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(54) Title: FURAN AND THIOPHENE CONTAINING PI-FUNCTIONAL EMITTERS

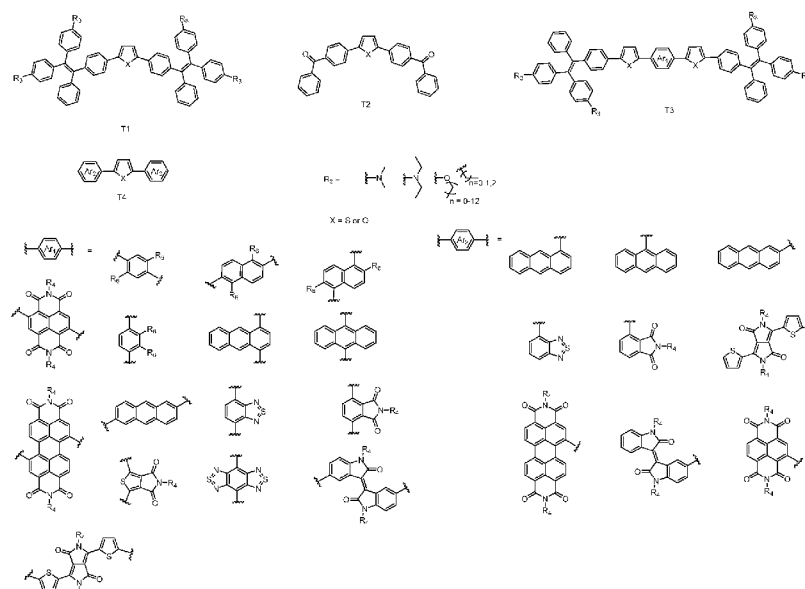


Fig. 1

(57) Abstract: The present disclosure relates to heteroaromatic containing organic compounds and methods of use and preparation thereof. The compounds disclosed herein can be used as organic semiconductors.

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FURAN AND THIOPHENE CONTAINING *Pi*-FUNCTIONAL EMITTERS

CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application claims priority from U.S. Provisional Patent Application Number 62/499,069, filed on January 17, 2017, which is incorporated herein by reference in its entirety.

5 FIELD OF THE INVENTION

[002] The present disclosure relates to furan and/or thiophene containing organic compounds and methods of use and preparation thereof. The compounds disclosed herein can be used as organic semiconductors.

BACKGROUND OF THE INVENTION

10 [003] Organic semiconductors with strong luminescence in the solid phase are useful in a number of applications, such as in components of organic light-emitting diodes (OLED), fluorescent imaging reagents, organic field-effect transistors (OFETs), and anti-counterfeit technology. π -functional (*Pi*-functional) materials have found wide spread use as organic semiconductors due to their unique optical-electrical properties.

15 [004] Heteroaromatic groups have been introduced in π -functional materials to tune their stability, charge mobility, absorption and emission properties. However, the synthesis of these heteroaromatic containing π -functional materials still heavily relies on traditional transition-metal catalyzed coupling reactions, which can require air sensitive and/or costly organometallic catalysts and expensive coupling starting materials. The synthesis of the
20 coupling starting material can also be tedious and can require the handling of toxic (e.g., organotin reagents) and flammable (e.g., Grignard reagents) compounds. In addition, the preparation of the coupling agents of certain heteroaromatic compounds, such as furan, and their subsequent coupling can be challenging due in part to their low reactivity, which has further limited the development of furan containing π -functional materials.

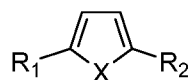
25 [005] In view of the foregoing, there is a need for improved methods of synthesizing π -functional materials containing furan and/or thiophene structures, which can be used in the preparation of new π -functional materials having distinct electrical and optical properties.

SUMMARY OF THE INVENTION

[006] Provided herein is an improved method of synthesizing furan and/or thiophene containing

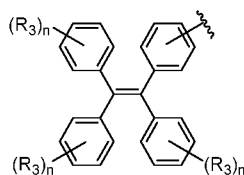
π -functional materials with, e.g., enhanced opto-electric properties. The compounds provided herein can exhibit strong emission and also aggregation induced emission, e.g., presents non- or weak emission in solution state, but enhanced emission in aggregation state.

[007] In a first aspect, provided herein is a compound of Formula 1:



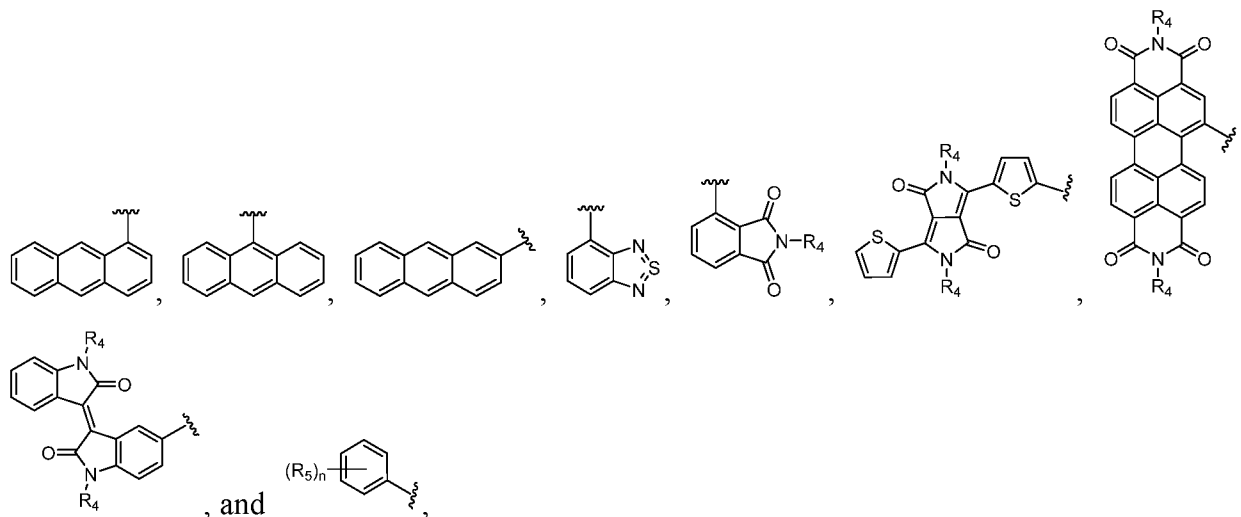
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wherein X is sulfur or oxygen; each of R₁ and R₂ is independently a moiety of Formula 2:

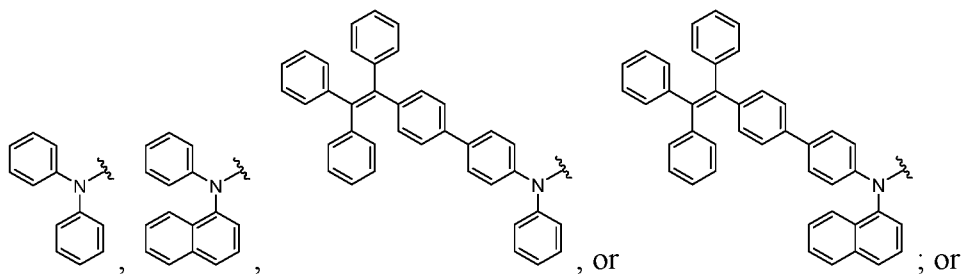


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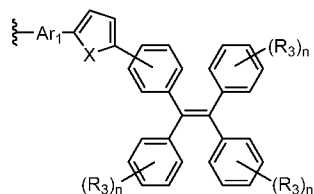
10 wherein each instance of n is independently selected between 1, 2, or 3; each instance of R₃ is independently selected from the group consisting of hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, alkoxy, and amino; each of R₁ and R₂ is independently selected from the group consisting:



wherein n is 1, 2, 3, or 4; R₄ is hydrogen, alkyl, cycloalkyl, aryl, or heteroaryl; each instance of R₅ is independently hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, amino, ketone, nitro, nitrile, halide, ester, sulfone,

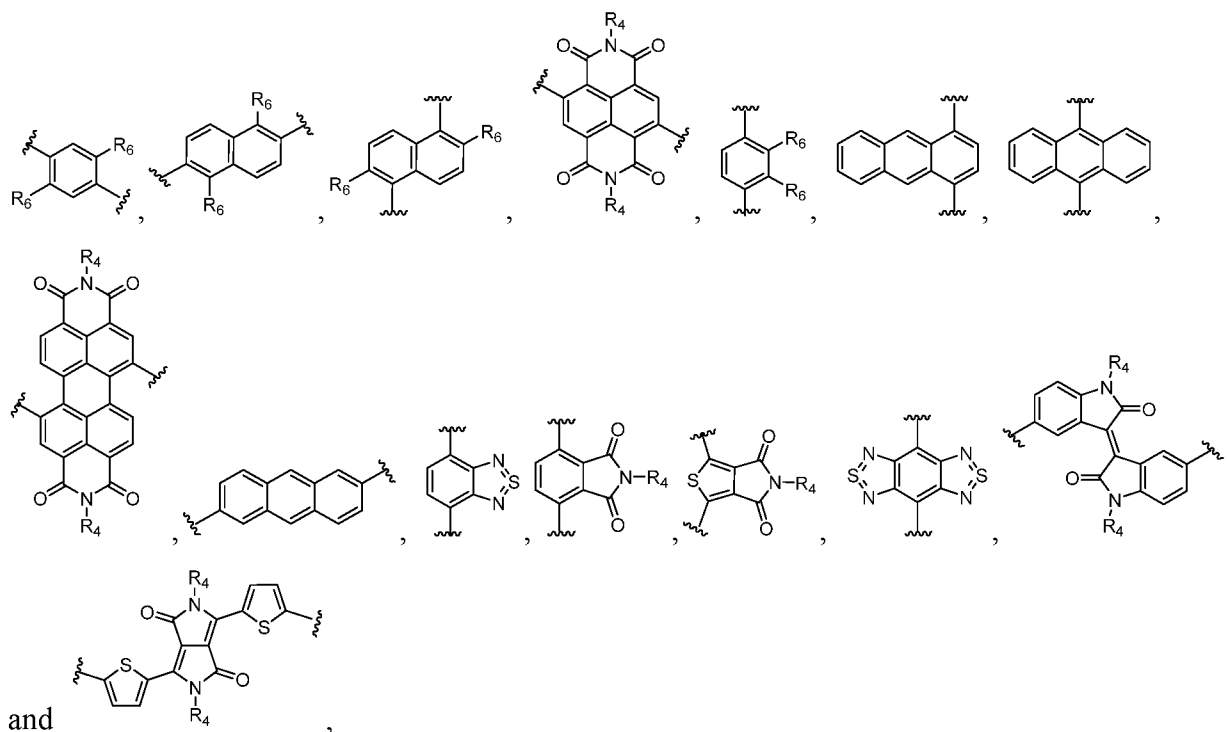


R_1 is the moiety of Formula 2 and R_2 is a moiety of Formula 3:

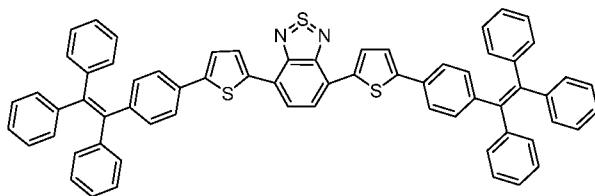


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5 wherein Ar_1 is selected from the group consisting of:

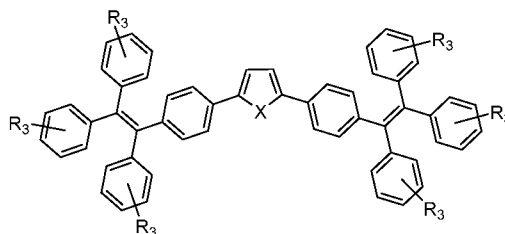


10 wherein independently for each instance R_6 is hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, alkoxy, amino, ester, sulfone, halide, nitrile or nitro; and with the proviso that a compound of Formula 4 is excluded:



4.

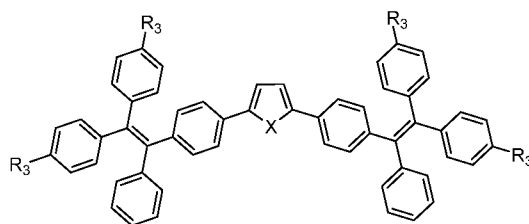
[008] In certain embodiments of the compound of Formula 1, the compound has Formula 5:



5

wherein X is sulfur or oxygen; for each instance of R_3 is independently selected from the group consisting of hydrogen, C_1 - C_{20} alkyl, C_1 - C_{20} alkoxy, and C_1 - C_{14} diakylamino.

[009] In certain embodiments, the compound of Formula 1 has Formula 6:

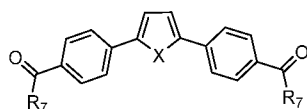


6

wherein X is sulfur or oxygen; each instance of R_3 is independently selected from the group consisting of hydrogen, C_1 - C_{13} alkyl, C_1 - C_{13} alkoxy, and C_1 - C_6 diakylamino.

[0010] In certain embodiments of the compound of Formula 6, R_3 is hydrogen or diethylamino.

[0011] In certain embodiments, the compound of Formula 1 has Formula 7:

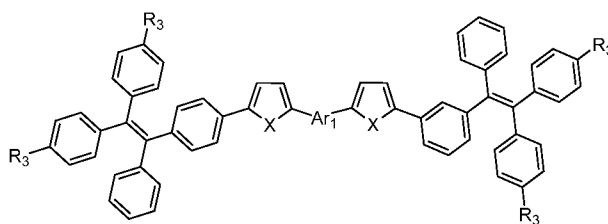


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wherein each instance of R_7 is independently selected from the group consisting of alkyl, cycloalkyl, optionally substituted aryl, and optionally substituted heteroaryl.

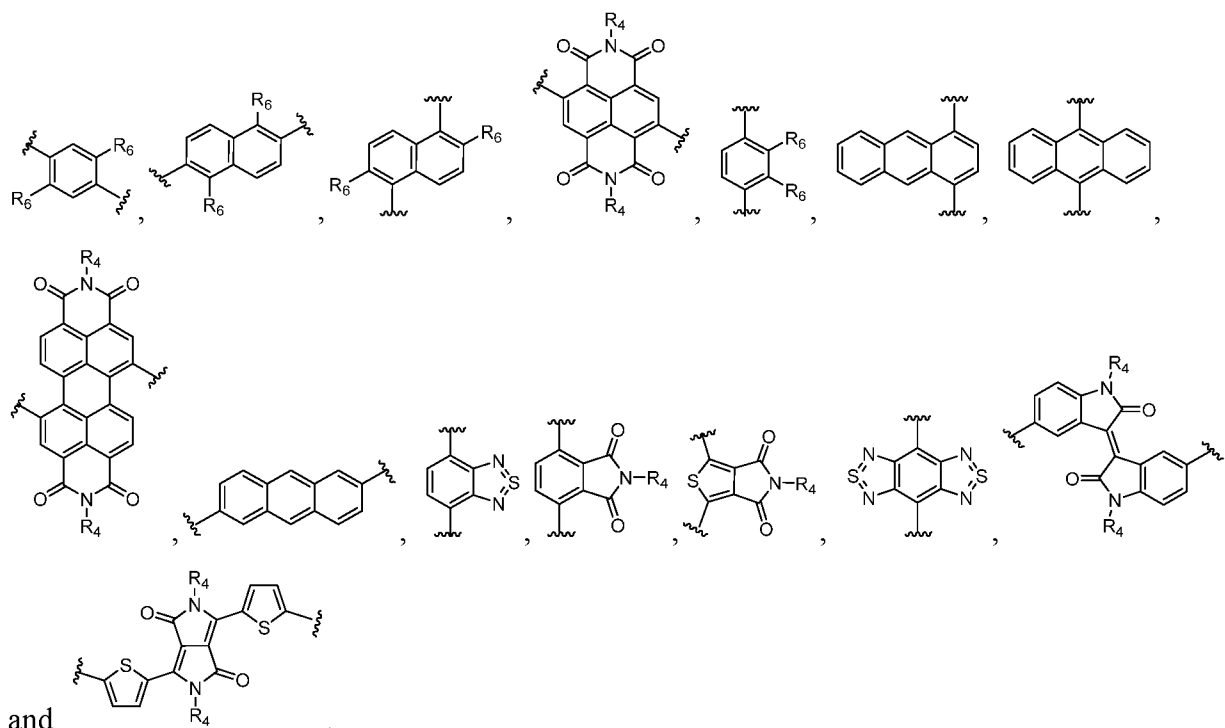
[0012] In certain embodiments of the compound of Formula 7, R_7 is phenyl.

[0013] In certain embodiments, the compound of Formula 1 has Formula 8:



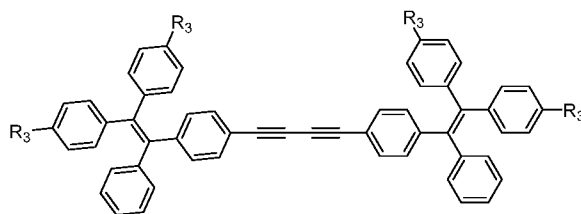
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wherein each instance of R_3 is independently selected from the group consisting of hydrogen, C_1 - C_{20} alkyl, C_1 - C_{20} alkoxy, and C_1 - C_{14} dialkylamino; and Ar_1 is:



[0014] In certain embodiments of the compound of any of the aforementioned embodiments, X is oxygen.

[0015] In a second aspect, provided herein is a method for preparing the compound of Formula 6 comprising the step of contacting a compound of Formula 8:

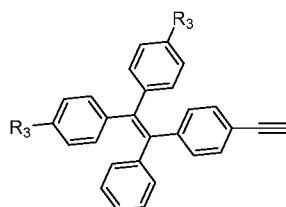
**8**

wherein R_3 is independently selected from the group consisting of hydrogen, C_1 - C_{13} alkyl, C_1 - C_{13} alkoxy, and C_1 - C_6 dialkylamino; with a nucleophile selected from the group consisting of
 5 a metal hydroxide, a metal sulfide, and a metal hydrosulfide; or S_8 and a Brønsted base; thereby forming the compound of Formula 6.

[0016] In certain embodiments of the method for preparing the compound of Formula 6, the metal hydroxide is NaOH, KOH, CsOH, or a combination thereof.

[0017] In certain embodiments of the method for preparing the compound of Formula 6, the
 10 step of contacting a compound of Formula 8 with a nucleophile or S_8 and a Brønsted base occurs in a solvent selected from dimethyl sulfoxide (DMSO), dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), hexamethylphosphoramide (HMPA), 1,3-dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone (DNPU), acetonitrile, or a combination thereof.

[0018] In certain embodiments of the method for preparing the compound of Formula 6, the
 15 method further comprises the step of contacting a compound of Formula 9:

**9**

[0019] wherein R_3 is independently selected from the group consisting of hydrogen, C_1 - C_{13} alkyl, C_1 - C_{13} alkoxy, and C_1 - C_6 dialkylamino; with a copper(I) salt thereby forming the
 20 compound of Formula 8.

[0020] In certain embodiments of the method for preparing the compound of Formula 6, the copper(I) salt is selected from copper(I)iodide, copper(I)bromide, copper(I)chloride, or a combination thereof.

[0021] In certain embodiments of the method for preparing the compound of Formula 6, the step of contacting the compound of Formula 9 with the copper(I) salt and the step of contacting the compound of Formula 8 with the nucleophile or S₈ and the Brønsted base occur in the same reaction vessel.

5 [0022] In certain embodiments of the method for preparing the compound of Formula 6, the step of contacting the compound of Formula 9 with the copper salt occurs in a solvent selected from dimethyl sulfoxide (DMSO), dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), hexamethylphosphoramide (HMPA), 1,3-dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone (DNPU), acetonitrile, or a combination thereof.

10 [0023] In certain embodiments of the method for preparing the compound of Formula 6, R₃ is hydrogen or diethylamino.

[0024] In certain embodiments of any of the aforementioned methods for preparing the compound of Formula 6, the nucleophile is a metal hydroxide.

15 [0025] In a third aspect, provided herein is a thin film comprising any one of the aforementioned compounds.

[0026] In a fourth aspect, provided herein is a nanoparticle comprising any one of the aforementioned compounds.

20 [0027] In a fifth aspect, provided herein is an organic field-effect transistor, organic light-emitting diode, or an organic photovoltaic cell comprising any one of the aforementioned compounds.

BRIEF DESCRIPTION OF DRAWINGS

[0028] The above and other objects and features of the present disclosure will become apparent from the following description of the invention, when taken in conjunction with the accompanying drawings, in which:

25 [0029] **FIG. 1** depicts certain embodiments of the compounds described herein.

[0030] **FIG. 2A** depicts certain embodiments of the synthetic methods for (A) a two-step, two pot method and a (b) two-step, one pot method for preparing the compounds described herein.

[0031] **FIG. 2B** depicts certain embodiments of the synthetic methods for preparing compounds described herein.

[0032] **FIG. 3A** depicts a ^1H NMR spectrum of TPE-F according to the procedure described in Examples 1 and 2.

[0033] **FIG. 3B** depicts a ^{13}C NMR spectrum of TPE-F according to the procedure described in Examples 1 and 2.

5 [0034] **FIG. 4A** depicts a ^1H NMR spectrum of TPE-T according to the procedure described in Examples 1 and 2.

[0035] **FIG. 4B** depicts a ^{13}C NMR spectrum of TPE-T according to the procedure described in Examples 1 and 2.

[0036] **FIG. 5A** depicts a high resolution mass spectrum (MALDI-TOF) of TPE-F according
10 to the procedure described in Examples 1 and 2.

[0037] **FIG. 5B** depicts a high resolution mass spectrum (MALDI-TOF) of TPE-T described in Examples 1 and 2.

[0038] **FIG. 6** depicts (A) UV-vis absorption spectra of TPE-F and TPE-T in dilute THF solutions (10 μM); (B) photoluminescence (PL) spectra of TPE-F (10 μM) in tetrahydrofuran
15 (THF)/water mixtures with different water fractions (f_w); and (C) a plot of relative emission intensity (I/I_0) of TPE-F and TPE-T in different percentages of THF/water mixtures. I_0 = PL intensity in 100% THF.

[0039] **FIG. 7** depicts the effect of solvent fuming and grinding on the emission color of TPE-F (A and C) and TPE-T and (B and D); and the effect of solvent fuming and grinding on
20 PL emission wavelength of solid state TPE-F (E) and TPE-T (F).

[0040] **FIG. 8** depicts (A) an electroluminescence (EL) device configuration comprising TPE-F: ITO/NPB/TPE-F/TPBi/LiF/Al and (B) the corresponding EL spectrum; (C) current density–voltage–luminance characteristics; and (D) change in external quantum efficiency with the applied current density of the device. Inset: photo of the device.

25 [0041] **Fig. 9** depicts the thermogravimetric analysis curves of (A) TPE-F and (B) TPE-T recorded under nitrogen at a heating rate of 10 $^\circ\text{C}/\text{min}$.

[0042] **Fig. 10** depicts the differential scanning calorimetry (DSC) thermograms of (A) TPE-F and (B) TPE-T recorded during the second heating cycle under nitrogen at a heating rate of 10 $^\circ\text{C}/\text{min}$.

