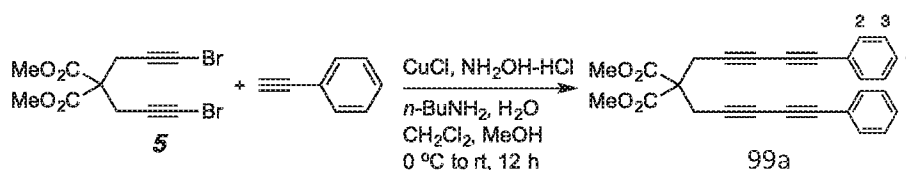
- Propargyl bromide (7.8 mL, 80 wt. % in toluene, 70 mmol) was added to a stirred suspension of dimethyl malonate (2.00 mL, 17.5 mmol) and K₂CO₃ (5.32 g, 38.5 mmol) in acetone (30 mL) under a N₂ atmosphere. This mixture was brought to reflux (ca. 60 °C). After 7 d the reaction mixture was filtered through Celite® (acetone eluent) and concentrated. The residue was partitioned between water and EtOAc and the aqueous phase further extracted with EtOAc. The combined organic layers were washed with brine, dried (MgSO₄), and concentrated.
- 20 This residue was dissolved in a mixture of DCM and hexanes (ca. 1:10). A portion of the more volatile DCM was removed under reduced pressure. A precipitate appeared; this slurry was cooled and the solid collected by filtration. The filtrate was treated in the same fashion, and the process was repeated 2-3 more times to give **S1** (3.15 g, 15.2 mmol, 87%) as a white solid. The NMR spectral data were consistent with reported values (Parsons, P. J.; Jones, D. R.; Padgham, A. C.; Allen, L. A. T.; Penkett, C. S.; Green, R. A.; White, A. J. P. *Chemistry - A European Journal* **2016**, 22, 3981–3984.)
- 25

Dimethyl 2,2-bis(3-bromoprop-2-yn-1-yl)malonate (5) (Parsons, P. J.; Jones, D. R.; Padgham, A. C.; Allen, L. A. T.; Penkett, C. S.; Green, R. A.; White, A. J. P. *Chemistry - A European Journal* **2016**, 22, 3981–3984.)



Powdered AgNO₃ (0.2 equiv) was added to a stirred solution of **4** (1.0 equiv) and *N*-bromosuccinimide (NBS, 2.4 equiv) in acetone (0.1 M) at room temperature. After 10 h the slurry was filtered through Celite® (acetone eluent) and concentrated. The residue was partitioned between water and EtOAc and the water layer was further extracted with EtOAc. The combined extracts were washed with brine, dried (MgSO₄), and concentrated. The crude material was purified by flash chromatography (hexanes:EtOAc 8:1) to give the known dibromodiyne **5** as a clear colorless oil (2.56 g, 12.6 mmol, 76%). The NMR spectral data were consistent with reported values (Yamamoto, Y.; Hattori, K.; Nishiyama, H. *J. Am. Chem. Soc.* **2006**, 128, 8336–8340).

Dimethyl 2,2-bis(5-phenylpenta-2,4-diyn-1-yl)malonate (99a)



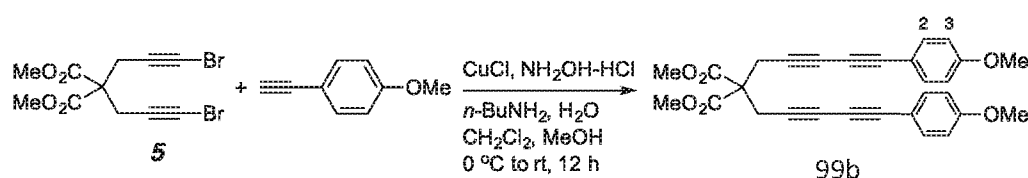
CuCl (198 mg, 2.0 mmol) was added to a 40% aqueous solution of *n*-butylamine (72 mL) at 0 °C with stirring. Hydroxylamine hydrochloride was added until the solution was colorless (~10 mg). A solution of ethynylbenzene (204 mg, 2.0 mmol) in dichloromethane (4 mL) was added, and a yellow precipitate, the copper acetylide, appeared. A solution of dimethyl 2,2-bis(3-bromoprop-2-yn-1-yl)malonate (**5**, 3.66 g, 10 mmol) and ethynylbenzene (2.24 g, 22 mmol) in 35 mL of CH₂Cl₂/MeOH (4/1 : v/v) was added dropwise to the yellow suspension with vigorous stirring, and the resulting mixture was allowed to stir at 0 °C for 2 h and then room temperature for 10 h. Aqueous NH₄Cl (35 mL) was added, the aqueous phase was extracted with EtOAc, and the combined organics were washed with brine, dried (MgSO₄), and concentrated. The crude product was purified by flash chromatography (hexanes:EtOAc 7:1) to give the known tetrayne

99a (2.77 g, 6.8 mmol, 68%) (Zhang, H.; Hu, Q.; Li, L.; Hu, Y.; Zhou, P.; Zhang, X.; Xie, H.; Yin, F.; Hu, Y.; Wang, S. *Chem. Commun.* 2014, 50, 3335–3337) as a pale yellow solid.

¹H NMR (CDCl₃, 400 MHz) δ 7.48 (nfod, *J* = 7 Hz, 4H, *H*2), 7.36 (nfot, *J* = 7 Hz, 2H, *H*4), 7.31 (nfot, *J* = 7 Hz, 4H, *H*3), 3.82 (s, 6H, OMe), and 3.22 (s, 4H, CH₂).

5 **mp:** 96-98 °C (lit. value: 96-97 °C) (Zhang, H.; Hu, Q.; Li, L.; Hu, Y.; Zhou, P.; Zhang, X.; Xie, H.; Yin, F.; Hu, Y.; Wang, S. *Chem. Commun.* **2014**, 50, 3335-3337).

Dimethyl 2,2-bis(5-(4-methoxyphenyl)penta-2,4-diyne-1-yl)malonate (99b)



CuCl (99 mg, 1 mmol) was added to a 40% aqueous solution of *n*-butylamine (36 mL) at 0 °C with stirring. Hydroxylamine hydrochloride was added until the solution was colorless (~10 mg). A solution of 1-ethynyl-4-methoxybenzene (264 mg, 1 mmol) in dichloromethane (3 mL) was added, and a yellow precipitate, the copper acetylide, appeared. A solution of dimethyl 2,2-bis(3-bromoprop-2-yn-1-yl)malonate (**5**, 1.83 g, 5 mmol) and 1-ethynyl-4-methoxybenzene (1.12 g, 11 mmol) in 18 mL of CH₂Cl₂/MeOH (4/1 : v/v) was added dropwise to the yellow suspension, which was being vigorously stirred. The resulting mixture was allowed to warm to rt. After 24 h aqueous NH₄Cl (25 mL) was added, the aqueous phase was extracted with EtOAc, and the combined organics were washed with brine, dried (MgSO₄), and concentrated. The crude product was purified by flash chromatography (hexanes:EtOAc 6:1 to 5:1 to 4:1) to give tetrayne **99b** (1.05 g, 2.25 mmol, 45%) as a pale yellow solid, whose spectral data correlated closely with the reported data (Zhang, M.-X.; Shan, W.; Chen, Z.; Yin, J.; Yu, G.-A.; Liu, S. H. *Tetrahedron Lett.* 2015, 56, 6833–6838).

Data for tetrayne 99b:

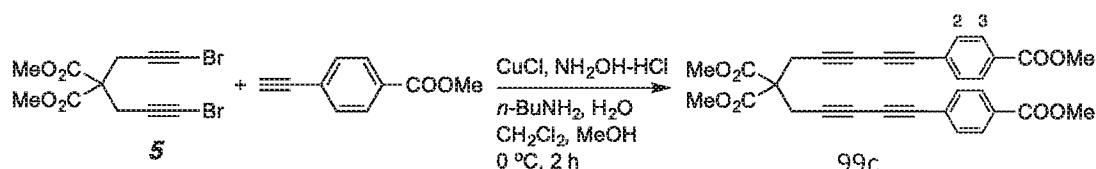
¹H NMR (CDCl₃, 400 MHz) δ 7.42 (d, *J* = 8.9 Hz, 2H, *H*2), 6.83 (d, *J* = 8.9, 2H, *H*3), 3.81 (s, 6H, malonyl-CO₂Me or ArOMe), 3.80 (s, 6H, malonyl-CO₂Me or ArOMe), and 3.20 (s, 4H, CH₂).

^{13}C NMR (100 MHz, CDCl_3) δ 168.9, 160.4, 134.3, 114.2, 113.6, 77.1, 76.3, 72.8, 68.8, 56.9, 55.5, 53.5, and 24.4.

IR (neat) 3007, 2969, 2954, 2839, 2246, 2146, 1740, 1603, 1510, 1436, 1336, 1261, 1251, and 1029 cm^{-1} .

5 mp (recrystallized from $\text{CH}_2\text{Cl}_2/\text{MeOH}$): 109–110 °C.

Dimethyl 2,2-bis(5-(4-(methoxycarbonyl)phenyl)penta-2,4-diyne-1-yl)malonate (99c)



CuCl (198 mg, 2 mmol) was added to a 40% aqueous solution of *n*-butylamine (72 mL) at 0 °C with stirring. Hydroxylamine hydrochloride was added until the solution was colorless (~10 mg). A solution of methyl 4-ethynylbenzoate Li, Q.; Rukavishnikov, A. V.; Petukhov, P. A.; Zaikova, T. O.; Jin, C.; Keana, J. F. W. J. Org. Chem. 2003, 68, 4862–4869) ((320.4 mg, 2 mmol) in dichloromethane (4 mL) was added, and a yellow precipitate, the copper acetylide, appeared. A solution of dimethyl 2,2-bis(3-bromoprop-2-yn-1-yl)malonate (**5**, 3.66 g, 10 mmol) and methyl 4-ethynylbenzoate (3.52 g, 22 mmol) in 35 mL of $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (4/1 : v/v) was added dropwise to the yellow suspension with robust stirring, and the resulting mixture was allowed to stir at 0 °C for 2 h. The poorly soluble product had partially precipitated. Aqueous NH_4Cl solution (60 mL) was added, and the amount of precipitate increased. This mixture was filtered, and the filter cake was washed by H_2O (100 mL), MeOH (50 mL), and EtOAc (50 mL). The combined filtrate was extracted with DCM and the organic extract was washed with brine, dried (MgSO_4), and filtered. A portion (ca. 25 vol%) of EtOAc was added and the solution was concentrated to remove nearly all of the DCM. The resulting slurry was filtered and combined solids were dried under vacuum to give **99c** (3.46 g, 6.6 mmol, 66%) as a white powder.

^1H NMR (CDCl_3 , 400 MHz) δ 7.98 (nfod, $J = 8.7$, 4H, H_3), 7.51 (nfod, $J = 8.7$, 4H, H_2), 3.92 (s, 6H, ArCO_2Me), 3.82 (s, 6H, malonyl- CO_2Me), and 3.22 (s, 4H, CH_2).

^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 166.2, 132.5, 130.3, 129.5, 126.2, 79.1, 76.5, 75.0, 68.2, 56.5, 53.5, 52.3, and 24.3.

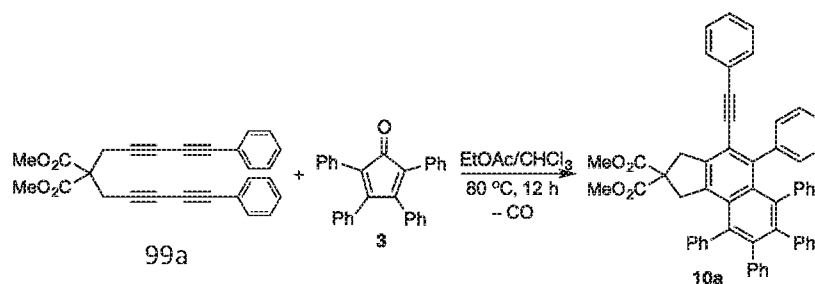
IR (neat) 3003, 2969, 2953, 2844, 2248, 1738, 1722, 1604, 1435, 1366, 1274, 1216, 1102, 851 and 764 cm^{-1} .

HRMS (ESI-TOF): Calcd for $(\text{C}_{31}\text{H}_{24}\text{O}_8\text{Na})^+$ 547.1363; found: 547.1369.

mp (recrystallized from $\text{CH}_2\text{Cl}_2/\text{MeOH}$): $>140\text{ }^\circ\text{C}$ (dec).

5

Dimethyl 5,6,7,8,9-pentaphenyl-4-(phenylethynyl)-1,3-dihydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (10a)



A solution of tetrayne **99a** (1.5 mmol, 612 mg) and 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (**3**, 2.2 mmol, 864 mg) in EtOAc (12 mL) and CHCl_3 (12 mL) was heated in an oil bath held at $80\text{ }^\circ\text{C}$ for 12 h in a round bottom flask fitted with a reflux condenser. The solvent was removed under reduced pressure, and the crude product, already of $>95\%$ purity (^1H NMR), was purified by flash chromatography (hexanes:EtOAc 9:1 to 4:1) to remove the excess of **3**. Subsequent recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ three times gave **10a** (940 mg, 1.23 mmol, 82%) as a white solid. It should be noted that compound **10a** may also be referred to herein as compound **1015a** and **28a**, and vice versa.

15

The thermogravimetric analysis scan for **10a** is seen in **FIG. 15A** and the differential scanning calorimetry scan for **10a** is seen in **FIG. 15B**

^1H NMR (CDCl_3 , 500 MHz) δ 7.22-7.16 (m, 8H), 7.12-7.08 (m, 2H), 7.94-7.88 (m, 5H), 6.83-6.77 (m, 3H), 6.77-6.73 (m, 2H), 6.73-6.69 (m, 3H), 6.69-6.64 (m, 1H), 6.63-6.56 (m, 4H), 6.52-6.48 (m, 2H), 3.83 (s, 2H, CH_2), 3.68 (s, 6H, malonyl- CO_2Me), and 2.99 (s, 2H, CH_2).

20

^{13}C NMR (125 MHz, CDCl_3) δ 172.4, 144.4, 142.4, 141.9, 141.5, 140.7, 140.5, 140.4, 140.3, 139.8, 139.3, 136.8, 134.9, 132.5, 132.1, 131.9, 131.5, 131.19, 131.17, 131.15, 130.3, 128.2, 128.1, 127.2, 126.9, 126.7, 126.5, 126.31, 126.28, 125.6, 125.3, 125.03, 125.00, 123.5, 120.1, 96.8, 88.0, 59.2, 53.0, 43.3, and 41.0.

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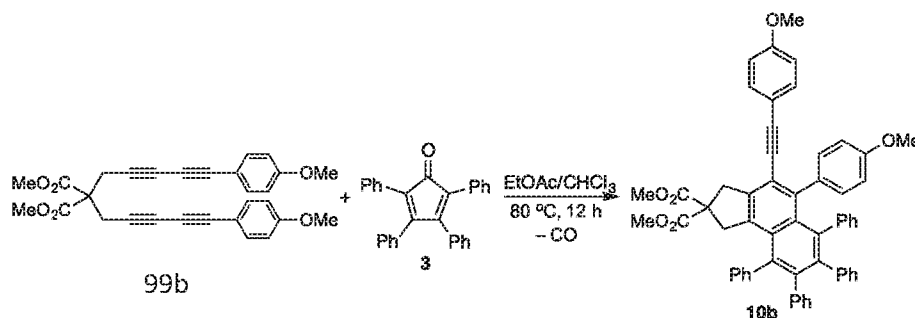
IR (neat) 3056, 3023, 2952, 2848, 2257, 1735, 1599, 1492, 1441, 1259, 1202, 1168, 1072, 1028, and 909 cm^{-1} .

HRMS (ESI-TOF): Calcd for $(\text{C}_{55}\text{H}_{40}\text{NaO}_4)^+$ 787.2819; found: 787.2813.

mp: 239-242 °C and 237 °C (from DSC data).

5

Dimethyl 5-(4-Methoxyphenyl)-4-((4-methoxyphenyl)ethynyl)-6,7,8,9-tetraphenyl-1,3-dihydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (10b)



A solution of tetrayne **99b** (1.2 mmol, 560 mg) and 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (**3**, 1.79 mmol, 689 mg) in EtOAc (10 mL) and CHCl_3 (10 mL) was heated in an oil bath held at 80 °C for 12 h in a round bottom flask fitted with a reflux condenser. The solvent was removed under reduced pressure, and the crude product, already of >95% purity (^1H NMR), was purified by flash chromatography (hexanes:EtOAc 10:1 to 4:1) to remove the excess of **3**. Subsequent recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ three times gave **10b** (841 mg, 1.02 mmol, 85%) as a white solid. It should be noted that compound **10b** may also be referred to herein as compound **1015b** and **28b**, and vice versa.

The thermogravimetric analysis scan for **10b** is seen in **FIG. 16A** and the differential scanning calorimetry scan for **10b** is seen in **FIG. 16B**. **FIG. 16C** shows a ORTEP rendering of the single crystal X-ray structure of **10b**

^1H NMR (CDCl_3 , 500 MHz) δ 7.22-7.15 (m, 5H), 7.09 (nfod, $J = 8.9$, 2H), 6.84-6.76 (m, 5H), 6.76-6.69 (m, 7H), 6.69-6.62 (m, 3H), 6.60-6.56 (m, 2H), 6.49 (m, 2H), 6.47 (nfod, $J = 8.8$, 2H), 3.81 (s, 2H, CH_2), 3.76 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 3.68 (s, 6H, malonyl- CO_2Me), and 2.98 (s, 2H, CH_2).

^{13}C NMR (125 MHz, CDCl_3) δ 172.4, 159.6, 157.5, 143.5, 142.2, 141.5, 140.6, 140.5, 140.4, 140.2, 139.7, 139.2, 136.7, 135.3, 134.7, 133.0, 132.9, 132.3, 131.94, 131.88, 131.22, 131.19,

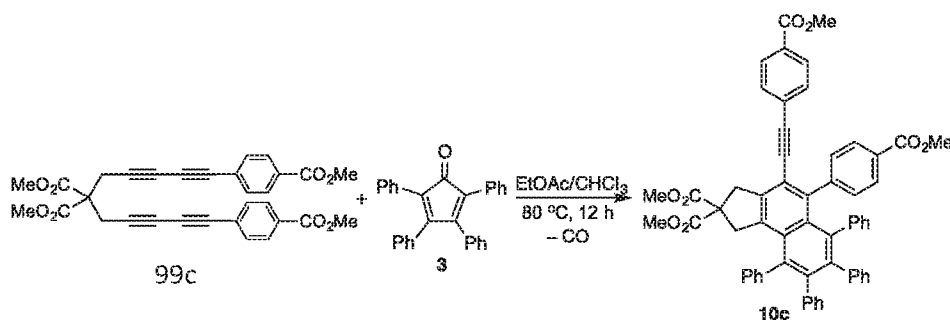
130.2, 127.2, 126.9, 126.4, 126.3, 126.2, 125.2, 125.0, 124.9, 120.6, 115.8, 113.9, 112.5, 96.9, 86.9, 59.2, 55.5, 55.4, 53.0, 43.2, and 41.0.

IR (neat) 3055, 3028, 2952, 2835, 2203, 1736, 1604, 1510, 1441, 1286, 1247, 1201, 1171, 1072, 1031, 909, 833, and 751 cm^{-1} .

5 **HRMS** (ESI-TOF): Calcd for $(\text{C}_{57}\text{H}_{44}\text{NaO}_6)^+$ 847.3030; found: 847.3051.

mp: 217-219 °C.

Dimethyl 5-(4-(methoxycarbonyl)phenyl)-4-((4-(methoxycarbonyl)phenyl)ethynyl)-6,7,8,9-tetraphenyl-1,3-dihydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (10c)



10

A solution of tetrayne **99c** (0.92 mmol, 480 mg) and 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (**3**, 1.37 mmol, 527 mg) in EtOAc (10 mL) and CHCl_3 (10 mL) was heated in an oil bath held at 80 °C for 12 h in a round-bottom flask fitted with a reflux condenser. The solvent was removed under reduced pressure, and the crude product, already of >95% purity (^1H NMR), was purified by
 15 flash chromatography (hexanes:EtOAc 6:1 to 4:1) to remove the excess of **3**. Subsequent recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ three times gave **10c** (672 mg, 0.76 mmol, 83%) as a white solid. It should be noted that compound **10c** may also be referred to herein as compound **1015c** and **28c**, and vice versa.

The thermogravimetric analysis scan for **10c** is seen in **FIG. 17A** and the differential scanning
 20 calorimetry scan for **10c** is seen in **FIG. 17B**.

^1H NMR (CDCl_3 , 500 MHz) δ 7.87 (nfod, $J = 8.7$ Hz, 2H), 7.62 (nfod, $J = 8.5$ Hz, 2H), 7.22-7.17 (m, 5H), 7.11 (nfod, $J = 8.7$ Hz, 2H), 6.98 (nfod, $J = 8.5$ Hz, 2H), 6.84-6.78 (m, 3H), 6.77-6.68 (m, 6H), 6.62-6.57 (m, 4H), 6.51-6.48 (m, 2H), 3.89 (s, 3H, CO_2CH_3), 3.88 (s, 3H, CO_2CH_3), 3.82 (s, 2H, CH_2), 3.69 (s, 6H, malonyl- CO_2Me), and 3.0 (s, 2H, CH_2).

¹³C NMR (125 MHz, CDCl₃) δ 172.2, 167.3, 166.6, 147.3, 143.6, 141.5, 141.23, 141.22, 140.7, 140.2, 140.0, 139.6, 139.2, 137.0, 135.8, 132.31, 132.27, 131.8, 131.3, 131.2, 131.1, 131.0, 130.6, 129.49, 129.47, 128.0, 127.9, 127.3, 127.2, 127.1, 126.52, 126.51, 126.4, 125.5, 125.4, 125.2, 119.2, 96.4, 90.5, 59.2, 53.1, 52.3, 52.1, 43.2, and 40.9.

5 **IR** (neat) 3056, 3023, 2952, 2848, 2262, 2207, 1721, 1604, 1495, 1435, 1404, 1307, 1274, 1199, 1173, 1107, 1073, 1019, 910, and 756 cm⁻¹.

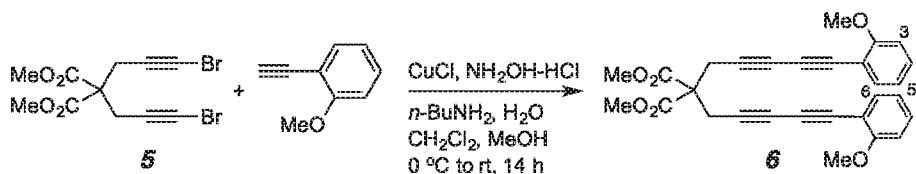
HRMS (ESI-TOF): Calcd for (C₅₉H₄₄NaO₈)⁺ 903.2928; found: 903.2946.

mp: 268-271 °C and 260 °C (from DSC data)

10 **FIGs. 18A, 18B and 18C** show the photoluminescence efficiency (solution quantum yield) for compounds **10a (FIG. 18A)**, **10b (FIG. 18B)** and **10c (Fig. 18C)** in THF/water mixtures.

Synthesis of 100 as a representative of the methods used to make many of the HDDA triyne or tetrayne precursors.

Dimethyl 2,2-bis(5-(2-methoxyphenyl)penta-2,4-diyn-1-yl)malonate (6) from 4



5 CuCl (198 mg, 2 mmol) was added to a 40% aqueous solution of *n*-butylamine (72 mL) at 0 °C with stirring. Hydroxylamine hydrochloride was added until the solution was colorless (~10 mg) followed by a solution of 1-ethynyl-2-methoxybenzene (232.2 mg, 2 mmol) in dichloromethane (2 mL). A yellow precipitate, the copper acetylide, appeared. A solution of 4 (3.66 g, 10 mmol) and 1-ethynyl-2-methoxybenzene (2.91 g, 22 mmol) in 15 mL of
10 CH₂Cl₂/MeOH (4/1 : v/v) was added dropwise to the yellow suspension with robust stirring, and the resulting mixture was allowed to come to rt. After 14 h aqueous NH₄Cl (35 mL) was added, the aqueous phase was extracted with EtOAc, and the combined organics were washed with brine, dried (MgSO₄), and concentrated. The crude product was purified by flash chromatography (hexanes:EtOAc 3:1) to give 6 (3.65 g, 7.8 mmol, 78%) as a pale yellow solid.

15 Data for 6

¹H NMR (CDCl₃, 500 MHz) δ 7.44 (ddd, *J* = 7.6, 1.7, 0.3 Hz, 2H, H6), 7.31 (ddd, *J* = 8.4, 7.5, 1.8 Hz, 2H, H4), 6.89 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 2H, H5), 6.86 (dd, *J* = 8.5, 1.0 Hz, 2H, H3), 3.88 (s, 6H, malonyl-CO₂Me), 3.80 (s, 6H, ArOCH₃), and 3.22 (s, 4H, CH₂).

20 ¹³C NMR (126 MHz, C₆D₆) δ 169.0, 162.6, 135.2, 130.9, 120.9, 112.0, 111.2, 79.3, 79.0, 73.7, 69.9, 57.5, 55.4, 53.1, and 25.0.

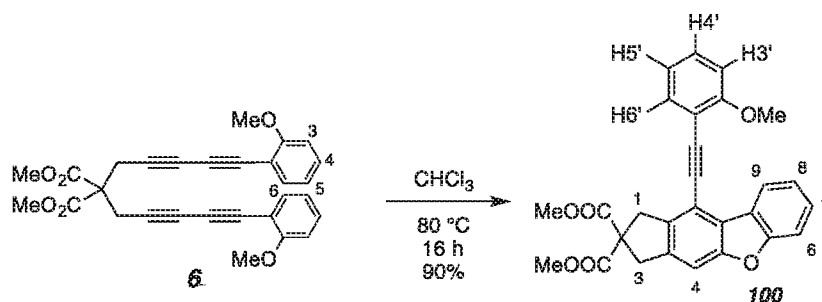
IR (neat) 2954, 2838, 2246, 1740, 1594, 1492, 1434, 1277, 1247, 1211, and 1022 cm⁻¹.

HRMS (ESI-TOF): Calcd for (C₂₉H₂₄O₆Na)⁺ 491.1465; found: 491.1460.

TLC: R_f 0.16 (3:1 Hex/EtOAc).

mp (recrystallized from CH₂Cl₂/MeOH): 154-156 °C.

Dimethyl 10-((2-Methoxyphenyl)ethynyl)-1,3-dihydro-2*H*-indeno[5,6-*b*]benzofuran- 2,2-dicarboxylate (100**)**



A solution of the tetrayne **6** (0.021 mmol, 10 mg) in CHCl_3 (2 mL) was placed in a dried glass vial. The reaction vessel was placed in an oil bath held at 80 °C for 16 hours. The solvent was removed under reduced pressure, and the crude product was subjected to MPLC (hexanes:EtOAc = 3:1) to yield **100** (8.7 mg, 0.019 mmol, 90%) as a white powder.

Data for 100

^1H NMR (CDCl_3 , 500 MHz) δ 8.76 (d, $J = 7.7$ Hz, 1H, H_9), 7.63 (br d, $J = 7.5$ Hz, 1H, H_6'), 7.53 (d, $J = 8.2$ Hz, 1H, H_6), 7.45 (br dd, $J = 8.3, 7.2$, 1H, H_7), 7.34–7.40 (m, 2H, H_4' and H_8), 7.36 (s, 1H, H_4), 7.02 (br dd, $J = 7.5, 7.5$ Hz, 1H, H_5'), 7.00 (br d, $J = 8.4$ Hz, 1H, H_3'), 4.03 (s, 3H, ArOCH_3), 3.91 (s, 2H, H_1 or H_3), 3.78 (s, 6H, malonyl- CO_2Me), and 3.77 (s, 2H, H_1 or H_3).

^{13}C NMR (100 MHz, CDCl_3) δ 172.1, 160.4, 156.7, 156.0, 139.3, 137.4, 133.6, 130.4, 127.1, 124.3, 123.8, 122.8, 122.4, 120.7, 113.0, 112.6, 111.3, 110.8, 107.7, 94.3, 89.8, 60.5, 55.8, 53.2, 41.2, and 39.9.

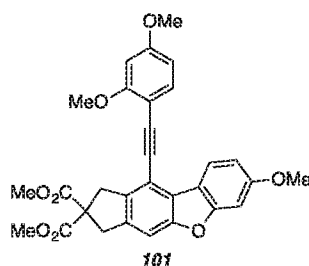
IR (neat) 3005, 2954, 2839, 2220, 1740, 1603, 1509, 1456, 1435, 1334, 1251, 1211, 1175, 1108, 1074, 1030, 835 cm^{-1} .

HRMS (ESI-TOF): Calcd for $(\text{C}_{28}\text{H}_{22}\text{O}_6\text{Na})^+$ 477.1309; found: 477.1369.

TLC: $R_f = 0.32$ (3:1 Hex/EtOAc).

mp (recrystallized from $\text{CH}_2\text{Cl}_2/\text{MeOH}$): 164–166 °C.

Dimethyl 10-((2,4-dimethoxyphenyl)ethynyl)-7-methoxy-1,3-dihydro-2H-indeno[5,6-b]benzofuran-2,2-dicarboxylate (101)



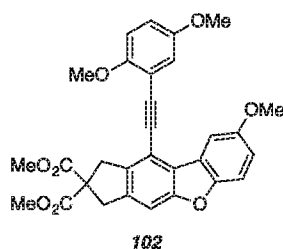
Compound 101 was obtained following general procedure.

¹H NMR (400 MHz, CDCl₃): δ 8.58 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.280 (s, 1H), 7.05 (d, *J* = 2.0 Hz, 1H), 6.94 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.56-6.53 (m, 2H), 3.99 (s, 3H), 3.90 (s, 3H), 3.87 (br s, 5H), 3.78 (s, 6H), and 3.74 (s, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 172.2, 161.7, 161.6, 159.9, 158.1, 156.1, 137.7, 136.9, 134.3, 123.9, 122.7, 117.7, 112.4, 111.1, 107.0, 105.3, 105.2, 98.6, 94.1, 88.7, 60.5, 55.88, 55.86, 55.7, 53.2, 41.2, and 39.9.

Melting point: 181–182 °C

Dimethyl 10-((2,5-dimethoxyphenyl)ethynyl)-8-methoxy-1,3-dihydro-2H-indeno[5,6-b]benzofuran-2,2-dicarboxylate (102)



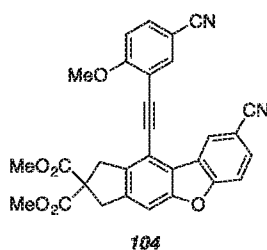
Compound 102 was obtained following general procedure.

