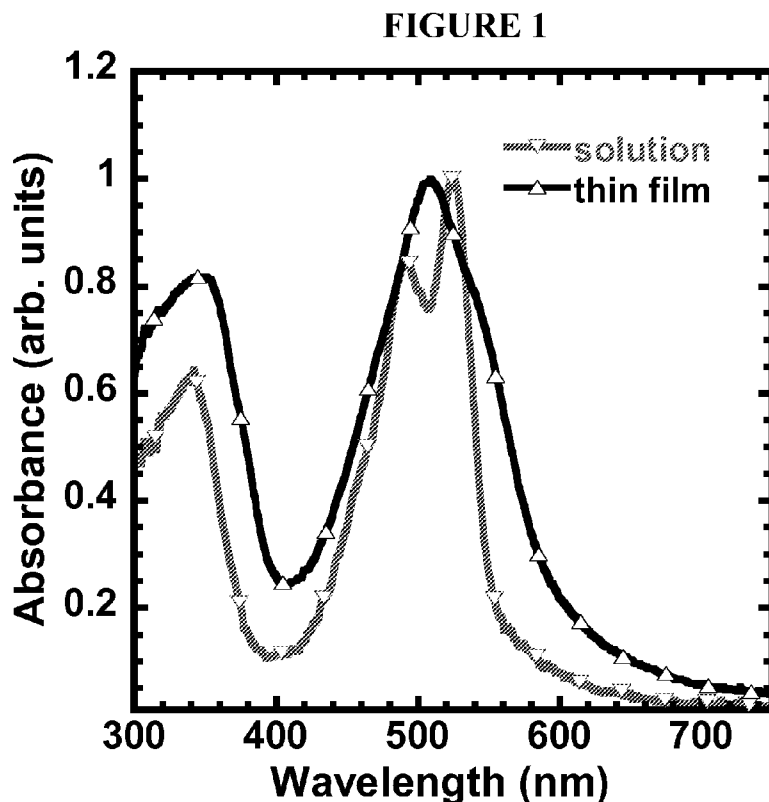




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[Continued on next page]

(54) Title: NAPHTHOBISAZOLE DIIMIDE BASED N-TYPE ORGANIC SEMICONDUCTORS



(57) Abstract: Synthesis of new class of conjugated molecules comprising electron accepting subunits that comprise, for example, naphthobisthiazole-, or naphthobisoxazole-diimides. The naphthobisazazole molecules are useful for manufacturing organic electronic devices, including n-channel transistors, and non-fullerene based solar cells. Methods for making the compounds and the derivative electronic devices are also described. A new synthetic method is described, Pure compounds or isomeric mixtures can be formed.



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Naphthobisazole Diimide Based n-Type Organic Semiconductors

BACKGROUND

Solution processable organic semiconductors are of growing interest in view of their applications in large area, flexible and low cost electronics such as organic light emitting diodes (OLEDs), thin film transistors and/ or solar cells. The electronic structure of most organic semiconductors constitutes a number of sp^2 orbitals with large delocalization of π -electrons and to some extent with the heteroatoms such as sulfur, nitrogen and oxygen. Small molecule-based organic semiconductors can have several advantages over polymers in terms of well-defined structure, monodisperse molecular weight, and convenient purification methods. However, the electronic properties of such small molecule-based semiconducting materials still too often remains low.

While some small molecule based semiconductors are known in the prior art, notably they are more often of the p-type semiconducting materials. They can have good thermal and oxidative stability, and have achieved reasonably good hole mobilities and good performance when used to make transistors or solar cells. However, there are relatively few for air-stable, durable, solution processable, high electron transport n-type semiconducting materials. This hinders the development of low cost complementary circuits and also other organic electronic devices for commercial applications.

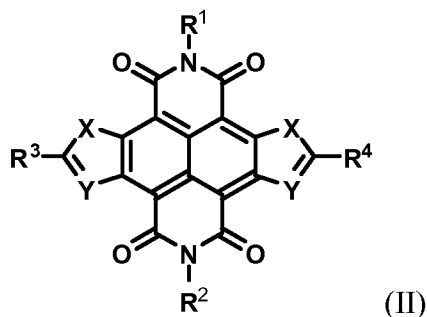
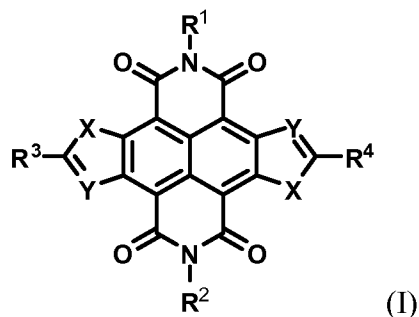
To date, the most common n-type semiconducting materials consist of aromatic molecules bearing electron withdrawing fluorine or cyano or carboxydiimide moieties. Among various diimides, naphthalene diimides (NDIs) and perylene diimides (PDIs) with suitable subunits were found to be promising candidates for n-type semiconductors, but most or all such prior art molecules lack good thermal or oxidative stability, or the practical processability characteristics needed in order to make commercially practical electronic devices.