[0043] **Fig. 11** depicts the PL spectra of TPE-T (10 μ M) in THF/water mixtures with different water fractions (f_w). Inset: fluorescence photos of TPE-T in dilute THF solution and at 99% aqueous mixture taken under 365 nm UV irradiation from a hand-hold lamp.

[0044] **Fig. 12** depicts the fluorescence decay curves of (A and B) TPE-F and (C and D) TPE-T in the solution and solid states.

[0045] **Fig. 13** depicts cyclic voltammetry curves of (A) TPE-F and (B) TPE-T with 0.1 M $\text{Bu}_4^+\text{NPF}_6^-$ in CH_2Cl_2

[0046] **Fig. 14** transfer characteristics of organic field-effect transistor based on (A) TPE-F and (B) TPE-T.

[0047] **Fig. 15A** depicts a ^1H NMR of other derivatives of compounds described herein.

[0048] **Fig. 15B** depicts a ^{13}C NMR of other derivatives of compounds described herein.

[0049] **Fig. 15C** depicts a high resolution mass spectrum (MALDI-TOF) of other derivatives of compounds described herein.

[0050] **Fig. 16** depicts a high resolution mass spectrum (MALDI-TOF) of other derivatives of compounds described herein.

[0051] **Fig. 17** depicts a high resolution mass spectrum (MALDI-TOF) of other derivatives of compounds described herein.

DETAILED DESCRIPTION OF THE INVENTION

[0052] The present disclosure provides improved methods for accessing 2,5-disubstituted furan- and/or thiophene-based compounds, which can be used as organic semiconductors. This methodology permits the efficient synthesis of heteroaromatic containing π -functional materials that have been hereto unstudied. Accordingly, this disclosure also provides novel π -functional materials. This new class of heteroaromatic containing π -functional materials exhibit unique properties that are useful in the preparation of organic semiconductors.

Definitions

[0053] The definitions of terms used herein are meant to incorporate the present state-of-the-art definitions recognized for each term in the chemical and semiconductor fields. Where appropriate, exemplification is provided. The definitions apply to the terms as they are used throughout this

specification, unless otherwise limited in specific instances, either individually or as part of a larger group.

[0054] The term "heteroatom" is art-recognized and refers to an atom of any element other than carbon or hydrogen. Illustrative heteroatoms include boron, nitrogen, oxygen, phosphorus, sulfur and selenium.

[0055] The term "alkyl" is art-recognized, and includes saturated aliphatic groups, including straight-chain alkyl groups, branched-chain alkyl groups, cycloalkyl (alicyclic) groups, alkyl substituted cycloalkyl groups, and cycloalkyl substituted alkyl groups. In certain embodiments, a straight chain or branched chain alkyl has about 30 or fewer carbon atoms in its backbone (e.g., C₁-C₃₀ for straight chain, C₃-C₃₀ for branched chain), and alternatively, about 20 or fewer. Likewise, cycloalkyls have from about 3 to about 10 carbon atoms in their ring structure, and alternatively about 5, 6 or 7 carbons in the ring structure.

[0056] Unless the number of carbons is otherwise specified, "lower alkyl" refers to an alkyl group, as defined above, but having from one to about ten carbons, alternatively from one to about six carbon atoms in its backbone structure. Likewise, "lower alkenyl" and "lower alkynyl" have similar chain lengths.

[0057] The term "aralkyl" is art-recognized and refers to an alkyl group substituted with an aryl group (e.g., an aromatic or heteroaromatic group).

[0058] The terms "alkenyl" and "alkynyl" are art-recognized and refer to unsaturated aliphatic groups analogous in length and possible substitution to the alkyls described above, but that contain at least one double or triple bond respectively.

[0059] The term "aryl" is art-recognized and refers to 5-, 6- and 7-membered single-ring aromatic groups that may include from zero to four heteroatoms, for example, benzene, naphthalene, anthracene, pyrene, pyrrole, furan, thiophene, imidazole, oxazole, thiazole, triazole, pyrazole, pyridine, pyrazine, pyridazine and pyrimidine, and the like. Those aryl groups having heteroatoms in the ring structure may also be referred to as "aryl heterocycles" or "heteroaromatics." The aromatic ring may be substituted at one or more ring positions with such substituents as described above, for example, halogen, azide, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, alkoxy, amino, nitro, sulfhydryl, imino, amido, phosphonate, phosphinate, carbonyl, carboxyl, silyl, ether, alkylthio, sulfonyl, sulfonamido, ketone, aldehyde, ester,

heterocyclyl, aromatic or heteroaromatic moieties, -CF₃, -CN, or the like. The term "aryl" also includes polycyclic ring systems having two or more cyclic rings in which two or more carbons are common to two adjoining rings (the rings are "fused rings") wherein at least one of the rings is aromatic, e.g., the other cyclic rings may be cycloalkyls, cycloalkenyls, cycloalkynyls, aryls and/or heterocyclyls.

[0060] The terms ortho, meta and para are art-recognized and refer to 1,2-, 1,3- and 1,4-disubstituted benzenes, respectively. For example, the names 1,2-dimethylbenzene and ortho-dimethylbenzene are synonymous.

[0061] The terms "heterocyclyl", "heteroaryl", or "heterocyclic group" are art-recognized and refer to 3- to about 10-membered ring structures, alternatively 3- to about 7-membered rings, whose ring structures include one to four heteroatoms. Heterocycles may also be polycycles. Heterocyclyl groups include, for example, thiophene, thianthrene, furan, pyran, isobenzofuran, chromene, xanthene, phenoxanthene, pyrrole, imidazole, pyrazole, isothiazole, isoxazole, pyridine, pyrazine, pyrimidine, pyridazine, indolizine, isoindole, indole, indazole, purine, quinolizine, isoquinoline, quinoline, phthalazine, naphthyridine, quinoxaline, quinazoline, cinnoline, pteridine, carbazole, carboline, phenanthridine, acridine, pyrimidine, phenanthroline, phenazine, phenarsazine, phenothiazine, furazan, phenoxazine, pyrrolidine, oxolane, thiolane, oxazole, piperidine, piperazine, morpholine, lactones, lactams such as azetidinones and pyrrolidinones, sultams, sultones, and the like. The heterocyclic ring may be substituted at one or more positions with such substituents as described above, as for example, halogen, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, amino, nitro, sulfhydryl, imino, amido, phosphonate, phosphinate, carbonyl, carboxyl, silyl, ether, alkylthio, sulfonyl, ketone, aldehyde, ester, a heterocyclyl, an aromatic or heteroaromatic moiety, -CF₃, -CN, or the like.

[0062] The term "optionally substituted" refers to a chemical group, such as alkyl, cycloalkyl aryl, and the like, wherein one or more hydrogen may be replaced with a substituent as described herein, for example, halogen, azide, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, alkoxyl, amino, nitro, sulfhydryl, imino, amido, phosphonate, phosphinate, carbonyl, carboxyl, silyl, ether, alkylthio, sulfonyl, sulfonamido, ketone, aldehyde, ester, heterocyclyl, aromatic or heteroaromatic moieties, -CF₃, -CN, or the like

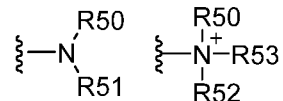
[0063] The terms "polycyclyl" or "polycyclic group" are art-recognized and refer to two or

more rings (e.g., cycloalkyls, cycloalkenyls, cycloalkynyls, aryls and/or heterocyclyls) in which two or more carbons are common to two adjoining rings, e.g., the rings are "fused rings". Rings that are joined through non-adjacent atoms are termed "bridged" rings. Each of the rings of the polycycle may be substituted with such substituents as described above, as for example, halogen, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, amino, nitro, sulfhydryl, imino, amido, phosphonate, phosphinate, carbonyl, carboxyl, silyl, ether, alkylthio, sulfonyl, ketone, aldehyde, ester, a heterocyclyl, an aromatic or heteroaromatic moiety, -CF₃, -CN, or the like.

[0064] The term "carbocycle" is art-recognized and refers to an aromatic or non-aromatic ring in which each atom of the ring is carbon.

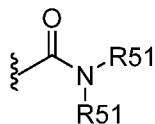
[0065] The term "nitro" is art-recognized and refers to -NO₂; the term "halogen" is art-recognized and refers to -F, -Cl, -Br or -I; the term "sulfhydryl" is art-recognized and refers to -SH; the term "hydroxyl" means -OH; and the term "sulfonyl" and "sulfone" is art-recognized and refers to -SO₂-. "Halide" designates the corresponding anion of the halogens.

[0066] The terms "amine" and "amino" are art-recognized and refer to both unsubstituted and substituted amines, e.g., a moiety that may be represented by the general formulas:



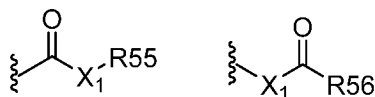
wherein R50, R51 and R52 each independently represent a hydrogen, an alkyl, an alkenyl, -(CH₂)_mR61, or R50 and R51, taken together with the N atom to which they are attached complete a heterocycle having from 4 to 8 atoms in the ring structure; R61 represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and m is zero or an integer in the range of 1 to 8. In other embodiments, R50 and R51 (and optionally R52) each independently represent a hydrogen, an alkyl, an alkenyl, or -(CH₂)_mR61. Thus, the term "alkylamine" includes an amine group, as defined above, having a substituted or unsubstituted alkyl attached thereto, i.e., at least one of R50 and R51 is an alkyl group.

[0067] The term "amido" is art recognized as an amino-substituted carbonyl and includes a moiety that may be represented by the general formula:



wherein R50 and R51 are as defined above.

[0068] The term "carboxyl" is art recognized and includes such moieties as may be represented by the general formulas:

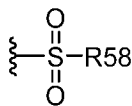


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wherein X_1 is a bond or represents an oxygen or a sulfur, and R55 and R56 represents a hydrogen, an alkyl, an alkenyl, $-(CH_2)_mR61$ or a salt, R56 represents a hydrogen, an alkyl, an alkenyl or $-(CH_2)_mR61$, where m and R61 are defined above. Where X_1 is an oxygen and R55 or R56 is not hydrogen, the formula represents an "ester". Where X_1 is an oxygen, and R55 is as defined above, the moiety is referred to herein as a carboxyl group, and particularly when R55 is a hydrogen, the formula represents a "carboxylic acid". Where X_1 is an oxygen, and R56 is hydrogen, the formula represents a "formate". In general, where the oxygen atom of the above formula is replaced by sulfur, the formula represents a "thiolcarbonyl" group. Where X_1 is a sulfur and R55 or R56 is not hydrogen, the formula represents a "thiolester." Where X_1 is a sulfur and R55 is hydrogen, the formula represents a "thiolcarboxylic acid." Where X_1 is a sulfur and R56 is hydrogen, the formula represents a "thiolformate." On the other hand, where X_1 is a bond, and R55 is not hydrogen, the above formula represents a "ketone" group. Where X_1 is a bond, and R55 is hydrogen, the above formula represents an "aldehyde" group.

[0069] The terms "alkoxyl" or "alkoxy" are art-recognized and refer to an alkyl group, as defined above, having an oxygen radical attached thereto. Representative alkoxyl groups include methoxy, ethoxy, propyloxy, tert-butoxy and the like. An "ether" is two hydrocarbons covalently linked by an oxygen. Accordingly, the substituent of an alkyl that renders that alkyl an ether is or resembles an alkoxyl, such as may be represented by one of -O-alkyl, -O-alkenyl, -O-alkynyl, $-(CH_2)_mR61$, where m and R61 are described above.

[0070] The term "sulfonyl" is art-recognized and refers to a moiety that may be represented by the general formula:



in which R58 is one of the following: hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, heterocyclyl, aryl or heteroaryl.

[0071] Compounds of the present disclosure can include a “divalent group” defined herein as a linking group capable of forming a covalent bond with two other moieties.

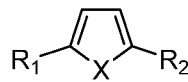
[0072] The representation “ --- ” as used herein in connection to chemical a group or moiety is intended to represent the covalent bond that the aforementioned chemical group or moiety is covalently bonded to another chemical group or moiety.

[0073] At various places in the present specification, substituents of compounds are disclosed in groups or in ranges. It is specifically intended that the description include each and every individual sub-combination of the members of such groups and ranges. For example, the term “C₁₋₆ alkyl” is specifically intended to individually disclose C₁, C₂, C₃, C₄, C₅, C₆, C₁-C₆, C₁-C₅, C₁-C₄, C₁-C₃, C₁-C₂, C₂-C₆, C₂-C₅, C₂-C₄, C₂-C₃, C₃-C₆, C₃-C₅, C₃-C₄, C₄-C₆, C₄-C₅, and C₅-C₆ alkyl. By way of other examples, an integer in the range of 0 to 40 is specifically intended to individually disclose 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, and 40, and an integer in the range of 1 to 20 is specifically intended to individually disclose 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20. Additional examples include that the phrase “optionally substituted with 1-4 substituents” is specifically intended to individually disclose a chemical group that can include 0, 1, 2, 3, 4, 0-4, 0-3, 0-2, 0-1, 1-4, 1-3, 1-2, 2-4, 2-3, and 3-4 substituents.

[0074] The present disclosure addresses the need for improved methods of preparing novel furan and thiophene containing π -functional materials. The methods described herein enable a highly efficient two step one-pot method to access 2,5-disubstituted furan and/or thiophene containing π -functional materials, which traditionally have been prepared by metal catalyzed cross coupling reactions or oxidative coupling reactions. The provided method addresses this problem by providing a copper (I) mediated reaction of terminal alkynes to yield 1,3-diynes, which are cyclized in the presence of an oxygen or sulfur based nucleophile to yield the desired 2,5-disubstituted furan and/or thiophene product.

[0075] The methods described herein allow access to novel furan and/or thiophene containing π -functional materials. These materials exhibit unique and advantageous electroptical and conducting properties, which enables their use as organic semiconductors and/or in organic field-effect transistors, organic light-emitting diode, or an organic photovoltaic cell devices.

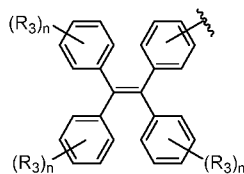
5 [0076] Provided herein are π -functional compounds of Formula 1:



1

10 wherein X is sulfur or oxygen. The compound of Formula 1 can be prepared using the methodologies described herein. Advantageously, the method enables the preparation of 2,5-substituted furans, which as discussed in detail below exhibit unique properties.

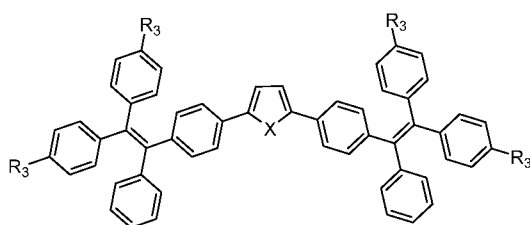
[0077] In certain embodiments, each of R_1 and R_2 of the compound of Formula 1 is independently a moiety of Formula 2:



[0080] In certain embodiments, n is 1 and R_3 is independently attached at either the para or ortho position of each of the aryl groups of the moiety of Formula 2.

[0081] In certain embodiments, R_3 is independently selected from the group consisting of hydrogen, alkyl, alkoxy, and amino. In certain embodiments, R_3 is independently selected from the group consisting of hydrogen, C_1 - C_{20} alkyl, C_1 - C_{20} alkoxy, and C_1 - C_{14} dialkylamino. When R_3 is C_2 - C_{20} , C_3 - C_{20} , or C_4 - C_{20} alkyl, the alkyl group can be a primary, a secondary or a tertiary alkyl group. In certain embodiments, the alkyl group is a C_3 - C_{20} secondary alkyl group. When R_3 is C_2 - C_{20} , C_3 - C_{20} , or C_4 - C_{20} alkoxy or C_2 - C_{14} , C_3 - C_{14} , or C_4 - C_{14} dialkylamino the alkyl group can be a primary, a secondary or a tertiary alkyl group.

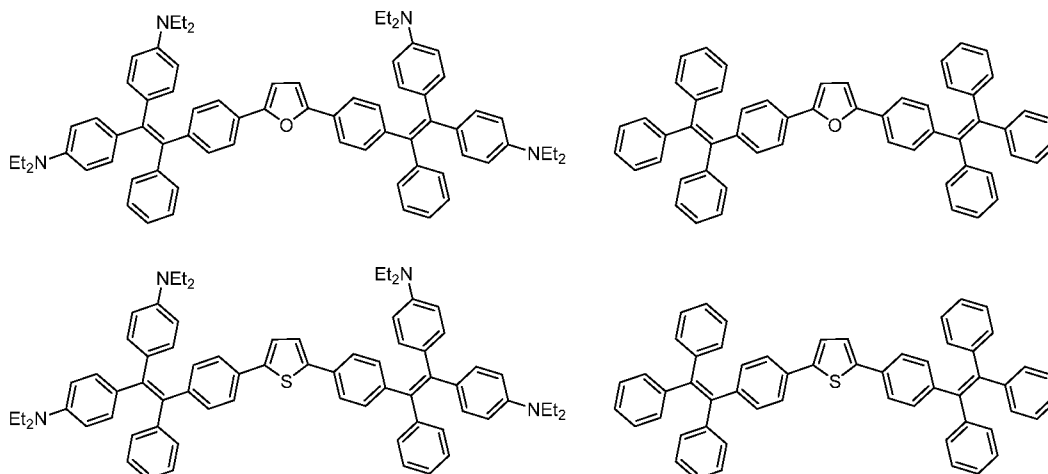
[0082] In certain embodiments, the compound has Formula 6:



6

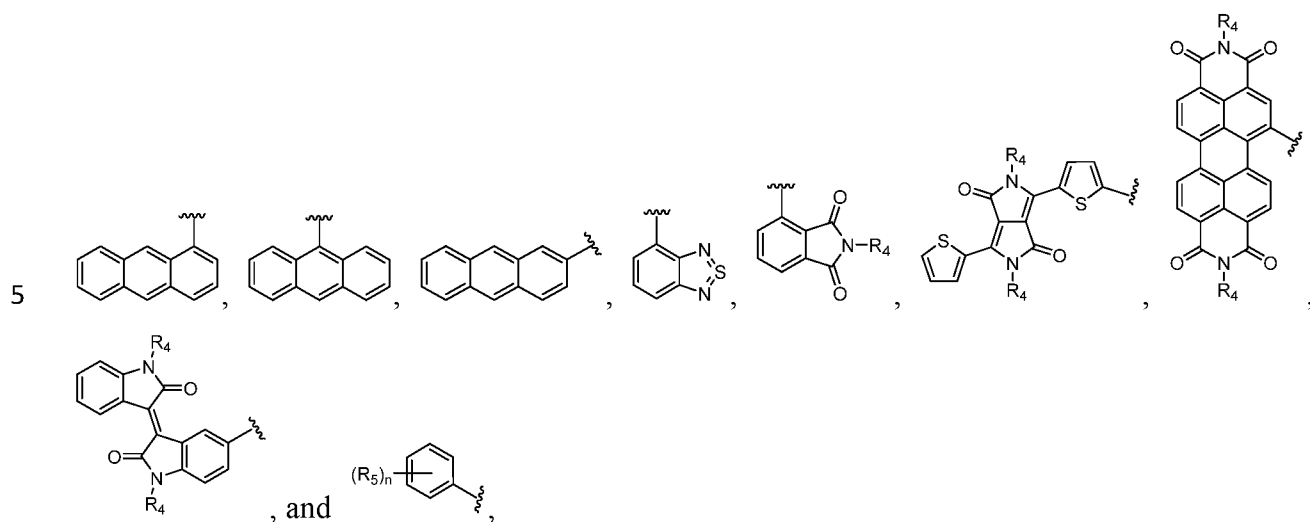
wherein X is sulfur or oxygen; each instance of R_3 is independently selected from the group consisting of hydrogen, C_1 - C_{13} alkyl, C_1 - C_{13} alkoxy, and C_1 - C_6 dialkylamino. In certain embodiments, X is oxygen.

[0083] In certain embodiments, the compound of Formula 1 is selected from the following compounds:

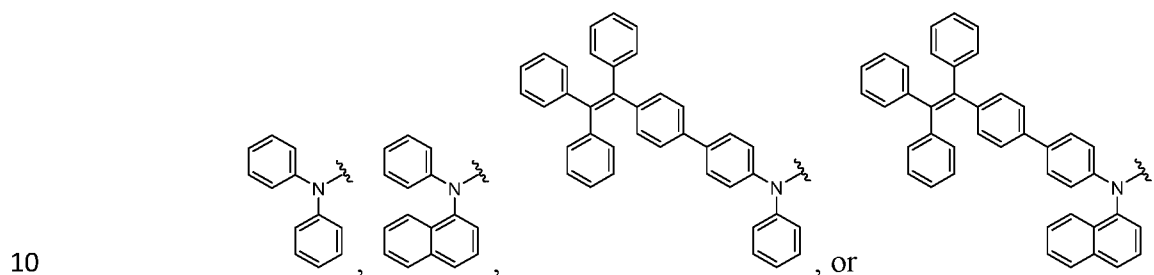


wherein X is sulfur or oxygen; each instance of R_3 is independently selected from the group consisting of hydrogen, C_1 - C_{13} alkyl, C_1 - C_{13} alkoxy, and C_1 - C_6 dialkylamino.