¹H NMR (400 MHz, CDCl₃): δ 8.24 (d, *J* = 2.4 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.320 (s, 1H), 7.15 (d, *J* = 2.4 Hz, 1H), 7.03 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.91 (m, 2H), 3.98 (s, 3H), 3.89 (br s, 5H), 3.83 (s, 3H), 3.78 (s, 6H), and 3.75 (s, 2H).

^{13}C NMR (101 MHz, CDCl_3): δ 172.1, 156.8, 155.9, 155.0, 153.4, 151.5, 139.4, 137.3, 124.9, 123.9, 118.3, 116.2, 114.2, 113.1, 112.8, 112.2, 111.5, 107.8, 106.8, 94.2, 89.7, 60.5, 56.4, 56.3, 56.1, 53.2, 41.2, and 39.8.

Melting point: 149.5–151 °C.

5 **Dimethyl 8-cyano-10-((5-cyano-2-methoxyphenyl)ethynyl)-1,3-dihydro-2H-indeno[5,6-b]benzofuran-2,2-dicarboxylate (104)**



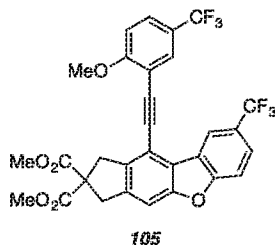
Compound 104 was obtained following general procedure.

10 ^1H NMR (400 MHz, CDCl_3): δ 9.04 (d, J = 1.7 Hz, 1H), 7.91 (d, J = 2.1 Hz, 1H), 7.75 (dd, J = 8.5, 1.7 Hz, 1H), 7.70 (dd, J = 8.7, 2.1 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.44 (s, 1H), 7.10 (d, J = 8.8 Hz, 1H), 4.22 (s, 3H), 3.89 (s, 2H), 3.81 (s, 6H), and 3.80 (s, 2H).

Solubility was insufficient for ^{13}C NMR.

Melting point: >230 °C.

15 **Dimethyl 10-((2-methoxy-5-(trifluoromethyl)phenyl)ethynyl)-8-(trifluoromethyl)-1,3-dihydro-2H-indeno[5,6-b]benzofuran-2,2-dicarboxylate (105)**



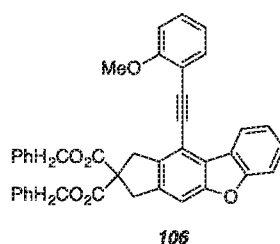
20 ^1H NMR (400 MHz, CDCl_3): δ 8.92 (s, 1H), 7.86 (d, J = 2.5 Hz, 1H), , 7.72 (dd, J = 8.7, 2.0 Hz, 1H), 7.66-7.61 (m, 2H), 7.42 (s, 1H), 7.07 (d, J = 8.8 Hz, 1H), 4.03 (s, 3H), 3.90 (s, 2H), 3.80 (s, 6H), and 3.78 (s, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 171.9, 162.5, 158.1, 156.6, 140.7, 138.5, 130.8 (q, *J* = 3.7 Hz), 127.6 (q, *J* = 3.9 Hz), 125.4 (q, *J* = 32.5 Hz), 124.7 (d, *J* = 272.2 Hz), 124.5, 124.3 (q, *J* = 3.6 Hz), 124.1 (d, *J* = 271.4 Hz), 123.3 (q, *J* = 32.9 Hz), 122.8 (s), 119.7 (q, *J* = 4.1 Hz), 112.8, 112.8, 111.8, 110.8, 108.4, 93.4, 90.1, 60.5, 56.4, 53.3, 41.2, and 39.8.

5 ¹⁹F NMR (375 MHz, CDCl₃): δ -60.59 (s, 3F), -61.71 (s, 3F)

Melting point: 219.5–221 °C

Dibenzyl 10-((2-methoxyphenyl)ethynyl)-1,3-dihydro-2H-indeno[5,6-b]benzofuran-2,2-dicarboxylate (106)



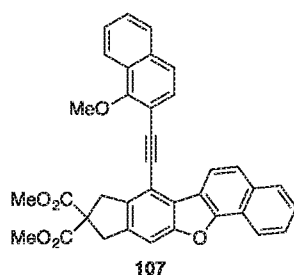
10 **106** was obtained following general procedure in 91% yield.

¹H NMR (CDCl₃, 400 MHz) δ 8.75 (d, *J* = 7.8 Hz, 1H, *H*9), 7.61 (br d, *J* = 7.6 Hz, 1H, *H*6'), 7.54 (d, *J* = 8.1 Hz, 1H, *H*6), 7.46 (br t, *J* = 7.7, 1H, *H*7), 7.41–7.33 (m, 2H, *H*4' and *H*8), 7.35 (s, 1H, *H*4), 7.32–7.23 (m, 10H, *PhH*), 7.02 (br t, *J* = 7.6, 1H, *H*5'), 7.00 (br d, *J* = 8.3 Hz, 1H, *H*3'), 5.17 (s, 4H, *PhCH*₂), 3.96 (s, 3H, *ArOCH*₃), 3.94 (s, 2H, *H*1 or *H*3), and 3.78 (s, 2H, *H*1 or *H*3).

15

¹³C NMR (100 MHz, CDCl₃) δ 171.2, 160.4, 156.7, 156.0, 139.3, 137.5, 135.5, 133.6, 130.3, 128.7, 128.4, 128.1, 127.1, 124.3, 123.7, 122.8, 122.4, 120.7, 113.1, 112.6, 111.3, 110.8, 107.7, 94.3, 89.8, 67.6, 60.8, 55.8, 41.2, and 39.8.

20 **Dimethyl 7-((1-methoxynaphthalen-2-yl)ethynyl)-8,10-dihydro-9H-indeno[5,6-b]naphtho[2,1-d]furan-9,9-dicarboxylate (107)**

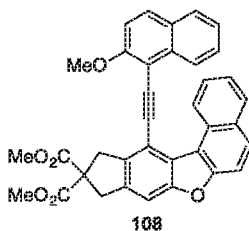


Compound 107 was obtained following general procedure.

¹H NMR (400 MHz, CDCl₃): δ 8.73 (d, *J* = 8.6 Hz, 1H), 8.42 (d, *J* = 8.1 Hz, 1H), 8.26 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.66-7.53 (m, 5H), 7.50 (s, 1H), 4.27 (s, 3H), 3.98 (s, 2H), 3.81 (s, 2H), and 3.80 (s, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 172.1, 158.6, 155.9, 152.6, 138.5, 137.9, 135.0, 133.2, 129.5, 128.6, 128.2, 128.1, 127.4, 126.7, 126.5, 126.3, 124.7, 124.0, 123.5, 122.5, 121.3, 121.0, 119.7, 119.5, 112.3, 111.9, 108.2, 94.4, 90.9, 62.4, 60.6, 53.3, 41.2, and 40.0

Dimethyl 12-((2-methoxynaphthalen-1-yl)ethynyl)-9,11-dihydro-10H-indeno[5,6-b]naphtho[1,2-d]furan-10,10-dicarboxylate (108)



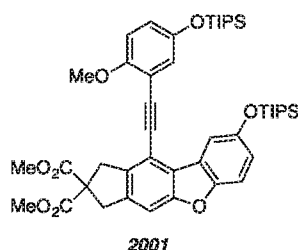
Compound 108 was obtained following general procedure.

¹H NMR (400 MHz, CDCl₃): δ 10.32 (d, *J* = 8.0 Hz, 1H), 8.49 (d, *J* = 8.5 Hz, 1H), 7.96 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.97-7.91 (m, 3H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.55 (ddd, *J*₁ = 8.2, 6.9, 1.2 Hz, 1H), 7.51 (s, 1H), 7.49-7.41 (m, 3H), 7.37 (d, *J* = 9.1 Hz, 1H), 4.15 (s, 2H), 4.11 (s, 3H), 3.85 (s, 2H), and 3.79 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3): δ 172.2, 159.9, 156.3, 155.0, 140.4, 138.1, 134.6, 130.84, 130.75, 129.4, 129.3, 128.9, 128.7, 128.4, 128.3, 127.8, 126.8, 125.9, 124.46, 124.49, 124.3, 118.5, 113.6, 112.62, 112.57, 108.2, 106.6, 98.7, 95.0, 60.2, 56.5, 53.2, 41.9, and 41.3.

Dimethyl 10-((2-methoxy-5-((triisopropylsilyl)oxy)phenyl)ethynyl)-8-

5 ((triisopropylsilyl)oxy)-1,3-dihydro-2H-indeno[5,6-b]benzofuran-2,2-dicarboxylate (2001)

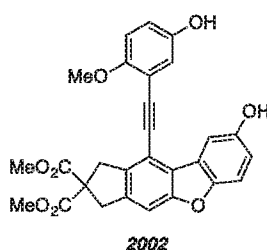


Compound 2001 was obtained following general procedure.

^1H NMR (400 MHz, CDCl_3): δ 8.01 (d, $J = 2.5$ Hz, 1H), 7.34 (d, $J = 8.8$ Hz, 1H), 7.32 (s, 1H), 7.10 (d, $J = 2.91$ Hz, 1H), 6.98 (dd, $J = 8.8$ Hz, 2.6 Hz, 1H), 6.88 (dd, $J = 8.9$ Hz, 3.0 Hz, 1H), 6.79 (d, $J = 9.0$ Hz, 1H), 3.89 (s, 3H), 3.88 (s, 2H), 3.77 (s, 6H), 3.74 (s, 2H), 1.33-1.17 (m, 6H), 1.13 (d, $J = 7.15$ Hz, 18H), and 1.04 (d, $J = 7.3$ Hz, 18H).

^{13}C NMR (101 MHz, CDCl_3): δ 172.1, 156.8, 155.0, 151.6, 149.5, 139.2, 137.6, 124.8, 124.3, 123.9, 121.2, 119.7, 112.95, 112.89, 112.2, 111.6, 111.3, 107.8, 94.0, 89.3, 60.5, 56.3, 53.2, 41.2, 40.0, 18.1, 18.0, 12.82, and 12.80.

15 Dimethyl 8-hydroxy-10-((5-hydroxy-2-methoxyphenyl)ethynyl)-1,3-dihydro-2H-indeno[5,6-b]benzofuran-2,2-dicarboxylate (2002)

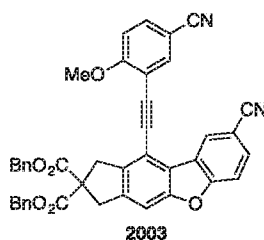


Compound 2002 was obtained following general procedure.

¹H NMR (400 MHz, acetone-D₆): (referenced to acetone = 2.05) δ 8.40 (br s, 1H), 8.25 (d, *J* = 2.6 Hz, 1H), 8.17 (br s, 1H), 7.45 (s, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.14 (d, *J* = 2.9 Hz, 1H), 7.05 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 1H), 6.91 (dd, *J* = 8.9, 2.9 Hz, 1H), 4.02 (s, 3H), 3.85 (s, 2H), 3.769 (s, 2H), and 3.765 (s, 6H).

5 ¹³C NMR (101 MHz, acetone-D₆): (referenced to acetone = 29.84 ppm) δ 172.3, 157.4, 155.2, 154.3, 151.6, 151.8, 140.7, 138.2, 125.5, 124.1, 120.0, 118.3, 116.4, 113.4, 113.3, 113.2, 112.2, 108.5, 108.5, 95.5, 89.7, 60.9, 56.4, 53.3, 41.5, and 40.2.

Dibenzyl 8-cyano-10-((5-cyano-2-methoxyphenyl)ethynyl)-1,3-dihydro-2H-indeno[5,6-b]benzofuran-2,2-dicarboxylate (2003)

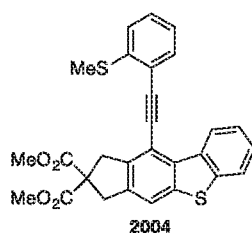


Compound 2003 was obtained following general procedure.

¹H NMR (400 MHz, CDCl₃): δ 9.02 (d, *J* = 1.8 Hz, 1H), 7.83 (d, *J* = 2.2 Hz, 1H), 7.74 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.69 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.41 (s, 1H), 7.33-7.30 (m, 6H), 7.27-7.24 (m, 4H), 7.08 (d, *J* = 8.8 Hz, 1H), 5.17 (s, 4H), 4.19 (s, 3H), 3.89 (s, 2H), and 3.79 (s, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 170.9, 163.2, 158.4, 156.5, 141.4, 139.0, 138.1, 137.3, 135.3, 134.7, 130.9, 128.7, 128.6, 126.9, 120.0, 118.3, 113.6, 112.7, 112.6, 111.7, 108.8, 108.7, 106.7, 104.7, 92.8, 90.6, 67.8, 60.7, 57.0, 56.5, 41.1, and 39.6.

Dimethyl 10-((2-(methylthio)phenyl)ethynyl)-1,3-dihydro-2H-benzo[b]indeno[5,6-d]thiophene-2,2-dicarboxylate (2004)



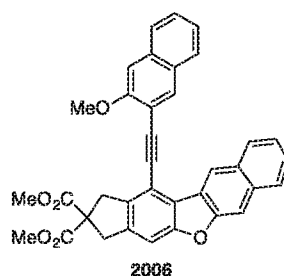
Compound 2004 was obtained following general procedure.

¹H NMR (400 MHz, CDCl₃): δ 9.36-9.34 (m, 1H), 7.83-7.80 (m, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.65 (s, 1H), 7.47-7.42 (m, 1H), 7.37 (td, *J* = 7.7, 1.0 Hz, 1H), 7.26 (d, *J* = 9.7 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 3.99 (s, 2H), 3.78 (s, 6H), 3.77 (s, 2H), and 2.56 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 172.1, 141.8, 141.7, 139.7, 139.4, 138.7, 135.5, 133.3, 132.9, 129.3, 126.6, 124.81, 124.76, 124.3, 122.5, 121.7, 118.6, 114.3, 96.8, 92.7, 60.3, 53.2, 40.9, 40.7, and 15.6.

Dimethyl 12-((3-methoxynaphthalen-2-yl)ethynyl)-1,3-dihydro-2H-indeno[5,6-b]naphtho[2,3-d]furan-2,2-dicarboxylate (2006)

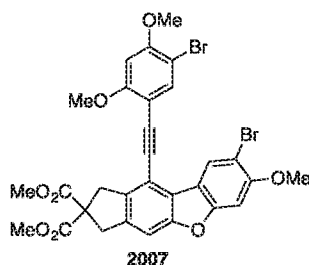
Compound 2006 was obtained following general procedure.



¹H NMR (400 MHz, CDCl₃): δ 9.18 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.86-7.84 (m, 2H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.53-7.49 (m, 2H), 7.47 (ddd, *J* = 8.0, 6.8, 1.4 Hz, 1H), 7.42 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.34 (s, 1H), 7.24 (s, 1H), 4.16 (s, 3H), 3.96 (s, 2H), 3.82 (s, 6H), and 3.78 (s, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 172.0, 157.4, 157.1, 155.4, 140.5, 137.5, 134.7, 134.0, 133.0, 130.5, 128.7, 128.6, 127.9, 127.8, 127.6, 126.8, 125.9, 125.3, 124.6, 124.2, 123.5, 121.1, 114.2, 113.5, 107.6, 106.6, 105.7, 95.0, 89.9, 60.5, 56.2, 53.3, 41.3, and 39.9.

Dimethyl 8-bromo-10-((5-bromo-2,4-dimethoxyphenyl)ethynyl)-7-methoxy-1,3-dihydro-2H-indeno[5,6-b]benzofuran-2,2-dicarboxylate (2007)



5

Compound 2007 was obtained following general procedure.

¹H NMR (400 MHz, CDCl₃): δ 8.82 (s, 1H), 7.75 (s, 1H), 7.30 (s, 1H), 7.10 (s, 1H), 6.56 (s, 1H), 4.13 (s, 3H), 4.00 (s, 3H), 3.99 (s, 3H), 3.86 (s, 2H), 3.79 (s, 6H), and 3.74 (s, 2H).

10 Solubility was too low for ¹³C NMR

Melting point: 228.1–231.0 °C.

V. Discussion of Computational Methods and Computational Results

DFT calculations were carried out within the Gaussian 09 software package (M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone,
 15 B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M.
 20 Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J.

Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox. Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.) Geometries were optimized using the M06-2X (Zhao, Y.; Truhlar, D. G. Theor. Chem. Acc. 2008, 120, 215–241) functional; the double- ζ split-valence 6-31G(d) basis set was also used. The geometry

- 5 optimization and frequency calculations for each ground state of **10a-c** were performed in the gas phase (i.e., no solvation model was used). Harmonic vibrational frequency calculations were done at 298 K and then used for the thermal correction of the enthalpies. The value for the “Sum of electronic and thermal Free Energies=” gave the free energy (G) that is reported for each of **10a-c**. Excited state properties for each of **10a-c** were obtained using time-dependent DFT
- 10 calculations by three different functions, using B3LYP/6-31G(d), BLYP/6-31G(d), and M06-2X/6-31G(d), the HOMO, LUMO and the HOMO-LUMO gaps are presented in the following Table.

	B3LYP		
	HOMO	LUOM	E _{gap}
10a	-5.196 eV	-1.486 eV	3.71 eV
10b	-4.984 eV	-1.351 eV	3.63 eV
10c	-5.406 eV	-1.865 eV	3.54 eV

	BLYP		
	HOMO	HOMO	HOMO
10a	-6.412 eV	-6.412 eV	-6.412 eV
10b	-6.215 eV	-6.215 eV	-6.215 eV
10c	-6.615 eV	-6.615 eV	-6.615 eV

15

	M06-2X		
	HOMO	HOMO	HOMO
10a	-4.349 eV	-4.349 eV	-4.349 eV
10b	-4.111 eV	-4.111 eV	-4.111 eV
10c	-4.548 eV	-4.548 eV	-4.548 eV

Energy and geometry 10a (optimized in the gas phase by M06-2X/6-31G(d) and given here in Å in Gaussian 09's format, electronic energies are given in a.u., all structures calculated are in the singlet spin state and have a neutral charge.)

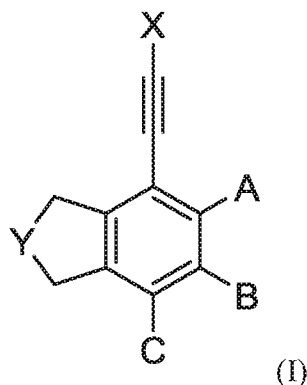
5 **FIGs. 19A, 19B and 19C** show electroluminescence for all nine devices including compound **10a** (**FIG. 19A**), **10b** (**FIG. 19B**) and **10c** (**FIG. 19C**) taken at 2 mA/cm².

FIGs. 20A show current-voltage and brightness-voltage data for compounds **10a** in 4%, 20% and 100% UGH2 (**FIG. 20A, 20B and 20C** respectively); **10b** in 4%, 20% and 100% UGH2 (**FIG. 21A, 21B and 21C** respectively); and **10c** in 4%, 20% and 100% UGH2 (**FIG.**
10 **22A, 22B and 22C** respectively).

 Thus, embodiments of compounds and devices containing such compounds are disclosed. The implementations described above and other implementations are within the scope of the following claims. One skilled in the art will appreciate that the present disclosure can be practiced with embodiments other than those disclosed. The disclosed embodiments are
15 presented for purposes of illustration and not limitation.

Claims:

1. Compounds of formula I



where Y can be selected from $(R^1)_2O_2C)_2C$, O, CH_2 , NR^2

with R^2 being SO_2R^3 , aryl, alkyl, $C(=O)R^4$; and

R^1 , R^3 and R^4 independently selected from H, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof;

X can be selected from SiR^5_3 , $C(=O)R^4$, CO_2R^4 , $CONR^4_2$, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof,

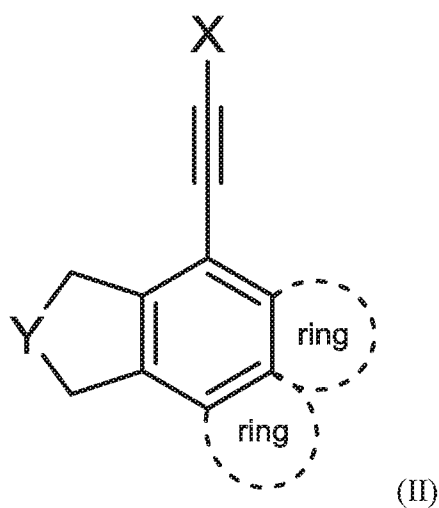
where R^4 is as defined above and

R^5 is selected from H, substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof; and

A, B, and C are independently selected from H, SiR^5_3 , substituted or unsubstituted branched or straight alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl (including multiple ring systems), substituted or unsubstituted heteroaryl, or combinations thereof, $C(=O)R^4$, CO_2R^4 , $CONR^4_2$, $C\equiv CR^2$

where R^2 , R^3 , R^4 and R^5 are independently defined as above.

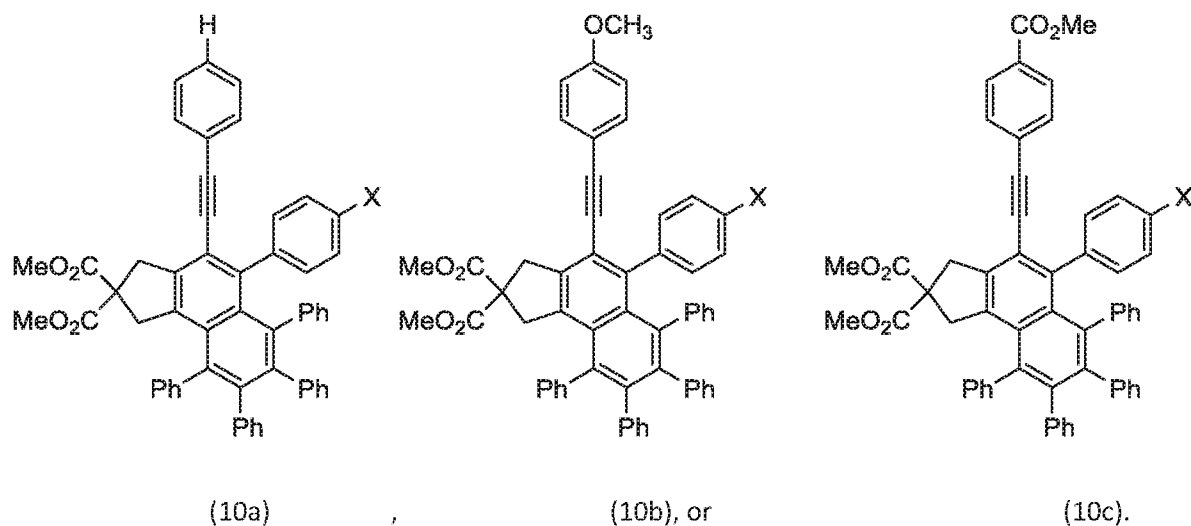
2. The compound according to claim 1, wherein X can be selected from substituted or unsubstituted aryl groups.
3. The compound according to claim 1, wherein X can be selected from phenyl, naphthyl, phenanthryl, carbazyl, or combinations thereof.
4. The compound according to claim 1 wherein X can be substituted with alkoxyl groups, hydroxyl groups, cyano groups, haloalkyl groups, alkyl groups, halides, protecting groups, or any combinations thereof.
5. The compound according to claim 1, of formula II



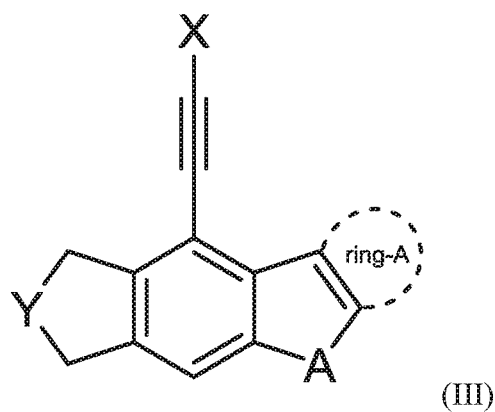
where X and Y are as defined above; and

ring is selected from benzo-, naphtheno-, or anthracenofurano, -thiofurano, or indolo, where the indolo nitrogen can bear R^2 .

6. The compound according to any of claims 1 to 5, wherein the compound is selected from:



7. The compound according to claim 1, of formula III:

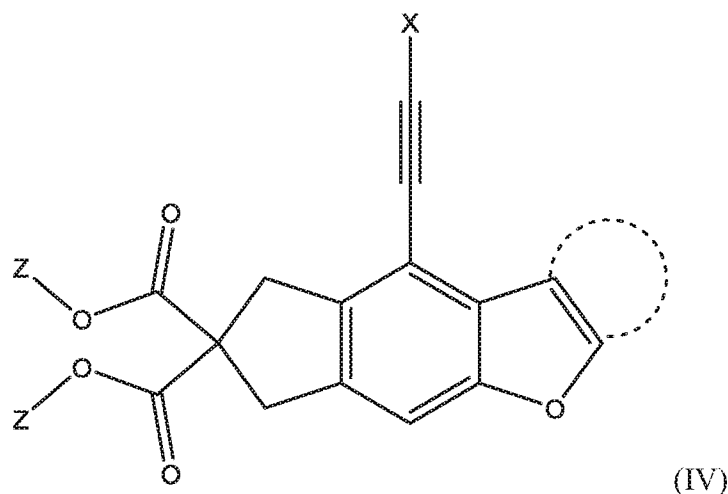


where X and Y are as defined above;

A is O, S, or NR^2 where R^2 is defined as above; and

ring-A is benzo- 1,2-naphtheno-, 2,3-naphtheno-, 1,2-anthraceno-, 2,3-anthraceno-, 9,10-phenanthreno- as well as substituted derivatives thereof.

8. The compound according to claim 1, of formula IV



where X can be selected from hydrogen (H), substituted or unsubstituted alkyl groups, fluoroalkyl groups, substituted or unsubstituted aryl groups, esters, halides, alkoxy groups, aryloxy groups, or combinations thereof; and

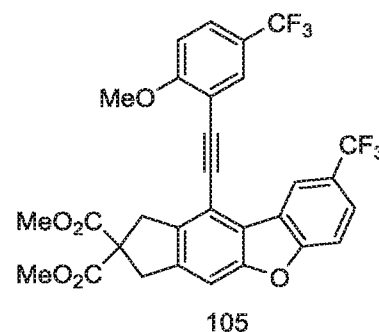
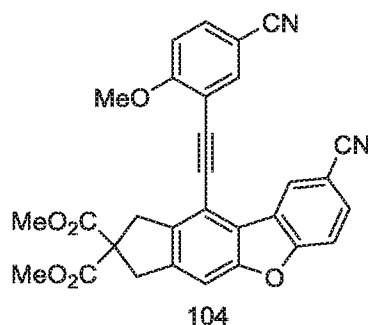
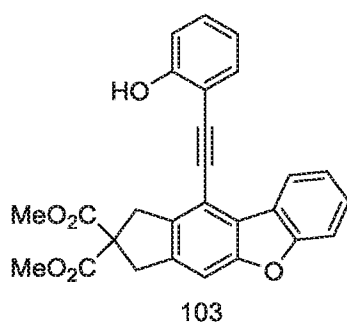
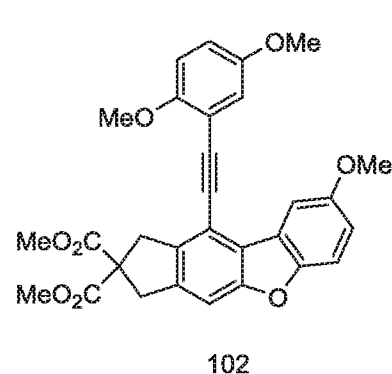
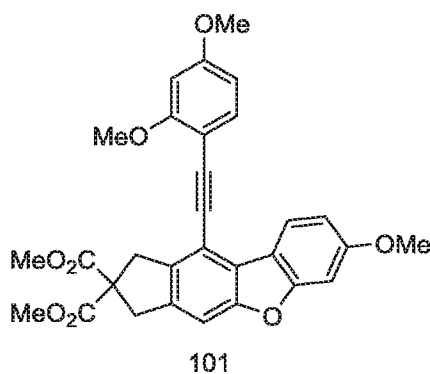
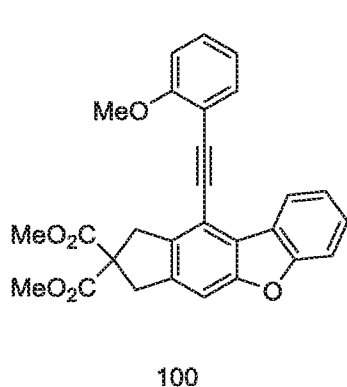
each Z can independently be selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted heteroaryls, or combinations thereof.

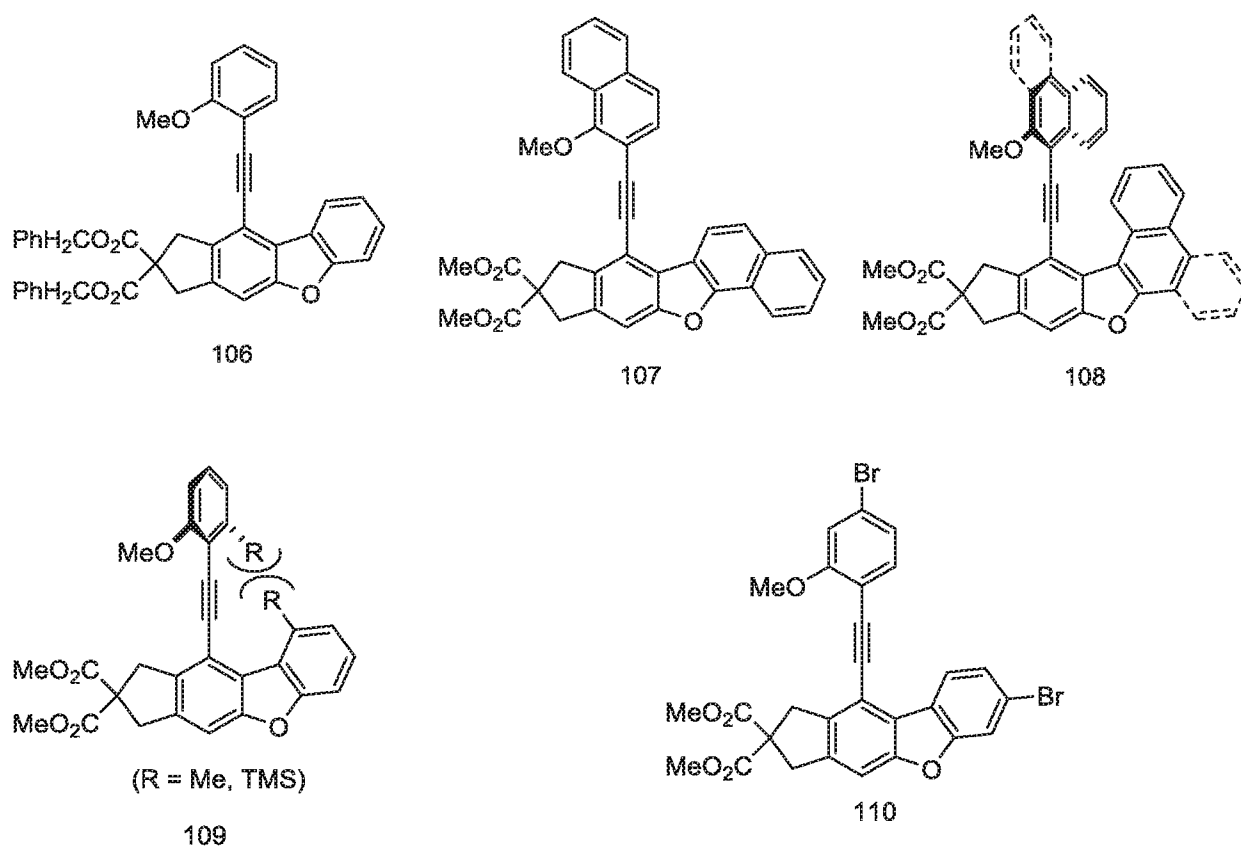
9. The compound according to claim 8, wherein X can be selected from substituted or unsubstituted aryl groups.