Therefore, there is a clear need in the art for new air-stable, durable, solution processable n-channel organic semiconductor materials for realization of printable, large area low-cost electronics, including complementary circuits, OLEDs, solar cells, capacitors, and sensors. The aim of the present inventions is to provide new compounds, and associated synthetic strategies, for use as n-channel organic semiconducting materials that do not have the drawbacks of prior art materials as described above and especially show good processability, high thermal, oxidative and electron transport properties. Another aim of the inventions was to obtain advantages from the structure-property relationships of the new organic semiconducting materials.

SUMMARY

The various embodiments disclosed herein relate to synthesis/manufacture of new conjugated molecules comprising naphthobisazole diimides, as well as associated methods of making and methods of using. The embodiments described herein also relate to organic electronic devices comprising the naphthobisazole diimide molecules or compounds disclosed and described herein, such as transistors, OLEDs, solar cells, and sensors.

One embodiment provides, for example, a compound represented by formulae (I) or (II):

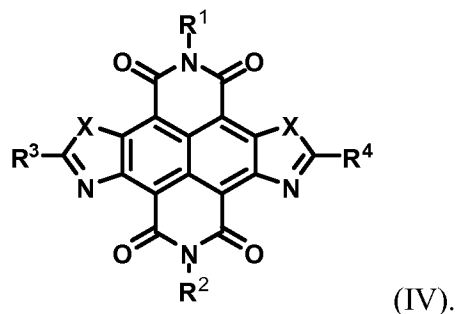
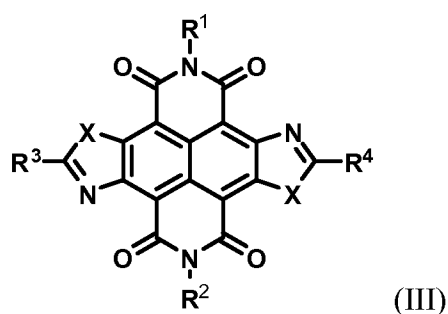


wherein:

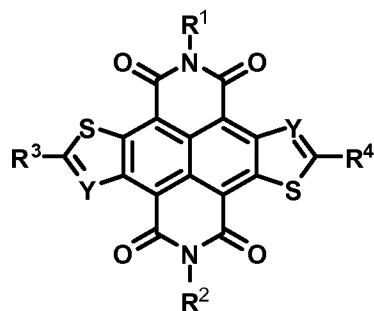
- (i) wherein X is O, S, Se, Te, or NR; and Y is N; wherein R is independently H, alkyl, heteroalkyl, aryl, or heteroaryl; wherein X and Y are different;
- (ii) R¹ and R² are independently selected from optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group;
- (iii) R³ and R⁴ are independently selected from hydrogen, halogen, optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group.

In another embodiment, the compound is represented by formula (I). In another embodiment, the compound is represented by formula (II).

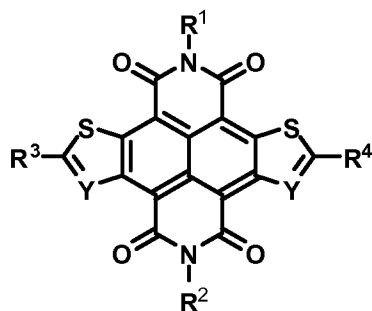
In other embodiments, the compound is represented by formulae (III) or (IV) and X is O, S, Se:



In other embodiments, wherein X is S and Y is N, and the compound is represented by formulae (V) or (VI):

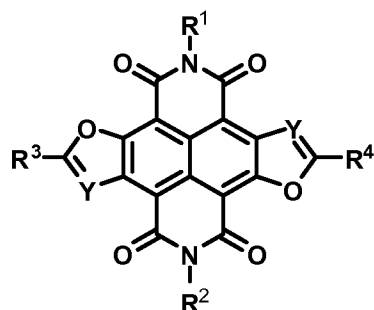


(V)

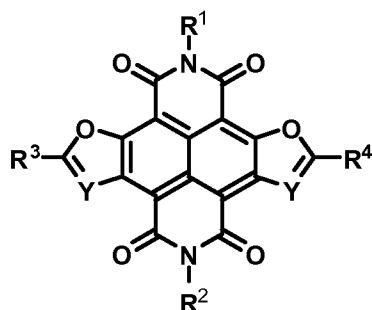


(VI).