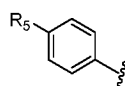
[0084] In certain embodiments, each of R_1 and R_2 of the compound of Formula 1 is independently selected from the group consisting:



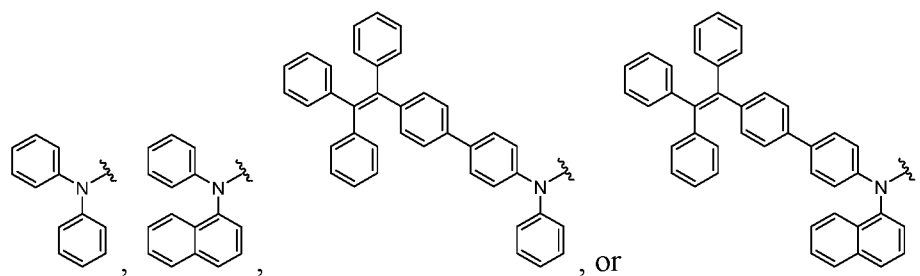
wherein n is 1, 2, 3, or 4; R_4 is hydrogen, alkyl, cycloalkyl, aryl, or heteroaryl; each instance of R_5 is independently hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, amino, ketone, nitro, nitrile, halide, ester, sulfone, diaryl amine,



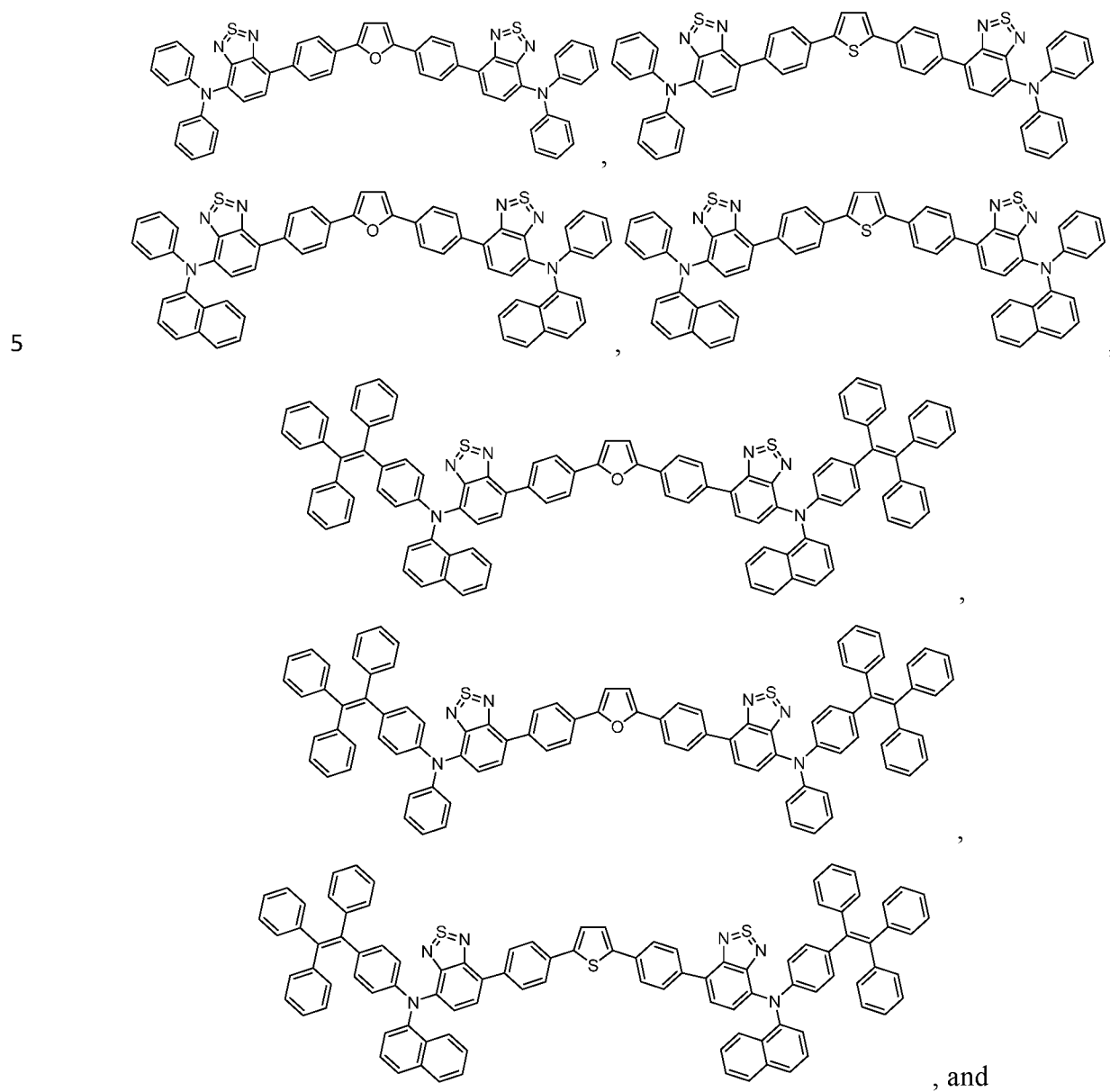
[0085] In certain embodiments, each of R_1 and R_2 is independently:

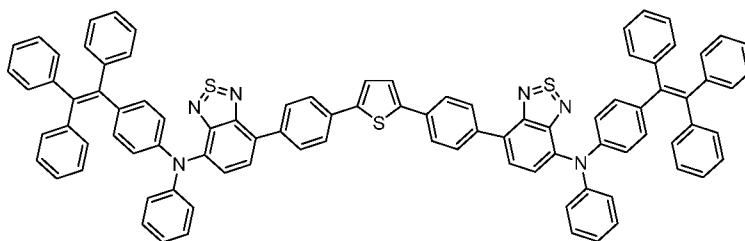


[0086] wherein each instance of R_5 is independently selected from the group consisting of diaryl amine,

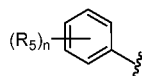


[0087] In certain embodiments, the compound of Formula 1 is a compound selected from the group consisting of:





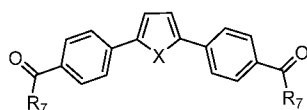
[0088] In certain embodiments, each of R_1 and R_2 is independently:



wherein n is 1 and R_5 is covalently attached at the ortho, meta or para position of the aryl group.

- 5 In certain embodiments, R_5 is an electron withdrawing group selected from the group consisting of ketone, nitro, nitrile, ester, or sulfone. In instances wherein R_5 is a ketone, the ketone can be an alkyl, cycloalkyl, heterocycloalkyl, aryl, or heteroaryl ketone. In certain embodiments, R_5 is an aryl ketone, wherein the aryl group is optionally substituted. In certain embodiments, R_5 is phenyl ketone attached at the para position and n is 1.

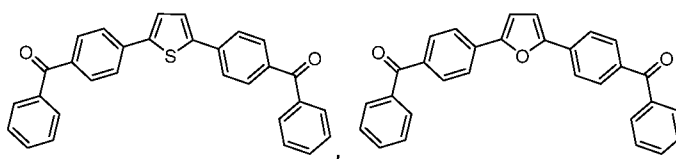
- 10 [0089] In certain embodiments, the compound of Formula 1 is a compound of Formula 7:

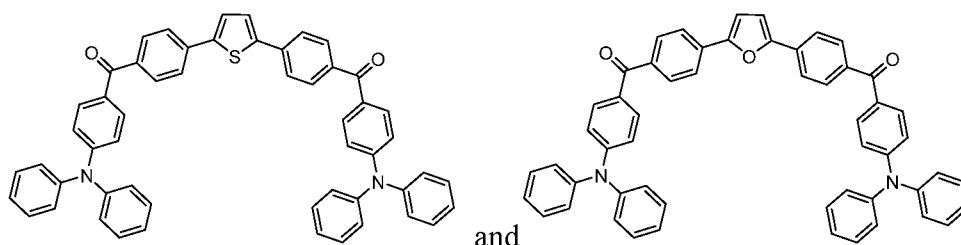


7

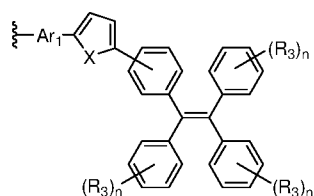
wherein each instance of R_7 is independently selected from the group consisting of alkyl, cycloalkyl, optionally substituted aryl, and optionally substituted heteroaryl.

- 15 [0090] In certain embodiments, the compound of Formula 7 is selected from the group consisting of:





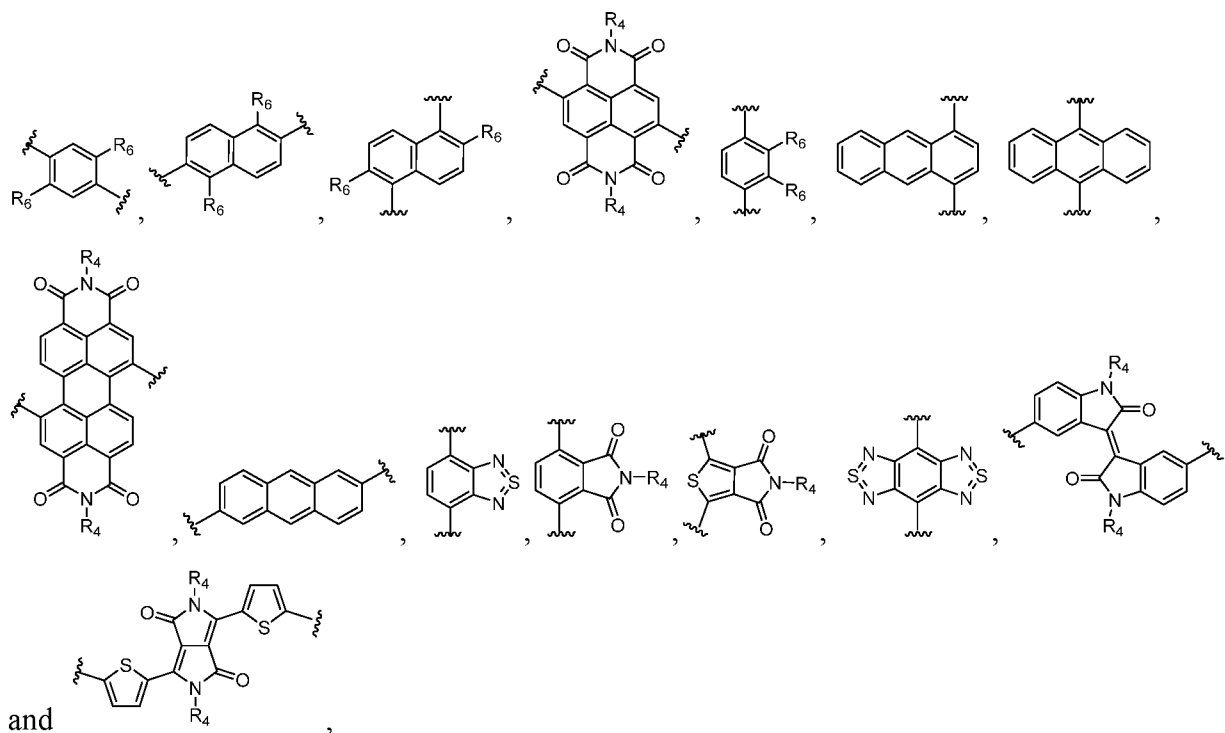
[0091] In certain embodiments, provided herein is the compound of Formula 1, wherein R₁ is the moiety of Formula 2 and R₂ is a moiety of Formula 3:



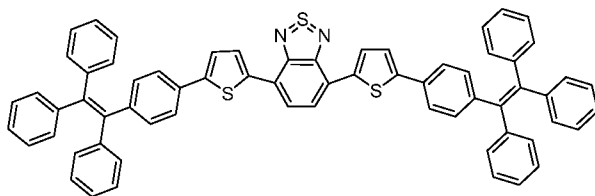
5

3

wherein Ar₁ is selected from the group consisting of:

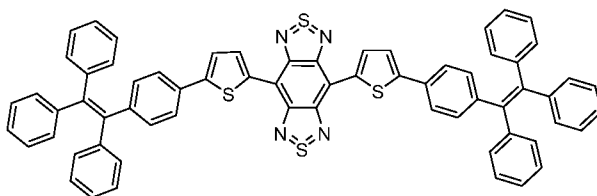


10 wherein independently for each instance R₄ is hydrogen, alkyl, cycloalkyl, aryl, or heteroaryl;
and R₆ is hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, alkoxy, amino, ester,
sulfone, halide, nitrile or nitro; with the proviso that a compound of Formula **4** is excluded:



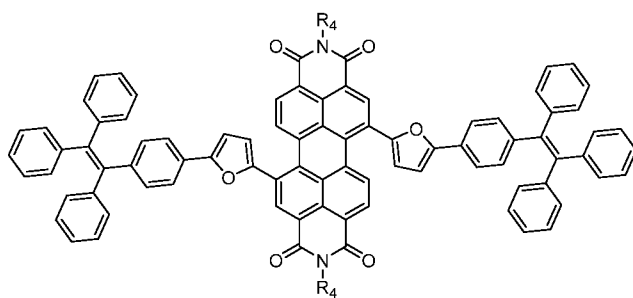
4.

[0092] In certain embodiments, the following compound is excluded from the scope of the compound of a Formula 1:

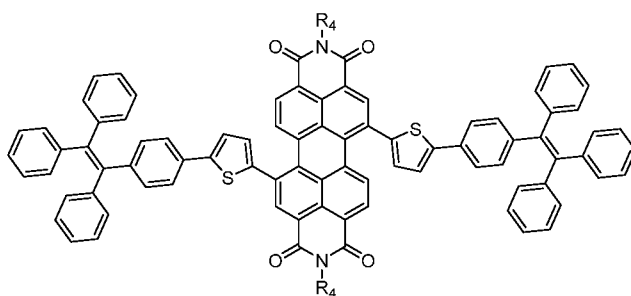


5

[0093] In certain embodiments, the compound of Formula 1 is:



or



wherein R_4 is hydrogen, alkyl, cycloalkyl, aryl, or heteroaryl.

10 [0094] The compounds described herein can exhibit a change in the emission frequency depending on the crystalline state of the compound. For example, when TPE-F and TPE- are treated with solvent fuming (to generate crystalline compounds) and gentle grinding (to create an amorphous solid) there is a change in the emission color of TPE-F (Fig. 6 A, C, and E) and TPE-T (Fig. 6 B, D, and E).

[0095] In certain embodiments, the compounds described herein can exist as an amorphous solid, as substantially a single crystal form, or a mixture of different crystal forms. When the compounds provided herein are present as an amorphous solid, at least 90%, at least 92%, at least 95%, at least 98%, at least 99%, or at least 99.9% or more of the material is present in amorphous form. When the compounds provided herein are present in substantially one crystal form, at least 90%, at least 92%, at least 95%, at least 98%, at least 99%, or at least 99.9% or more of the material is present as a single crystal form.

[0096] In certain embodiments, the compounds described herein are provided as a thin film. When provided as a thin film, the compounds described herein can be in crystalline form, amorphous form, or a combination thereof.

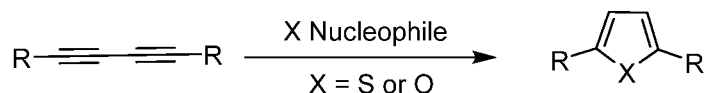
[0097] In certain embodiments, the method for preparing the provided 2,5-disubstituted furan and/or thiophene containing π -functional materials can be generally depicted as shown in Scheme 1 below.

Scheme 1.

Step 1.



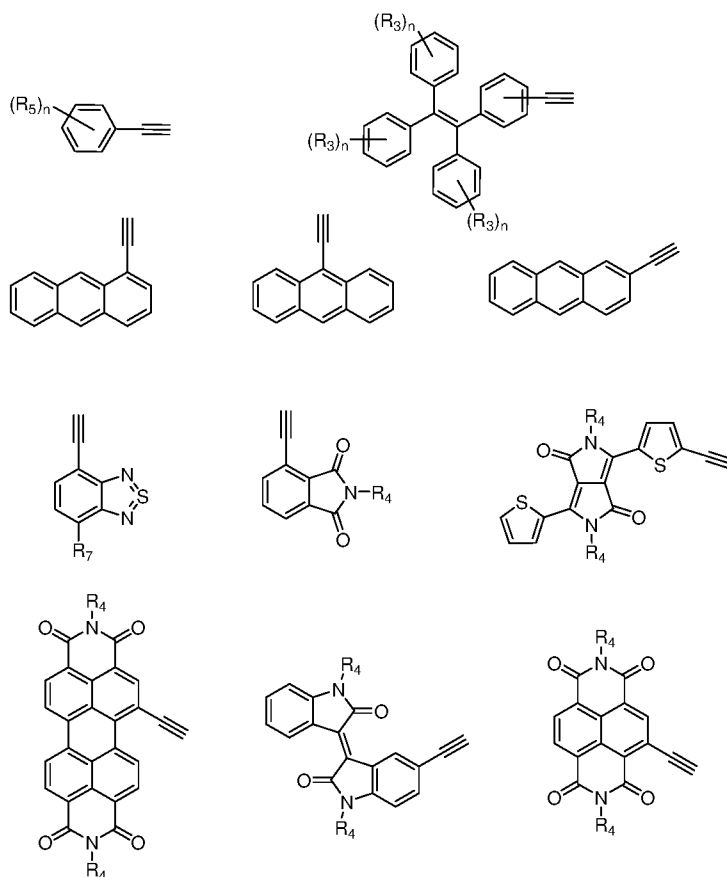
Step 2.



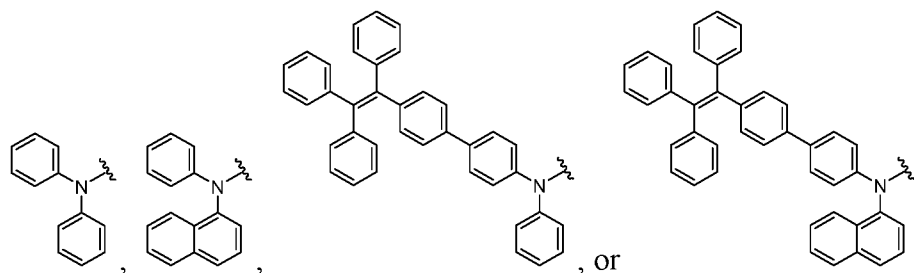
[0098] For simplicity, Scheme 1 depicts the homo-coupling of a terminal alkyne to yield a symmetrical 2,5-disubstituted thiophene and/or furan. However, the method can also be used to couple two distinct terminal alkynes to access unsymmetrical 2,5-disubstituted thiophene and/or furan.

[0099] In general, there is no restriction on the type of terminal alkyne that can be used in connection with the described method. Depending on the physical, chemical, optical, electrical properties desired in the prepared 2,5-disubstituted thiophene and/or furan, the appropriate alkynes can be selected. The selection of the appropriate alkyne and testing of the formed thiophene and/or furan π -functional material is well within the skill of a person in the art.

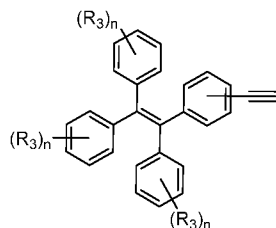
[00100] Exemplary terminal alkynes are shown below:



wherein each instance of n is independently selected between 1, 2, or 3; each instance of R_3 is independently selected from the group consisting of hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, alkoxy, and amino; R_4 is hydrogen, alkyl, cycloalkyl, aryl, or heteroaryl; and each instance of R_5 is independently hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, amino, ketone, nitro, nitrile, halide, ester, sulfone, diaryl amine,

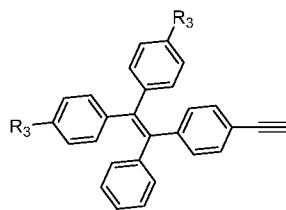


[00101] In certain embodiments, the alkyne has the formula:



wherein n is 1 and R_3 is independently selected from the group consisting of hydrogen, alkyl, alkoxy, and amino.

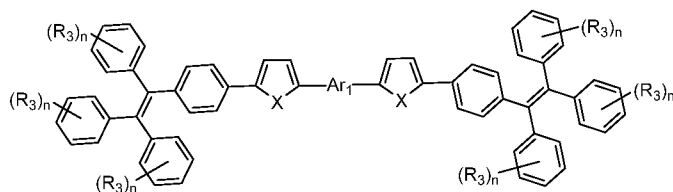
[00102] In certain embodiments, the terminal alkyne can be represented by Formula 9:



9

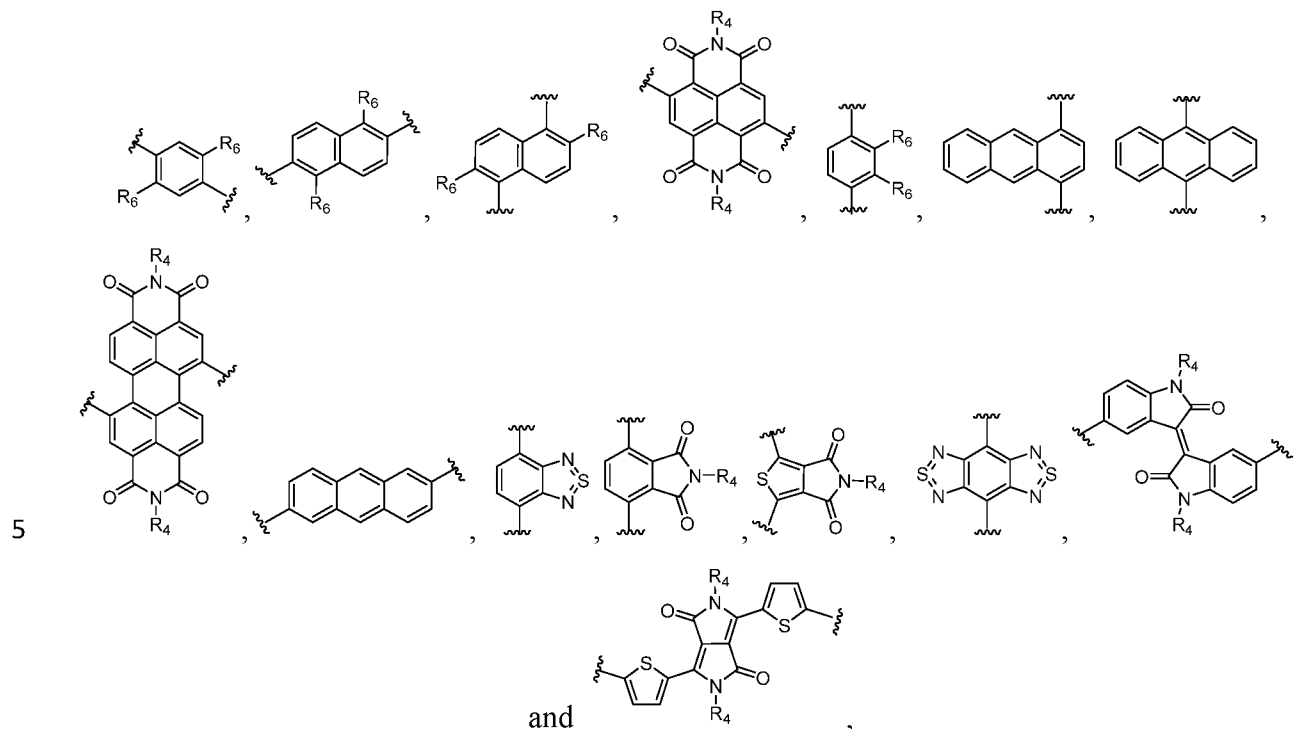
wherein R_3 for each instance is independently selected from the group consisting of hydrogen, C_1 - C_{13} alkyl, C_1 - C_{13} alkoxy, and C_1 - C_6 dialkylamino. In certain embodiments, each R_3 is the same substituent.

- 10 [00103] The method provided herein is a coupling method, which can be used to prepare complex furan and/or thiophenes from simple terminal alkynes. This approach can be further leveraged by using complex terminal alkynes, i.e., alkynes with more complicated chemical structures and/or of higher molecular weight to access even more complex furan and/or thiophene structures.
- 15 [00104] Complex 2,5-substituted furan and/or thiophene containing π -functional materials can be accessed using terminal alkynes containing moieties with more complex structures. For example, 2,5-substituted furan and/or thiophene containing π -functional materials of Formula 8A can be prepared using the alkynes shown in the listing of exemplary complex terminal alkynes below.