10. The compound according to claim 8, wherein X can be selected from phenyl, naphthyl, phenanthryl, carbazyl, or combinations thereof.

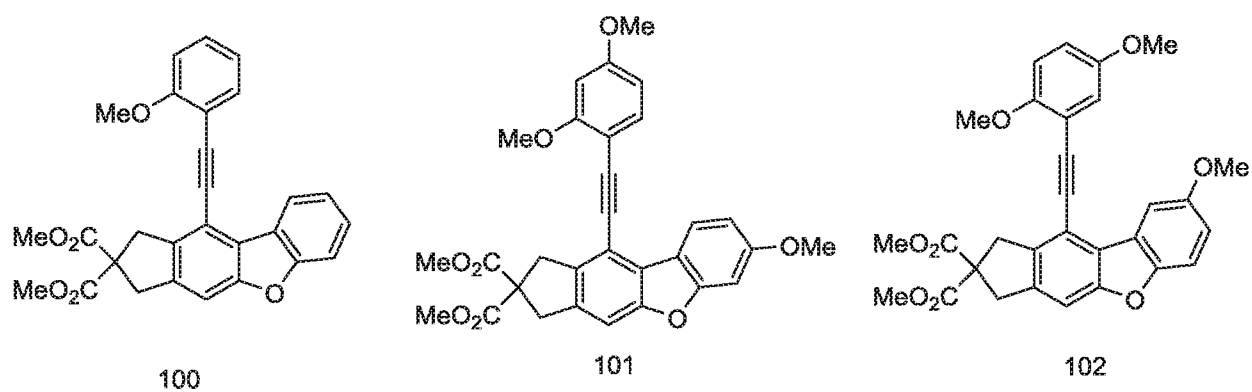
11. The compound according to claim 8 wherein X is substituted with alkoxy groups, hydroxyl groups, cyano groups, haloalkyl groups, alkyl groups, halides, protecting groups, or any combinations thereof.

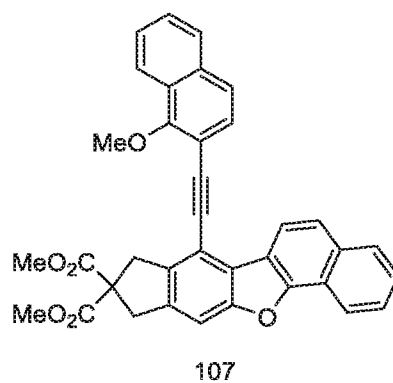
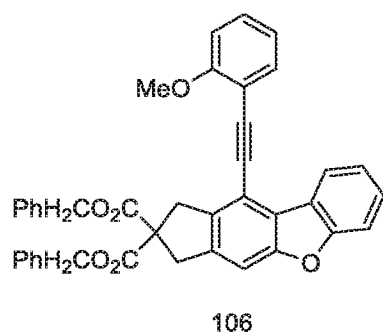
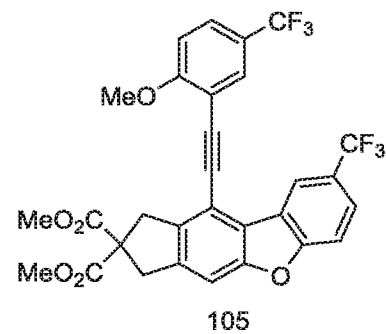
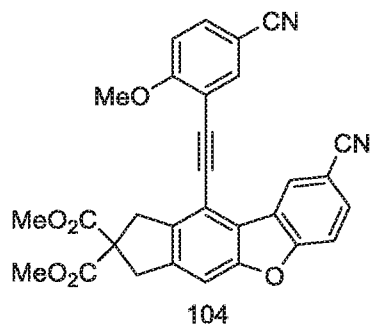
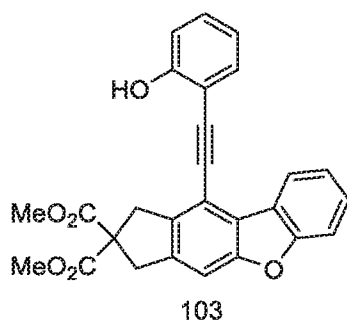
12. The compound according to claim 8, wherein Z are independently selected from substituted or unsubstituted C₁ to C₆ alkyl groups; or substituted or unsubstituted aryl groups.
13. The compound according to claim 8, wherein Z are independently selected from substituted or unsubstituted benzyl groups.
14. The compound according to claim 8, where the dashed ring is selected from benzo, 1,2-naphtheno-, 2,3-naphtheno-, 1,2-anthraceno-, 2,3-anthraceno-, 9,10-phenanthreno- as well as substituted derivatives thereof.
15. The compound according to claim 8, wherein the dashed ring is benzo and substituted with 1-3, alkoxy, aryloxy, halo, alkyl, amino, fluoroalkyl, trialksilyl, or combinations thereof.
16. The compound according to any of claims 1 to 5 or 7 to 15, wherein the compound is selected from:



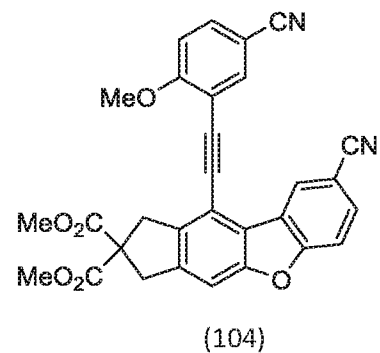
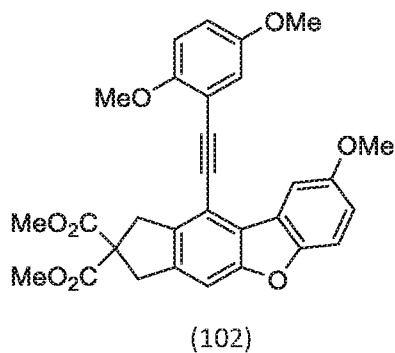
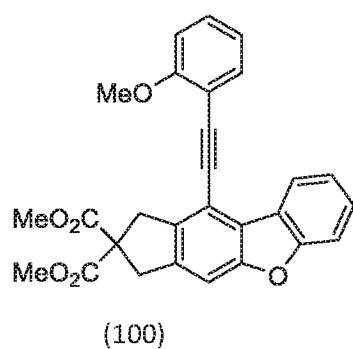


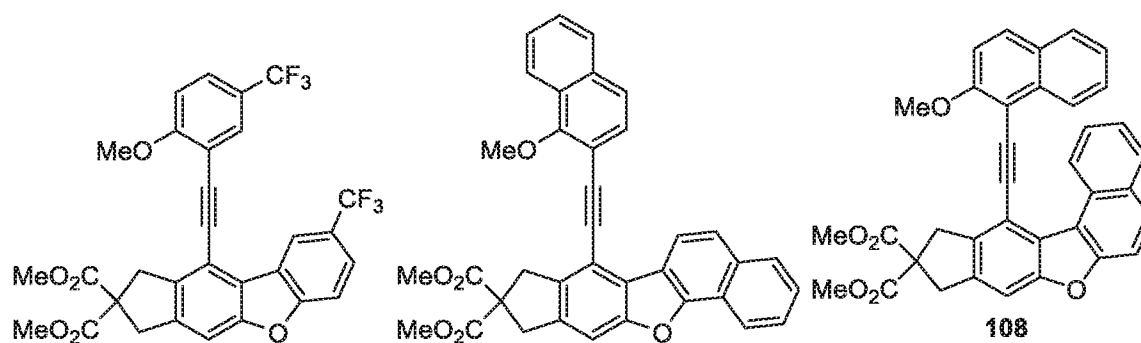
17. The compound according to any of claims 1 to 5 or 7 to 15, wherein the compound is selected from:



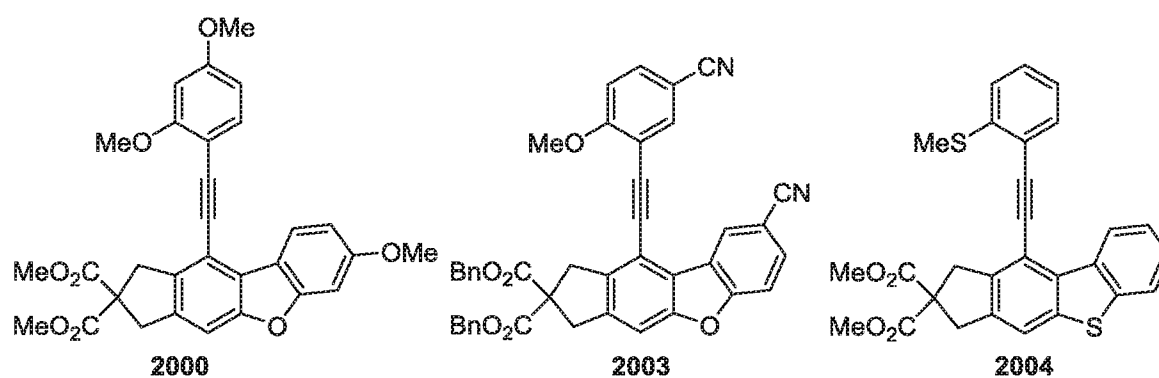


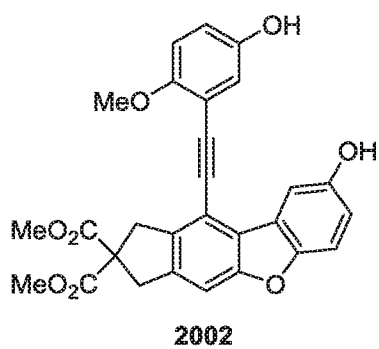
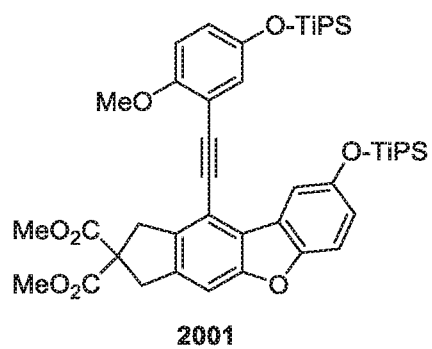
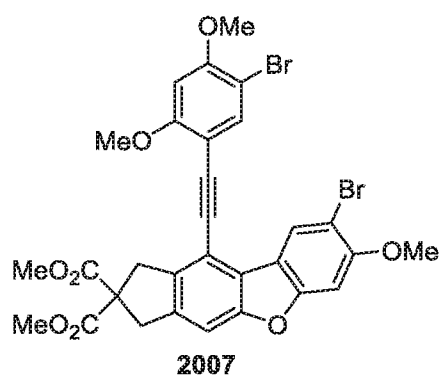
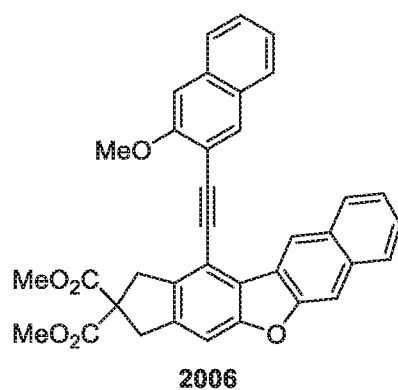
18. The compound according to any of claims 1 to 5 or 7 to 15, wherein the compound is selected from:



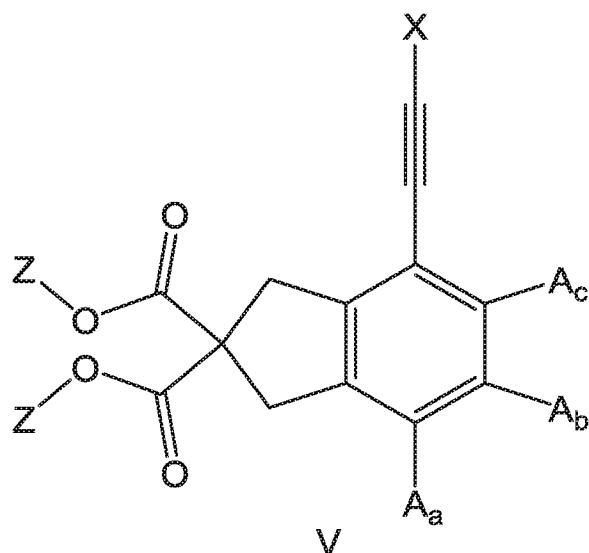


19. The compound according to any of claims 1 to 5 or 7 to 15, wherein the compound is selected from:



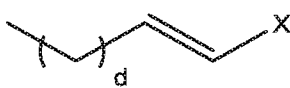
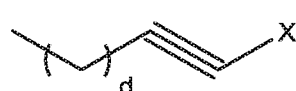


20. The compound according to claim 1, of formula V



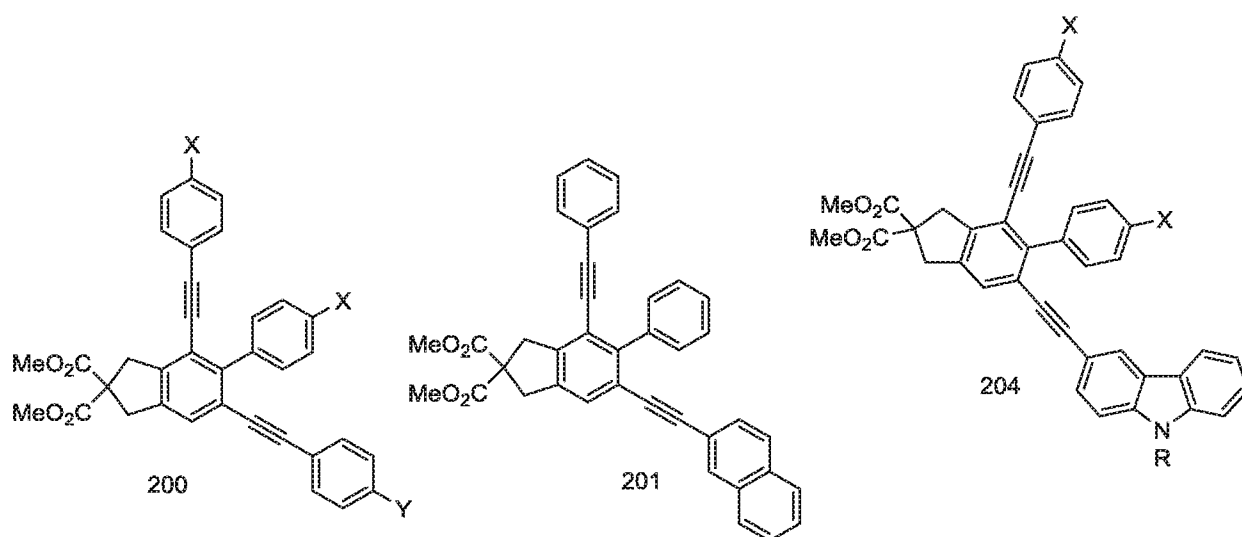
where X is as defined above;

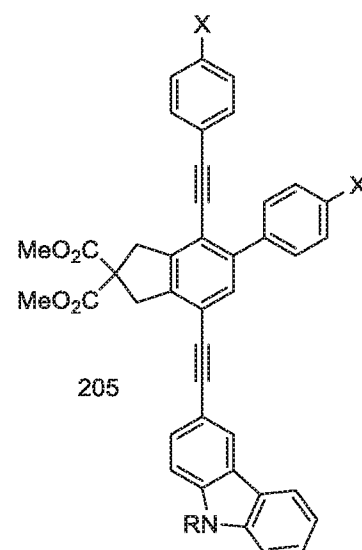
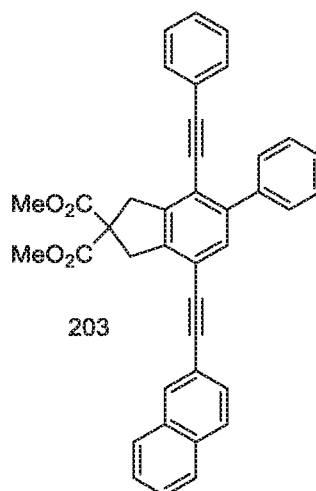
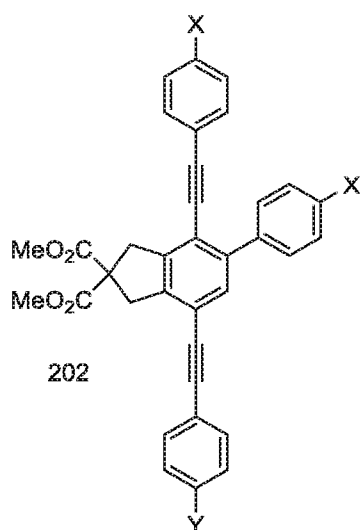
Z can independently be selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted heterocyclic aromatic groups;

A can be independently selected from , and , where X is as indicated above and d is an integer from 0 to 6; and a, b and c are 0 or 1 with the caveat that only 1 of a and b can be 1.

21. The compound according to claim 20, wherein X can be independently selected from hydrogen, substituted, or unsubstituted aryl groups.
22. The compound according to claim 20, wherein X can be independently selected from phenyl, naphthyl, phenanthryl, carbazyl, or combinations thereof.
23. The compound according to claim 20, wherein X is substituted with alkoxy groups, hydroxyl groups, cyano groups, haloalkyl groups, alkyl groups, halogens, protecting groups, or any combinations thereof.
24. The compound according to claim 20, wherein Z can independently be selected from substituted or unsubstituted cycloalkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted alkyls, or combinations thereof.
25. The compound according to claim 20, wherein Z can independently be selected from substituted or unsubstituted C₁ to C₆ alkyl groups, or substituted aryl groups.
26. The compound according to claim 20, wherein Z can independently be selected from substituted or unsubstituted benzyl groups.

27. The compound according to claim 20, wherein at least one X in Formula V is substituted.
28. The compound according to claim 27, wherein substituents of X can include methoxy, methanoate, N-phenyl, phenyl, naphthyl, and carbazyl.
29. The compound according to any of claims 1-5, 7 to 15, or 20 to 28, wherein the compound is selected from:



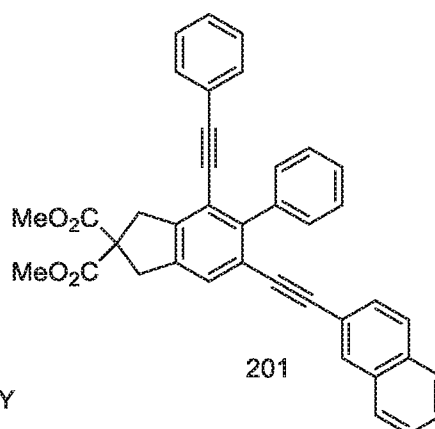
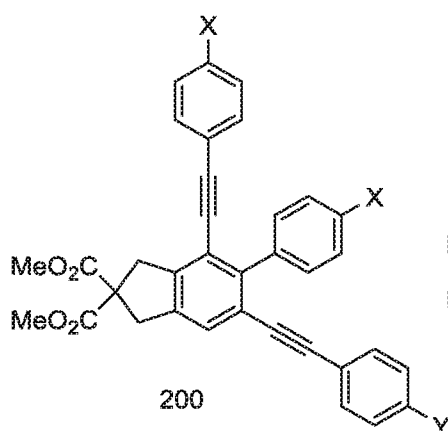


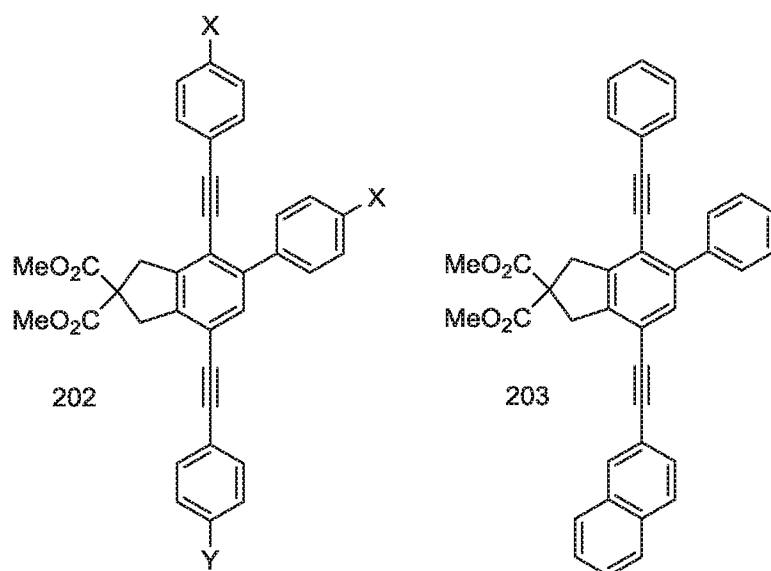
In compounds 200 to 205, the following substituents can include the following:

X=Y=H;	X=Y=OMe;	X=CO ₂ Me;
X=Y=CO ₂ Me;	Y=NPh ₂	
X=Y=CN		

In compound 205, R can be an alkyl, aryl, or sulfonyl group or a carbonyl-containing functional group.

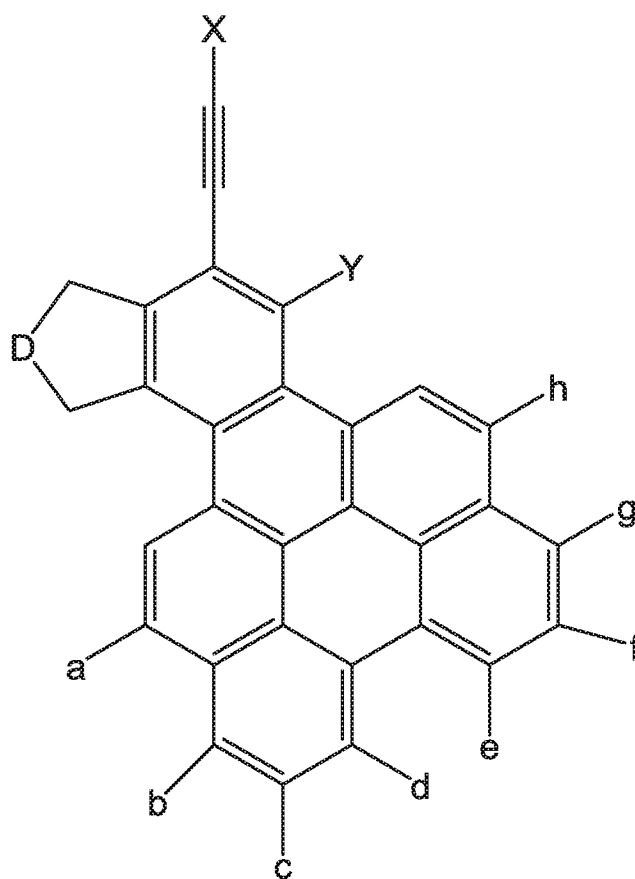
30. The compound according to any of claims 1-5, 7 to 15, or 20 to 28, wherein the compound is selected from:





X=Y=H;
X=Y=OMe; X=CO₂Me;
X=Y=CO₂Me; Y=NPh₂
X=Y=CN

31. A compound according to formula VI



VI

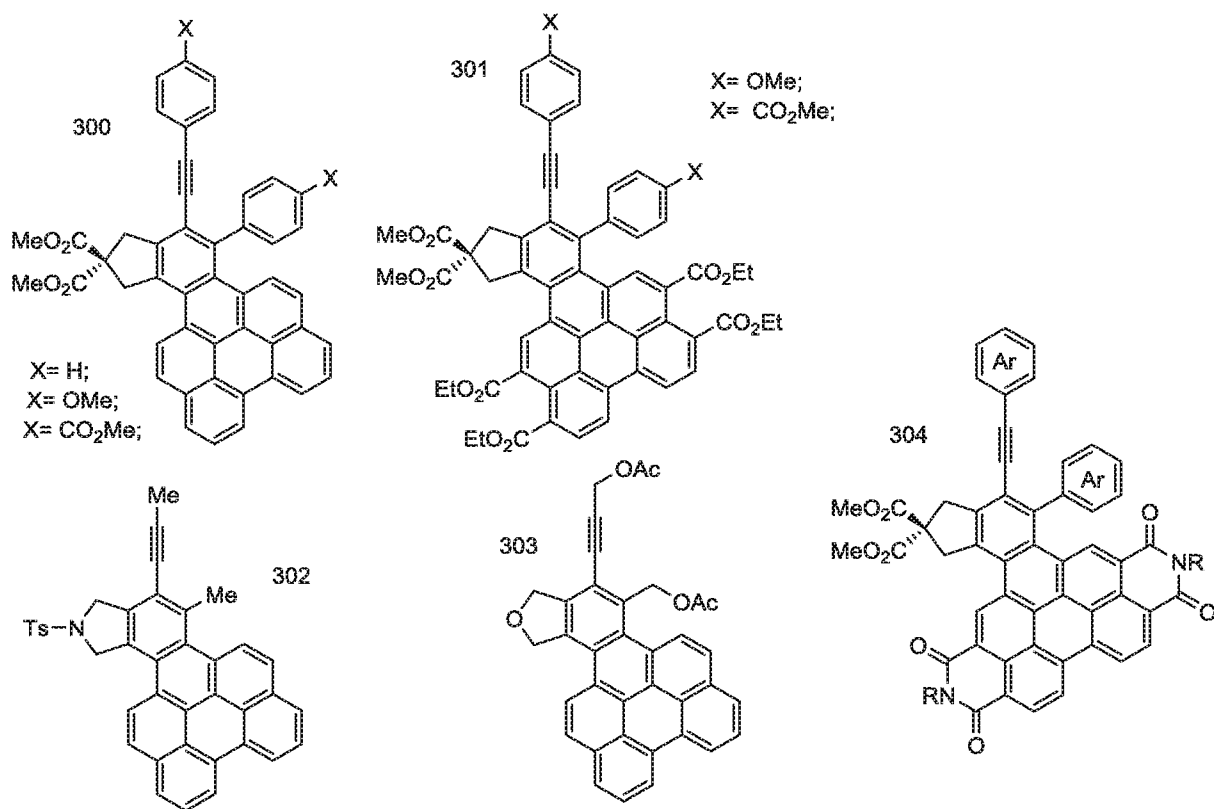
where X and Y can independently be selected from hydrogen, substituted or unsubstituted alkyl groups, aryl groups, esters, halides, alkoxy groups, aryloxy groups, or combinations thereof;

D is selected from N-alkyl, N-sulfonyl, N-acyl, N-protecting group, O, $C(CO_2Z)_2$, where Z can independently be selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted heterocyclic aromatic groups; and

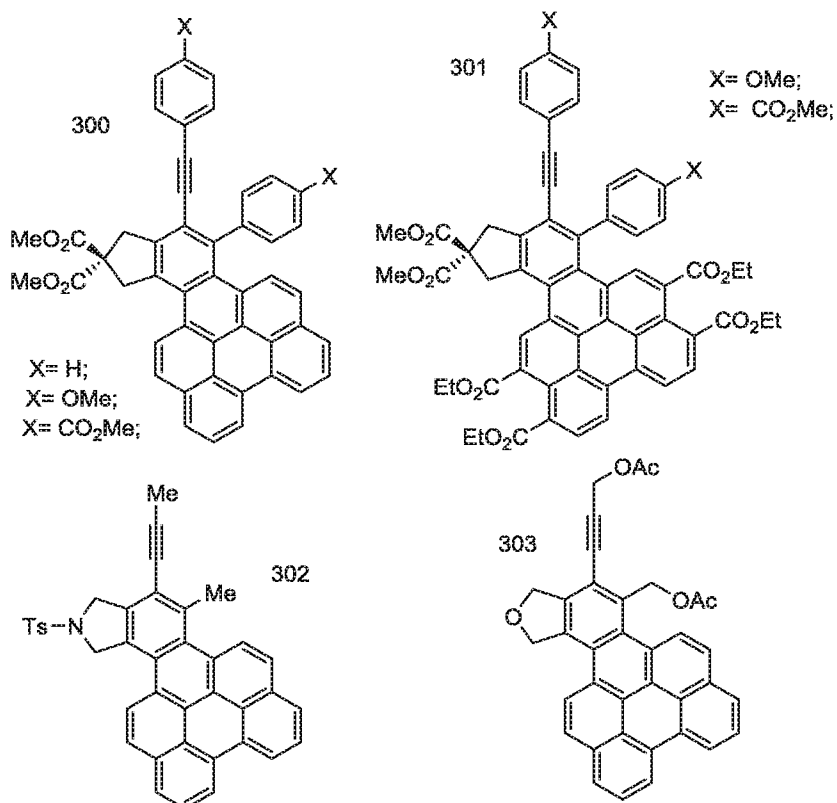
a, b, c, d, e, f, g and h are independently H or $C(O_2)$ alkyl, or a and b, g and h, or both a and b and g and h together are embedded in a common, five- or six-membered ring.

32. The compound according to claim 31, wherein a and b, g and h, or both a and b and g and h together are in a ring containing —CO—NR—CO—, where R can be H or an alkyl, cycloalkyl, or aryl substituent.
33. The compound according to claim 31, wherein X and Y can be independently selected from hydrogen, alkoxy, esters, or combinations thereof.
34. The compound according to claim 31, wherein only four of a to h are CO₂alkyl.
35. The compound according to claim 34, wherein the CO₂alkyl is CO₂CH₂CH₃.
36. The compound according to claim 31, wherein a and b, g and h, or both a and b and g and h together form a piperidine-2,6-dione group.