In other embodiments, wherein X is O and Y is N, and the compound is represented by formulae (VII) or (VIII):



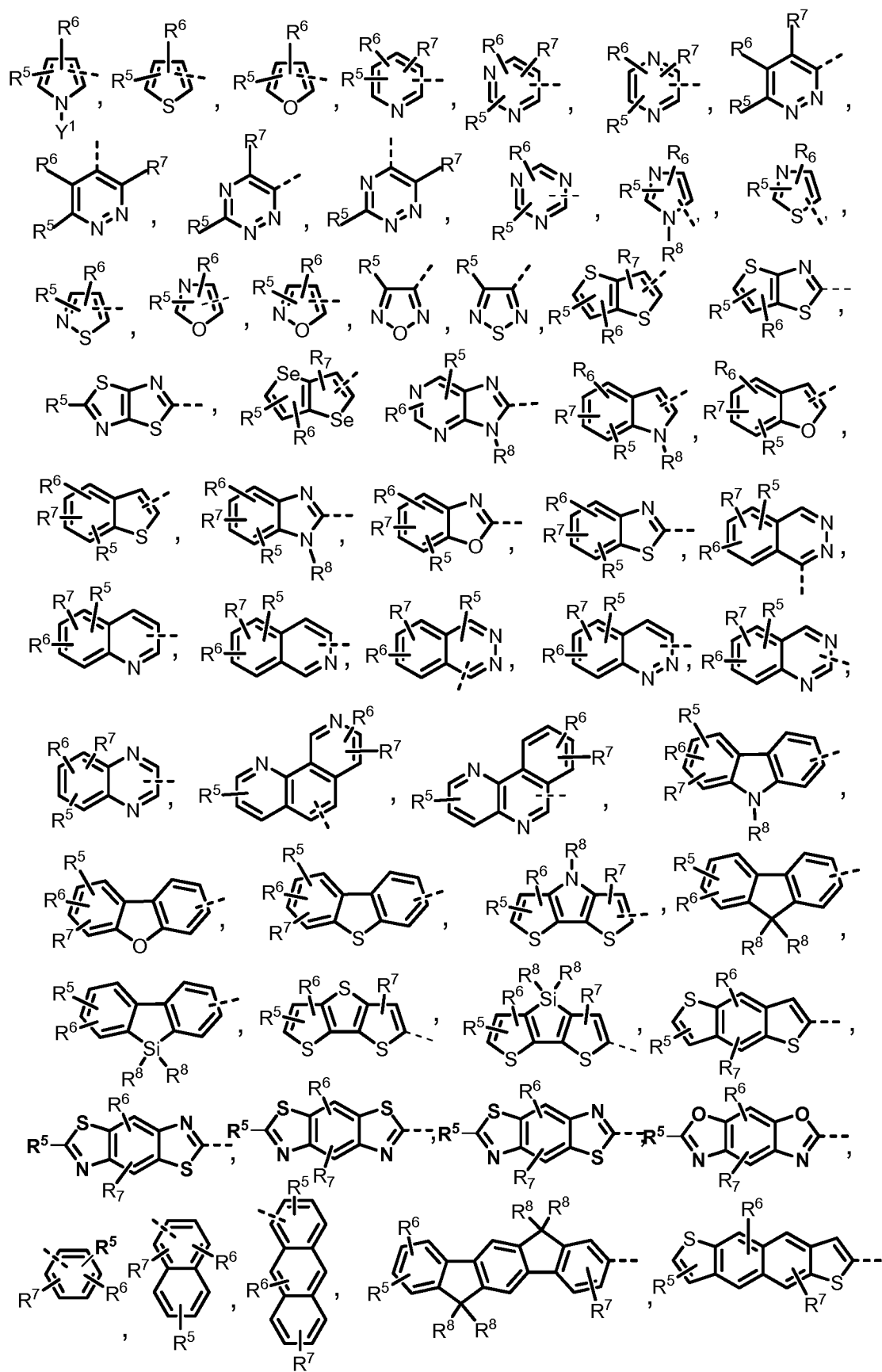
(VII)



(VIII).