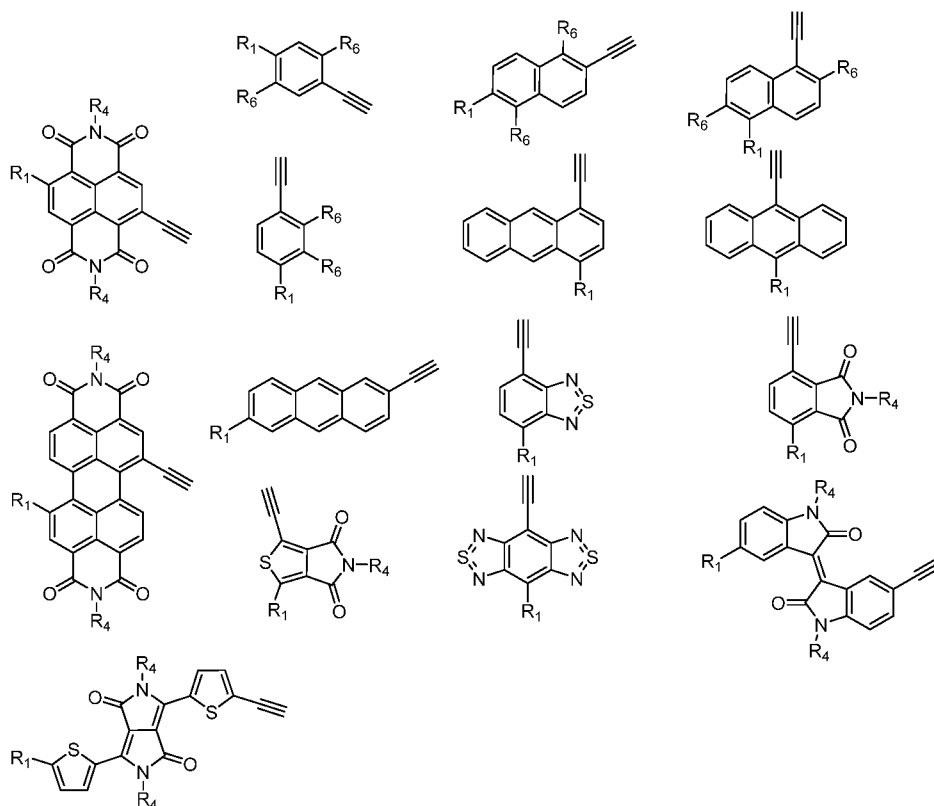
8A

wherein each instance of n is independently selected between 1, 2, or 3; X independently for each instance is selected from sulfur or oxygen; Ar₁ is selected from the group consisting of:

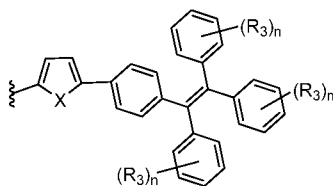


wherein independently for each instance R₄ is hydrogen, alkyl, cycloalkyl, aryl, or heteroaryl; and independently for each instance R₆ is hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, alkoxy, amino, ester, sulfone, halide, nitrile or nitro.

10 [00105] Exemplary terminal alkynes are shown below:

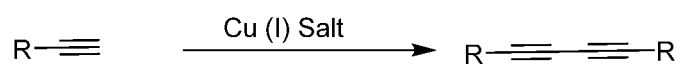


wherein R_1 is



wherein each instance of n is independently selected between 1, 2, or 3; X is sulfur or oxygen; and
 5 each instance of R_3 is independently selected from the group consisting of hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, alkoxy, and amino; R_4 is hydrogen, alkyl, cycloalkyl, aryl, or heteroaryl; and R_6 is hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, amino, ketone, nitro, nitrile, halide, ester, or sulfone.

[00106] The copper coupling reaction depicted below is a redox reaction in which a copper (I)
 10 species mediates an oxidative carbon-carbon forming reaction between the two terminal alkynes, which results in reduction of the copper (I) salt and the formation of copper (0).



[00107] The reaction can be conducted with a stoichiometric amount of the copper (I) salt or in

the alternative can use a catalytic amount (e.g., 0.1-20 mol %; 0.5-5 mol %; or 0.5-3 mol %) of the copper (I) salt and an agent that is capable of oxidizing the formed copper (0) species back to copper (I). In the examples below, copper is used in a catalytic amount in the presence of oxygen, which converts copper (0) to copper (I).

- 5 [00108] Any copper (I) salt can be used for the terminal alkyne coupling step. Exemplary copper (I) salts include copper (I) chloride, copper (I) bromide, copper (I) iodide, copper (I) sulfate, and copper (I) cyanide.

[00109] In the alternative, any source of copper (I) can be used. For example, copper (0) can be used and oxidized *in situ* by the reaction with the appropriate oxidant or a copper (II) salt can be
10 used and the copper (I) salt form therefrom by reaction with the appropriate reductant.

[00110] The copper mediated terminal alkyne coupling reaction is typically conducted in polar aprotic solvents, such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), hexamethylphosphoramide (HMPA), 1,3-dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone (DNPU), acetonitrile, or a combination thereof.
15 Other solvents can be used for the terminal alkyne coupling reaction, such as tetrahydrofuran, tetrahydropyran, 1,4-dioxane, and the like. In certain embodiments, the solvent is DMF or DMSO.

[00111] The copper mediated terminal alkyne coupling reaction is typically conducted at elevated temperature. For example, the reaction can be conducted at 40-120 °C. In certain
20 embodiments, the copper mediated terminal alkyne coupling reaction is conducted at about 50 to about 120; about 50 to about 110; about 50 to about 100; about 60 to about 100; about 60 to about 90; or about 70 to about 90 °C. The copper mediated terminal alkyne coupling reaction usually requires 20 minutes to 3 hours.

[00112] The cyclization of the 1,3-diyne occurs by reaction with a suitable nucleophile. Suitable
25 nucleophiles include metal hydroxides, metal sulfides, and metal hydrosulfides. The nucleophile can be added to the reaction vessel directly or can be generated *in situ*, e.g., by reaction of the conjugate acid of the metal hydroxide, metal sulfide, and metal hydrosulfide with a suitable base or the reaction of S₈ and a Brønsted base or the conjugate base of the metal hydroxide with a suitable acid (e.g., water).

30 [00113] Exemplary metal hydroxides include hydroxides of alkali metals (Group I) and alkaline

earth metals (Group II). In certain embodiments, the metal hydroxide is LiOH, NaOH, KOH, CsOH, Mg(OH)₂, Ca(OH)₂, Sr(OH)₂, and Ba(OH)₂.

[00114] In certain embodiments, the nucleophile is a metal oxide, such as Li₂O, Na₂O, K₂O, CsO, MgO, CaO, SrO, and BaO, which upon reaction with a suitable conjugate acid, such as water,
5 generates the metal hydroxide.

[00115] Exemplary metal hydrosulfides include hydrosulfides of alkali metals (Group I) and alkaline earth metals (Group II). In certain embodiments, the metal hydroxide is LiSH, NaSH, KSH, CsSH, Mg(SH)₂, Ca(SH)₂, Sr(SH)₂, and Ba(SH)₂.

[00116] Exemplary metal sulfides include sulfides of alkali metals (Group I) and alkaline earth
10 metals (Group II). In certain embodiments, the metal hydroxide is Li₂S, Na₂S, K₂S, CsS, MgS, CaS, SrS, and BaS.

[00117] The nucleophile may also be generated *in situ* from the reaction of S₈ and a Brønsted base. Suitable Brønsted bases include LiOH, NaOH, KOH, and LiO*t*Bu, NaO*t*Bu, and KO*t*Bu.

[00118] The copper mediated terminal alkyne coupling reaction and the cyclization of the
15 1,3-diyne can advantageously occur sequentially in the same reaction vessel (i.e., two steps in one pot) without the need for purification between each step. In the alternative, the reactions can be conducted in different reaction vessels, with or without purification of the intermediary 1,3-diyne.

[00119] If the copper mediated terminal alkyne coupling reaction and the cyclization of the
20 1,3-diyne are conducted in the same reaction vessel, then reactants for the cyclization of the 1,3-diyne are simply added to the reaction vessel once the copper mediated terminal alkyne coupling reaction has substantially completed or halted and/or once undesired side products reach a certain concentration/begin to form.

[00120] The temperature that the cyclization of the 1,3-diyne reaction is conducted is determined in part on the reactivity of the nucleophile. Reactions that employ reactive nucleophiles (e.g.,
25 metal hydrosulfides) can generally be conducted at lower temperatures, whereas less reactive nucleophiles can require higher temperatures and/or longer reaction times. The cyclization of the 1,3-diyne reaction is typically conducted at elevated temperature. For example, the reaction can be conducted at 80-150 °C. In certain embodiments, the cyclization of the 1,3-diyne reaction is conducted at about 90 to about 150; about 100 to about 150; about 100 to about 140; about 100

to about 130; or about 110 to about 130 °C.

[00121] The present disclosure further provide articles of manufacture, for example, devices, that include a compound of the present disclosure and a substrate and/or a dielectric material. The substrate can be selected from, but is not limited to, doped silicon, an indium tin oxide (ITO), ITO-coated glass, ITO-coated polyimide or other plastics, aluminum or other metals alone or coated on a polymer or other substrate, a doped polythiophene, and the like. The device can include one or more electrical contacts. Such electrical contacts can be made of a metal (e.g., gold) and can function as source, drain, or gate terminal. One or more of the devices described above can be included within various organic electronic devices such as organic thin film transistors (OTFTs), as well as capacitors, and the like.

[00122] As certain embodiments of the compounds disclosed herein can be soluble in common solvents, the compounds described herein can offer processing advantages when used to fabricate electronic devices, such as organic thin film semiconductor devices, organic field-effect devices, organic light emitting diodes (OLEDs), organic photovoltaic systems, organic photodetectors, organic capacitors, and organic sensors.

[00123] The present disclosure, therefore, further provides methods of preparing an organic semiconductor material. The methods can include preparing a precursor composition, prepared in accordance with the methods described herein, that includes a compound disclosed herein in one or more organic solvents, depositing the precursor composition on a substrate to provide a semiconductor material precursor, and heating the semiconductor precursor to provide a semiconductor material that includes a compound disclosed herein. In some embodiments, the depositing step can be carried out by printing, including inkjet printing and various contact printing techniques (e.g., screen-printing, gravure, offset, pad, and microcontact printing). In certain embodiments, the depositing step can be carried out by spin coating, drop-casting, dip coating, blade coating, or spraying.

[00124] Another aspect of the present disclosure relates to methods for fabricating organic field effect transistors that incorporate a compound described herein. The compounds described herein can be used to fabricate various types of organic field effect transistors.

[00125] Various articles of manufacture, structures, and devices that make use of the compounds disclosed herein are also within the scope of the present disclosure. Examples of such articles

include, but are not limited to, organic field effect transistors.

Synthesis, Characterization Representative Compounds of TPE-F and TPE-T

Example 1

[00126] Synthesis of TPE-F and TPE-T by diyne cyclization

- 5 [00127] To a round bottom flask were added compound **10** (100 mg, 0.14 mmol), CuCl (0.7 mg, 5 % mmol) and KOH (2 mg, 0.04 mmol) in dimethylsulfoxide (DMSO) (2 mL), and H₂O (0.1 mL) or Na₂S·9H₂O (33.6 mg, 0.14 mmol). The mixture was stirred at 120 °C for 30 min, giving TPE-F in a yield of 82% or TPE-T in quantitative yield.

Example 2

- 10 [00128] Synthesis of TPE-F and TPE-T by one-pot method

[00129] A mixture of compound **10** (200 mg, 0.56 mmol) and CuCl (3 mg, 5 % mmol) in DMSO (4 mL) was stirred at 80°C for 8 h. KOH (31 mg, 0.56 mmol) and H₂O (0.2 mL) or KOH (9.4 mg, 0.17 mmol) and Na₂S·9H₂O (33.6 mg, 0.14 mmol) were then added and after the reaction mixture was stirred at 120 °C for 30 min, TPE-F and TPE-T were obtained in 75% and
15 90% yields, respectively. TPE-F and TPE-T were purified by column chromatography and characterized by standard spectroscopic methods.

[00130] TPE-F: ¹H NMR (400 MHz, CDCl₃, δ): 7.45–7.43 (d, *J* = 8 Hz, 4H), 7.20–7.09 (m, 36H); ¹³C NMR (100 MHz, CDCl₃, δ): 153.3, 143.7, 143.6, 142.9, 141.2, 131.8, 131.4, 131.3, 128.7, 127.8, 127.7, 127.6, 126.5, 126.4, 122.9, 107.3; HRMS (MALDI-TOF): *m/z*: [M]⁺ calcd for C₅₆H₄₀O, 728.3079; found, 728.3107.
20

[00131] TPE-T: ¹H NMR (400 MHz, CDCl₃, δ): 7.43–7.40 (d, *J* = 8 Hz, 4H), 7.11–7.02 (m, 34H), 6.62 (s, 2H); ¹³C NMR (100 MHz, CDCl₃, δ): 143.7, 143.6, 143.2, 143.0, 141.2, 140.3, 132.2, 131.9, 131.4, 131.3, 127.8, 127.7, 127.6, 126.6, 126.5, 126.4, 124.7, 123.8; HRMS (MALDI-TOF): *m/z*: [M]⁺ calcd for C₅₆H₄₀S, 744.2851; found, 744.2873.

- 25 [00132] Other derivatives were synthesized by diyne cyclization

Photophysical Properties

[00133] The optical properties of TPE-F and TPE-T were characterized by UV-visible and PL spectroscopies. The UV spectra of TPE-F and TPE-T were similar and peaked at 378 nm, which was indicative of their similar electronic structure in the ground state.

[00134] Both TPE-F and TPE-T showed aggregation induced emission (AIE) characteristics, e.g., their weak emission in dilute THF solutions was enhanced upon aggregate formation.

[00135] The AIE characteristics of TPE-F and TPE-T were further demonstrated by studying their PL behaviors in THF and THF/water mixtures with different water fractions (f_w). In dilute THF solution, both TPE-F and TPE-T were weakly emissive owing to the active intramolecular motion, which consumed the energy of the excited state through non-radiative relaxation pathway (Figure 6 and 11). Addition of a large amount of water into the THF solutions caused aggregates to form, which enhanced their PL. The highest emission was achieved at a f_w of 99%.

[00136] Compared with TPE-T, the aggregates of TPE-F surprisingly showed a stronger PL. The quantum yields of TPE-F and TPE-T in dilute THF solutions were determined to be 3.5% and 3.7% by a calibrated integrating sphere. In the solid state, their quantum yields were measured to be 50% and 18%. These results indicate that TPE-F advantageously shows a more efficient emission than TPE-T in the solid state, demonstrating that furan is more favorable in affording luminophores with stronger emission than thiophene.

Table 1. Fluorescence lifetime and decay of TPE-F and TPE-T

	$\langle\tau\rangle$ (ns)		$k_r/k_{nr} (\times 10^8 \text{ s}^{-1})$	$k_r/k_{nr} (\times 10^8 \text{ s}^{-1})$
	soln	solid	soln	solid
TPE-F	0.44	3.57	0.79/21.9	1.4/1.4
TPE-T	0.50	0.96	0.74/19.3	1.9/8.5

^{a)} Abbreviation: $\langle\tau\rangle$ = fluorescence lifetime, k_r = radiative decay rate,

k_{nr} = non-radiative decay rate

Chromic Properties of TPE-F and TPE-T

[00137] Chromic materials are a class of smart materials which can switch between different colors in the presence of external stimuli, and have attracted great attention for their importance in both fundamental research and practical applications. Many AIE-active materials have been reported with reversible mechanochromic or thermochromic properties, but the associated mechanism for guiding their design and synthesis has not been well investigated. We thus studied the chromic properties of TPE-F and TPE-T and explained the change in their chromic

properties in the presence of external perturbation by X-ray diffraction and crystallographic analysis. Both TPE-F and TPE-T exhibited color and fluorescence changes upon solvent fuming and mechanical grinding. Compared with TPE-T, TPE-F showed larger color and fluorescence contrast (Figure 7). For example, the crystalline powder of TPE-F precipitated from hexane was white in color and showed deep blue luminescence. After fuming with DCM or mechanical grinding, the powder was amorphorized, red-shifting its color and fluorescence to yellow and yellowish-green, respectively. The powder of TPE-T turned to pale yellow color and emitted sky-blue light after fumed by hexane, while that treated with DCM vapor fuming or mechanical grinding force appeared yellow and now showed green fluorescence.

[00138] By measuring their PL spectra after treatment with solvent vapor, we found that the emission of TPE-F red-shifted by 61 nm, while TPE-T showed a PL red-shift of 30 nm. The longer-wavelength absorption and emission indicates that the molecular structure becomes more planar when transformed from crystalline to amorphous state. The larger torsion angles in TPE-F may endow it with a greater conformation change when an external stimulus is applied, thus explaining its larger chromic shift as compared with TPE-T.

[00139] It is also worthy to note that the fluorescence of ground powder of TPE-F can be fully recovered to the original blue one in the absence of hexane vapor fuming, as supported by the recuperative diffraction peaks that appeared in its X-ray diffractogram after 12 h storage. Without wishing to be bound by theory, it is believed that this observation stems from stronger intermolecular interactions and more dense molecular packing of TPE-F in the solid state.

The Electrochemical, Charge Transporting Properties and OLED performance

[00140] The HOMO and LUMO of the TPE-F and TPE-T were determined by cyclic voltammetry (CV) measurement (Figure 13). Both TPE-F and TPE-T showed two reversible or quasi-reversible oxidation waves with onset oxidative potentials of 0.83 and 1.03 V, respectively. The HOMO/LUMO of TPE-F and TPE-T estimated from CV were -5.31/-2.41 and -5.41/-2.51 eV, respectively. The higher HOMO energy level of TPE-F is an advantage for hole injection. This data is summarized in Table 2 below.

Table 2. Optical and Thermal Properties of TPE-F and TPE-T

λ_{abs} (nm)	λ_{em} (nm)		Φ_F (%)		HOMO (eV)	LUMO (eV)	T_d/T_g (°C)
	soln	aggregate	soln	solid			

TPE-F	378	488	491	3.5	50	-5.31	-2.41	388/129
TPE-T	378	479	487	3.7	18	-5.41	-2.51	407/125

^{a)} Abbreviation: λ_{abs} = absorption maximum, λ_{em} = emission maximum, Φ_F = fluorescence quantum yield, HOMO = highest occupied molecular orbitals, LUMO = lowest unoccupied molecular orbitals, T_d = temperature for 5% weight loss measured by TGA, T_g = glass transition temperature determined by DSC.

- 5 [00141] The charge-transporting properties of TPE-F and TPE-T were evaluated from their OFET devices with top-gate bottom-contact configurations (Figure 14) and the corresponding data is summarized in Table 3.

Table 3. Characteristics of OFETs based on TPE-F at different annealing temperatures.

Active layer	T (°C)	V_T (V)	I_{on}/I_{off}	μ_h (max) ($10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$)
TPE-F	25	-36	10^4	0.35
	80	-37	10^4	0.7
	120	-37	10^3	0.37
TPE-T	25	-51	10^2	0.0075
	80	-61	10^3	0.0043
	120	-37		

- 10 [00142] Films TPE-F and TPE-T were deposited by spin-coating method of their from dichlormethane solutions of TPE-F and TPE-T, which gave an amorphous film. The hole mobility of TPE-F was two orders magnitude higher than TPE-T, thanks to its better charge injection and more compact molecular packing.

- 15 [00143] The strong solid-state PL, higher charge transporting property and good thermal and morphological stabilities of TPE-F inspired the investigation of its EL properties. A non-doped multilayer EL device with a configuration of ITO/NPB (60 nm)/TPE-F (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm) (device I) was fabricated by vapor deposition process, in which TPE-F served as emitter, NPB worked as hole-transporting layer, 2,2',2''-(1,3,5-benzinetriyl)tris(1-phenyl-1-H-benzimidazole) (TPBi) functioned as both a hole-blocking and electron-transporting material, respectively.

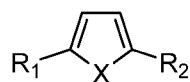
- 20 [00144] Figure 8 shows the EL spectrum and the device performance. The device radiated bright green light with a low turn-on voltage of 3.3 V. The maximum luminescence (L), current efficiency (η_c), power efficiency (η_p) and external quantum efficiency attained by the device

were 24298 cd/m², 9.98 cd/A, 7.02 lm/W and 3.67%, respectively. Comparing these values with properties of other AIEgens bridged with different heteroaromatics such as benzo-2,1,3-thiadiazole and silole with the same device structure, the performance of TPE-F was better.

- 5 [00145] It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are included within the spirit and purview of this application and scope of the appended claims.