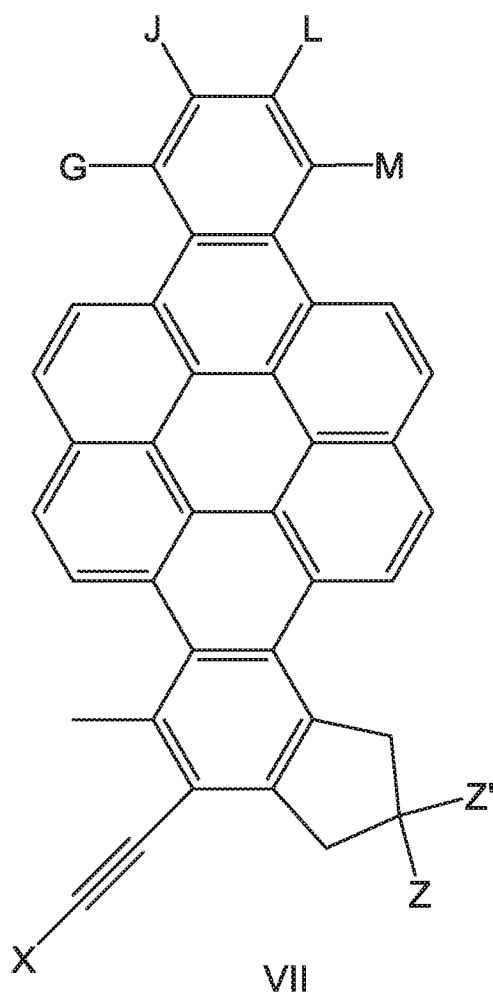
37. The compound according to claim 31, wherein the compound is selected from:



38. The compound according to claim 31, wherein the compound is selected from:



39. A compound according to Formula VII:



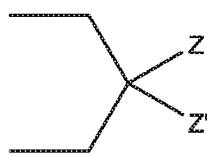
where X can be selected from hydrogen, substituted or unsubstituted alkyl groups, aryl groups, esters, esters, halides, alkoxy groups, aryloxy groups, or combinations thereof;

Z and Z' can independently be selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted alkoxy groups, substituted or unsubstituted ester groups, substituted or unsubstituted heterocyclic aromatic groups; and

G and M are independently selected from hydrogen, substituted or unsubstituted alkyl groups, aryl groups, esters, or combinations thereof;

J and L are $\text{---}\equiv\text{---X}$, where X is as defined above, or

G together with J, L together with M, or both G together with J and L together with M forms

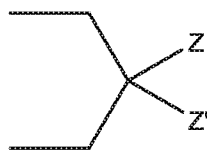


, where Z and Z' can be independently selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted alkoxy groups, substituted or unsubstituted ester groups, substituted or unsubstituted heterocyclic aromatic groups.

40. The compound according to claim 39, wherein X is a substituted aryl group.

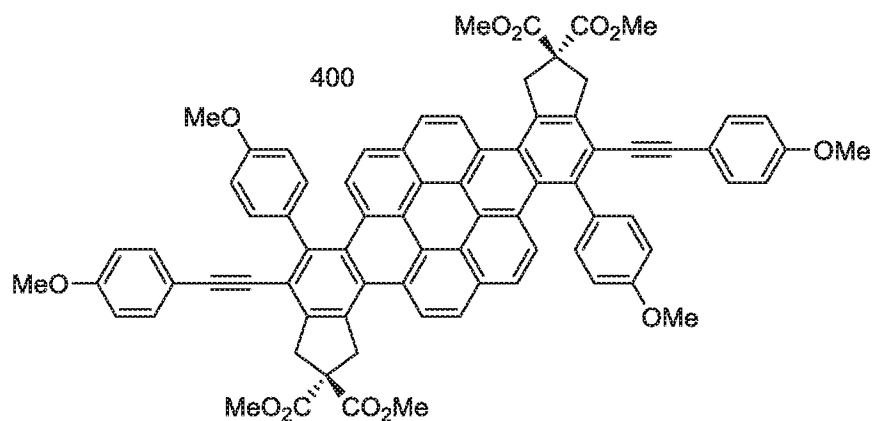
41. The compound according to claim 40, wherein X is a substituted phenyl group.

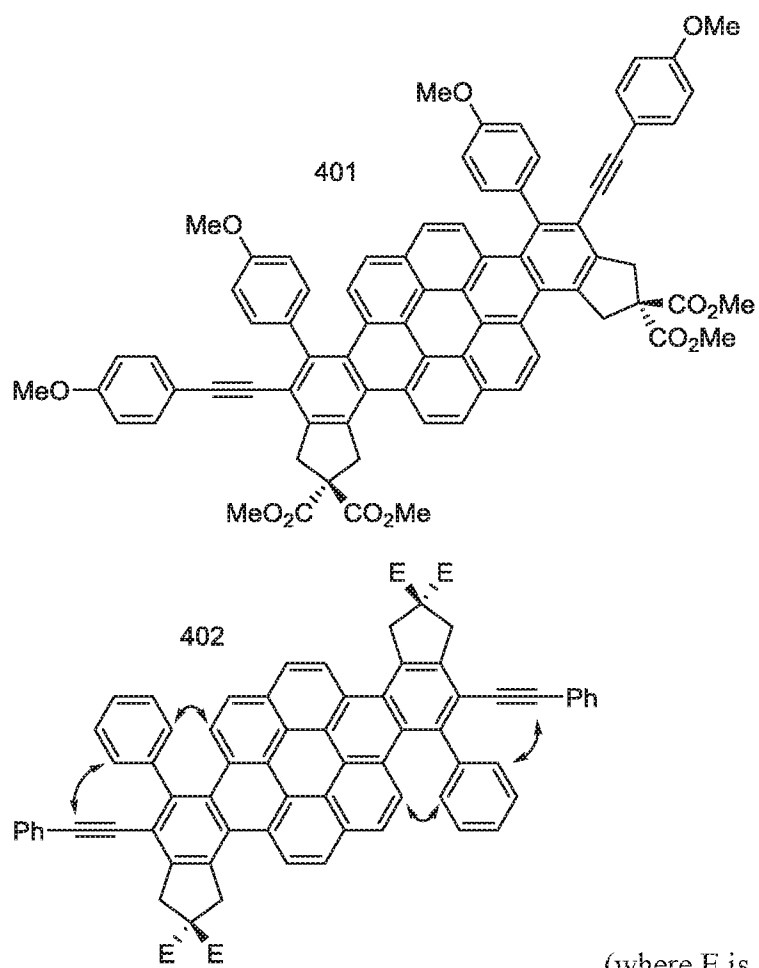
42. The compound according to claim 39, wherein G together with J, L together with M, or both G together with J and L together with M forms



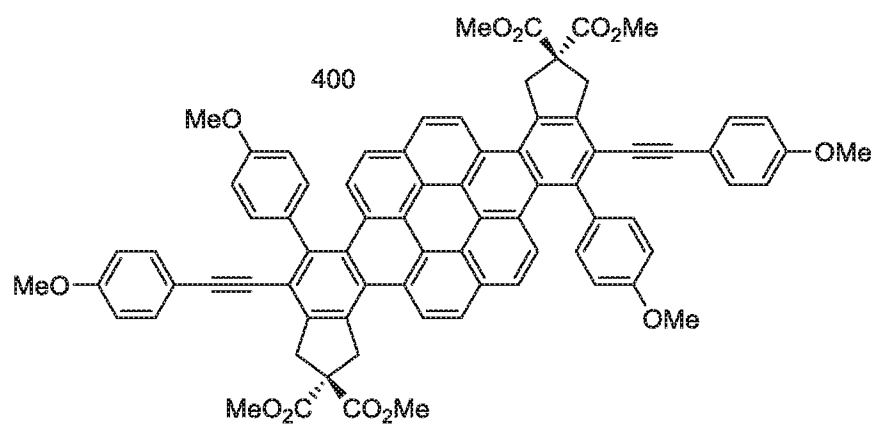
43. The compound according to claim 42, wherein Z and Z' are independently selected from substituted or unsubstituted ester groups.

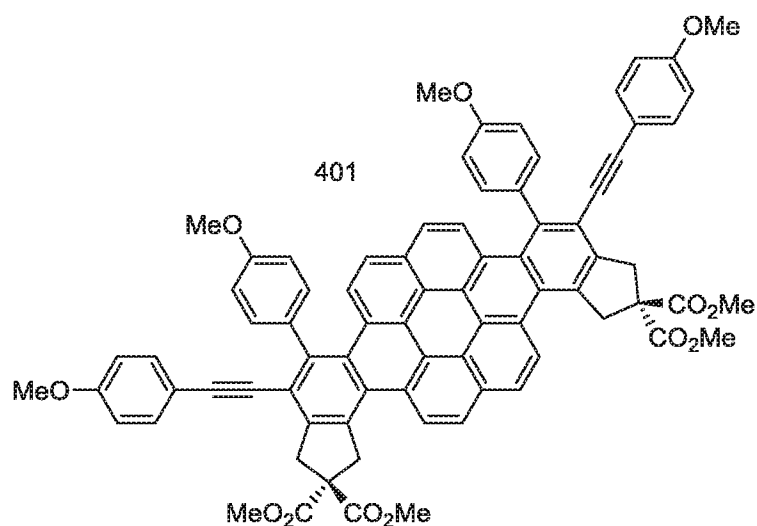
44. The compound according to claim 39, wherein the compound is selected from:



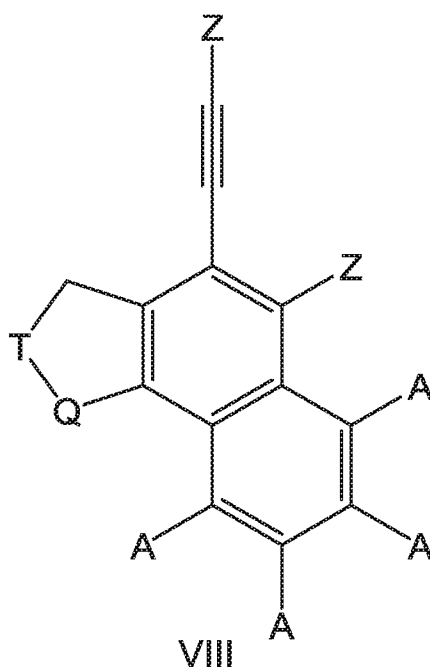


45. The compound according to claim 39, wherein the compound is selected from:





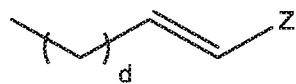
46. A compound according to Formula VIII



where Q is a substituted or unsubstituted N or substituted or unsubstituted C;

Z are independently selected from substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted alkoxy groups, substituted or unsubstituted ester groups, substituted or unsubstituted heterocyclic aromatic groups;

A are independently selected from substituted or unsubstituted aryl groups,



where Z is as indicated above and d is an integer from 0 to 6, or two

adjacent A can together form a conjugated ring structure having at least 3 additional members in the ring; and

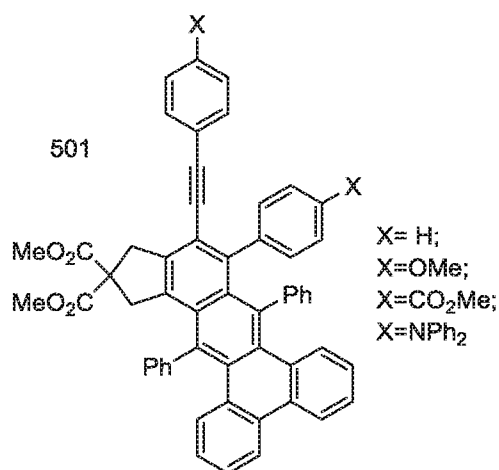
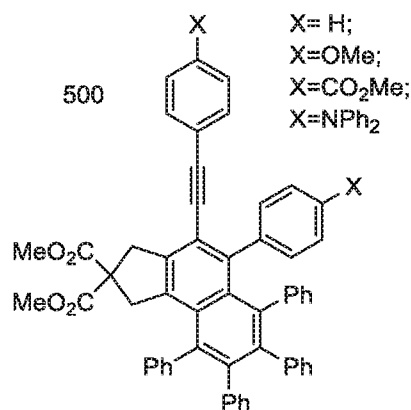
T is $-\text{C}(\text{CO}_2\text{Z})$ where Z is as indicated above, a substituted or unsubstituted N, or a substituted or unsubstituted C.

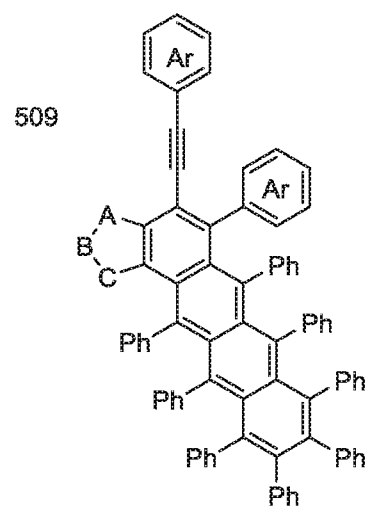
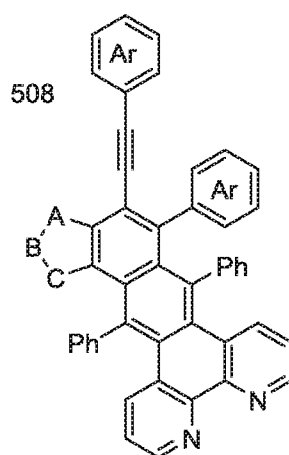
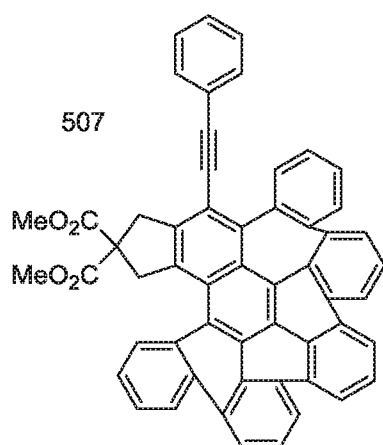
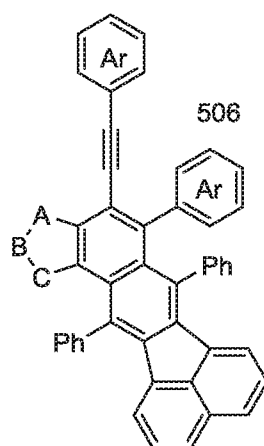
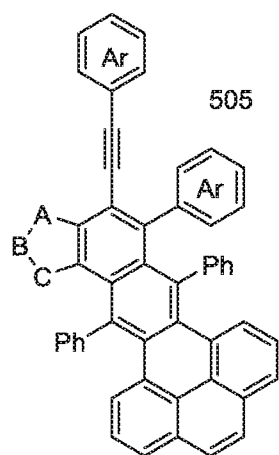
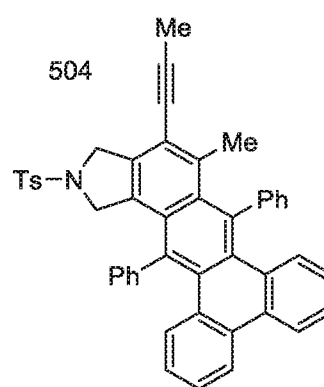
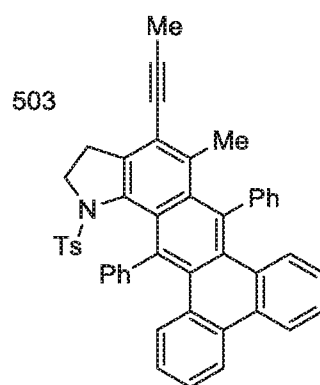
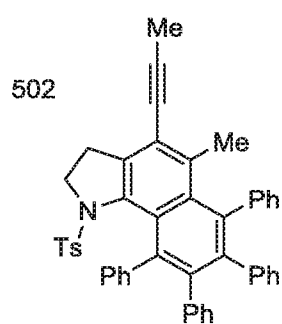
47. The compound according to claim 46, wherein T is $-\text{C}(\text{CO}_2\text{Z})$.

48. The compound according to claim 47, where Z are substituted or unsubstituted ester groups.

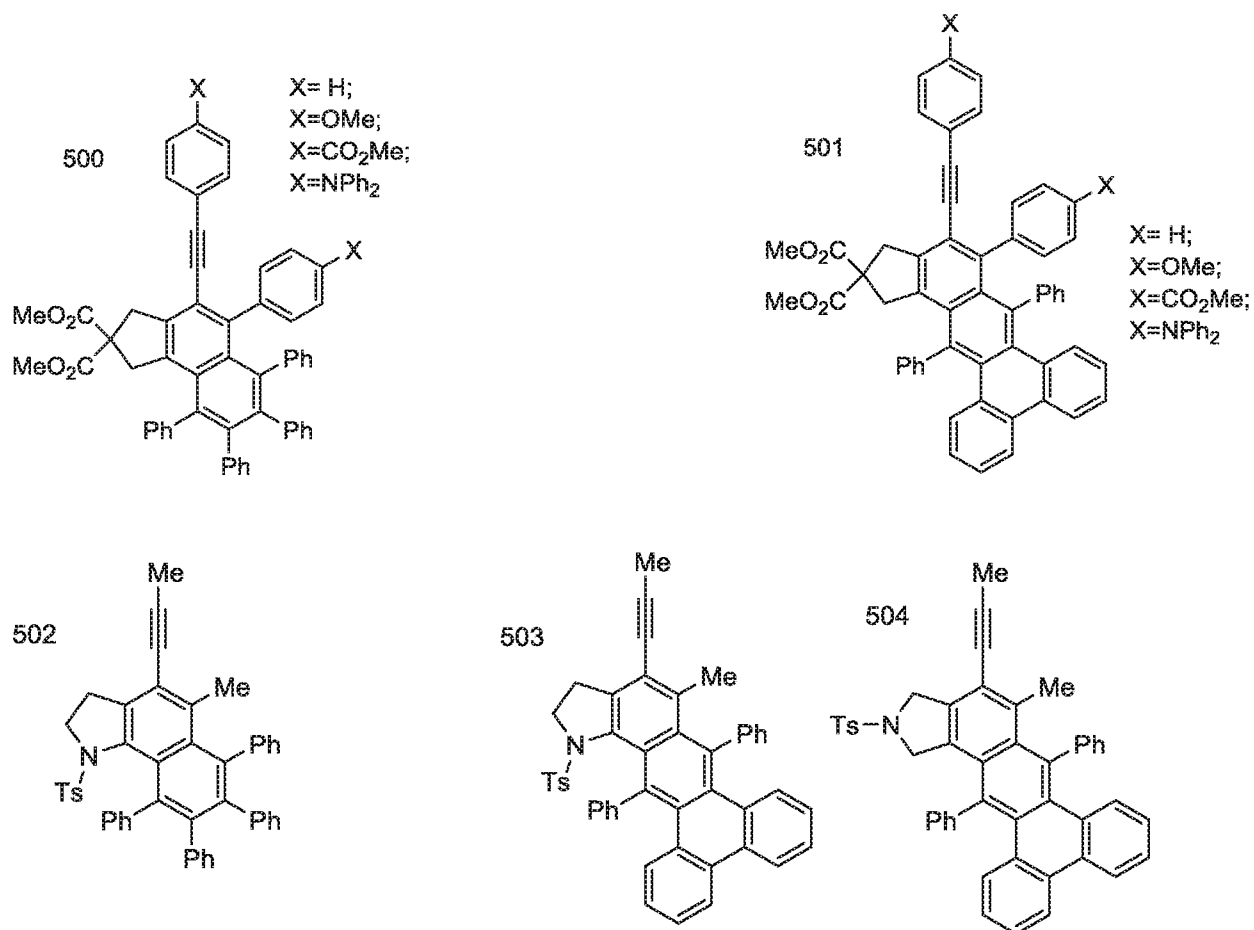
49. The compound according to claim 46, wherein Z are independently substituted or unsubstituted aryl groups.

50. The compound according to claim 46, wherein the compound is selected from:

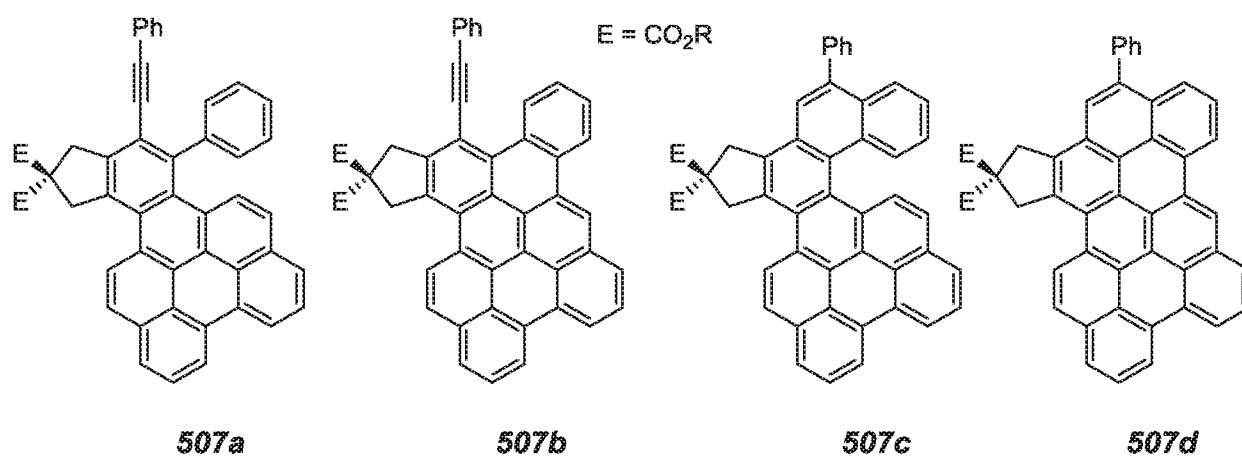




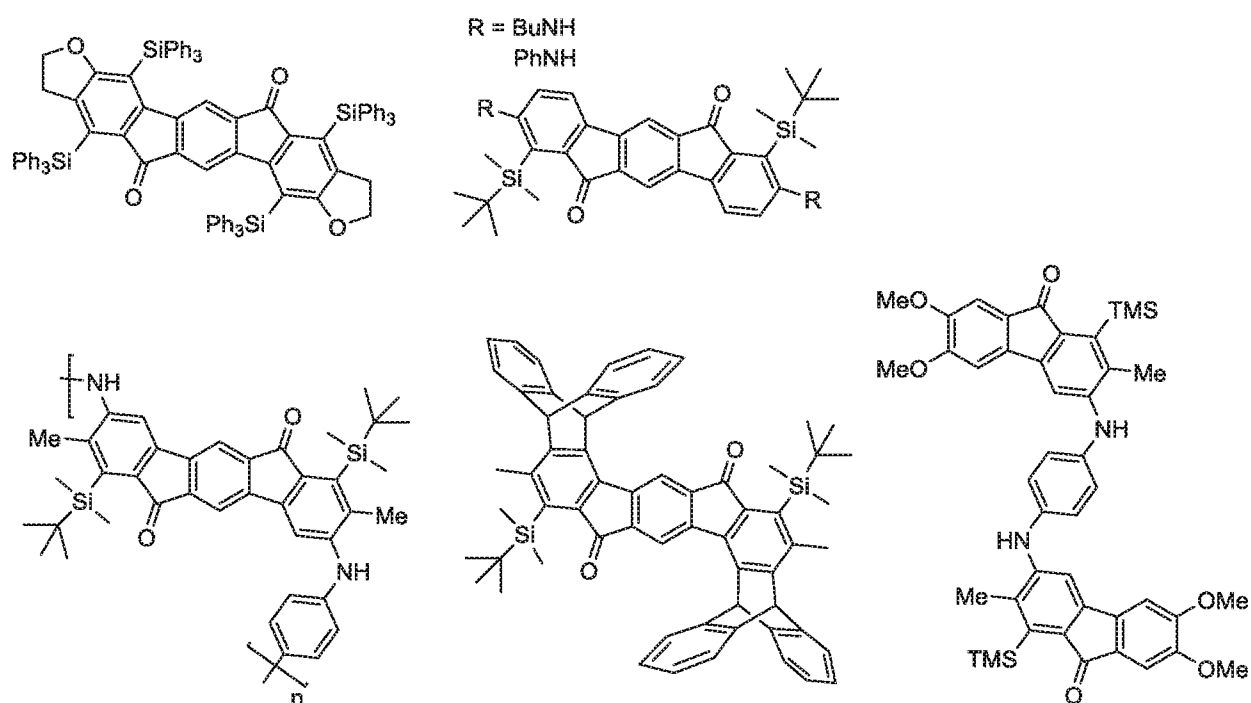
51. The compound according to claim 46, wherein the compound is selected from:

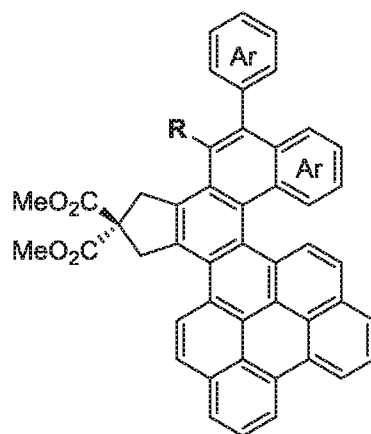
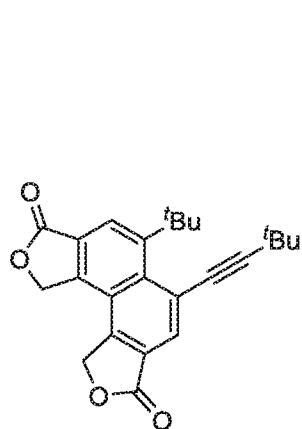


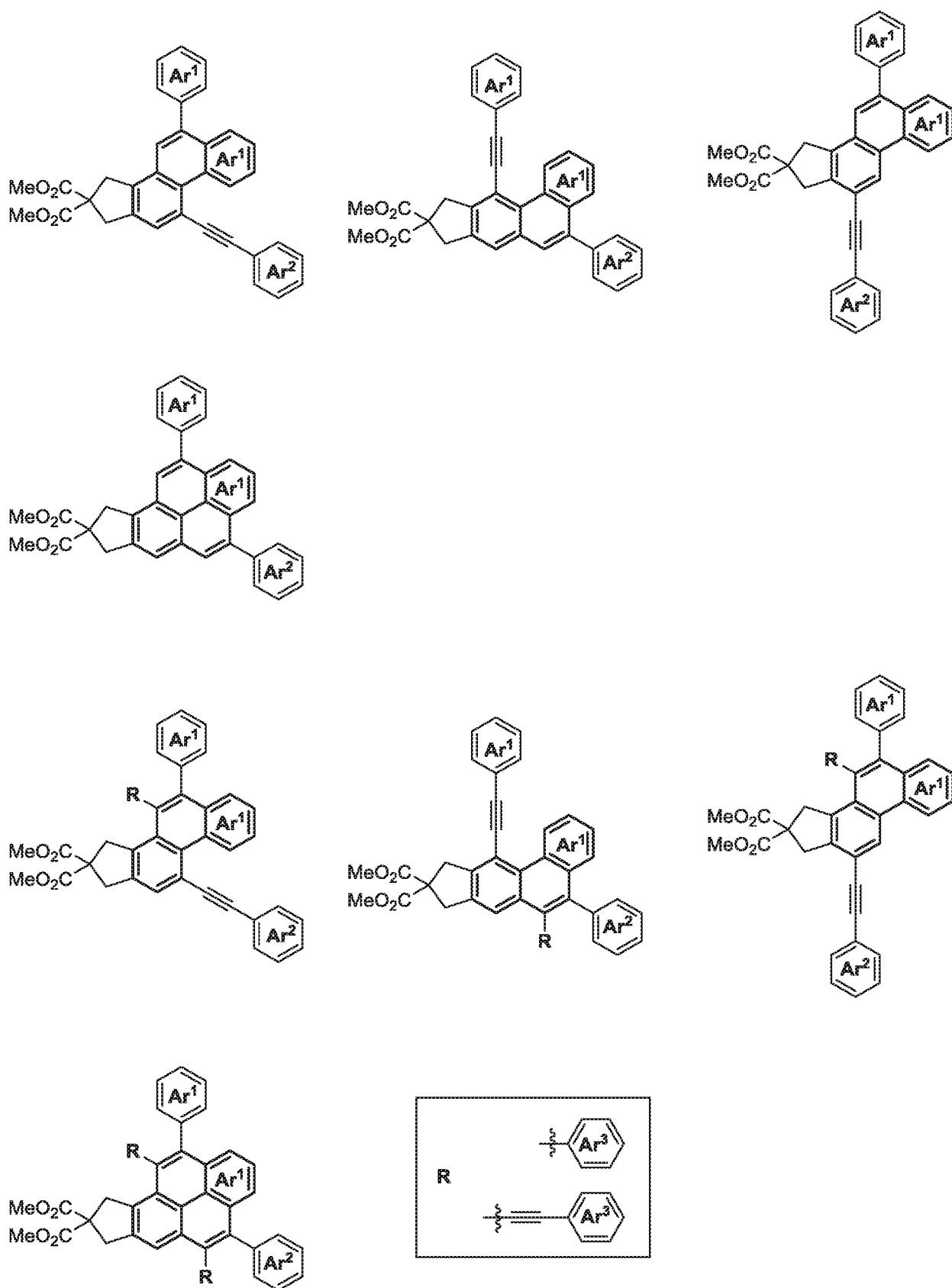
52. The compound according to claim 46, wherein the compound is selected from:



53. A compound selected from:

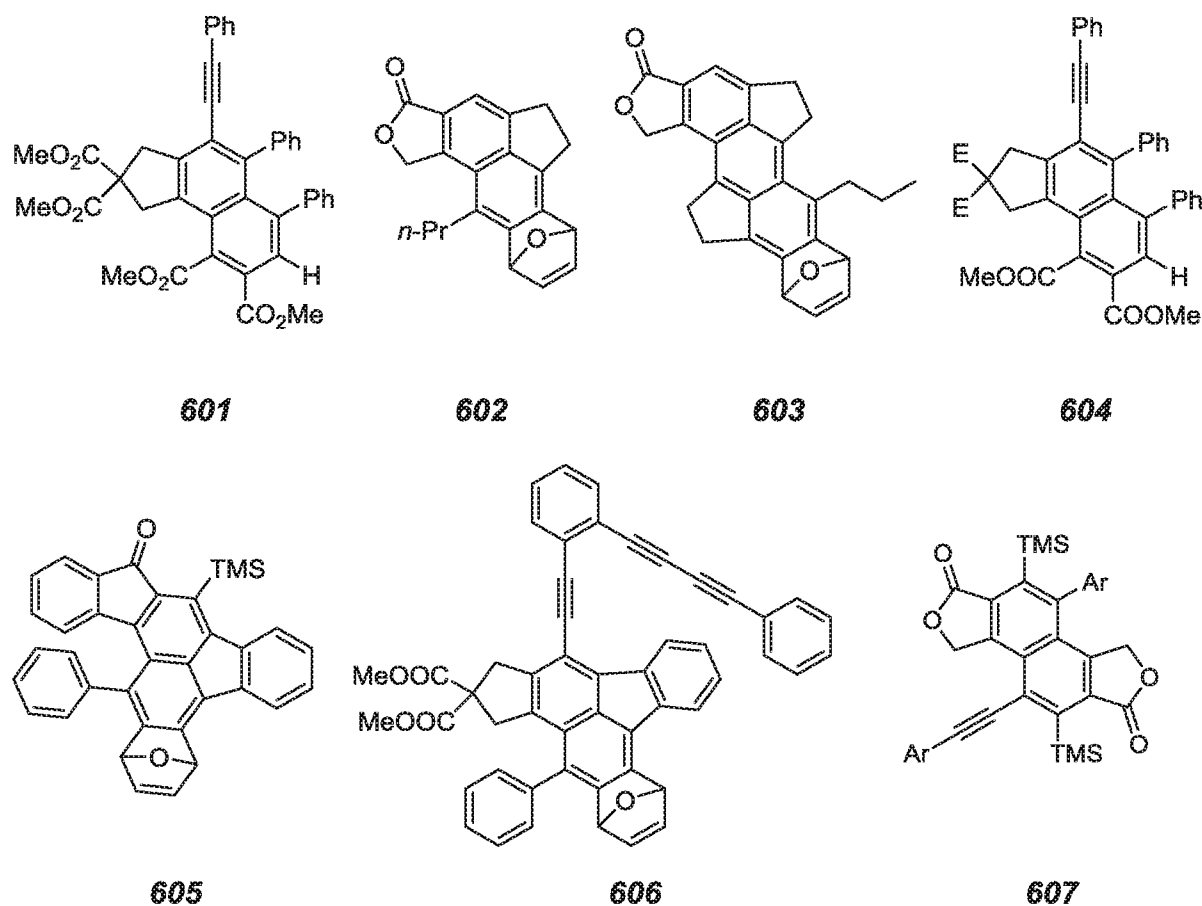






, where A-B-C is a cyclic group; R¹ and R² are substituted or unsubstituted alkyl groups; and Ar,

Ar¹, Ar² and Ar³ are independently selected from substituted or unsubstituted aryl groups; and



54. An organic device comprising one or more compounds according to any of claims 1 to 45.
55. The organic device according to claim 54, wherein the organic device is an organic electronic device or an organic photonic device.
56. The organic device according to claim 54, wherein the device is an organic light-emitting diode (OLED), an organic photovoltaic (OPV) device, an organic field-effect transistor (OFET), or a combination thereof.
57. A compound according to any one of claims 1 to 56 synthesized using a hexadehydro-Diels-Alder (HDDA) reaction.