CLAIMS

1. A compound of Formula 1:

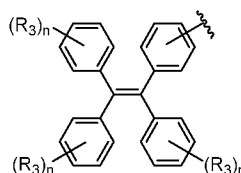


1

wherein

X is sulfur or oxygen;

each of R₁ and R₂ is independently a moiety of Formula 2:



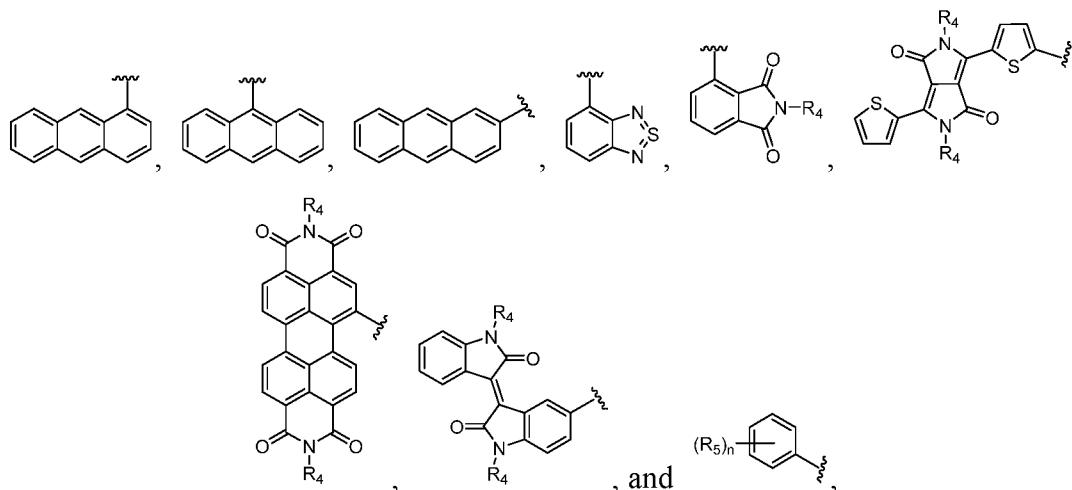
2

wherein

each instance of n is independently selected between 1, 2, or 3;

each instance of R₃ is independently selected from the group consisting of hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, alkoxy, and amino;

each of R_1 and R_2 is independently selected from the group consisting:

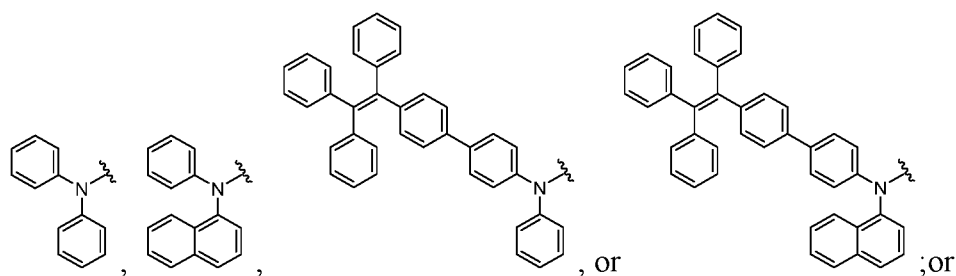


wherein

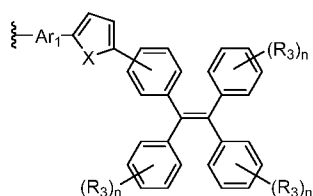
n is 1, 2, 3, or 4;

R₄ is hydrogen, alkyl, cycloalkyl, aryl, or heteroaryl;

each instance of R₅ is independently hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl,
heteroaryl, amino, ketone, nitro, nitrile, halide, ester, sulfone,

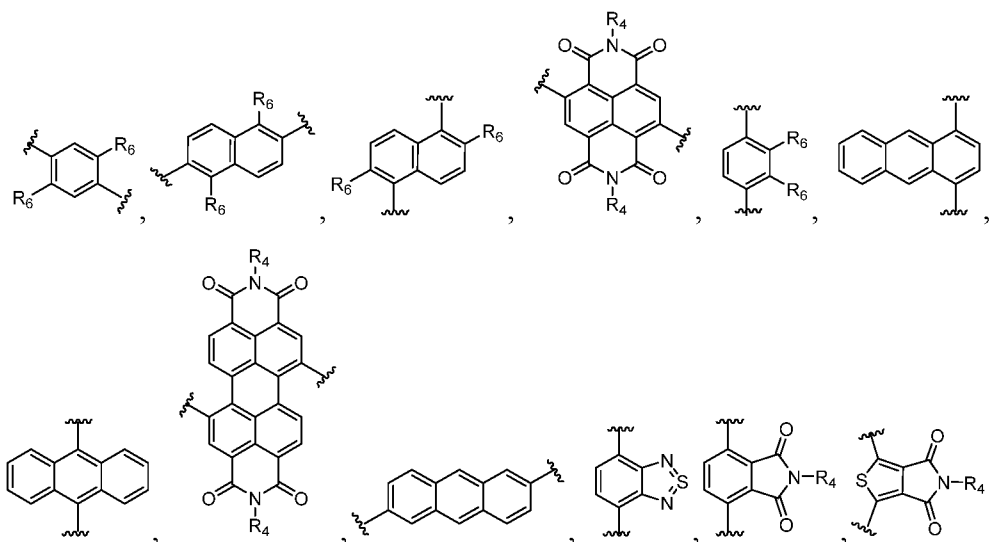


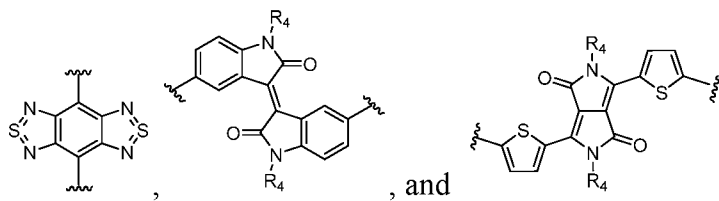
R₁ is the moiety of Formula 2 and R₂ is a moiety of Formula 3:



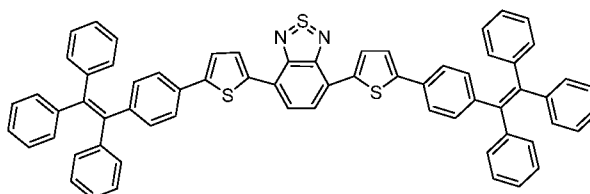
3

wherein Ar₁ is selected from the group consisting of:



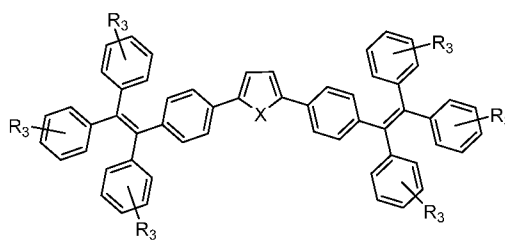


wherein independently for each instance R₆ is hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, alkoxy, amino, ester, sulfone, halide, nitrile or nitro; and with the proviso that a compound of Formula 4 is excluded:



4.

2. The compound of claim 1, wherein the compound has Formula 5:



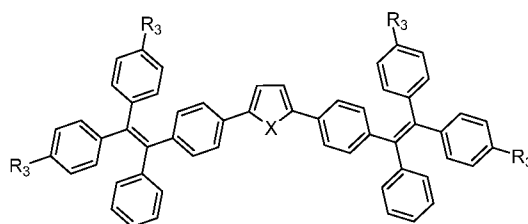
5

wherein

X is sulfur or oxygen;

each instance of R₃ is independently selected from the group consisting of hydrogen, C₁-C₂₀ alkyl, C₁-C₂₀ alkoxy, and C₁-C₁₄ diacylamino.

3. The compound of claim 2, wherein the compound has Formula 6:



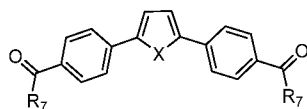
6

wherein

X is sulfur or oxygen;

each instance of R_3 is independently selected from the group consisting of hydrogen, C_1 - C_{13} alkyl, C_1 - C_{13} alkoxy, and C_1 - C_6 dialkylamino.

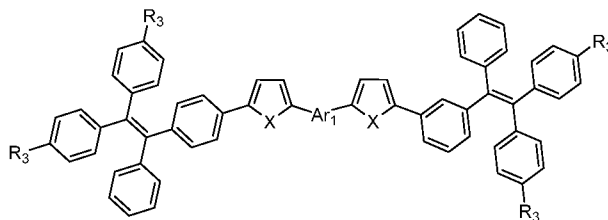
- 5 4. The compound of claim 3, wherein R_3 is hydrogen or diethylamino.
5. The compound of claim 1, wherein the compound has Formula 7:



7

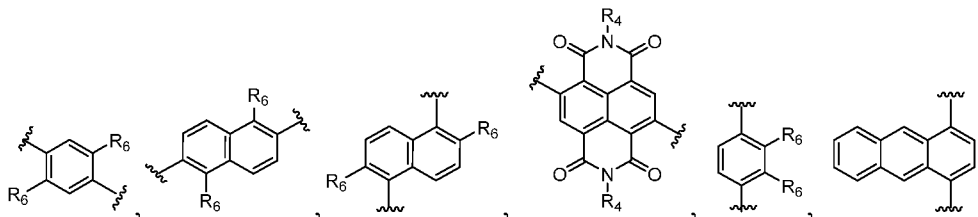
wherein

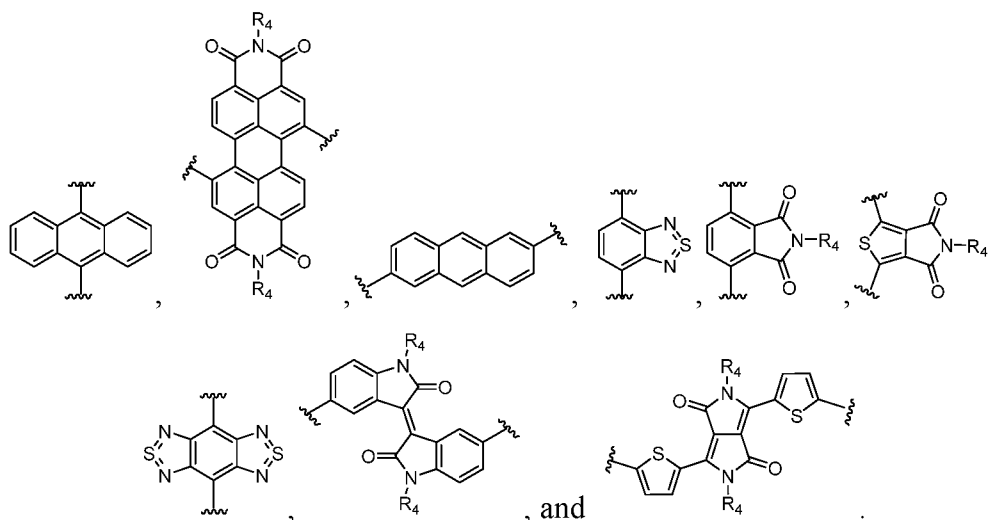
- 10 each instance of R_7 is independently selected from the group consisting of alkyl, cycloalkyl, optionally substituted aryl, and optionally substituted heteroaryl.
6. The compound of claim 5, wherein R_7 is phenyl.
7. The compound of claim 1, wherein the compound has Formula 8:



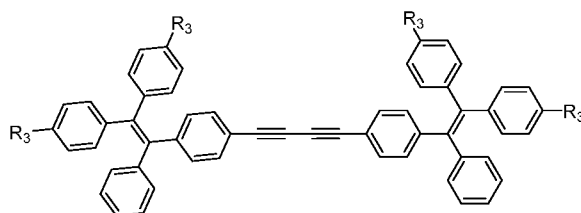
8

wherein each instance of R_3 is independently selected from the group consisting of hydrogen, C_1 - C_{20} alkyl, C_1 - C_{20} alkoxy, and C_1 - C_{14} dialkylamino; and Ar_1 is





8. The compound of any one of claims 1-7, wherein X is oxygen.
9. A method for preparing the compound of claim 3 comprising the step of contacting a compound of Formula 8

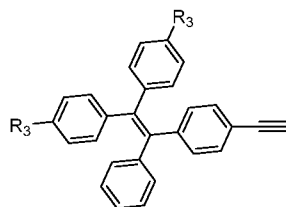


8

wherein R₃ is as defined in claim 3, with a nucleophile selected from the group consisting of a metal hydroxide, a metal sulfide, and a metal hydrosulfide; or S₈ and a Brønsted base; thereby forming the compound of claim 3.

10. The method of claim 9, wherein the metal hydroxide is NaOH, KOH, CsOH, or a combination thereof.
11. The method of claim 9, wherein the step of contacting a compound of Formula **8** with a nucleophile or S₈ and a Brønsted base occurs in a solvent selected from dimethyl sulfoxide (DMSO), dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), hexamethylphosphoramide (HMPA), 1,3-dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone (DNPU), acetonitrile, or a combination thereof.
12. The method of claim 9, further comprising the step of contacting a compound of

Formula 9

**9**

wherein R_3 is as defined in claim 3, with a copper(I) salt thereby forming the compound of Formula 8.

13. The method of claim 12, wherein the copper(I) salt is selected from copper(I)iodide, copper(I)bromide, copper(I)chloride, or a combination thereof.

14. The method of claim 12, wherein the step of contacting the compound of Formula 9 with the copper(I) salt and the step of contacting the compound of Formula 8 with the nucleophile or S_8 and the Brønsted base occur in the same reaction vessel.

15. The method of claim 14, wherein the step of contacting a compound of Formula 9 with the copper salt occurs in a solvent selected from dimethyl sulfoxide (DMSO), dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), hexamethylphosphoramide (HMPA), 1,3-dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone (DNPU), acetonitrile, or a combination thereof.

16. The method of claim 14, wherein R_3 is hydrogen or diethylamino.

17. The method of any one of claims 9-16, wherein the nucleophile is a metal hydroxide.

18. A thin film comprising the compound of any one of claims 1-8.

19. A nanoparticle comprising the compound of any one of claims 1-8.

20. An organic field-effect transistor, organic light-emitting diode, or an organic photovoltaic cell comprising the compound of any one of claims 1-8.

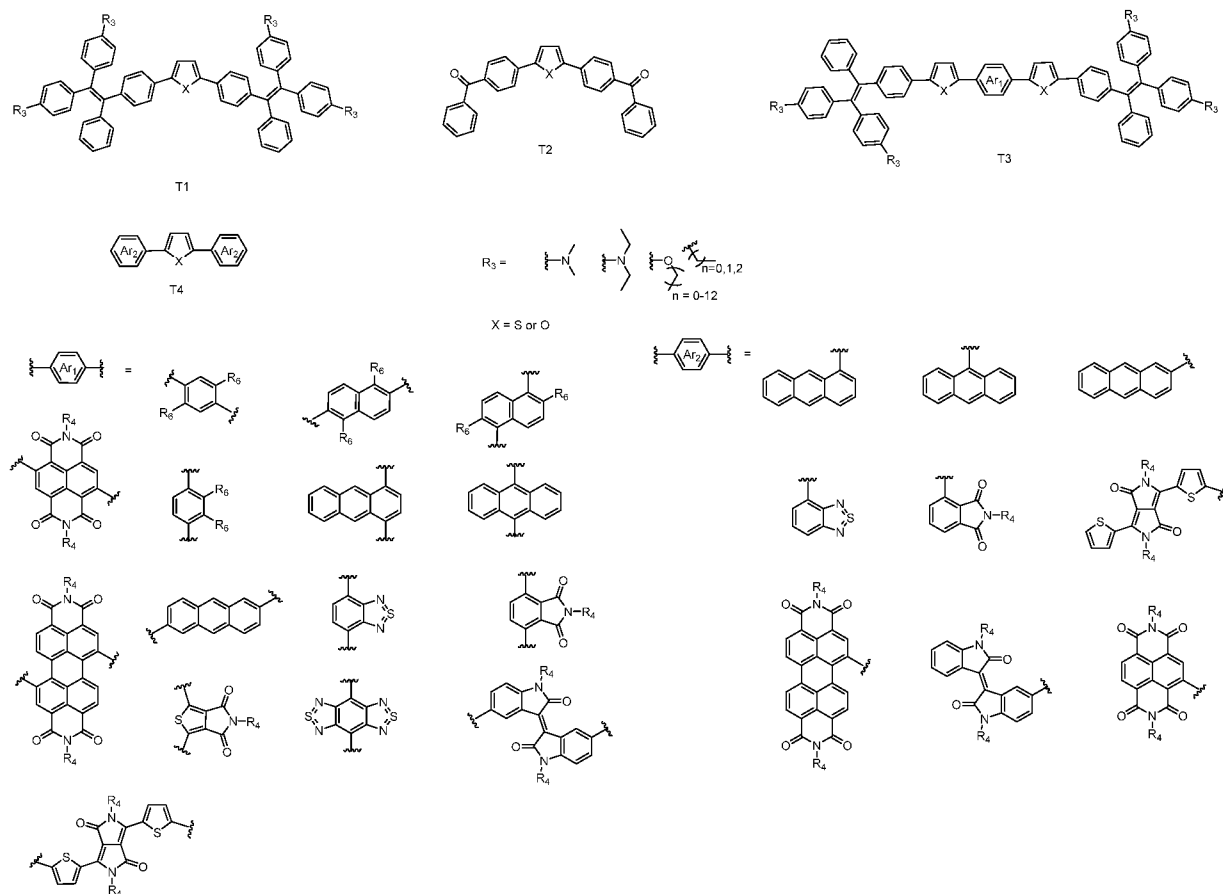


Fig. 1

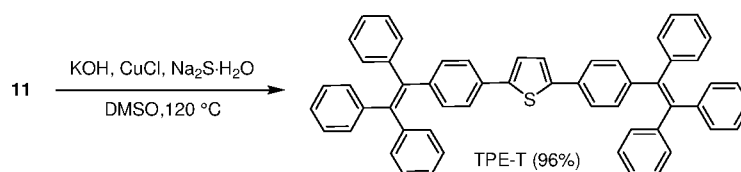
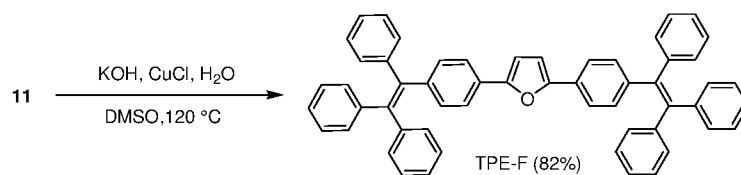
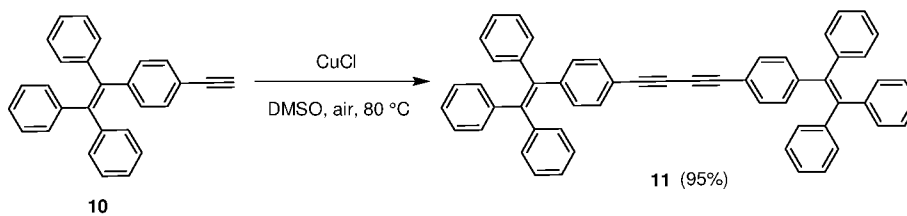
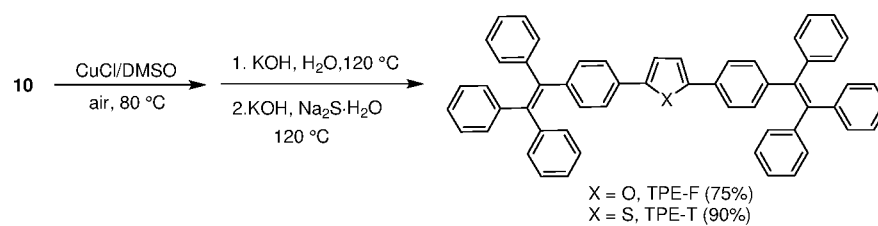
A Diyne cyclization**B** One-pot method

Fig. 2A

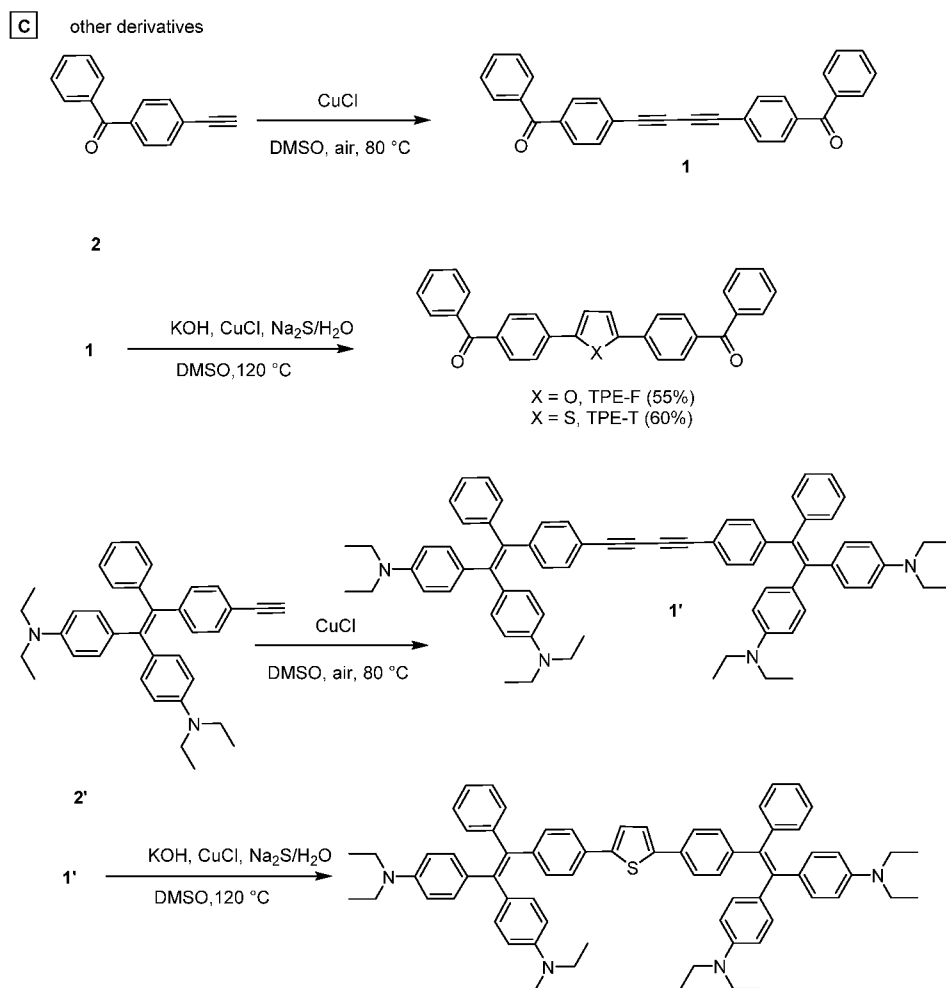


Fig. 2B

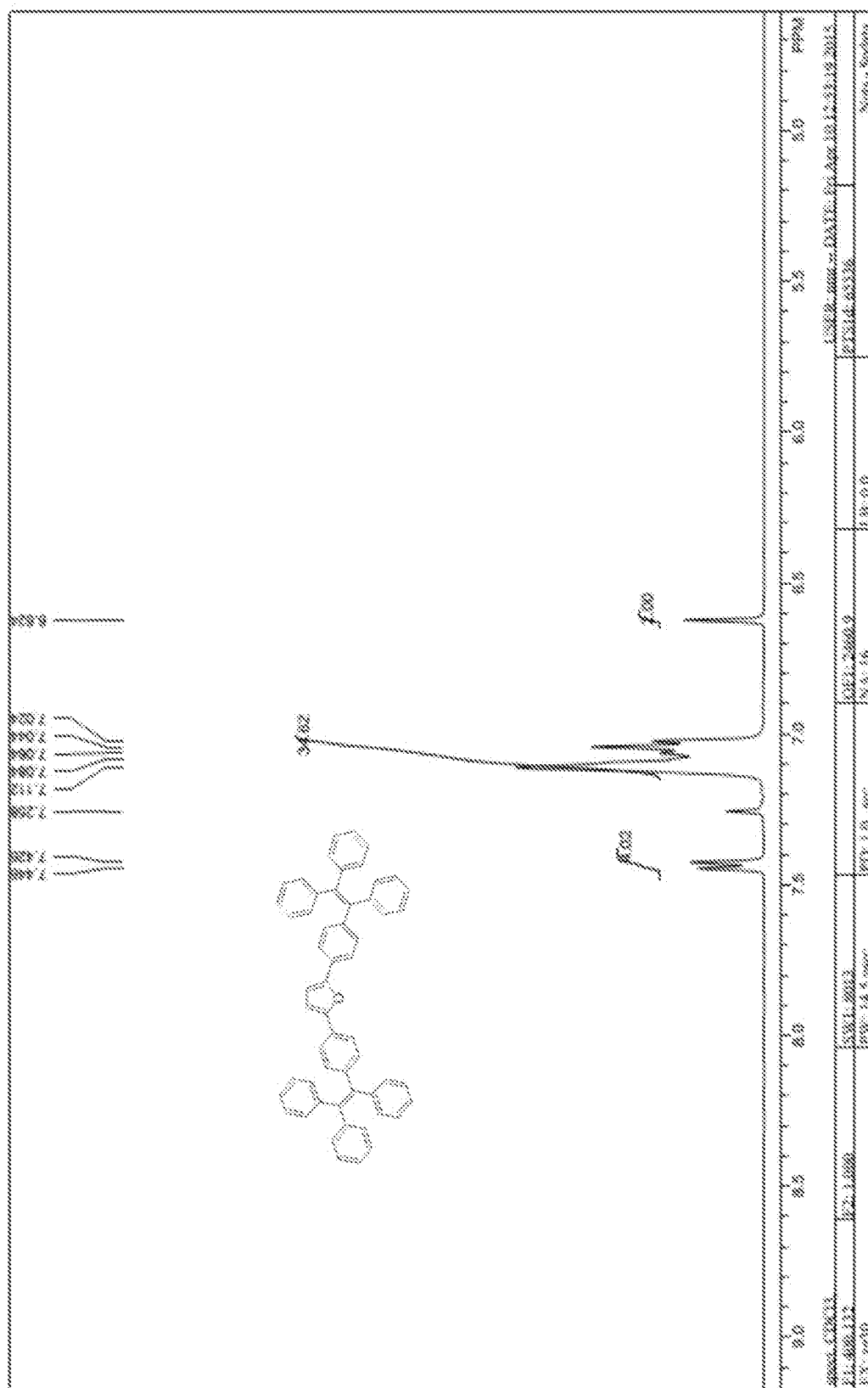


Fig. 3A

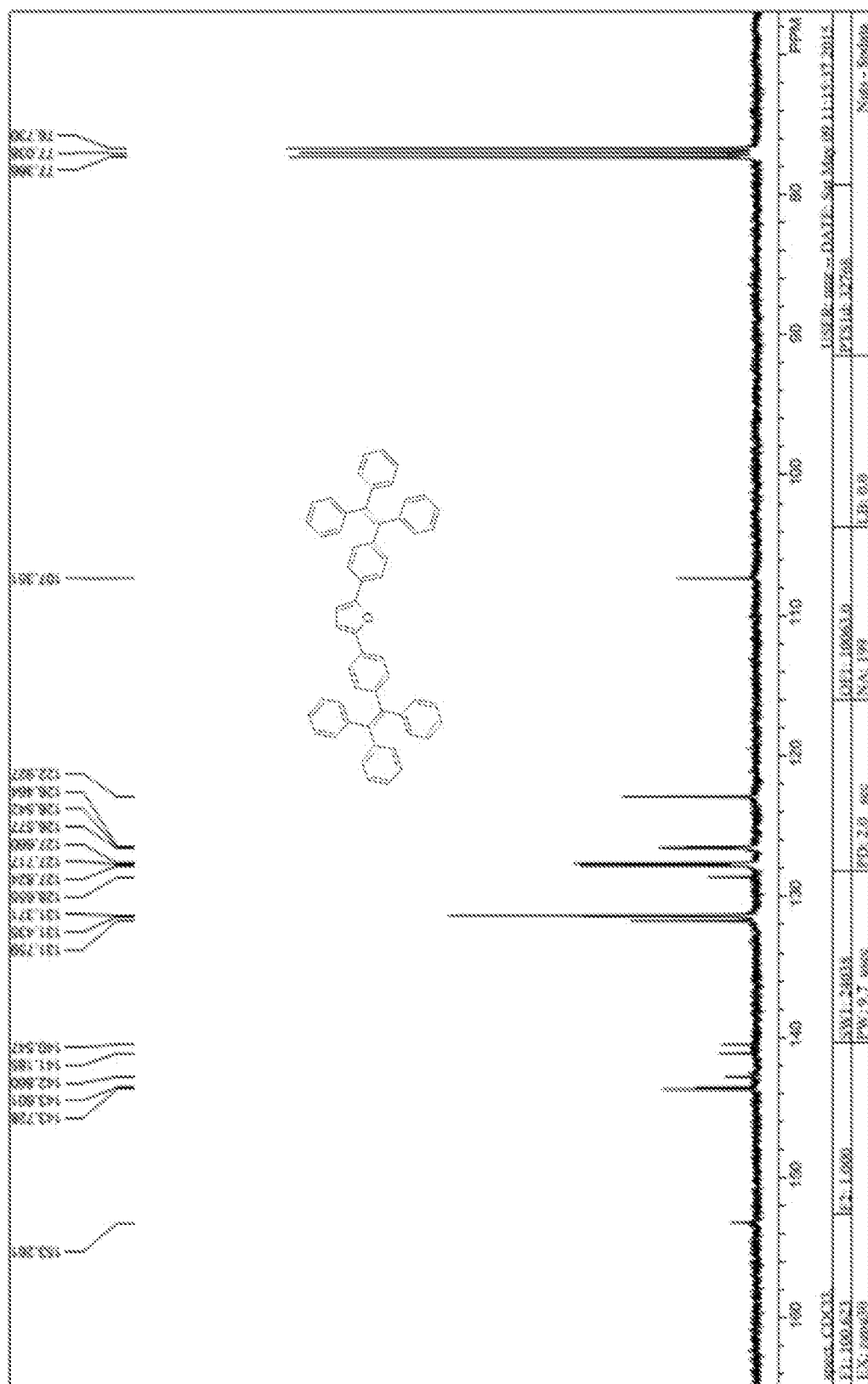


Fig. 3B

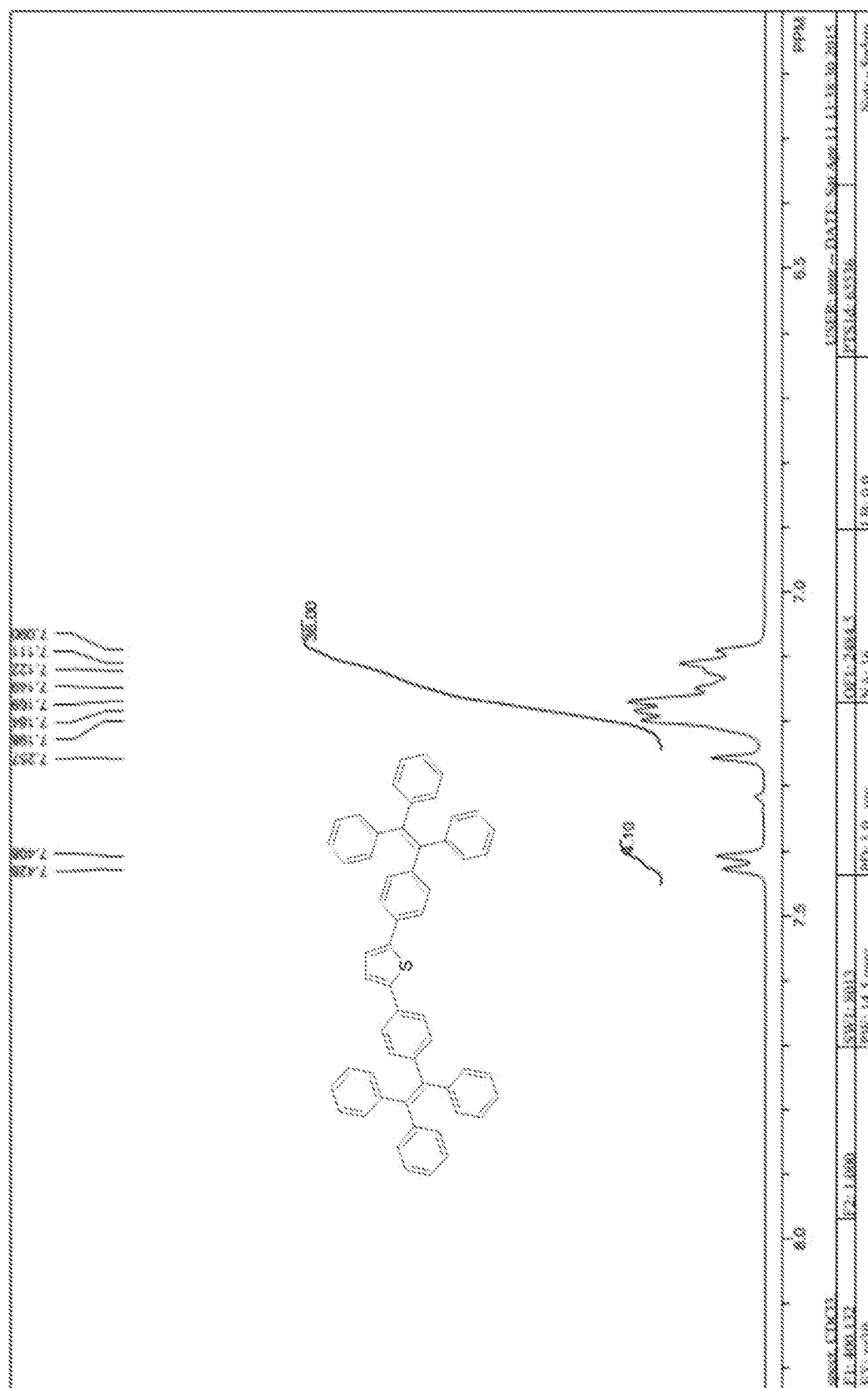


Fig. 4A

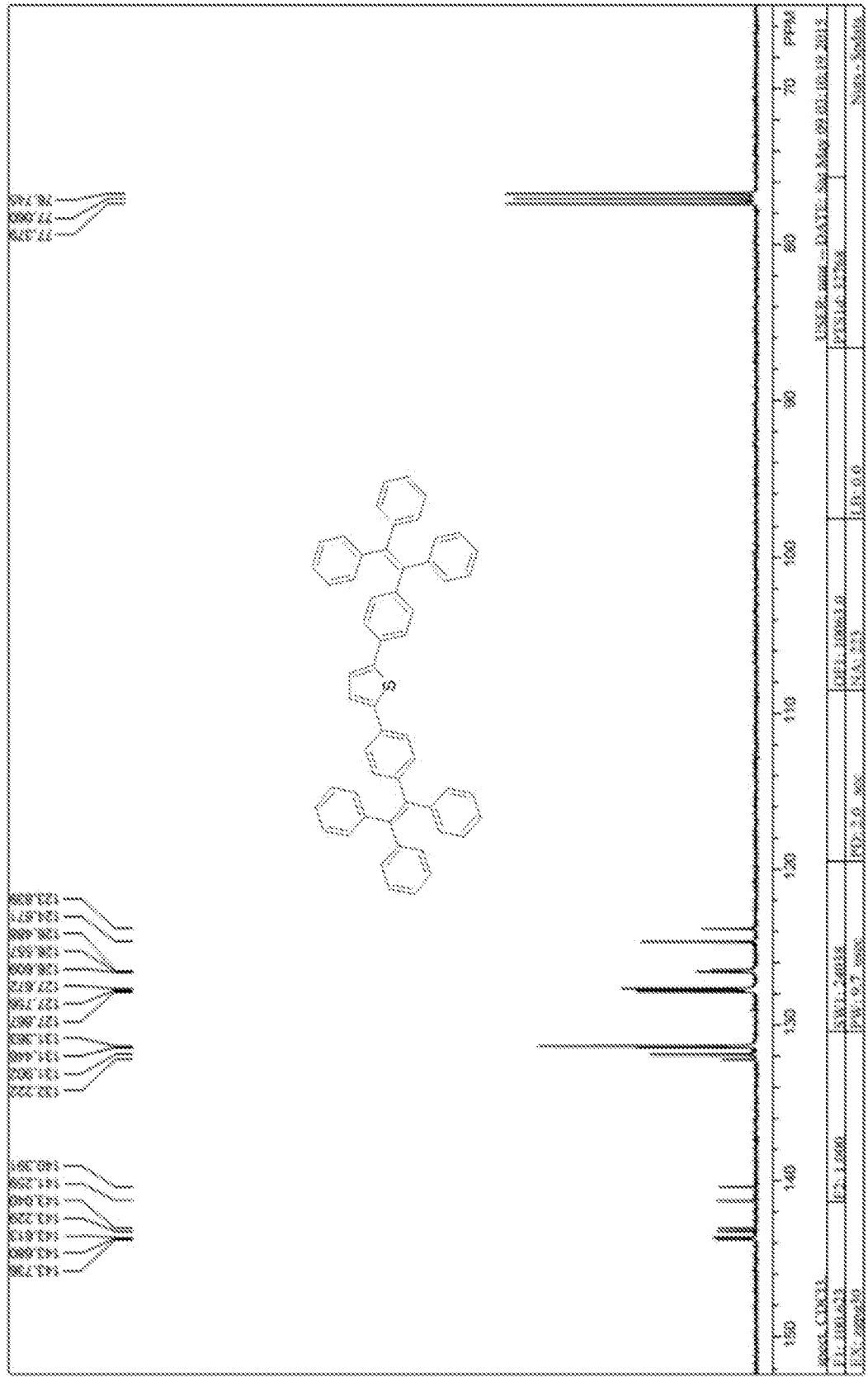


Fig. 4B

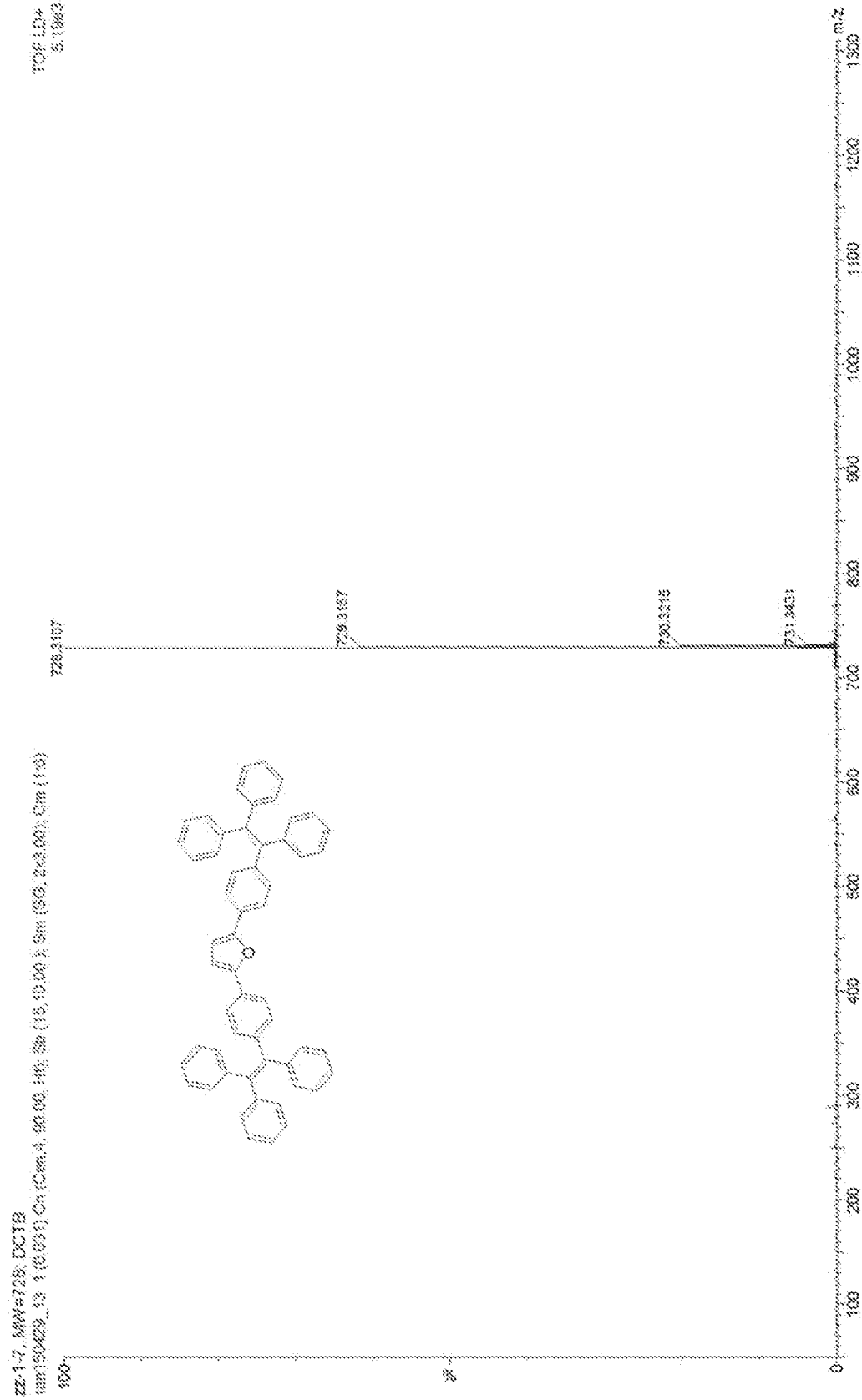
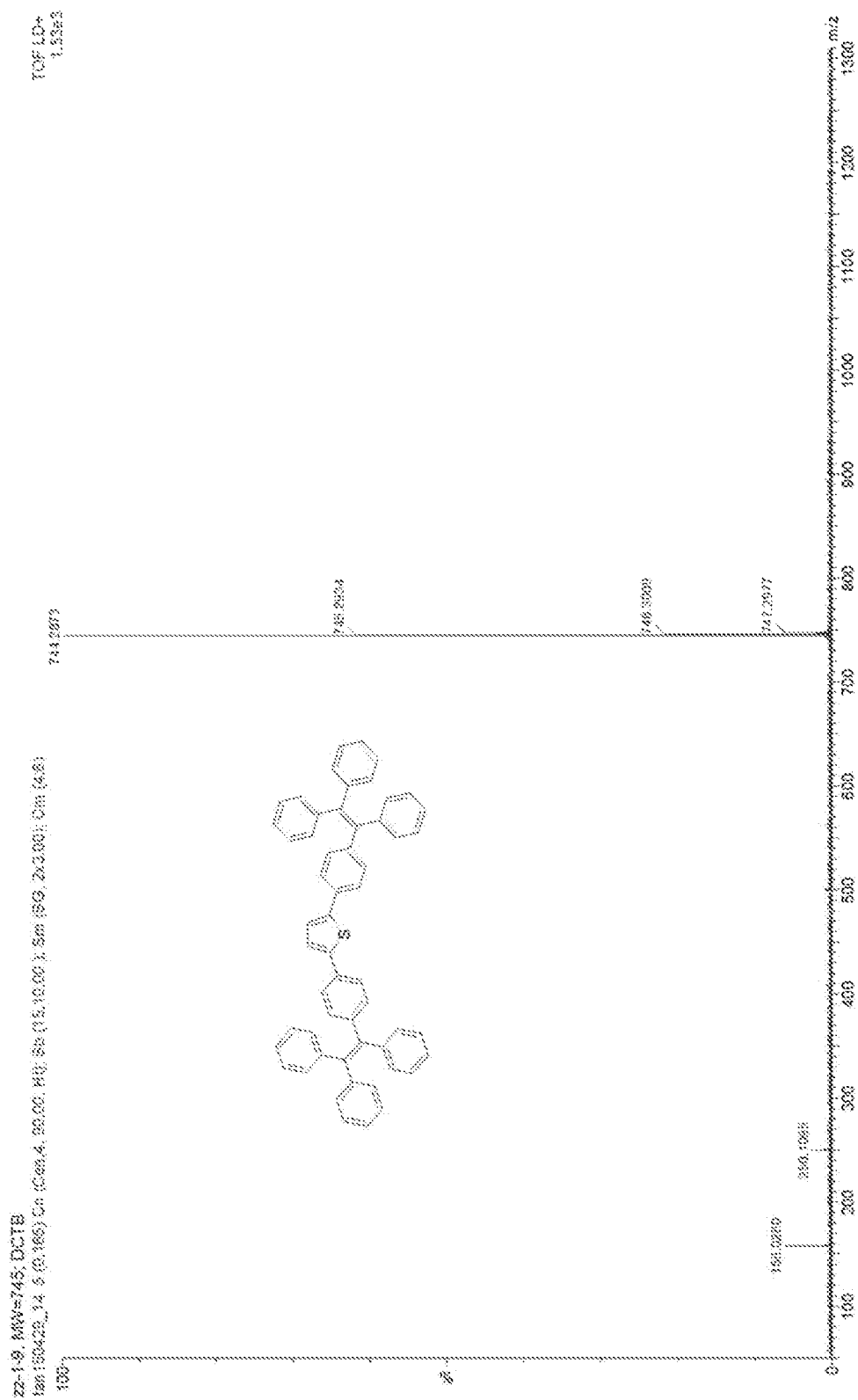