FIG. 1A

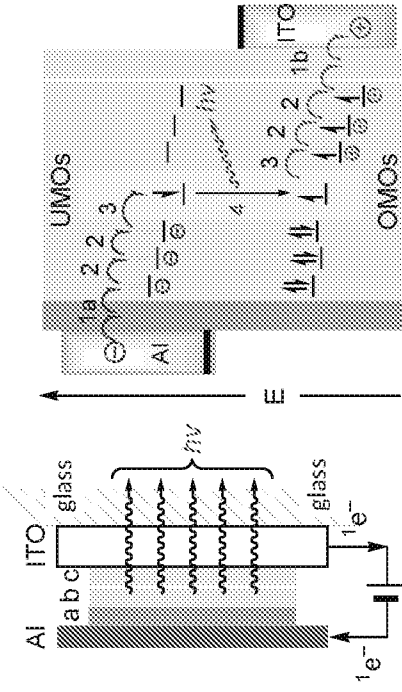
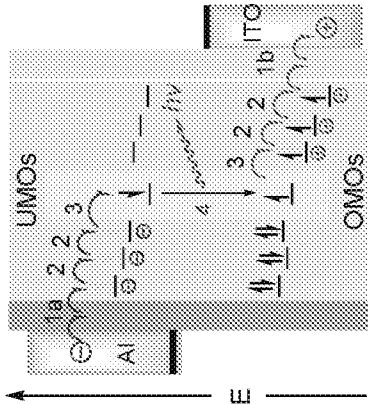


FIG. 1B

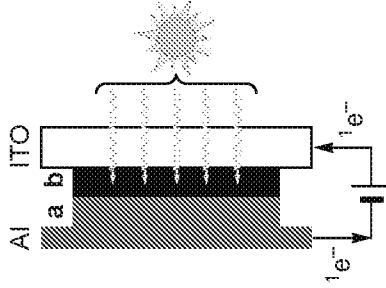


layers not to scale

layers/films:
a = electron transporter (electron donor)
b = fluorophore (emitter or active layer)
c = hole transporter (electron acceptor)

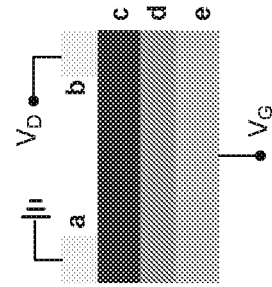
key processes:
1a. electron injection
1b. hole injection (electron removal)
2. charge migration/hopping
3. exciton formation
4. photon emission

FIG. 1C



layers/films:
a = electron acceptor (from the donor excited state)
b = active layer [photon acceptor and electron donor to (a)]

FIG. 1D



layers/films:
a = source
b = drain
c = organic semiconductor
d = insulator
e = gate
voltages
 V_D = drain voltage
 V_G = gate voltage

FIG. 1E

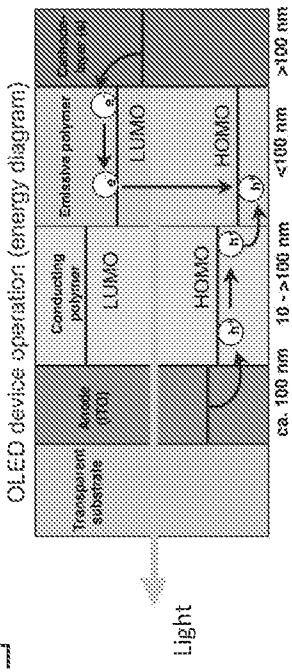


FIG. 2A

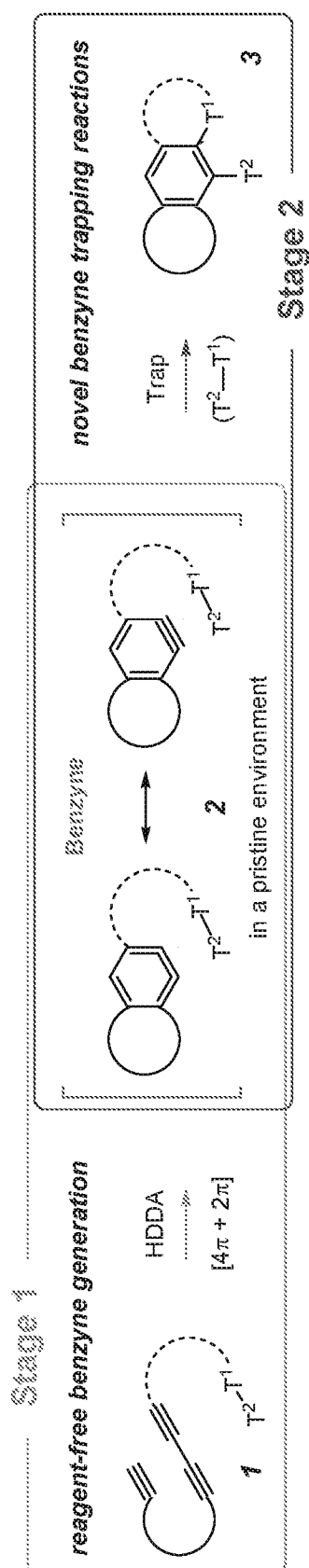


FIG. 2B

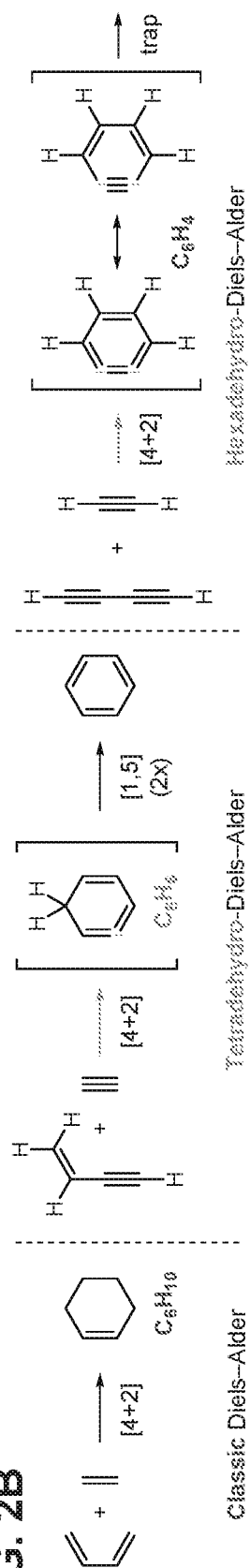


FIG. 3A

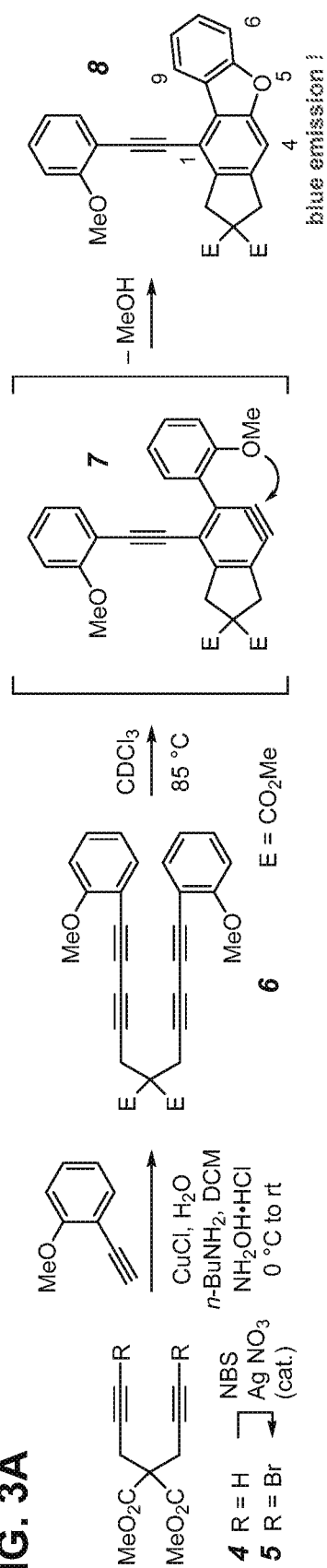


FIG. 3B

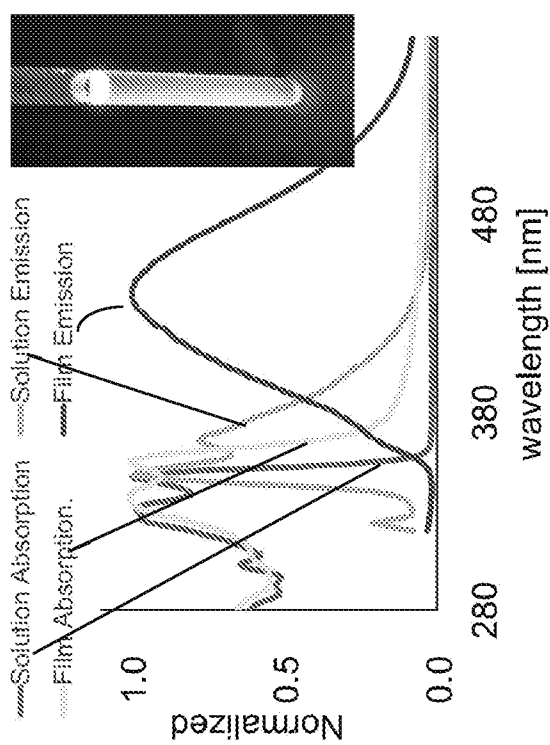


FIG. 3C

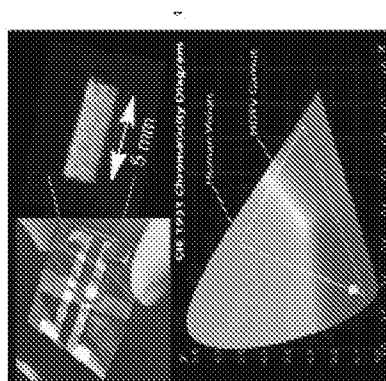


FIG. 3D

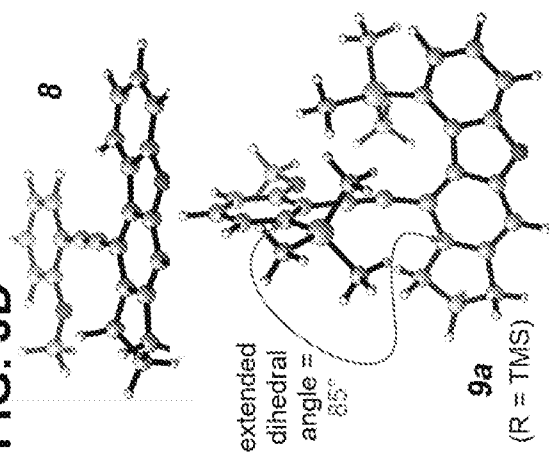
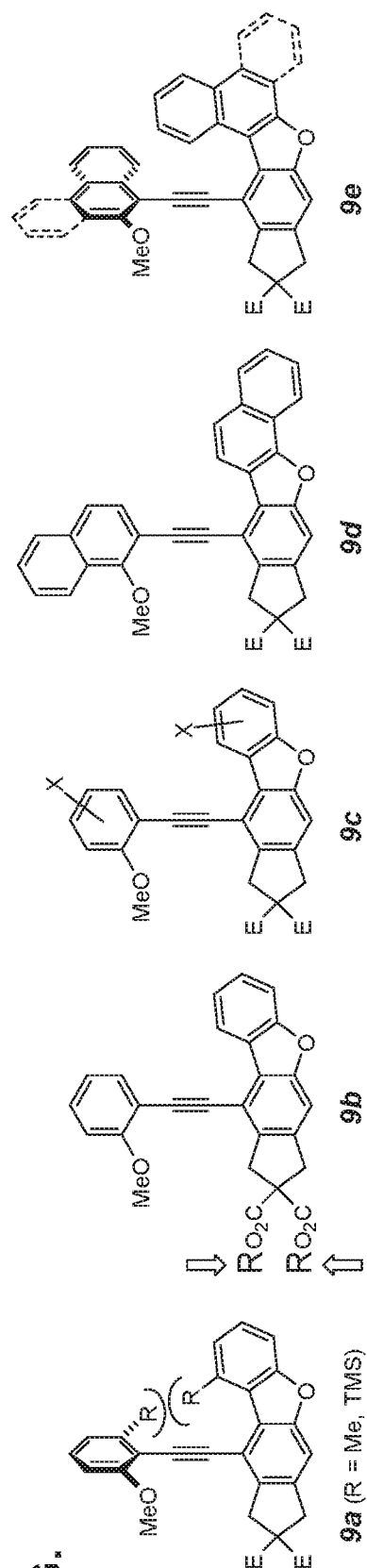
FIG.
3E

FIG. 4A

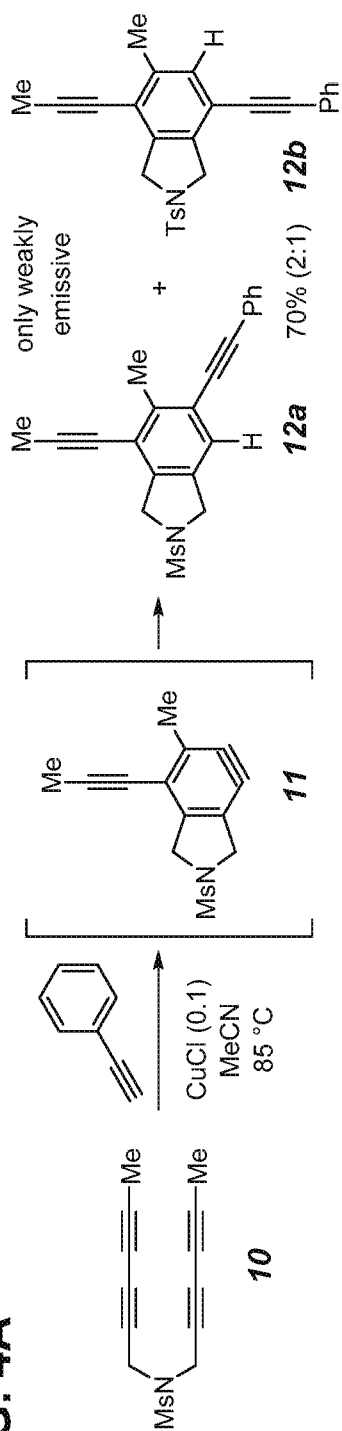
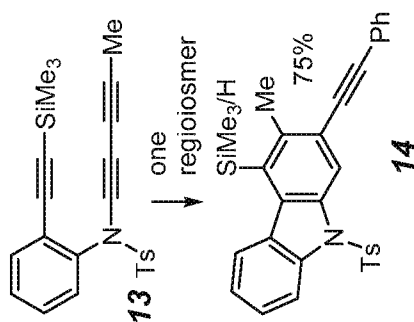


FIG. 4B



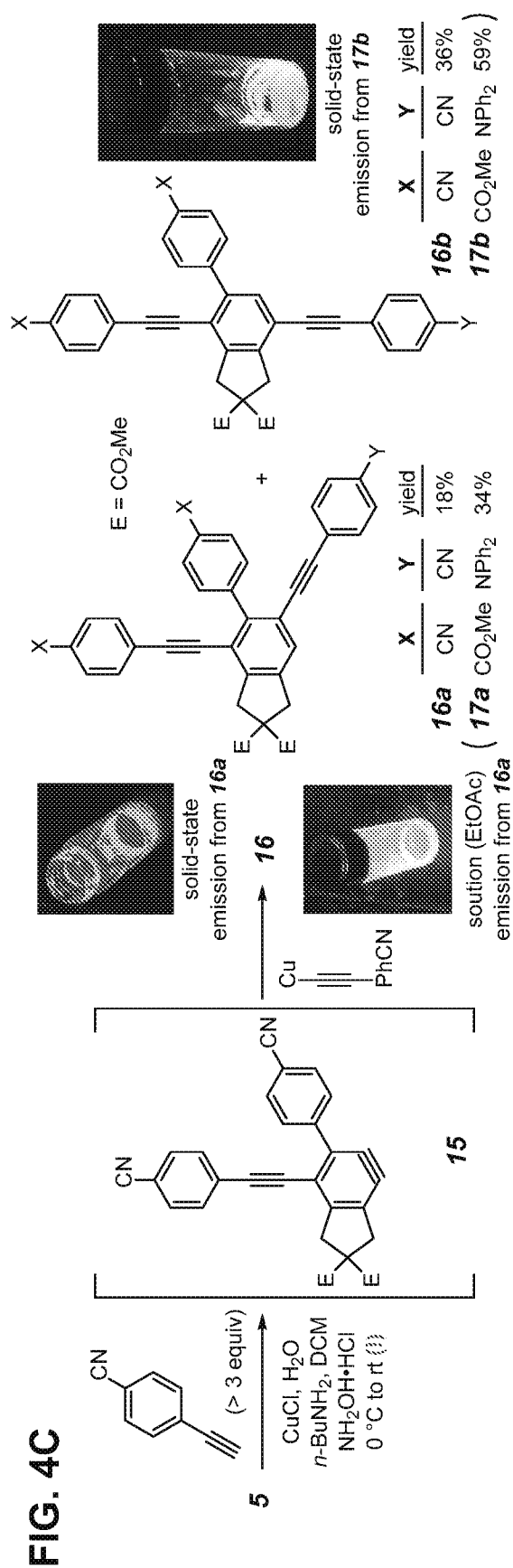
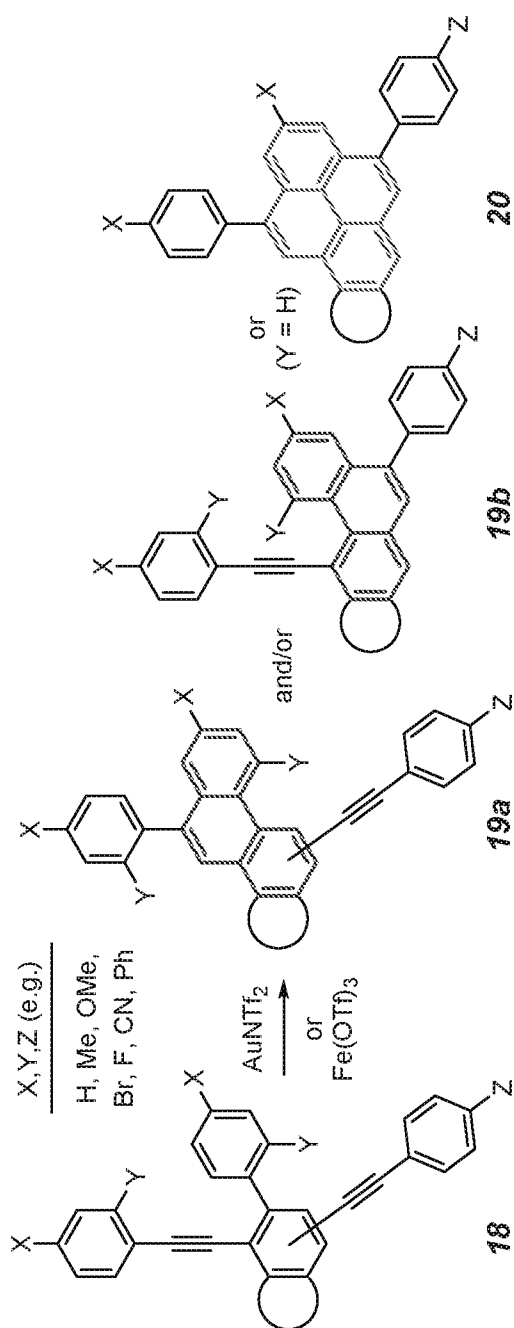
**FIG. 4D**

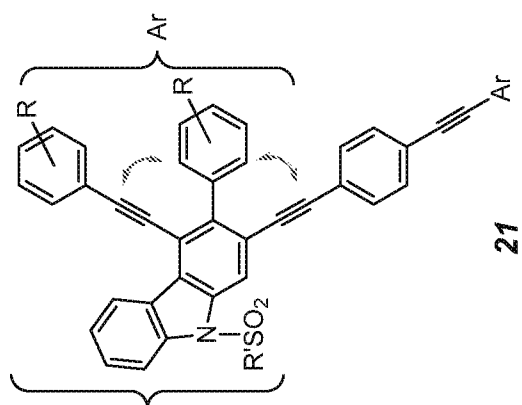
FIG.
4E

FIG. 5A

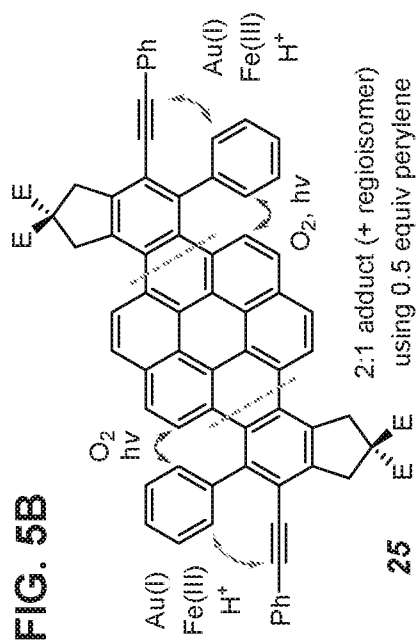
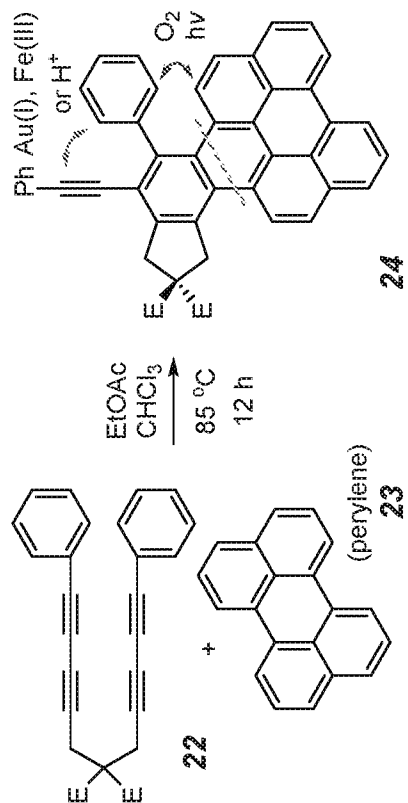
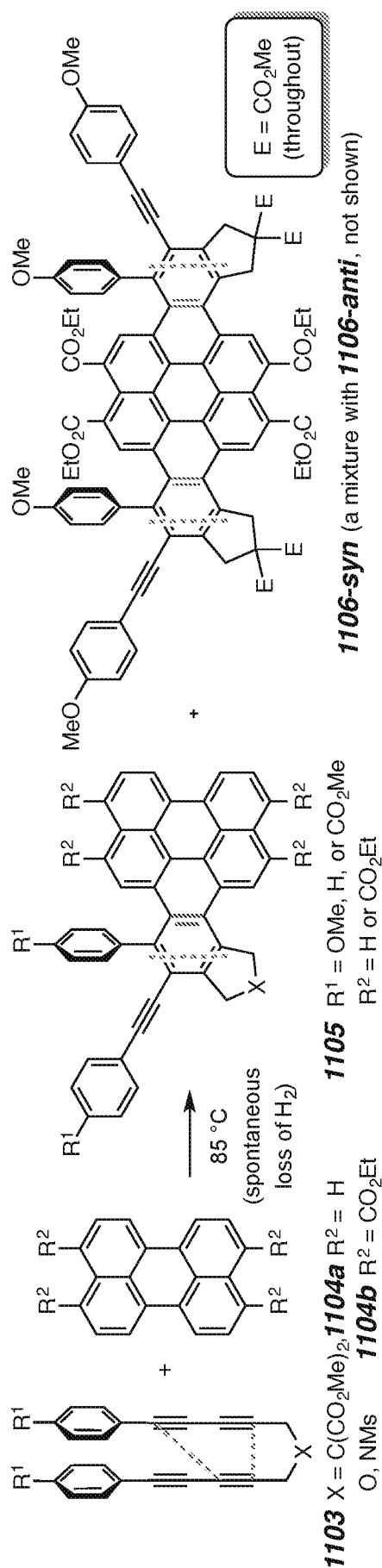
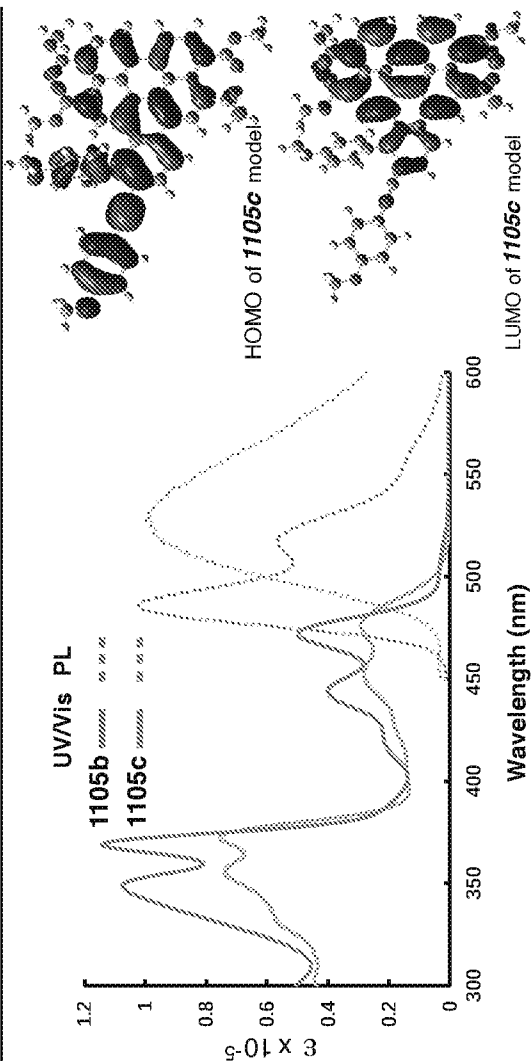
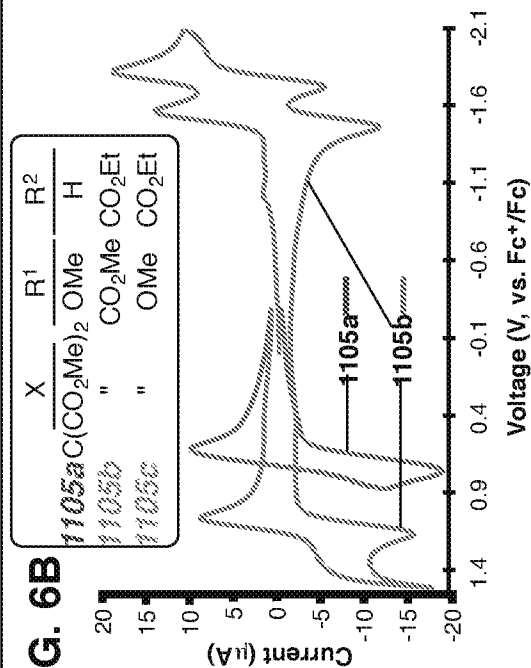


FIG. 5B

2.1 adduct (+ regioisomer)
using 0.5 equiv perylene



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66

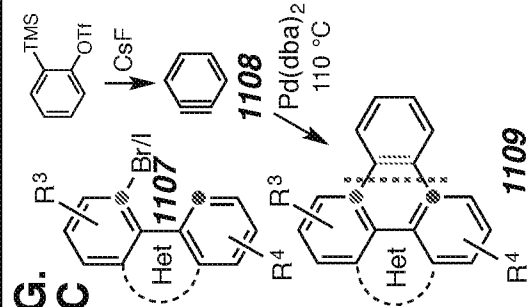


FIG. 1103

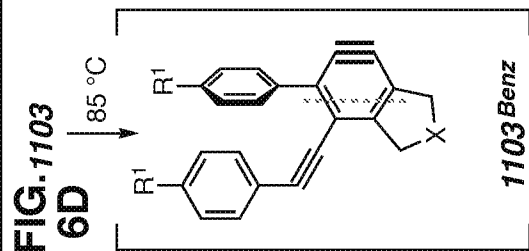
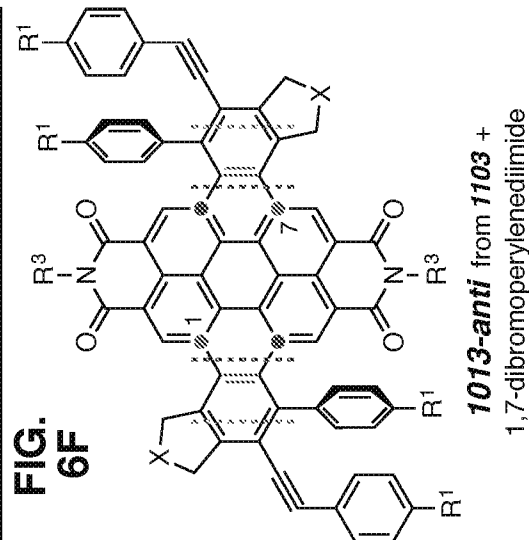
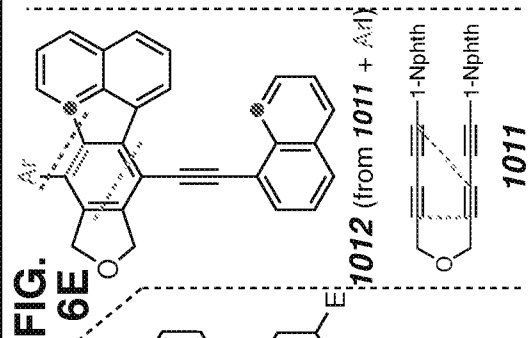
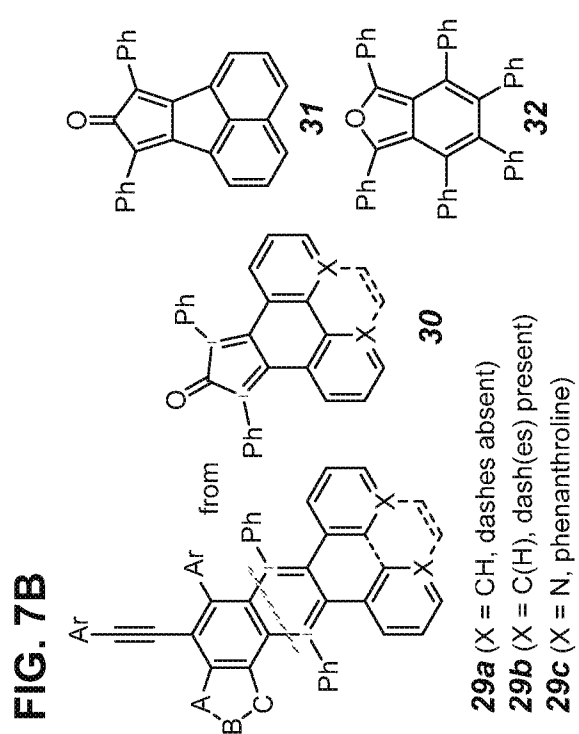
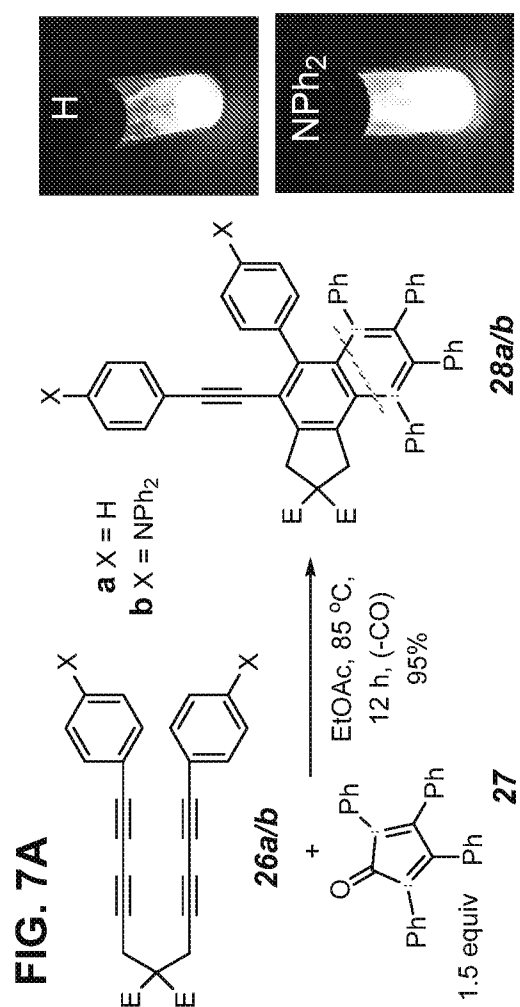


Fig.





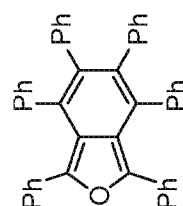
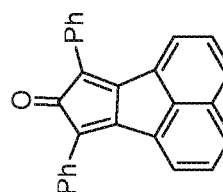
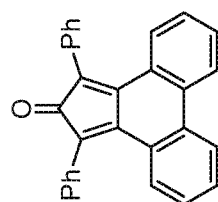
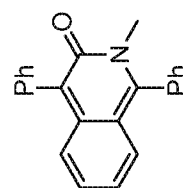
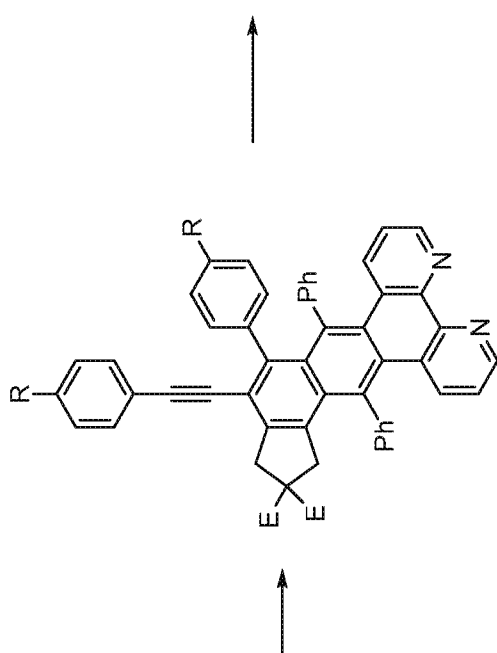
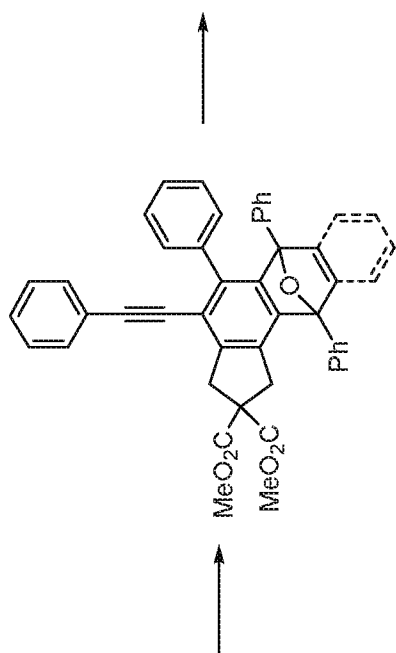
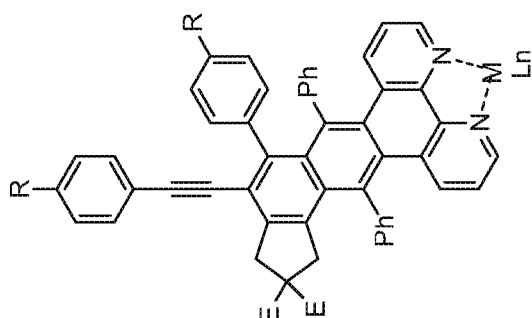
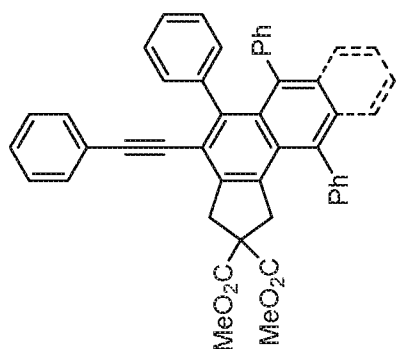


FIG. 7C

FIG. 7D

FIG. 7E

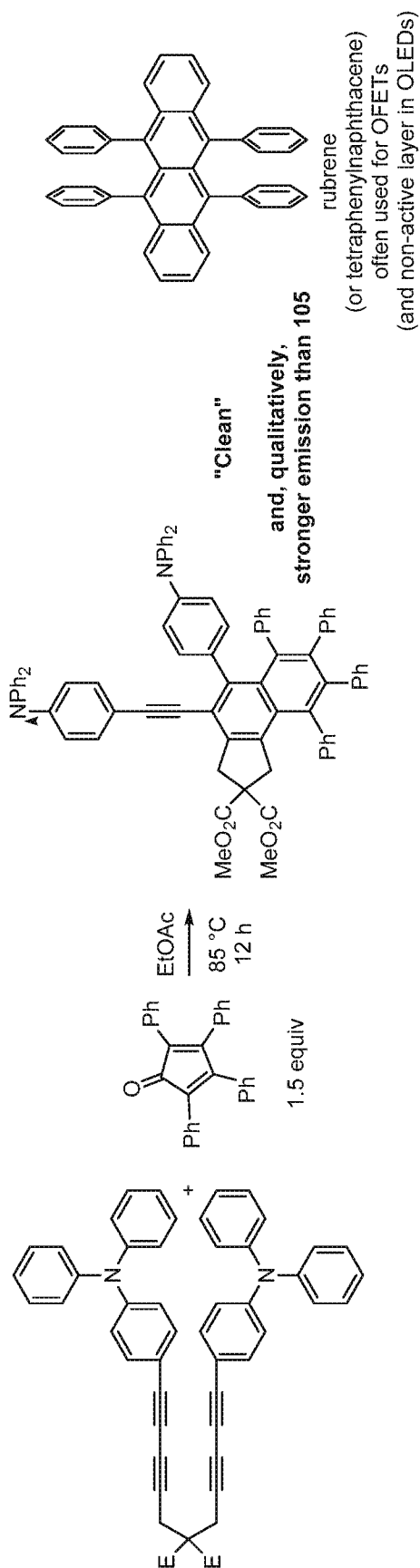


FIG. 8A

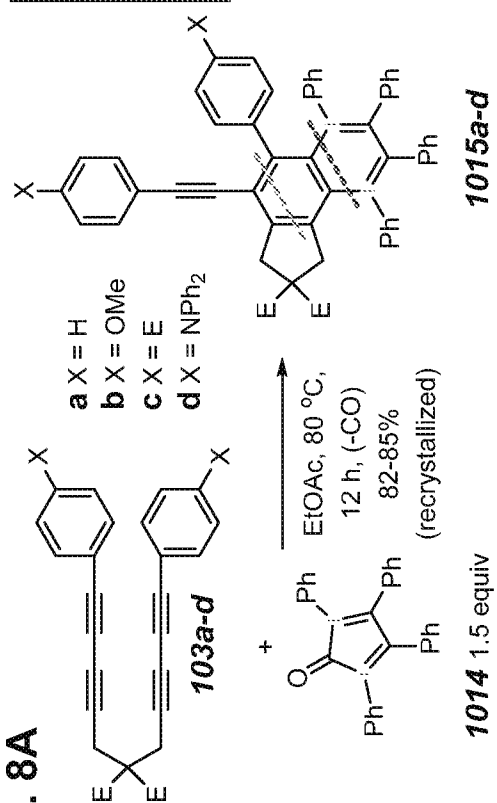
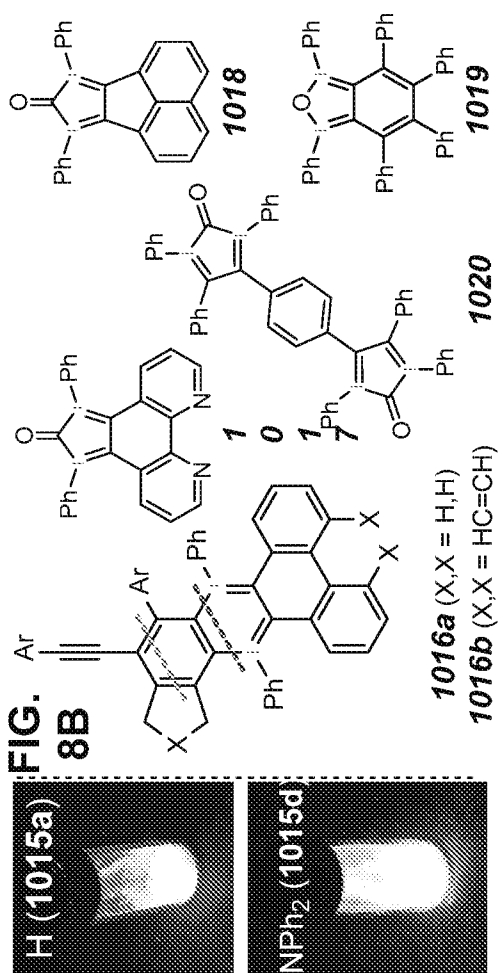


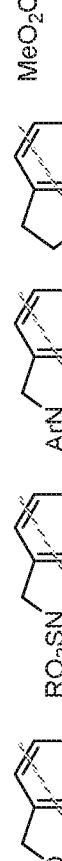
FIG. 8B





33

symmetrical



unsymmetrical

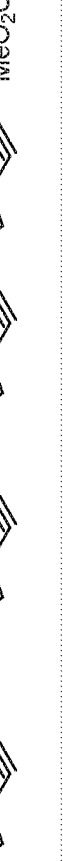


FIG. 9B

Reaction scheme for the synthesis of compounds 36 and 37b:

Starting materials: $\text{Me}-\text{C}\equiv\text{C}-\text{Me}$ and a substituted benzene derivative (34) containing a $\text{C}\equiv\text{C}-\text{R}$ group. The benzene ring in 34 is labeled with A, B, and C, and is associated with the text "HDA chromo phore".

Reaction 1: $\text{Me}-\text{C}\equiv\text{C}-\text{Me}$ + 34 $\xrightarrow{\text{alkyne metathesis}}$ 35

Structure 35: A central $\text{C}\equiv\text{C}$ bond connecting two substituted benzene rings. The left ring has a methyl group (Me) at position 1 and a substituent Ar^2 at position 2. The right ring has a methyl group (Me) at position 1 and a substituent Ar^1 at position 2.

Reaction 2: 35 $\xrightarrow{\text{xs } \text{Ar}^2-\text{C}\equiv\text{C}-\text{Me}}$ 36

Structure 36: A central $\text{C}\equiv\text{C}$ bond connecting a substituted benzene ring (left) and a phenyl ring (right). The left ring has a methyl group (Me) at position 1 and a substituent Ar^1 at position 2. The right ring has a methyl group (Me) at position 1 and a substituent Ar^2 at position 2.

Reaction 3: 36 $\xrightarrow{\Delta}$ 37b + 2 MeNCO

Structure 37b: A central $\text{C}\equiv\text{C}$ bond connecting two substituted benzene rings. The left ring has a methyl group (Me) at position 1 and a substituent Ar^1 at position 2. The right ring has a methyl group (Me) at position 1 and a substituent Ar^2 at position 2.

Structure 37a: A substituted benzene ring with a methyl group (Me) at position 1 and a substituent Ar^1 at position 2.

Structure 38: A substituted benzene ring with a methyl group (Me) at position 1 and a substituent Ar^1 at position 2.

Structure 39: A substituted benzene ring with a methyl group (Me) at position 1 and a substituent Ar^1 at position 2.

FIG. 9D

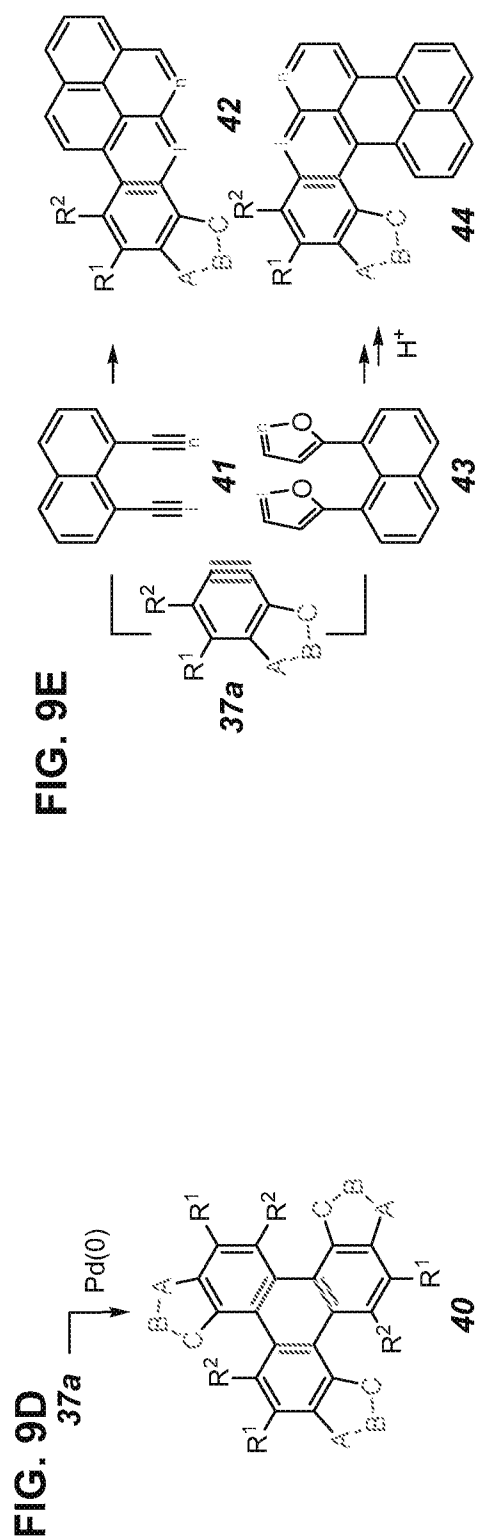


FIG. 9F

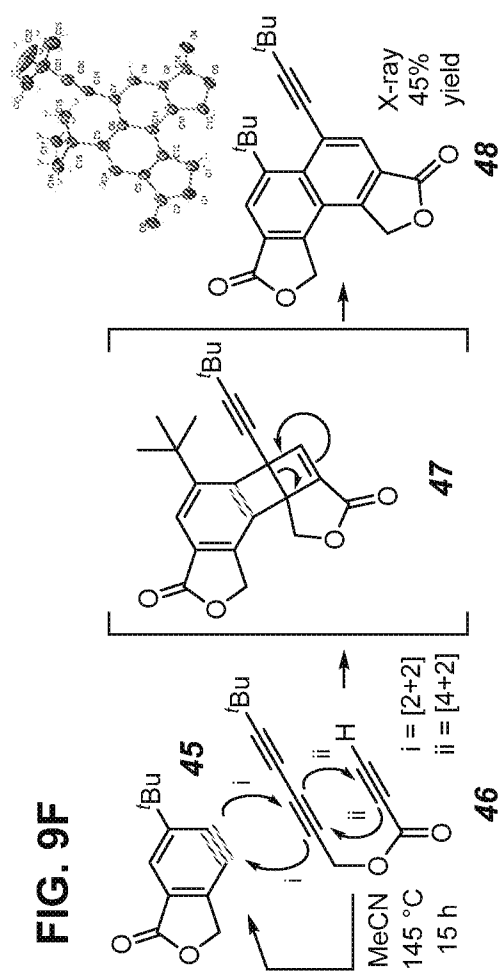


FIG. 10A

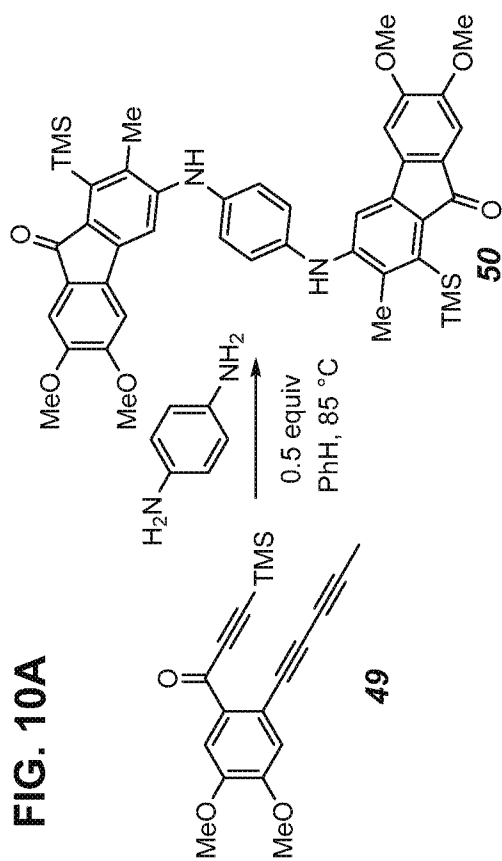


FIG. 10B

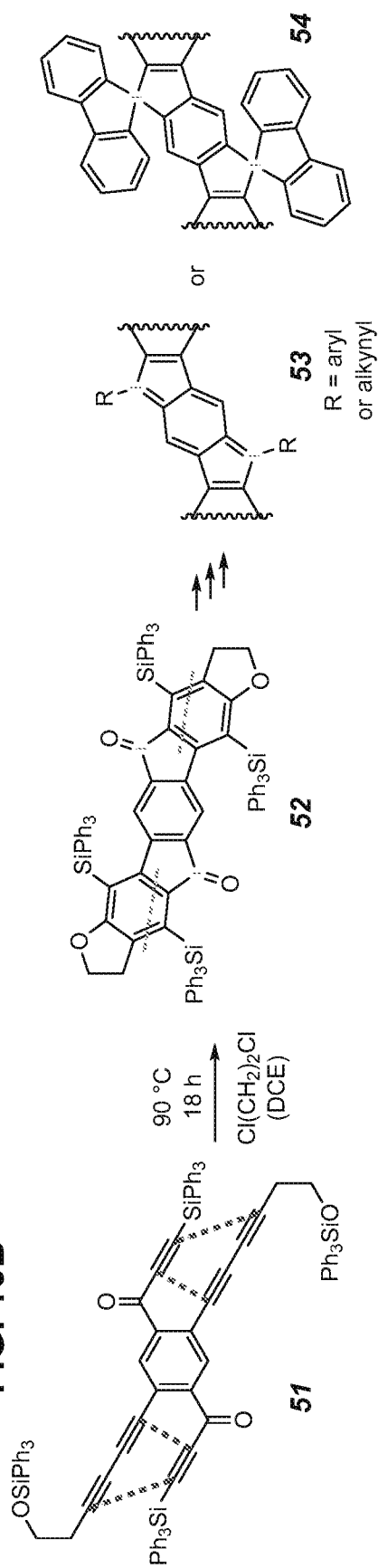


FIG. 10C

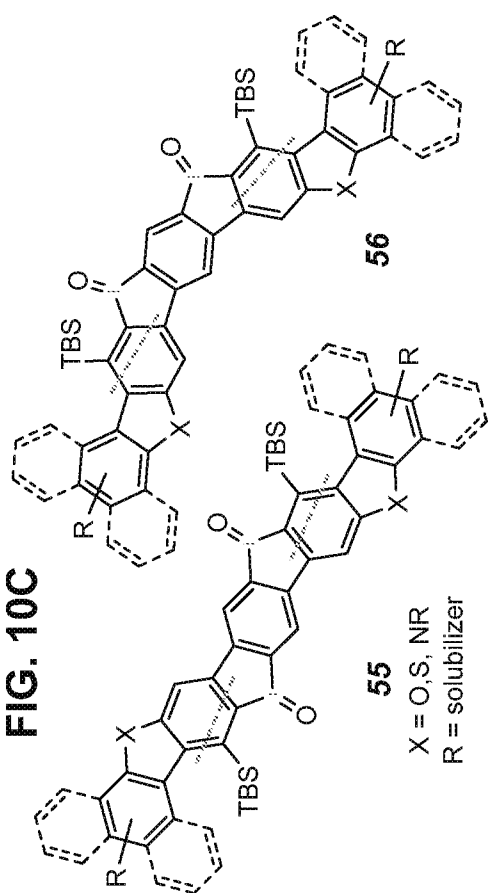


FIG. 10D

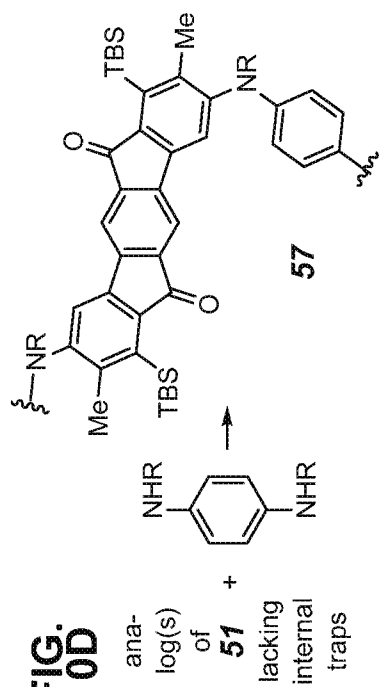
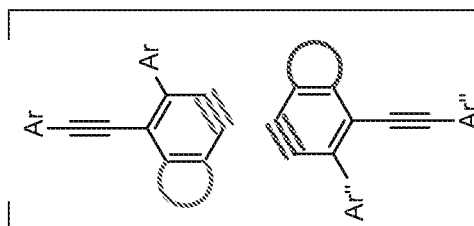
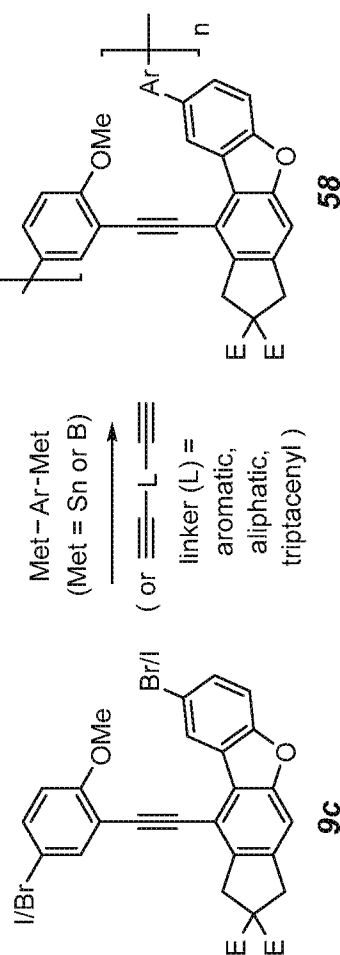
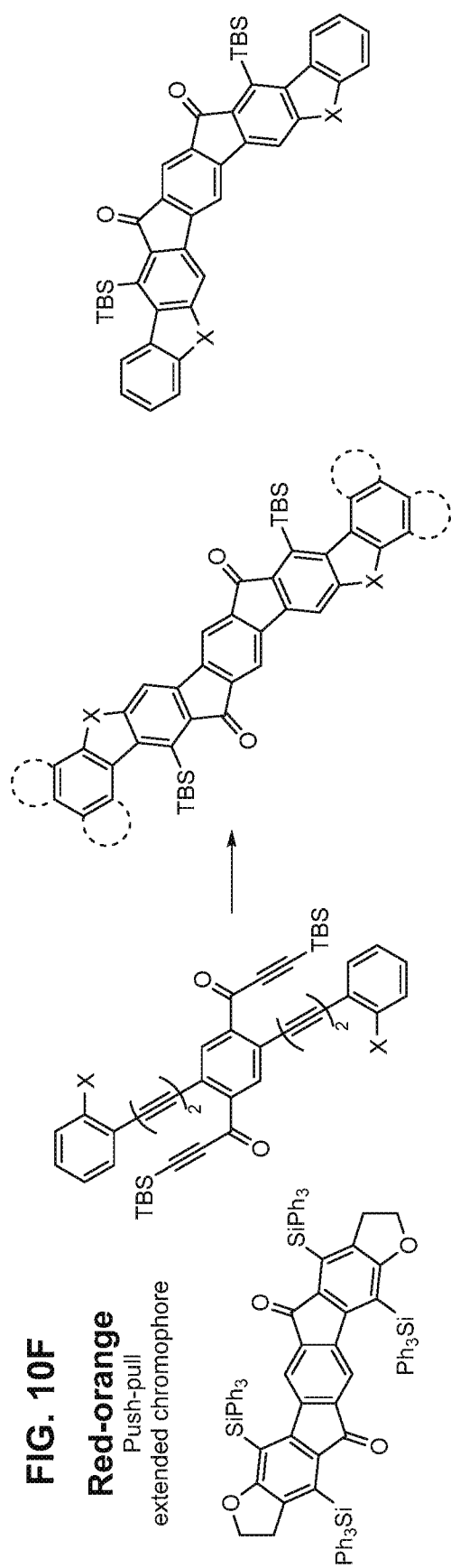