Fig. 5A



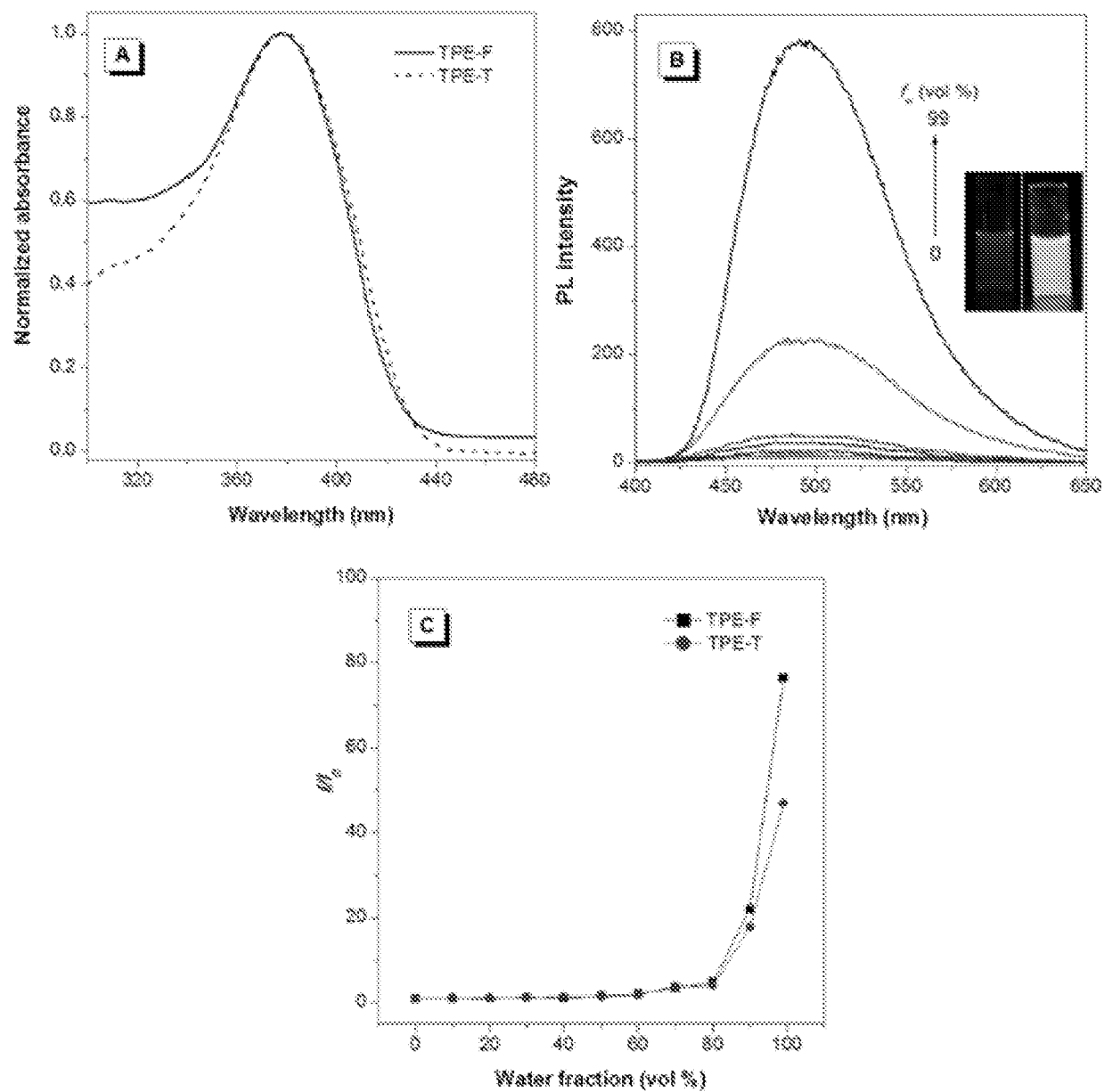


Fig. 6

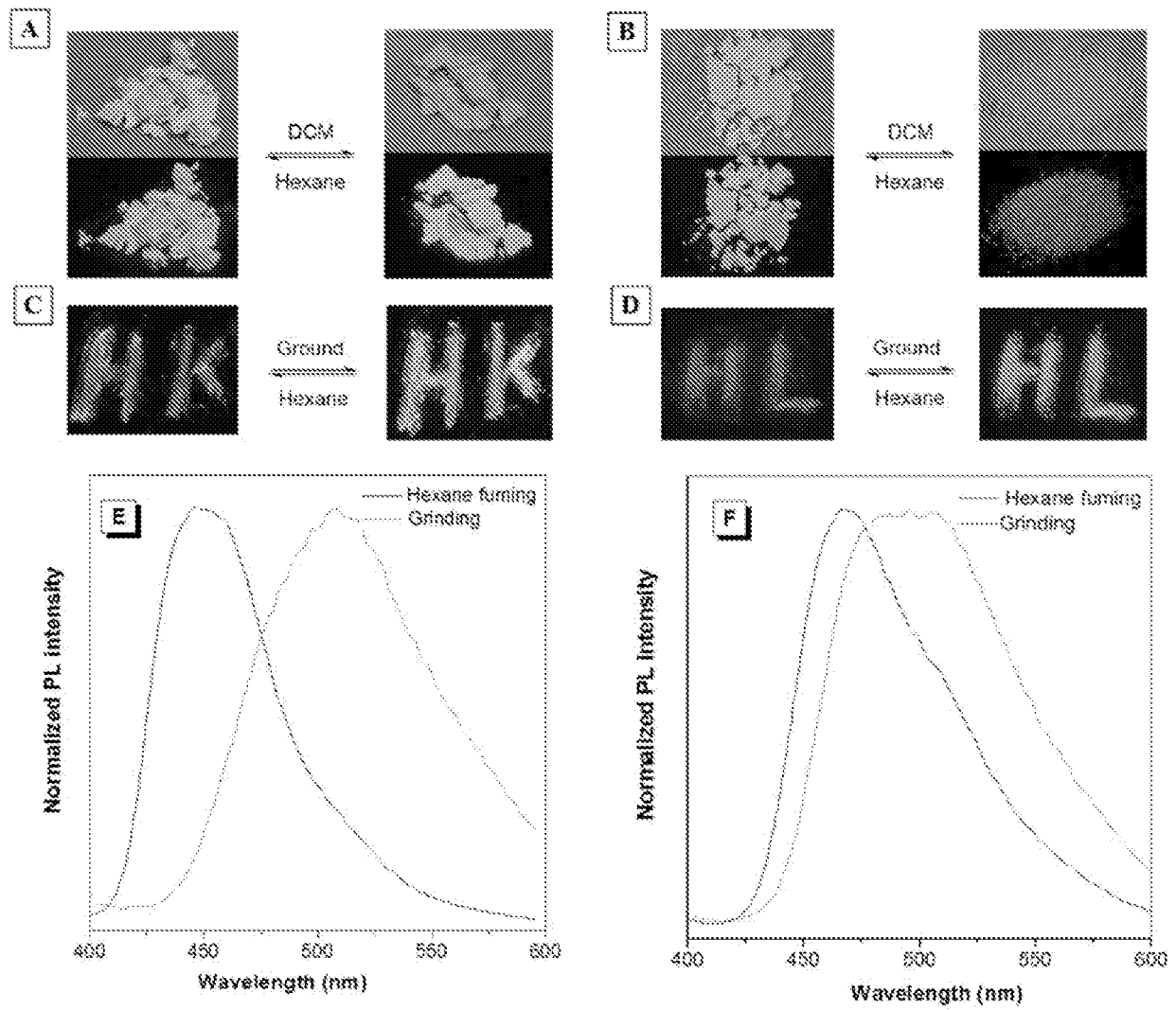


Fig. 7

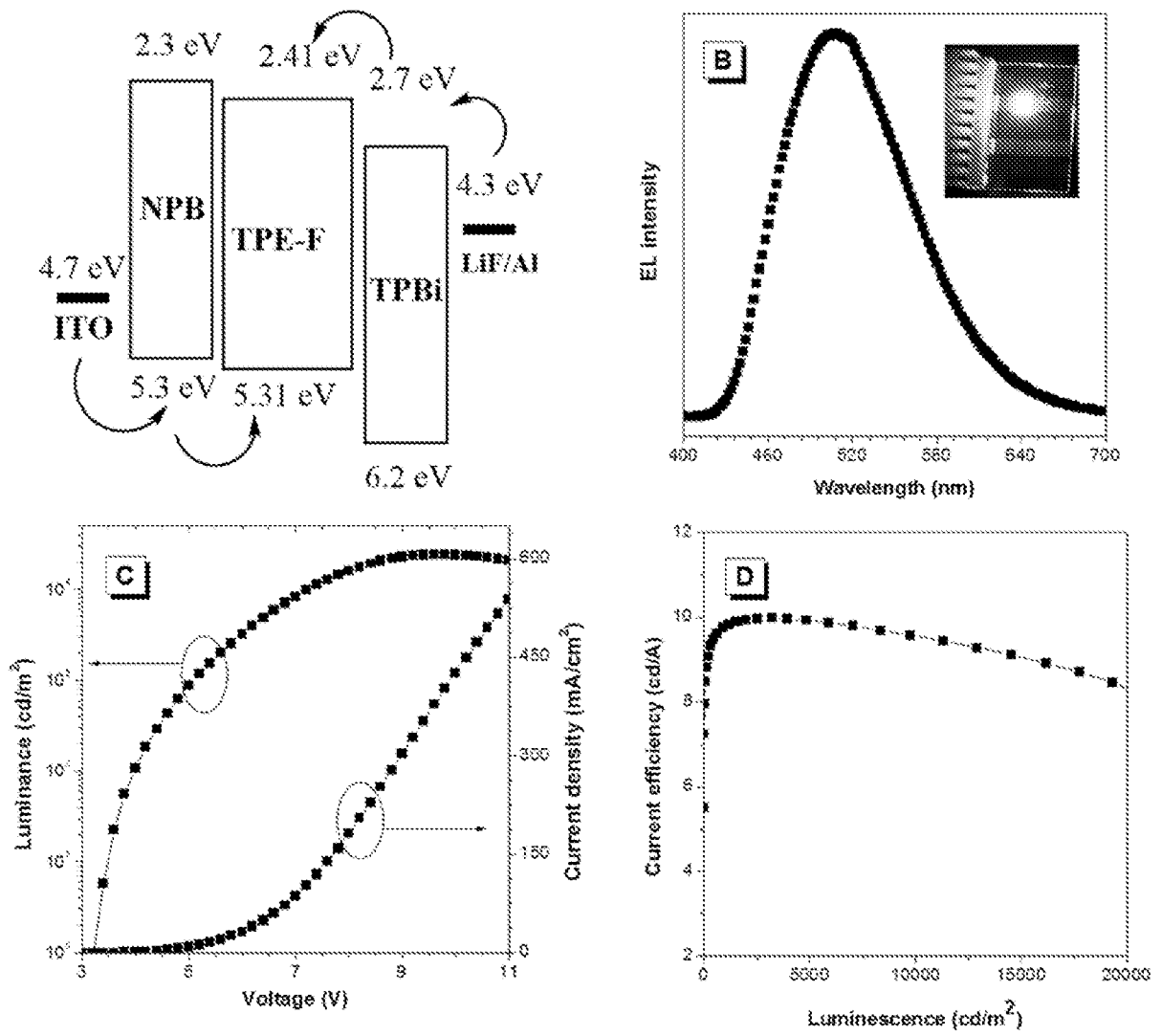


Fig. 8

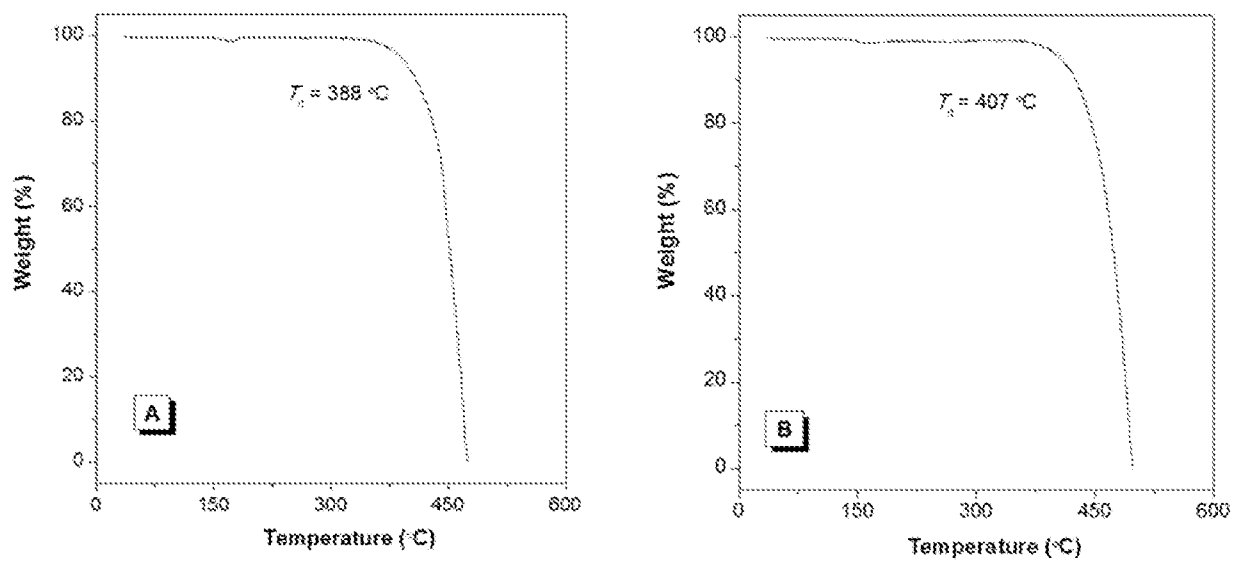


Fig. 9

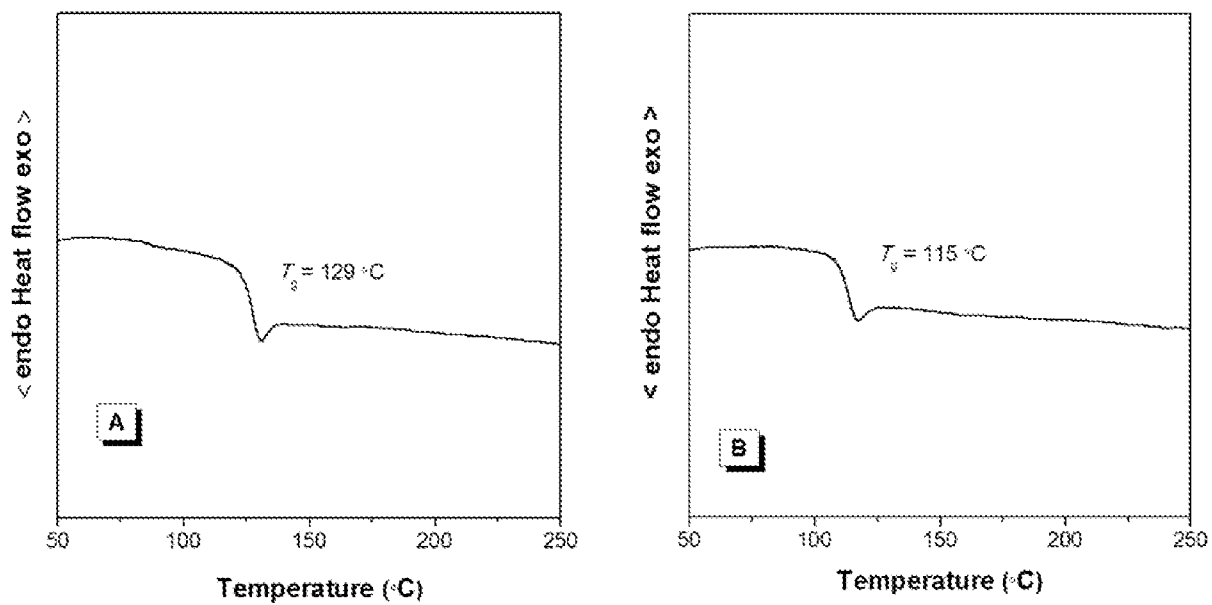


Fig. 10

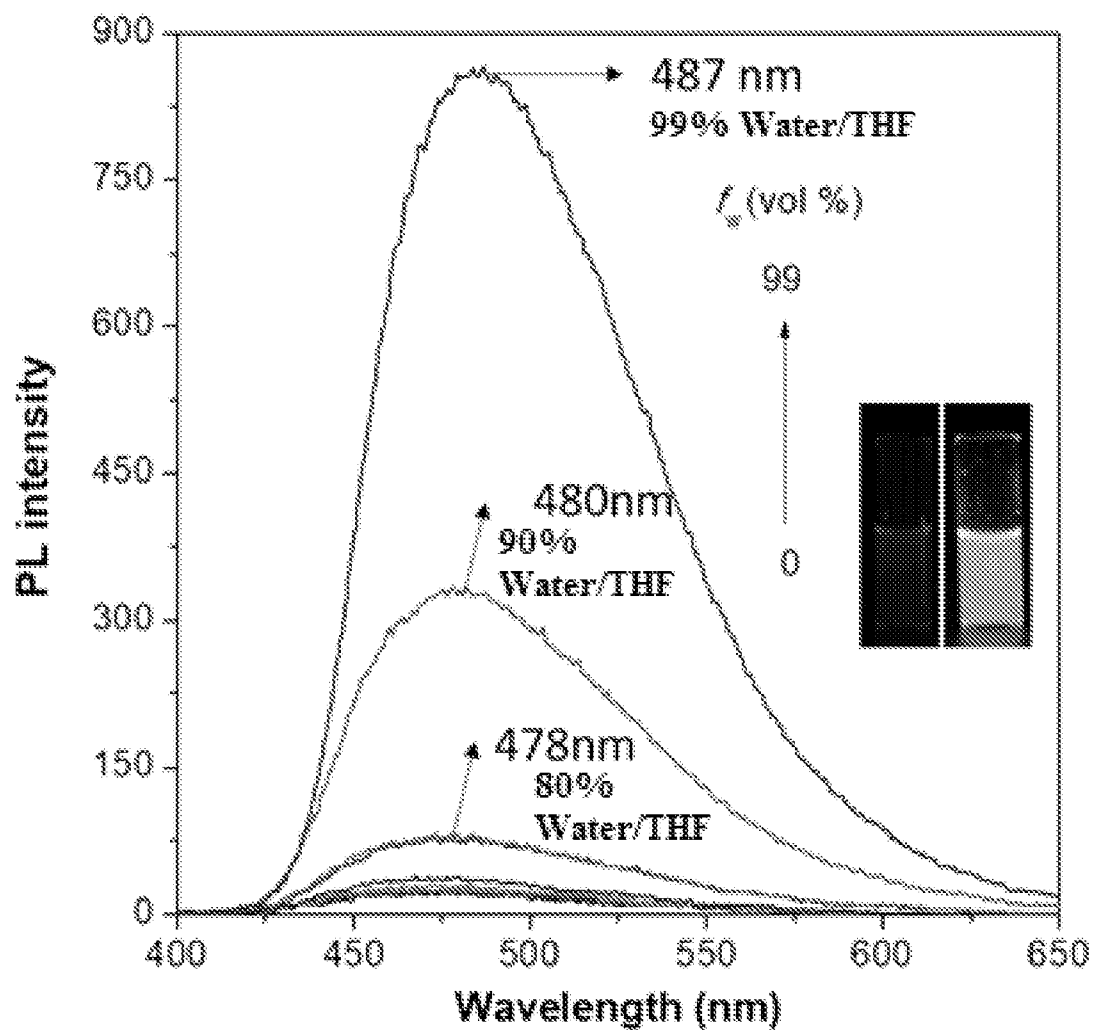
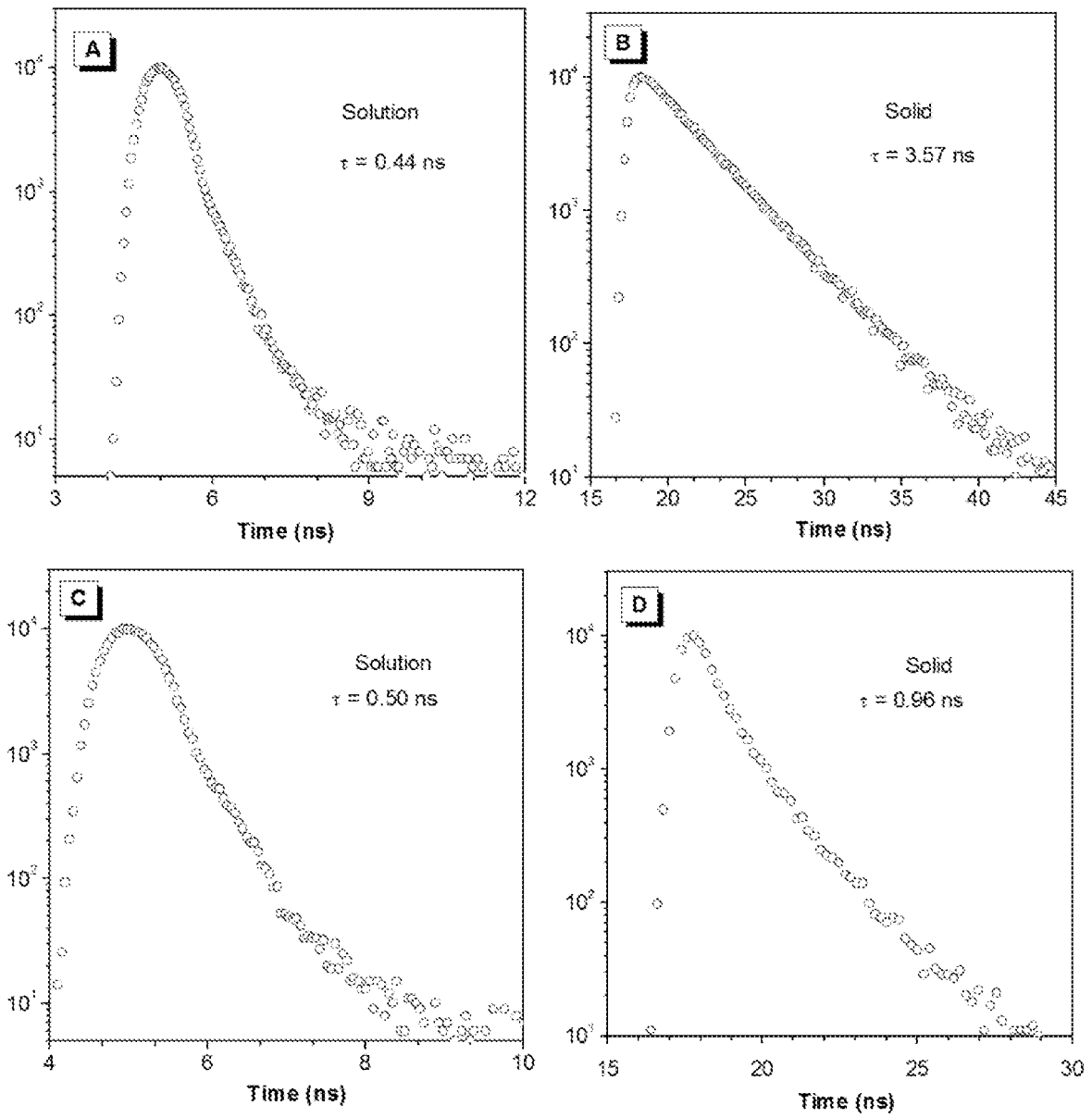
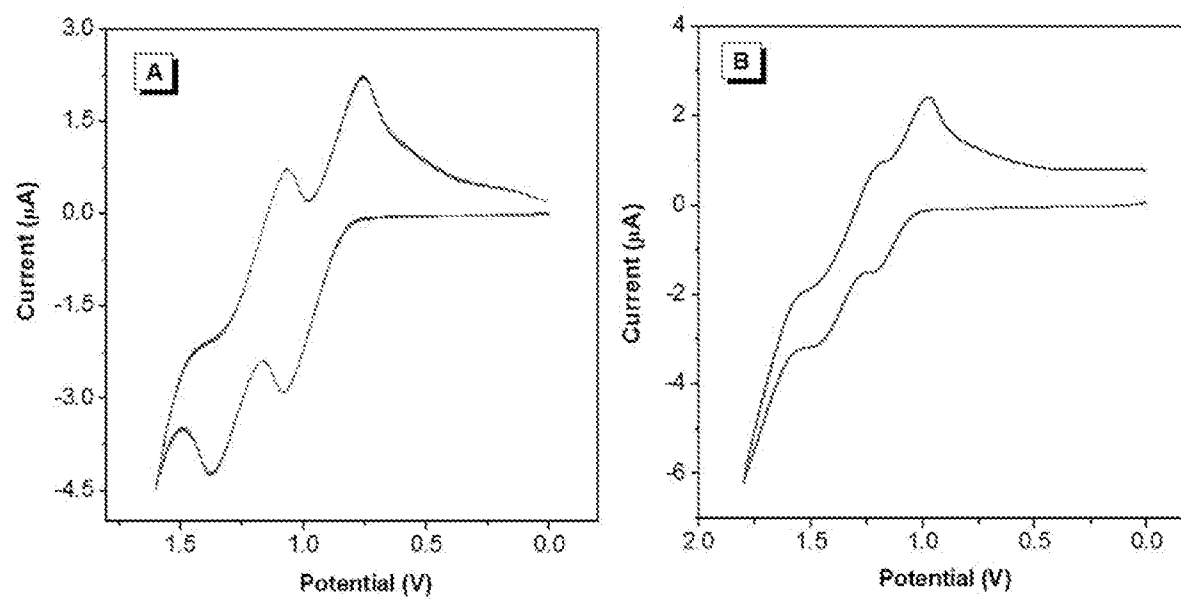
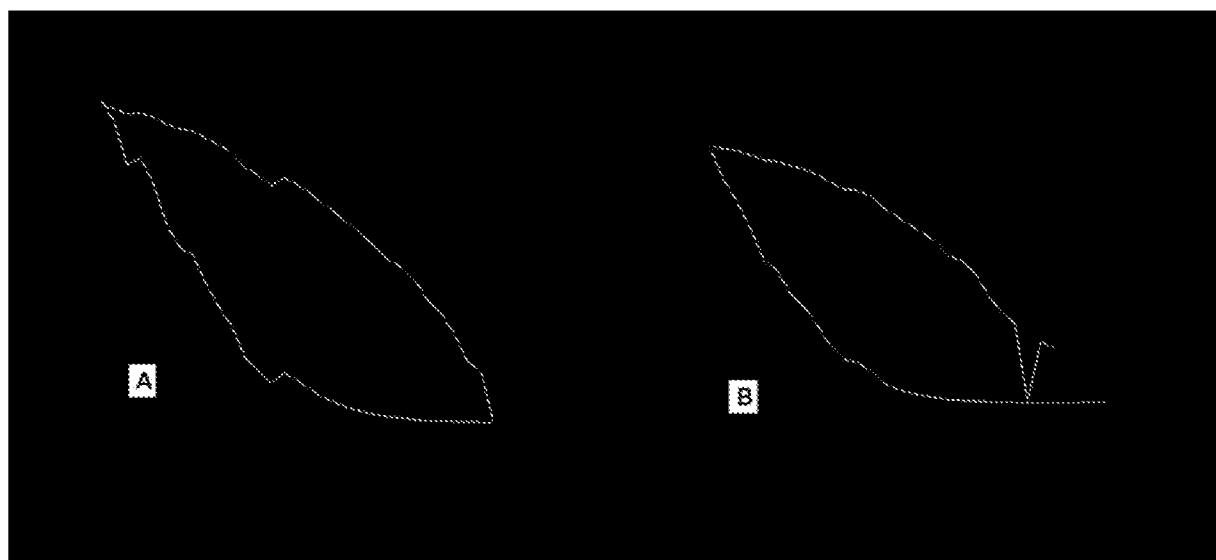