FIG. 10E





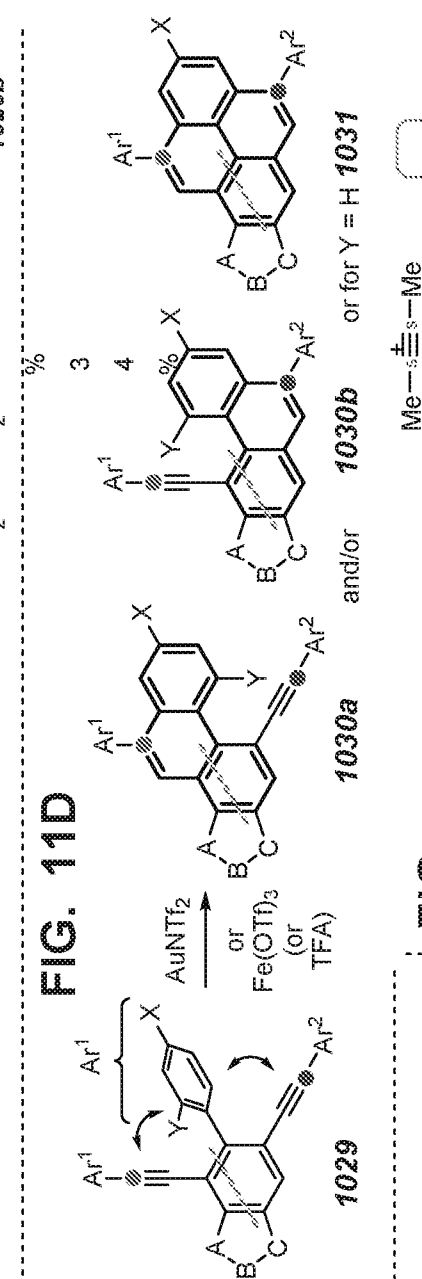
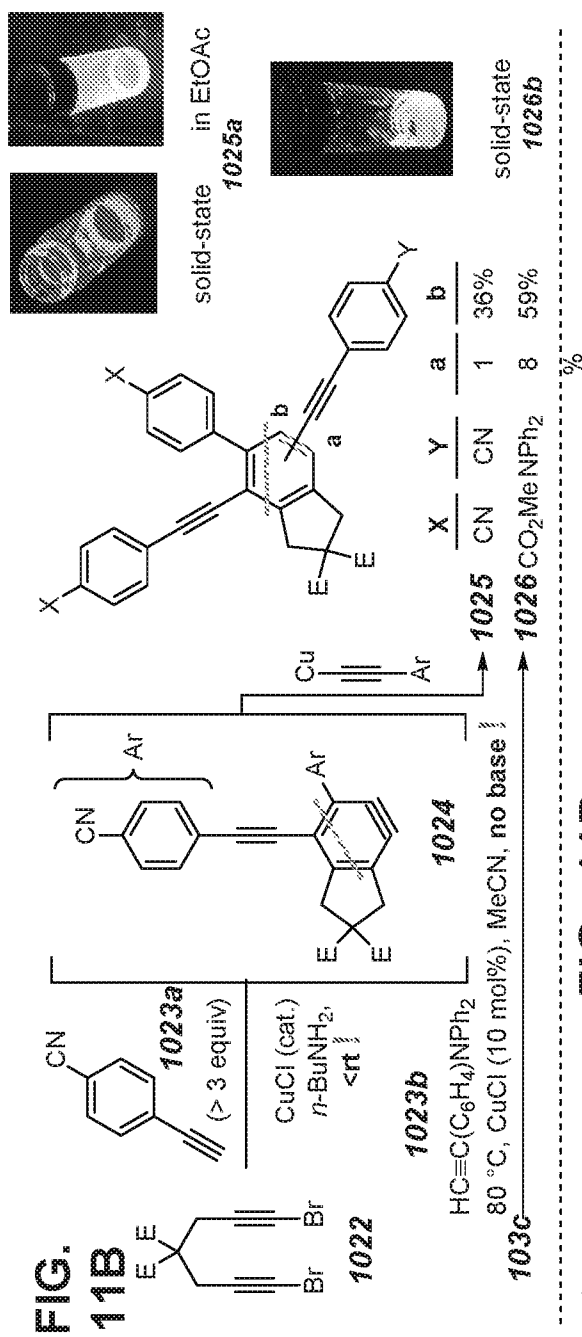


FIG. 12A

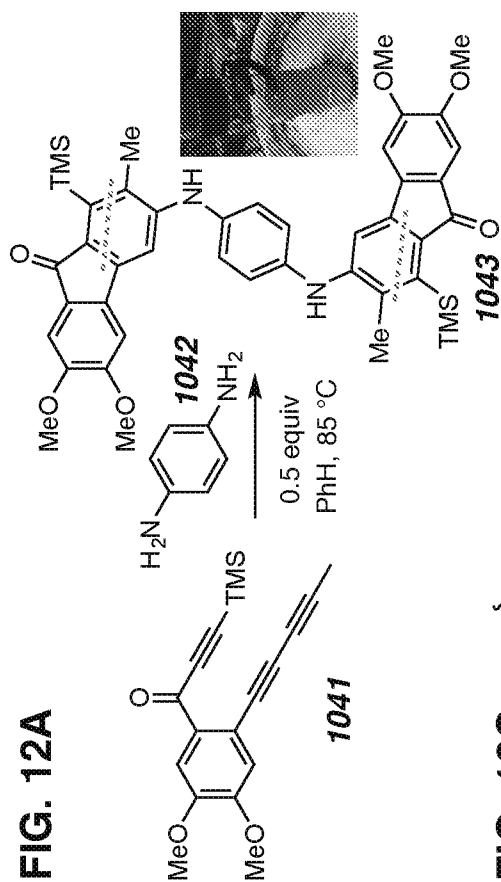


FIG. 12B

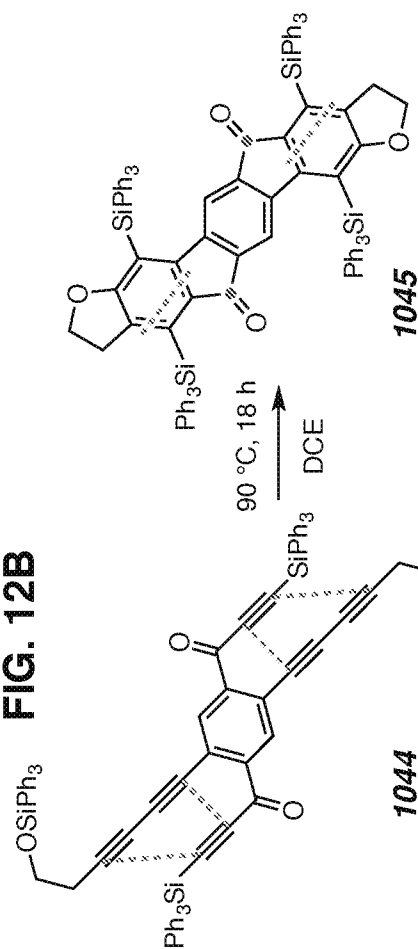


FIG. 12C

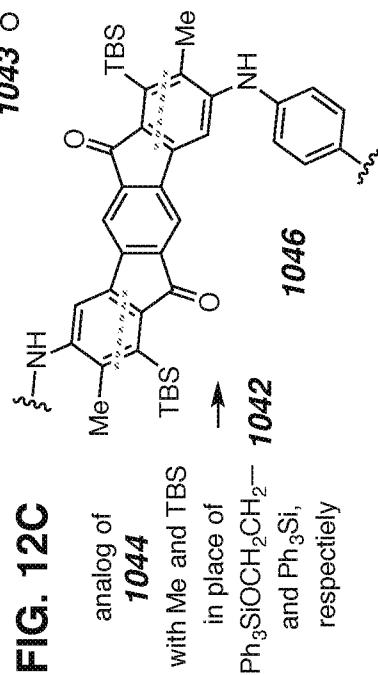


FIG. 12D

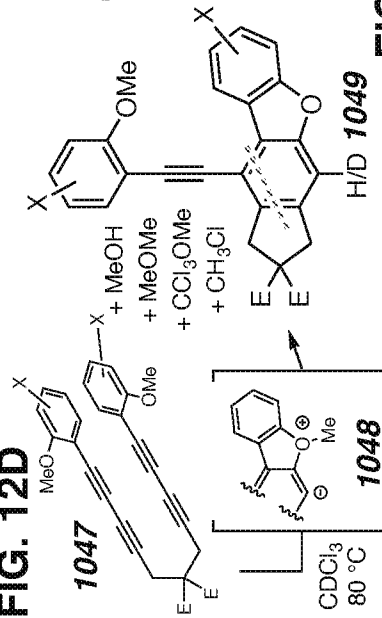


FIG. 12E

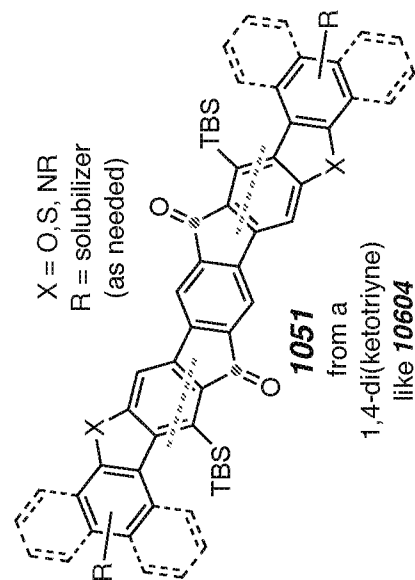
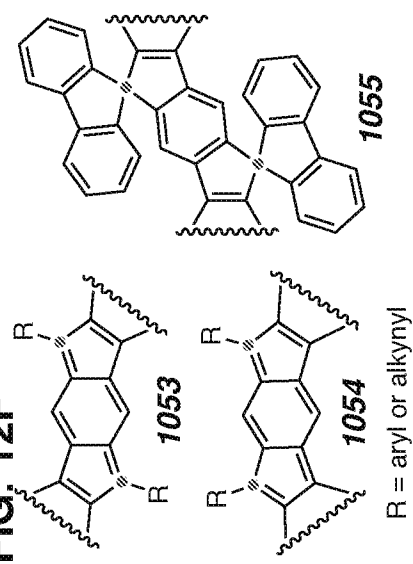


Fig. 12



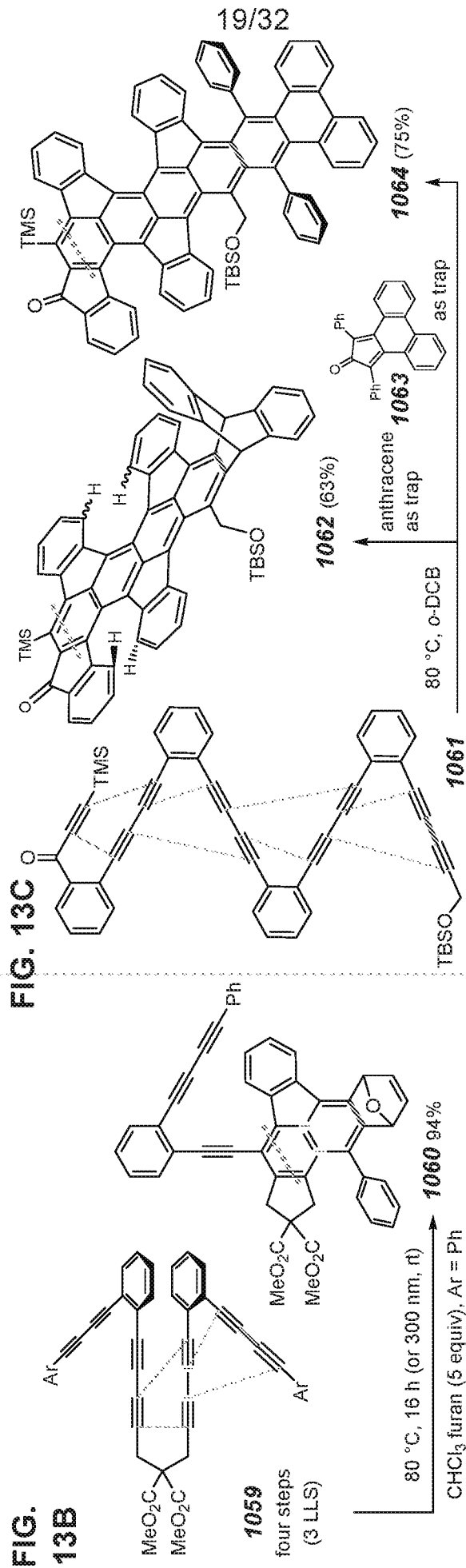
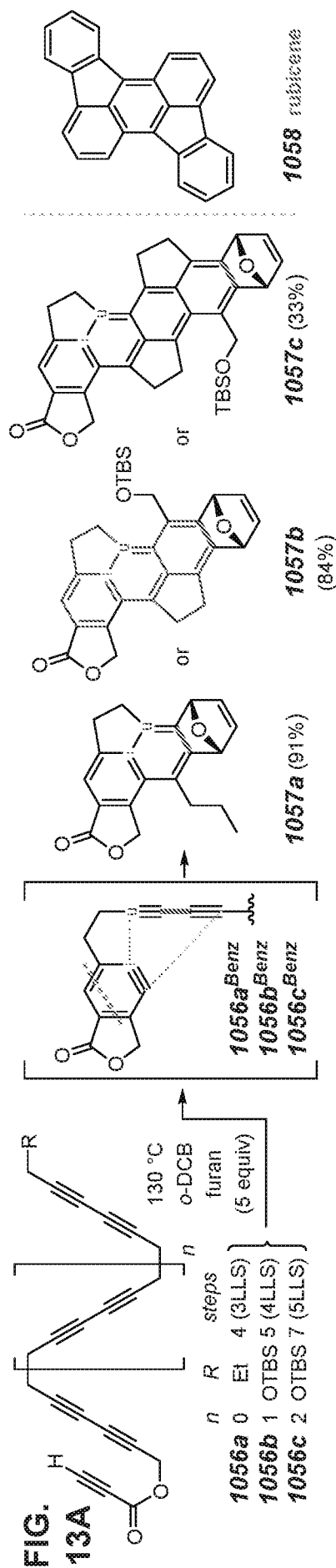
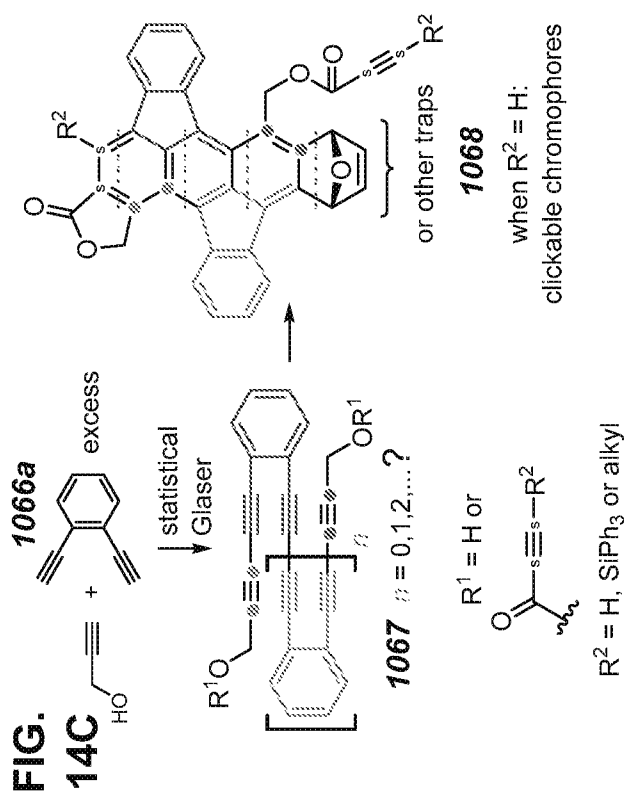
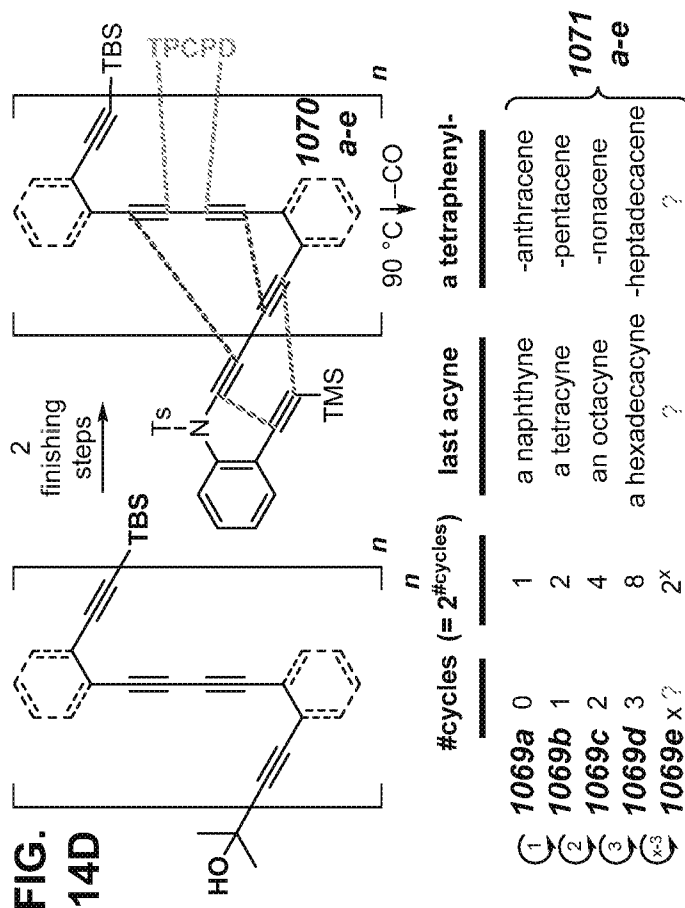
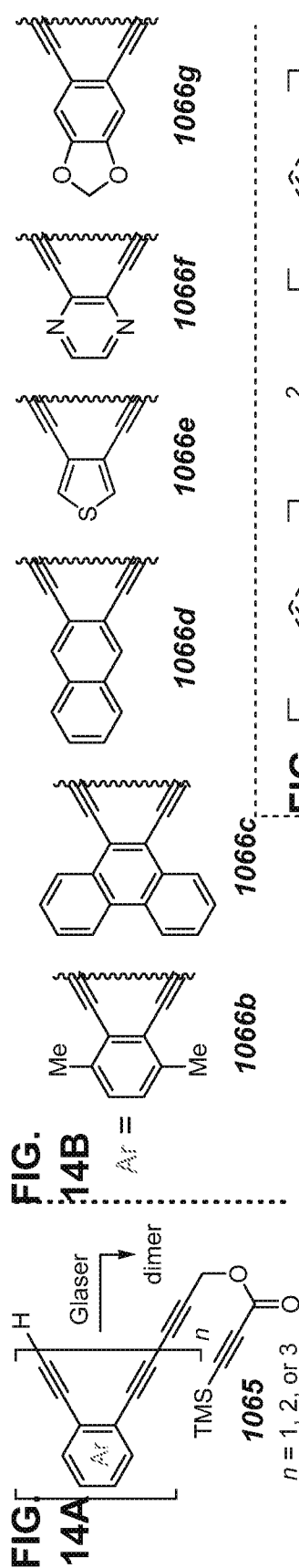


FIG. 13C



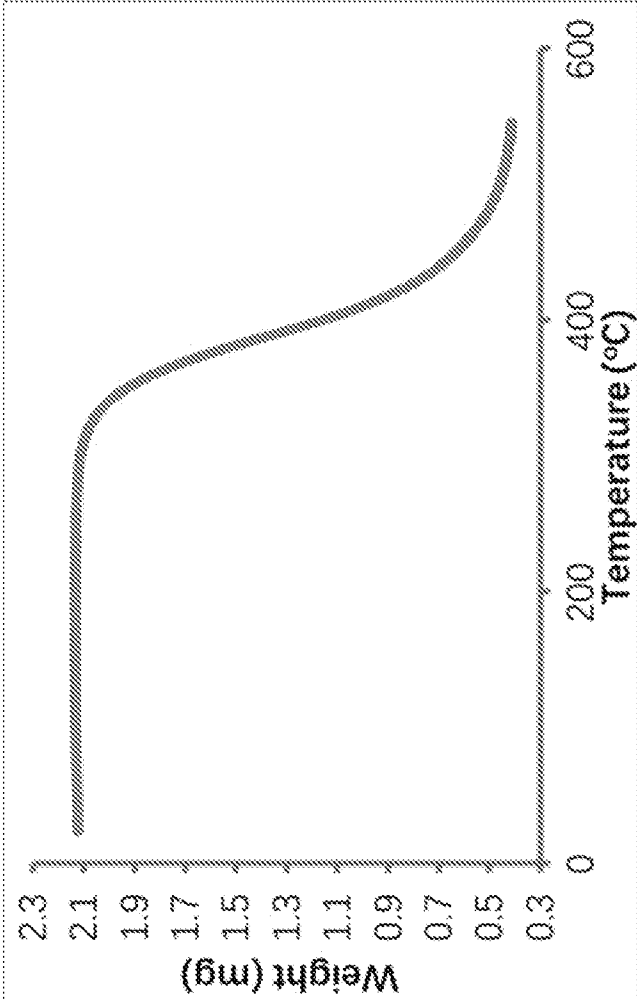


FIG. 15A

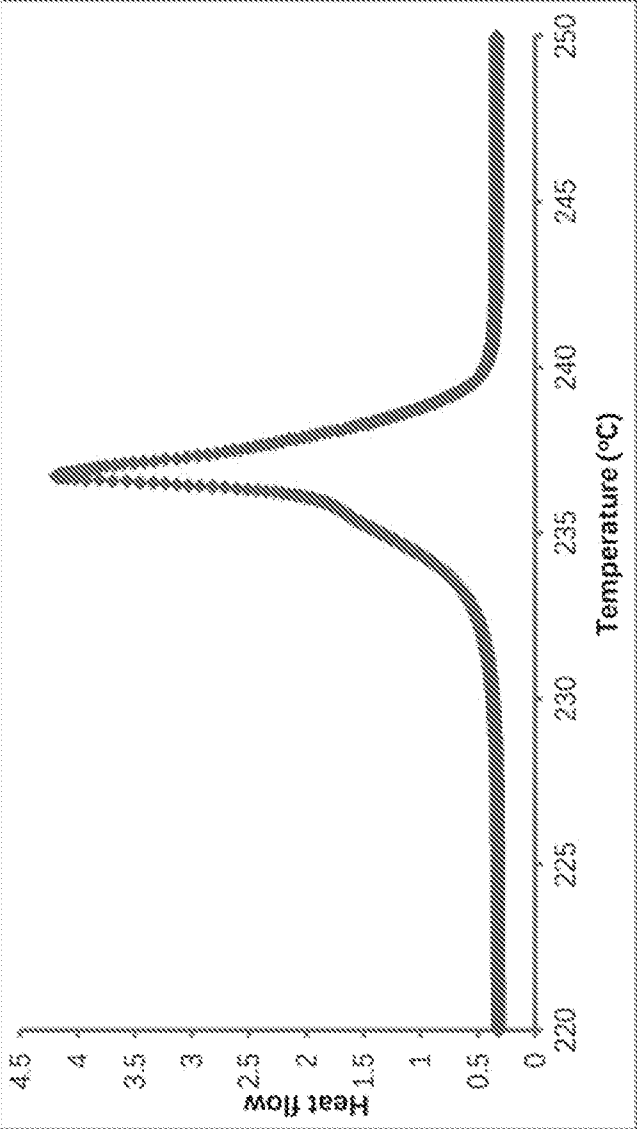


FIG. 15B

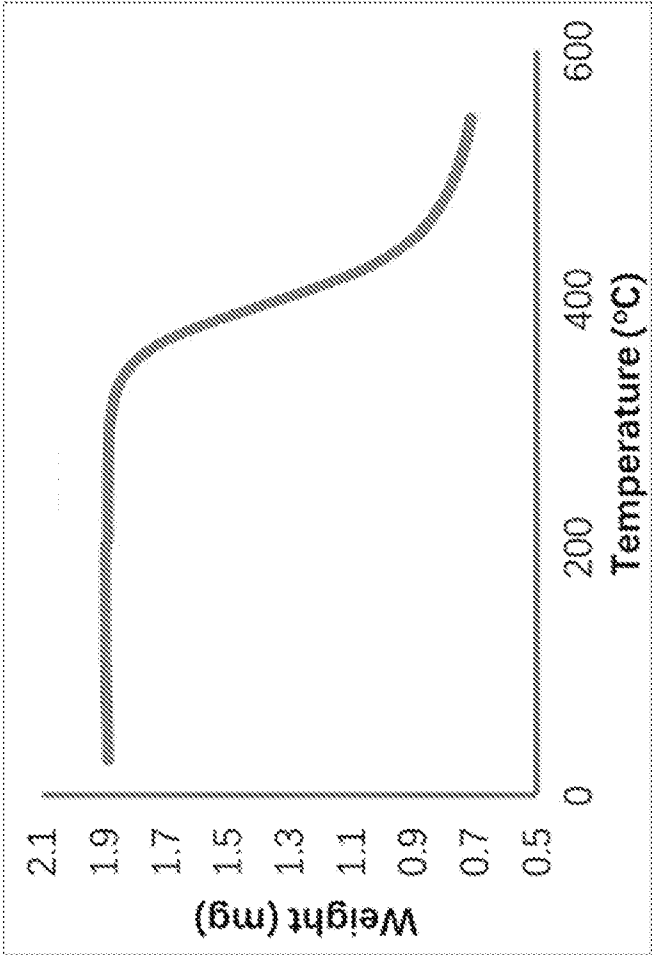


FIG. 16A

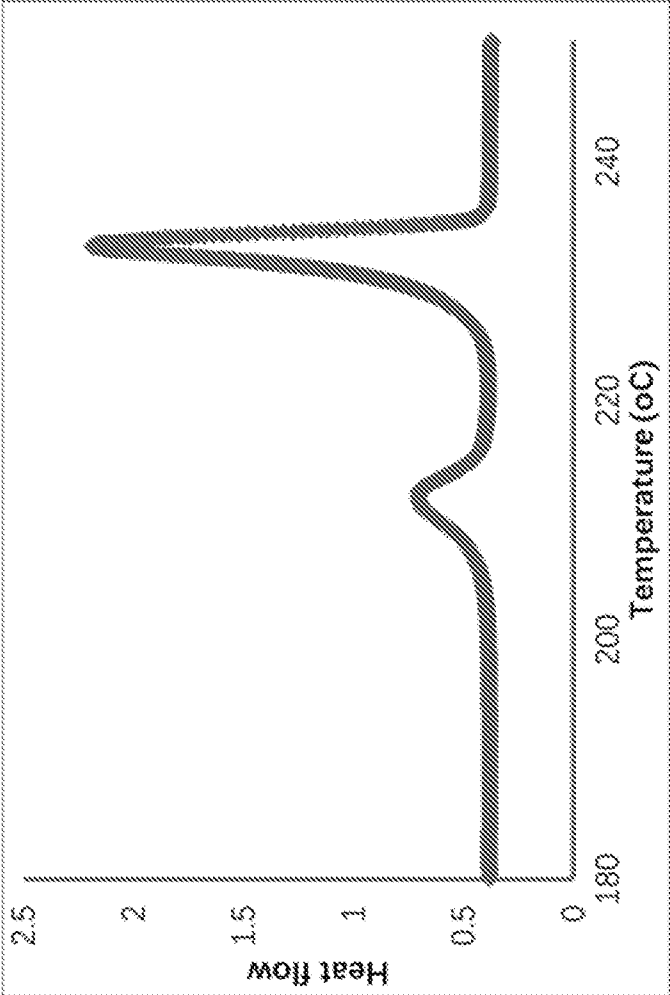
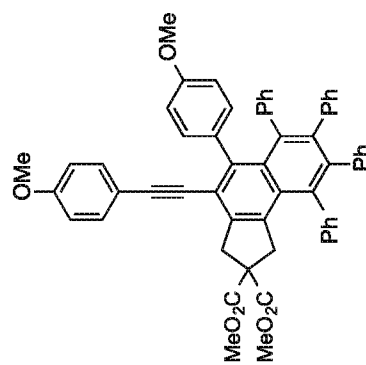
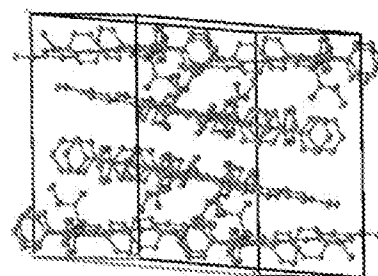
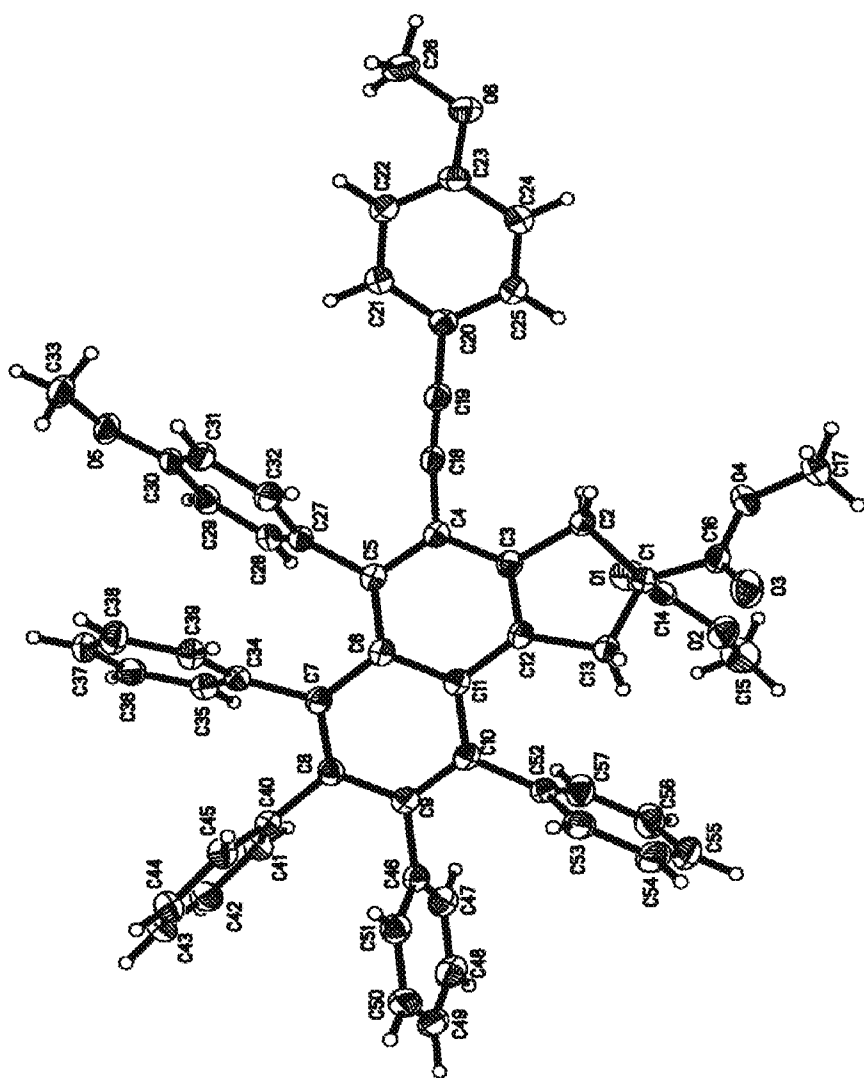