Fig. 11

**Fig. 12**

**Fig. 13****Fig. 14**

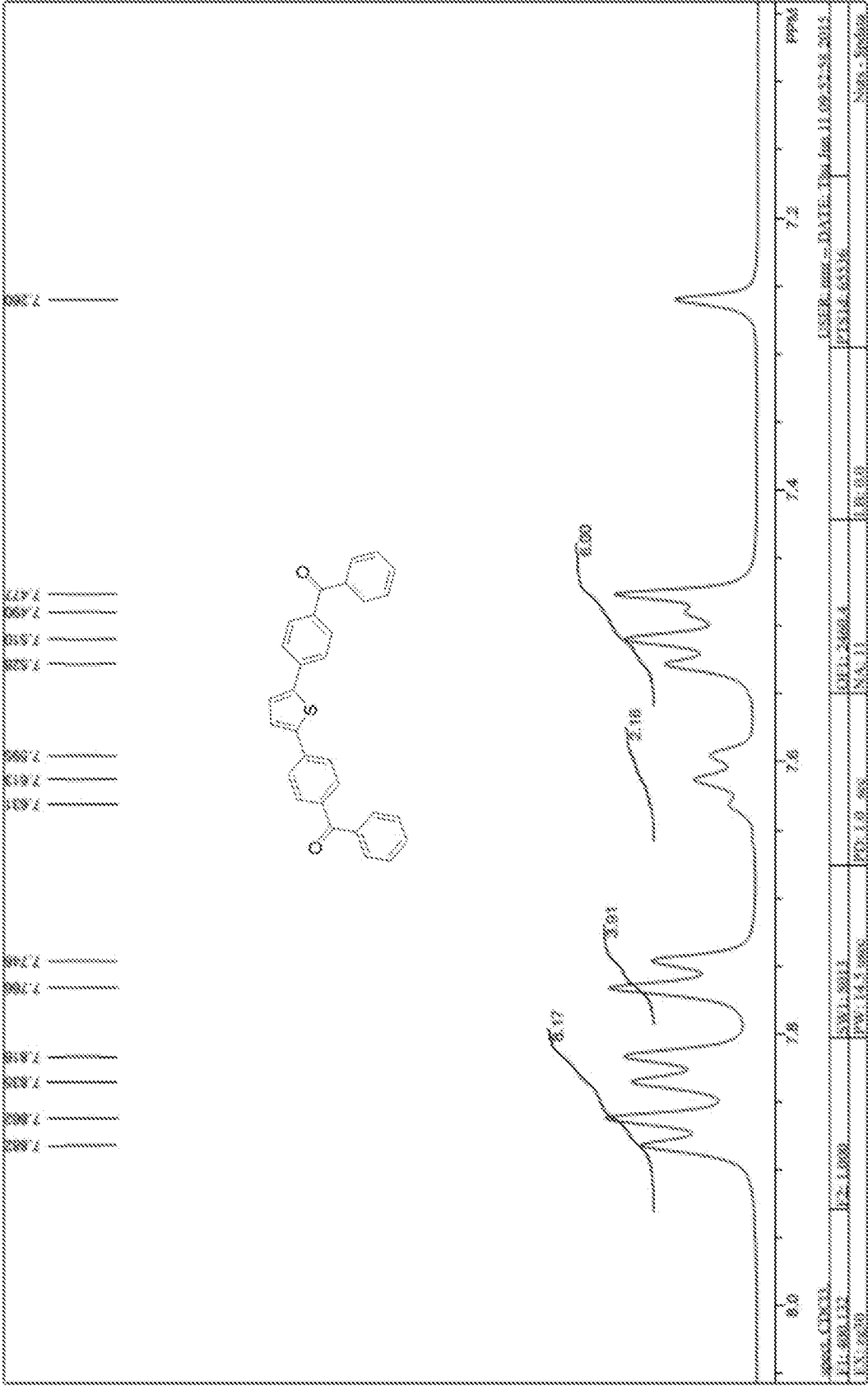
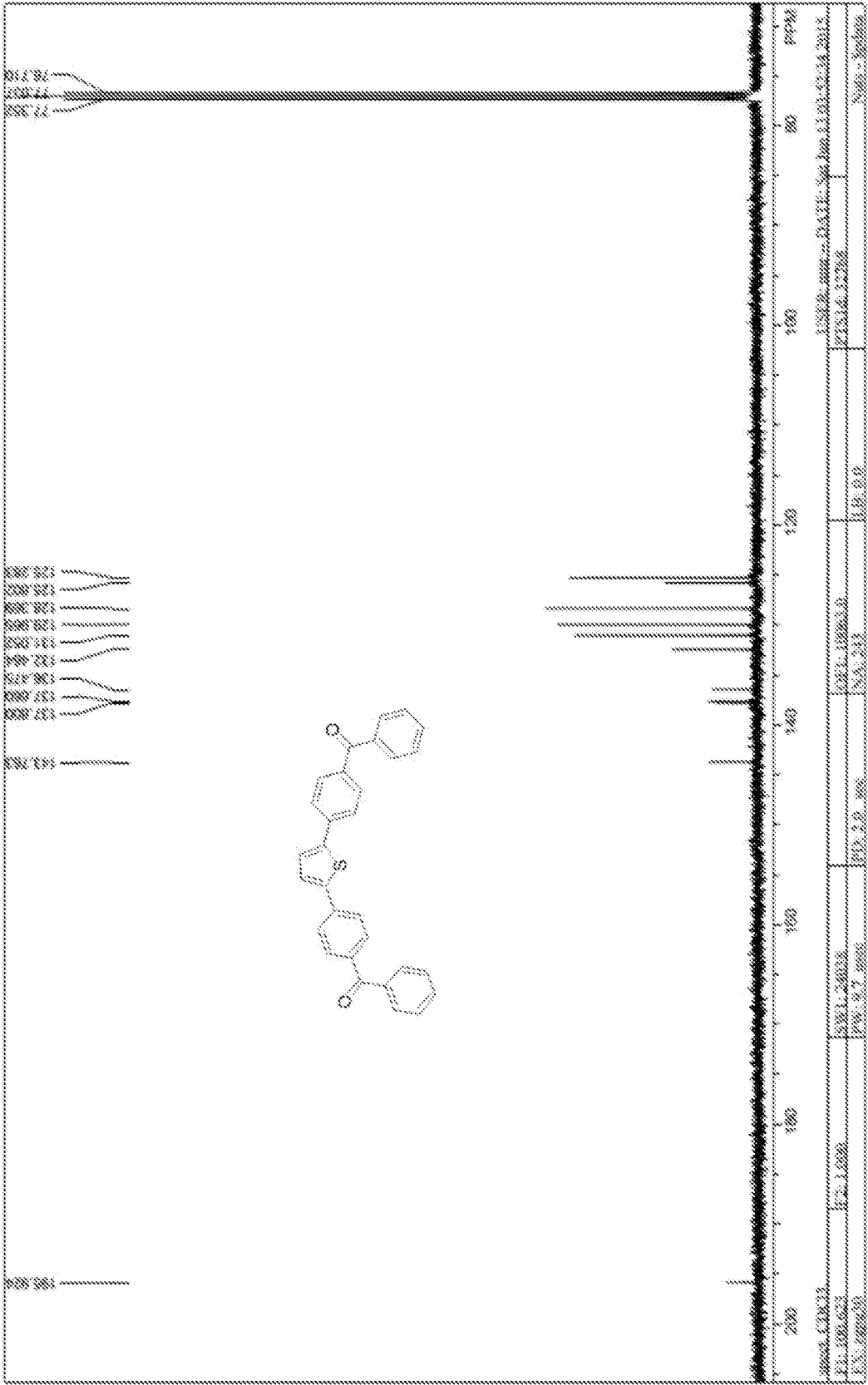


Fig. 15A



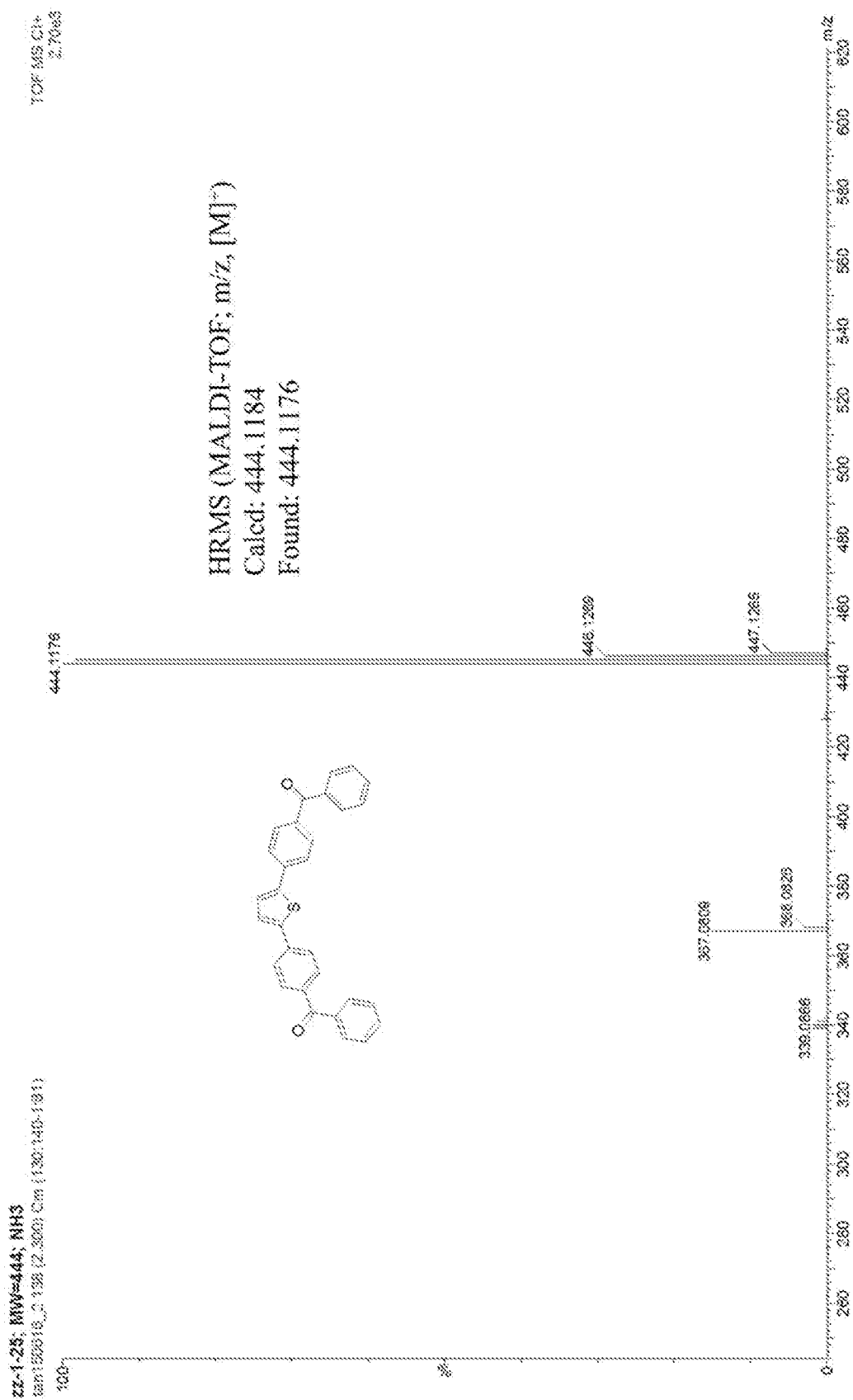


Fig. 15C

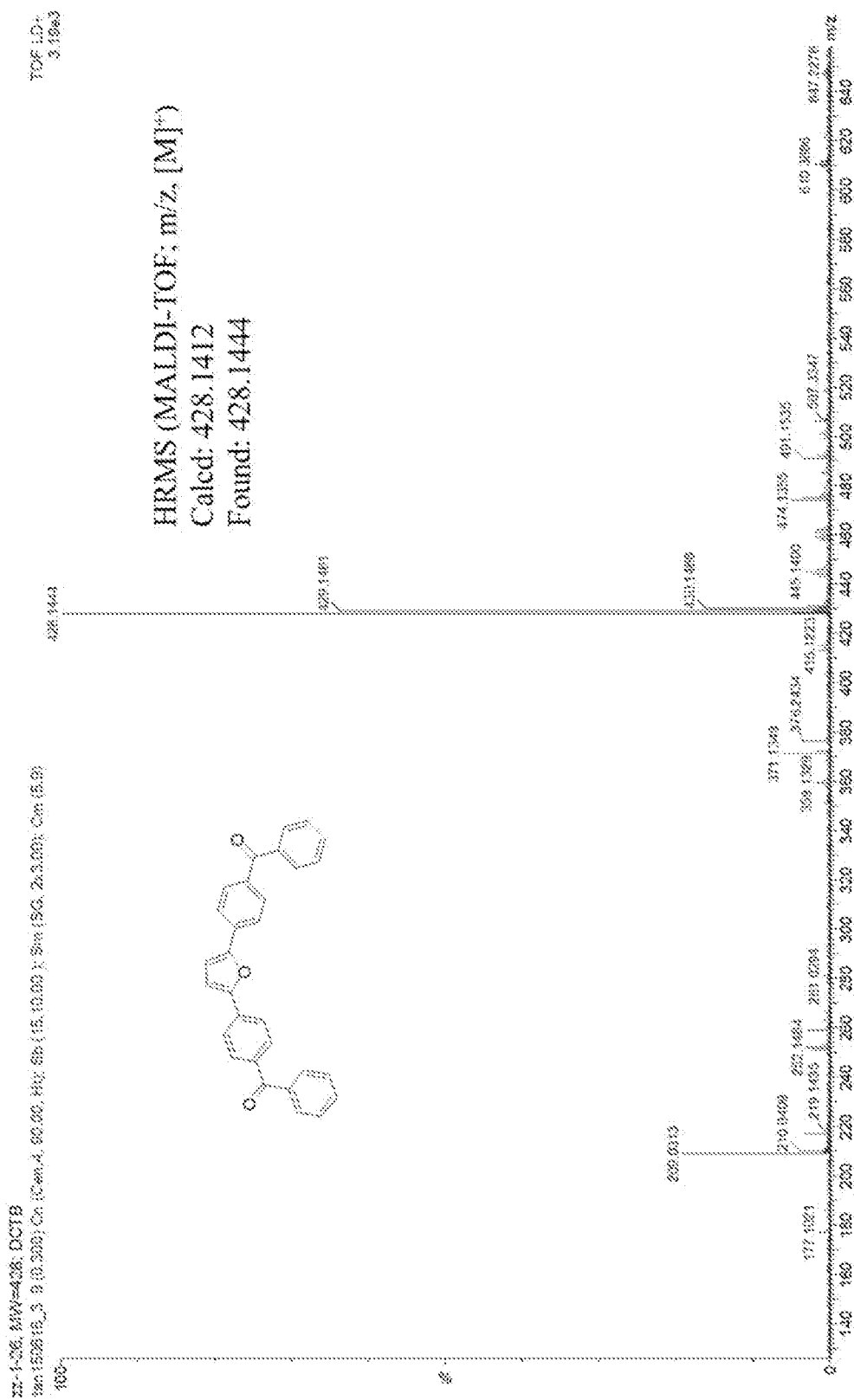
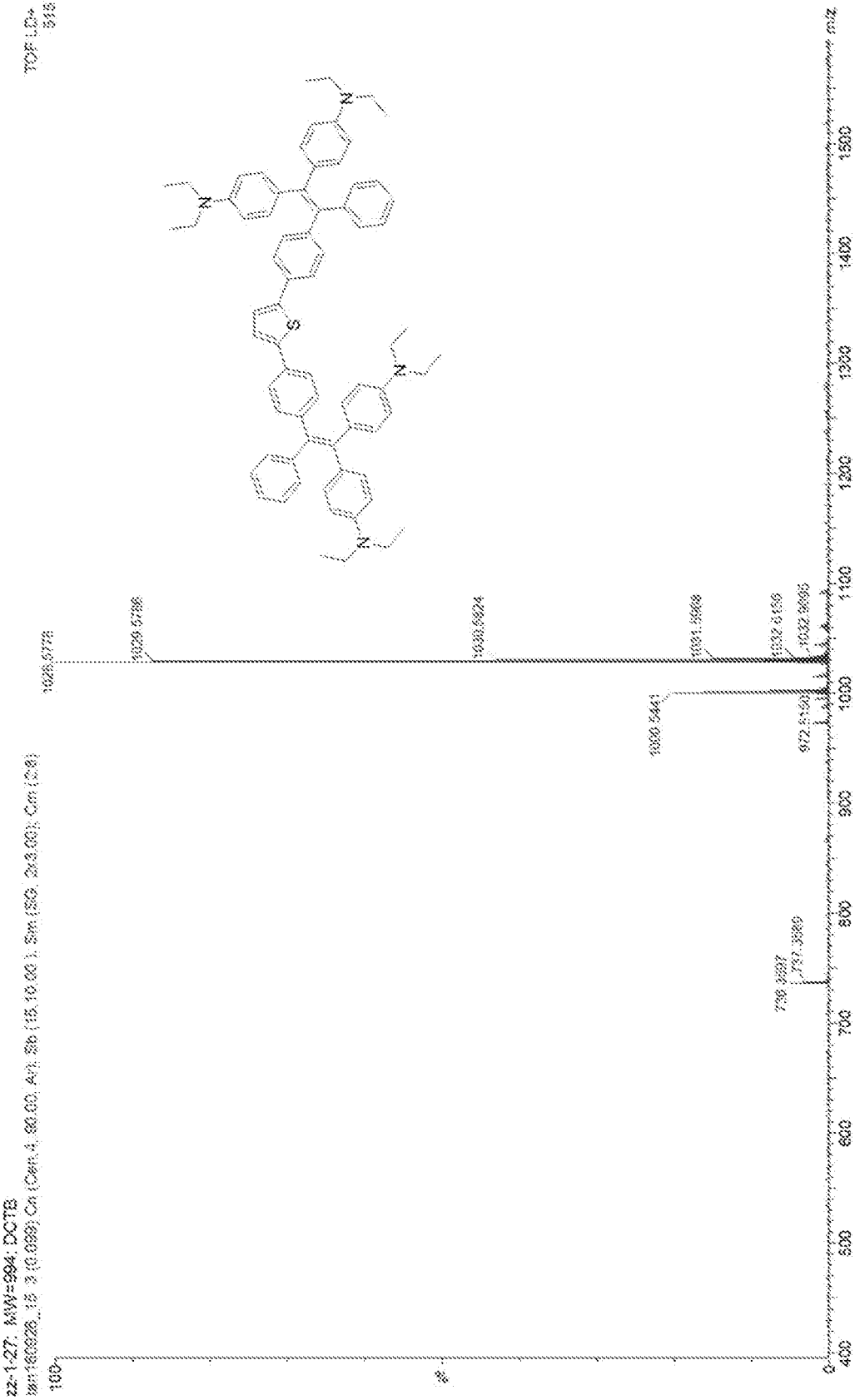


Fig. 16



INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2018/072934

A. CLASSIFICATION OF SUBJECT MATTER

C07D 333/08(2006.01)i; C07D 307/00(2006.01)i; C09K 11/06(2006.01)i; H01L 51/46(2006.01)i

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)

C07D C09K H01L

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

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

WPI,EPODOC,CNKI,CNABS,REGISTRY(STN),CAPLUS(STN):furan, thiophene, tetraphenylethylene,organic electroluminescent,OLED

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 104094435 A (BASF SE) 08 October 2014 (2014-10-08) see abstract, claim 9	1, 18-20
X	CN 105683193 A (LG CHEM, LTD.) 15 June 2016 (2016-06-15) see example 11, page 32	1, 18, 20
X	WO 2011106990 A1 (THE HONG KONG UNIVERSITY OF SCIENCE AND TECHNOLOGY ET AL.) 09 September 2011 (2011-09-09) see page 15	1, 7, 18-20
X	US 3013019 A (NATIONAL DISTILLERS AND CHEMICAL CORPORATION) 12 December 1961 (1961-12-12) see lines 45-50, column 1	5, 6
X	TOYATA Shinji et al. "Synthesis, structures, and properties of 2, 5-dianthrylthiophene derivatives" <i>Can. J. Chem.</i> , Vol. 95, 08 September 2016 (2016-09-08), pages 286-291 see Fig. 1, page 287	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

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"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

30 March 2018

Date of mailing of the international search report

16 April 2018

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2018/072934

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HARTNETT Patrick E et al. "Ring-fusion as a perylenediimide dimer design concept for high-performance non-fullerene organic photovoltaic acceptors" <i>Chem. Sci.</i> , Vol. 7, 09 February 2016 (2016-02-09), pages 3543–3555 see scheme 1, page 3547	1, 18, 20
X	ZHONG Hongliang et al. "Rigidifying Nonplanar Perylene Diimides by Ring Fusion Toward Geometry-Tunable Acceptors for High-Performance Fullerene-Free Solar Cells" <i>Advanced Materials</i> , Vol. 28, 31 December 2016 (2016-12-31), pages 951–958 see Fig.1, page 952	1, 8, 18, 20
A	JP 2003081969 A (MITSUI CHEMICALS INC) 19 March 2003 (2003-03-19) see paragraph [0013]	1-20

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2018/072934

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	104094435	A	08 October 2014	CN	104094435	B	22 February 2017
				US	2014217329	A1	07 August 2014
				KR	20140118977	A	08 October 2014
				WO	2013030325	A1	07 March 2013
				EP	2751855	A1	09 July 2014
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				US	9209412	B2	08 December 2015
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				JP	2016538272	A	08 December 2016
				EP	3064500	A2	07 September 2016
				KR	20150048636	A	07 May 2015
				EP	3064500	A4	02 August 2017
				WO	2015064937	A2	07 May 2015
				TW	201529586	A	01 August 2015
				KR	101702183	B1	06 February 2017
				WO	2015064937	A3	25 June 2015
WO	2011106990	A1	09 September 2011	US	2012299474	A1	29 November 2012
				CN	102858911	A	02 January 2013
				CN	102858911	B	17 December 2014
US	3013019	A	12 December 1961	None			
JP	2003081969	A	19 March 2003	JP	4010871	B2	21 November 2007