FIG. 16B

FIG. 16C



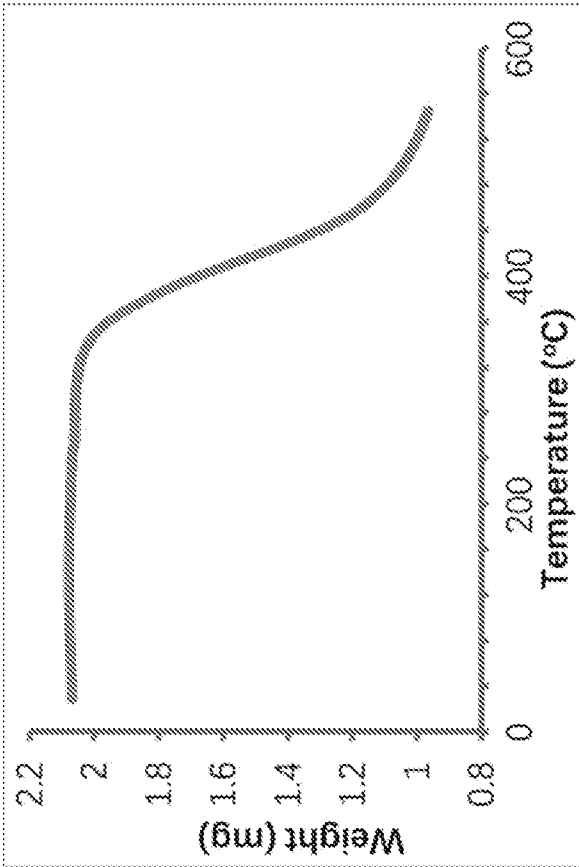


FIG. 17A

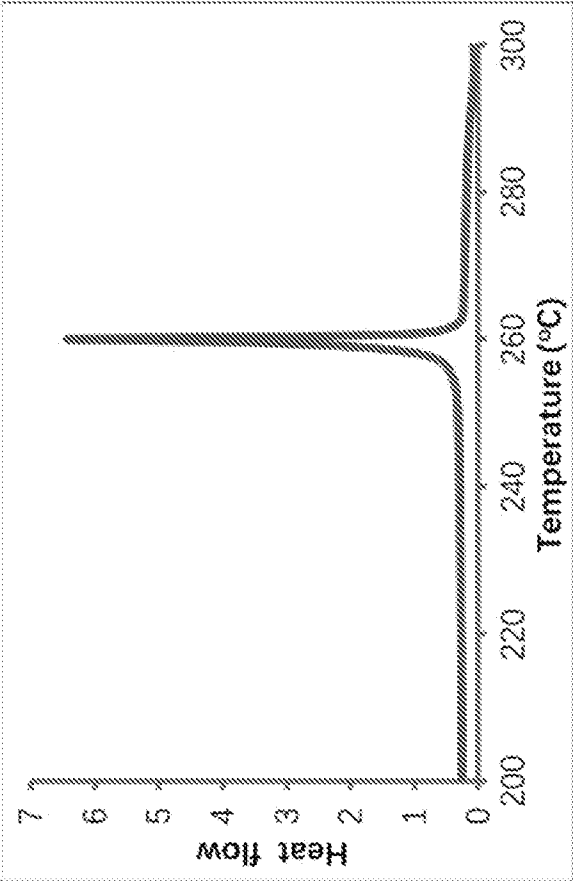


FIG. 17B

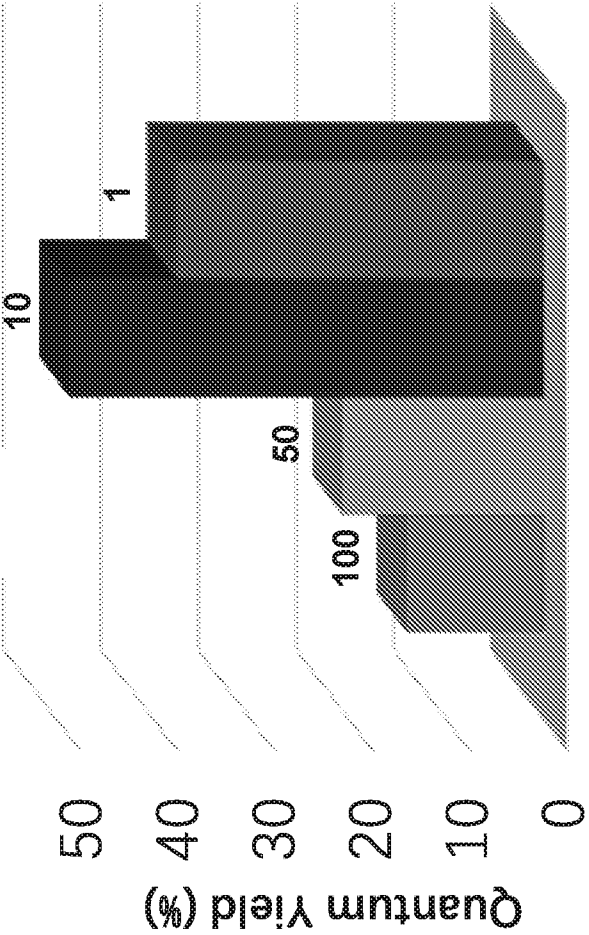


FIG. 18A

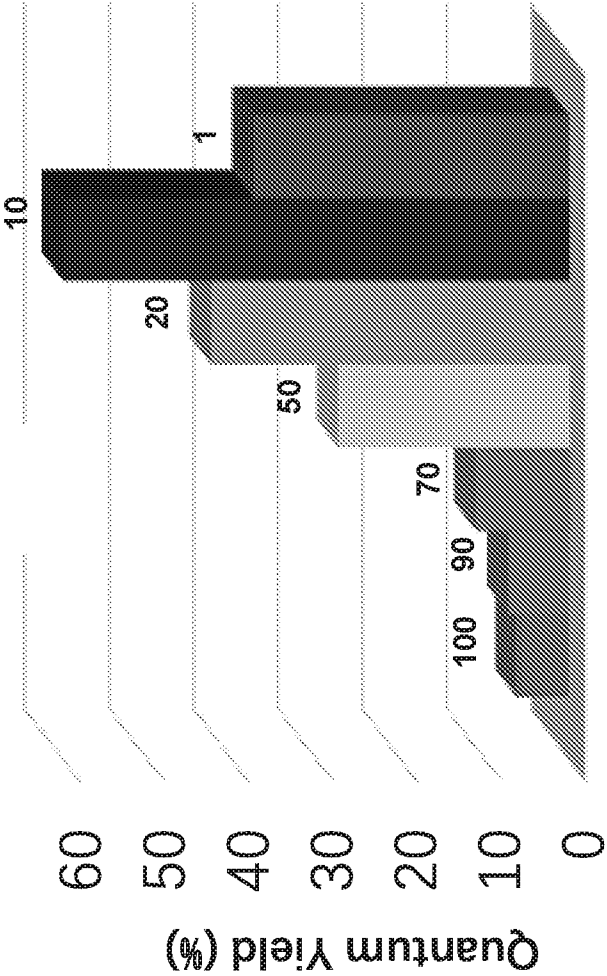


FIG. 18B

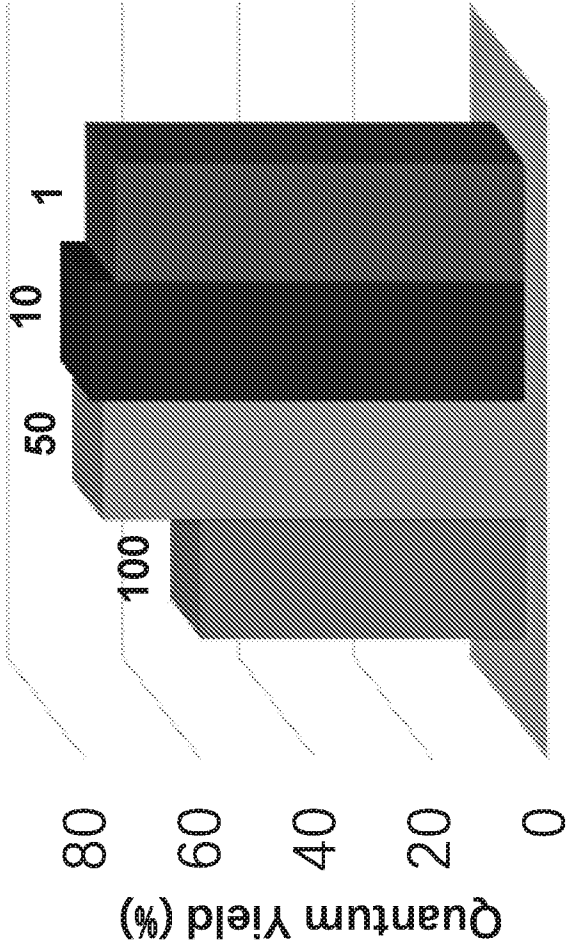


FIG. 18C

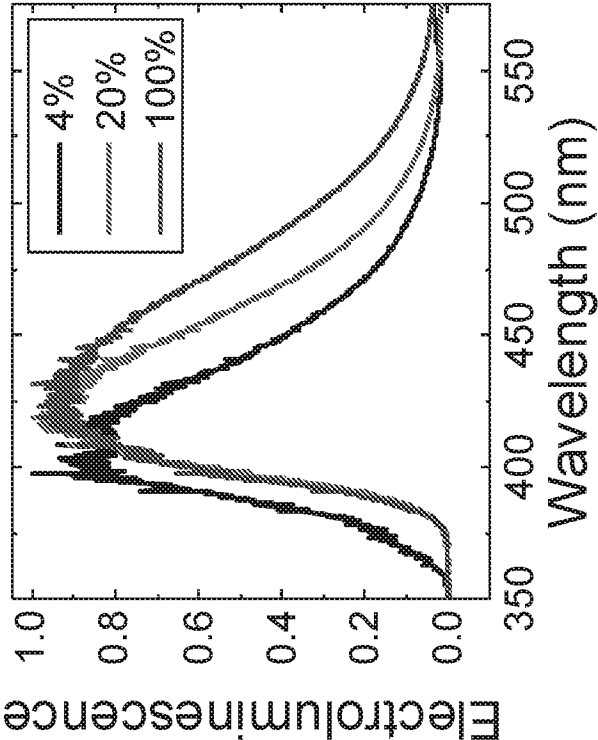


FIG. 19A

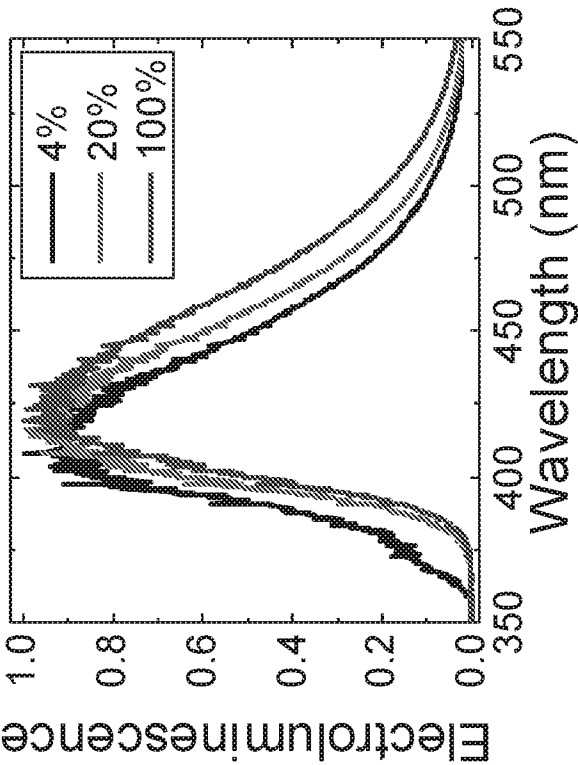


FIG. 19B

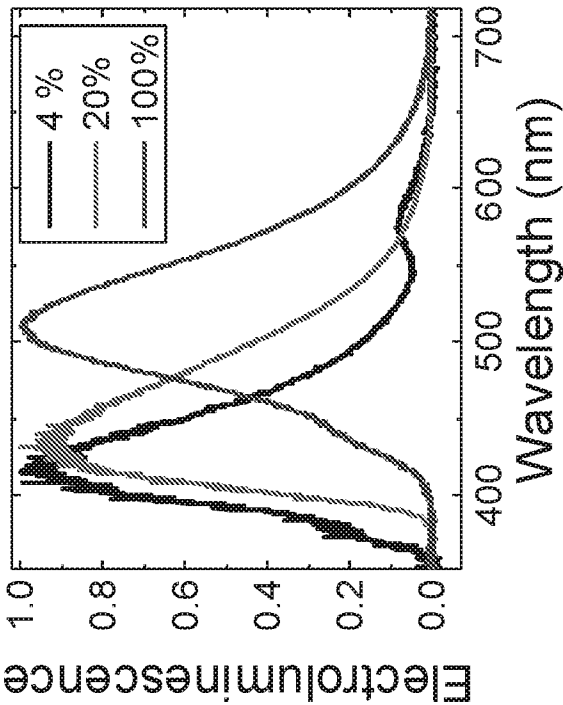


FIG. 19C

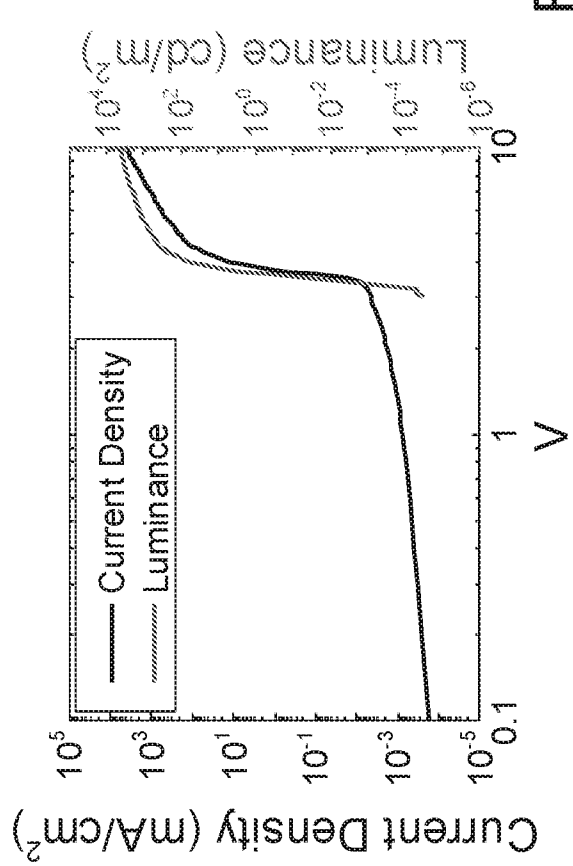


FIG. 20A

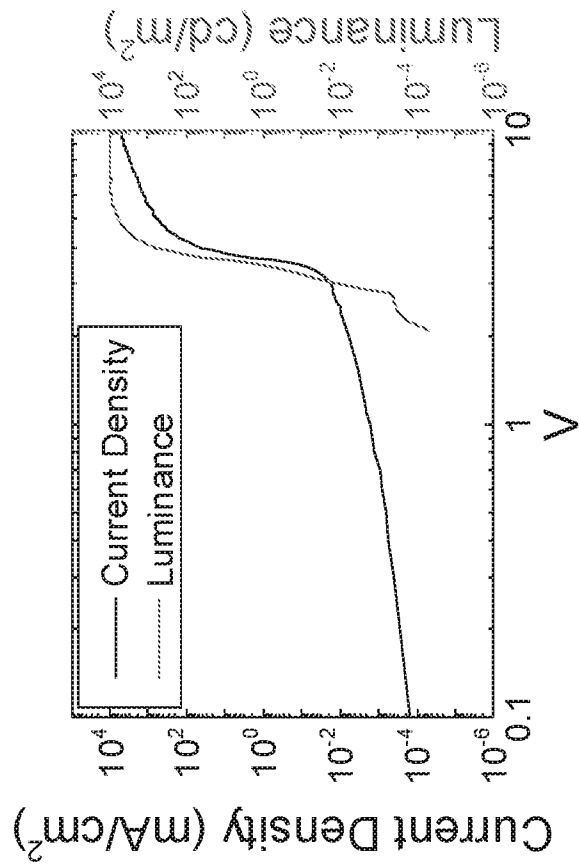


FIG. 20B

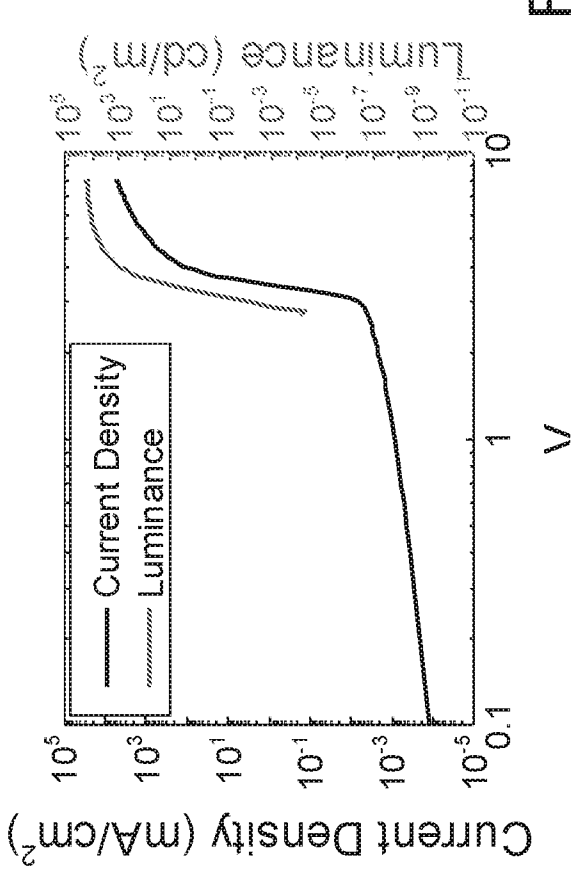


FIG. 20C

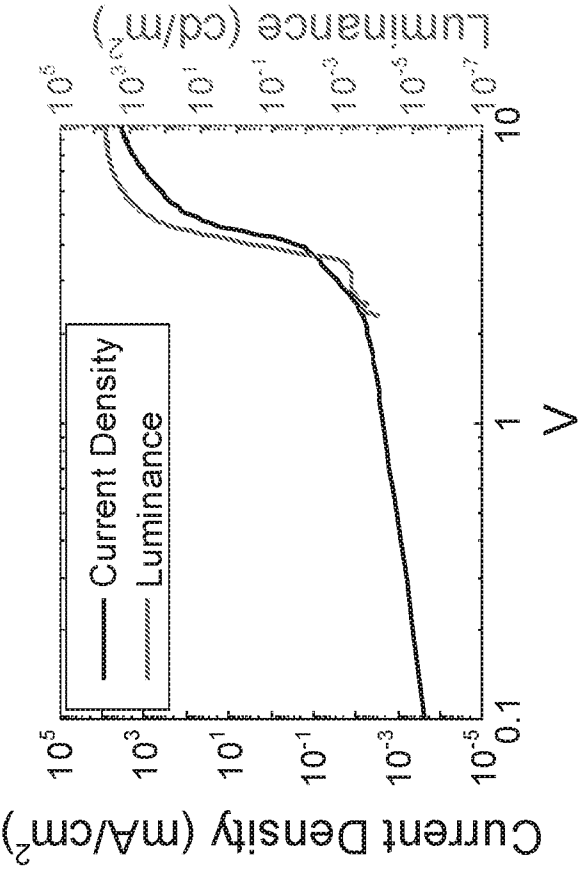


FIG. 21A

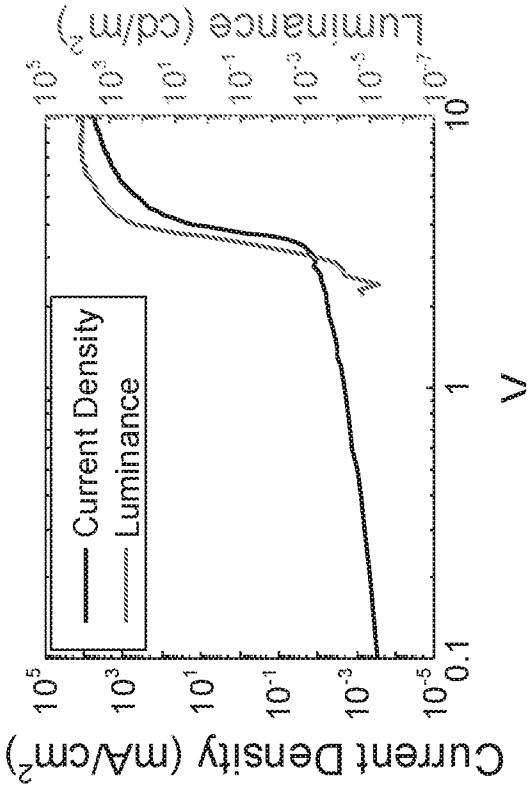


FIG. 21B

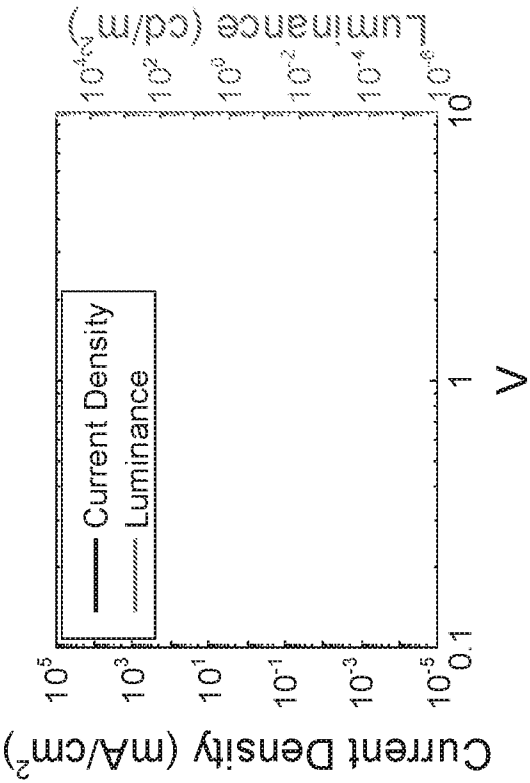


FIG. 21C

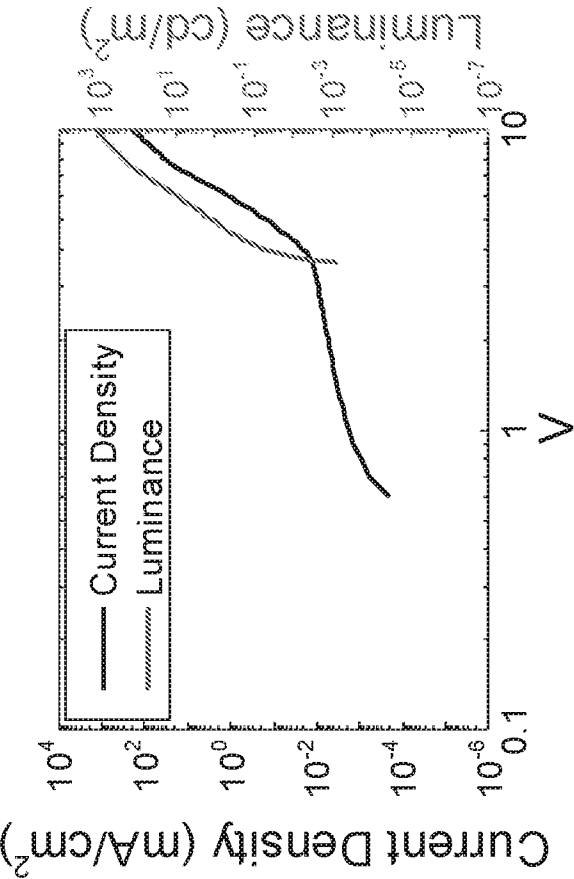


FIG. 22A

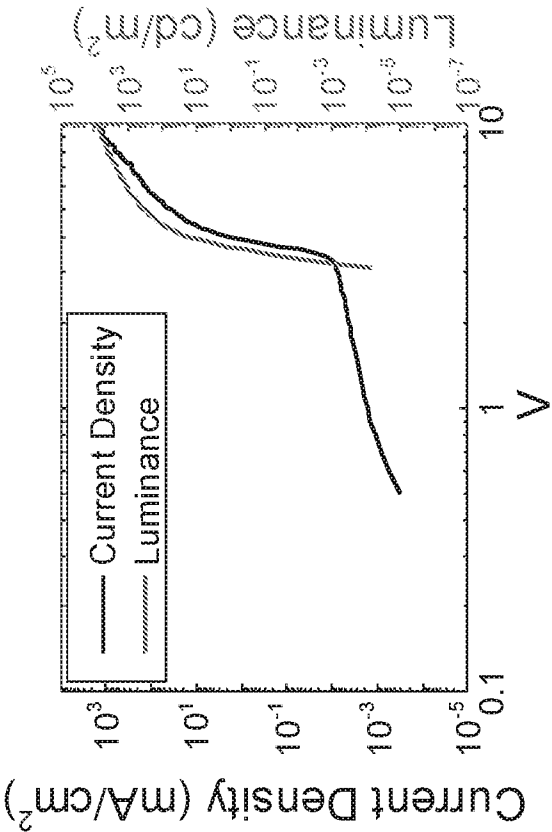
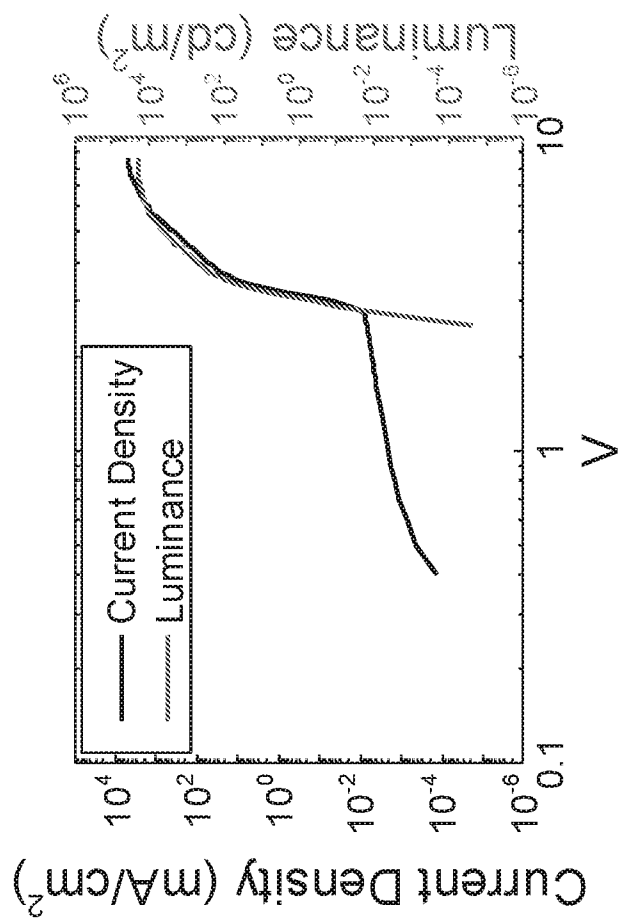


FIG. 22B

FIG. 22C



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US17/42424

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 54-57
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

---Continued Within the Next Supplemental Box---

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

1

Remark on Protest

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

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US17/42424

A. CLASSIFICATION OF SUBJECT MATTER
 IPC - C07D 311/94; C07F 7/08, 7/18 (2017.01)
 CPC - C07D 311/94; C07F 7/1876, 7/1892

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2013/0197241 A1 (REGENTS OF THE UNIVERSITY OF MINNESOTA) 01 August 2013; paragraphs [0005], [0164]	1
Y	US 2001/0011144 A1 (MORI, H) 02 August 2001; paragraphs [0011], [0014]	1
A	US 2,230,233 A (DANE, E et al.) 04 February 1941; entire document	1

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

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

07 September 2017 (07.09.2017)

Date of mailing of the international search report

07 NOV 2017

Name and mailing address of the ISA/

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Shane Thomas

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

-----Continued from Box No. III Observations where unity of invention is lacking -----

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid. Groups I+, Claims 1-53 (in-part); compound of Formula (I), where Y is ((R1)2O2C)2 with R1 being unsubstituted alkyl; X is Si(R5)3 wherein R5 is unsubstituted alkyl; A is Si(R5)3 wherein R5 is unsubstituted alkyl; B is H; and C is H (first exemplary compound structure).

The compound, compositions and methods will be searched to the extent the compound encompasses a compound of Formula (I), where Y is ((R1)2O2C)2 with R1 being unsubstituted alkyl; X is Si(R5)3 wherein R5 is unsubstituted alkyl; A is Si(R5)3 wherein R5 is unsubstituted alkyl; B is H; and C is H (first exemplary compound structure). Applicant is invited to elect additional compound(s), with fully specified structure (e.g. no optional or variable atoms or substituents) for each, to be searched. Additional compound(s) will be searched upon the payment of additional fees. It is believed that claim 1 (in-part) encompasses this first named invention and thus this claim will be searched without fee to the extent that it encompasses a compound of Formula (I), wherein X is -O-; R1 is H; R2 and R3 are H; R4 is H; R5 is H; R6 is (C5-C16)alkyl; and R8 is H (first exemplary compound structure). Applicants must specify the claims that encompass any additionally elected compound structure(s). Applicants must further indicate, if applicable, the claims which encompass the first named invention, if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the "+" group(s) will result in only the first claimed invention to be searched/examined. An exemplary election would be a compound of Formula (I), where Y is O; X is Si(R5)3 wherein R5 is unsubstituted alkyl; A is Si(R5)3 wherein R5 is unsubstituted alkyl; B is H; and C is H (first exemplary elected compound structure).

Groups I+ share the technical features including: a compound of Formula (I), where Y is ((R1)2O2C)2 with R1 being unsubstituted alkyl; X is Si(R5)3 wherein R5 is unsubstituted alkyl; A is Si(R5)3 wherein R5 is unsubstituted alkyl; B is H; and C is H.

However, these shared technical features are previously disclosed by US 2013/0197241 A1 (REGENTS OF THE UNIVERSITY OF MINNESOTA) (hereinafter 'Minnesota') in view of US 2001/0011144 A1 (MORI).

Minnesota discloses a compound of formula I, as shown, where Y is ((R1)2O2C)2 with R1 being unsubstituted alkyl; X is Si(R5)3 wherein R5 is unsubstituted alkyl; A is Si(R5)3 wherein R5 is unsubstituted alkyl; and C is H (compound as shown in example 35; paragraph [0164]), but Minnesota does not disclose wherein B is H. However, Mori discloses wherein B is H (compound of formula II wherein R3-R6 are hydrogen; paragraphs [0011], [0014]). It would have been obvious to a person of ordinary skill in the art, at the time of the invention, to have modified the compound, as previously disclosed by Minnesota, in order to have provided wherein B is H, as previously disclosed by Mori, for providing a method of cycloaddition useful in a Diels-Alder reaction wherein the compound has less steric hindrance with hydrogen atoms substituted on the phenyl ring (Minnesota; paragraph [0005]; Mori; paragraph [0014]).

Since none of the special technical features of the Groups I+ inventions is found in more than one of the inventions, and since all of the shared technical features are previously disclosed by the Minnesota and Mori references, unity of invention is lacking.