In some embodiments, R^1 and R^2 are independently selected from optionally substituted C_1 - C_{25} alkyl group and optionally substituted C_1 - C_{25} heteroalkyl group. In other embodiments, R^1 and R^2 are independently selected from linear, mono- or pluri-cyclic, or branched alkyl group, linear, mono- or pluri-cyclic, or branched fluoroalkyl group, and linear, mono- or pluri-cyclic, or branched heteroalkyl group.

In other embodiments, R^3 and R^4 are each an optionally substituted aryl group or an optionally substituted heteroaryl group selected from



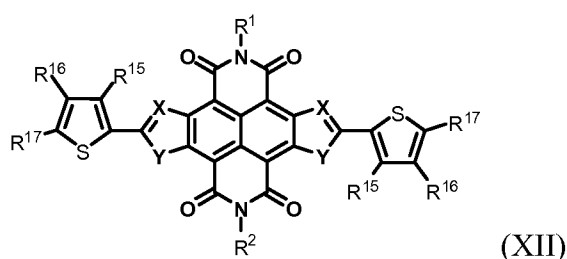
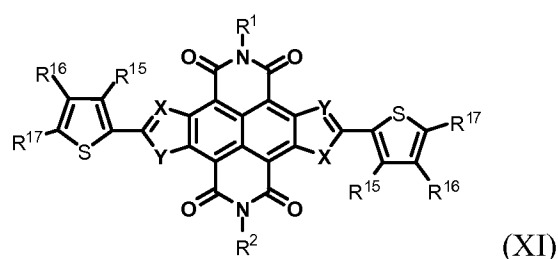
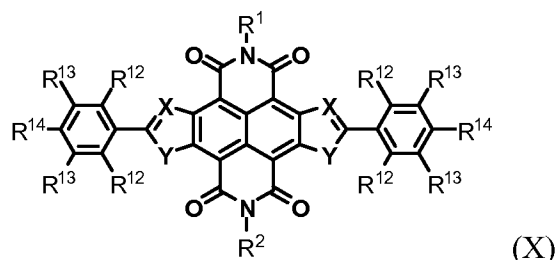
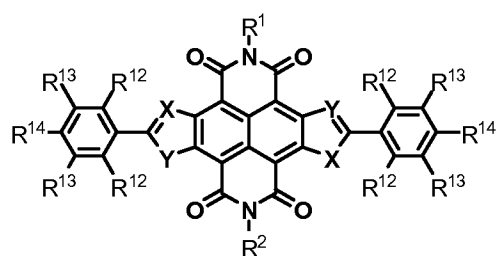
wherein R^5 , R^6 and R^7 are selected from hydrogen, halogen, hydroxyl, cyano, nitro, amine, silyl, siloxanyl, and optionally substituted linear, branched, or cyclic C_1 - C_{30} organic

group, wherein optionally two or more of adjacent R^5 , R^6 and R^7 form a ring; and

wherein R^8 is selected from hydrogen, optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group.

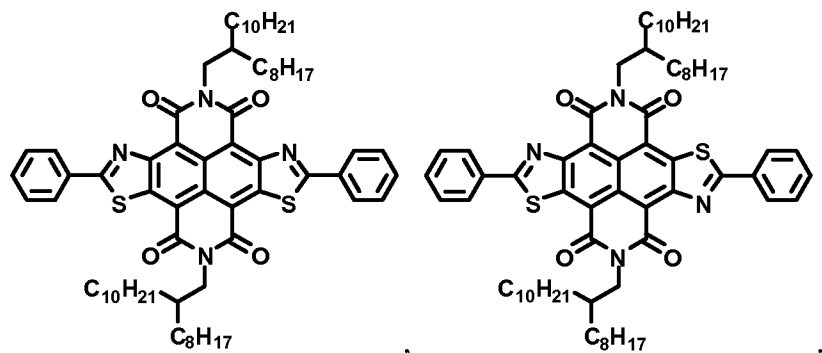
In other embodiments, R^3 and R^4 are independently selected from optionally substituted thiophenyl, optionally substituted furanyl, optionally substituted phenyl, optionally substituted pyridinyl, optionally substituted pyrimidinyl, optionally substituted pyridazinyl, optionally substituted pyrazinyl, optionally substituted 1,2,4-triazine, optionally substituted 1,3,5-triazine, optionally substituted 1,2,4,5-tetrazine.

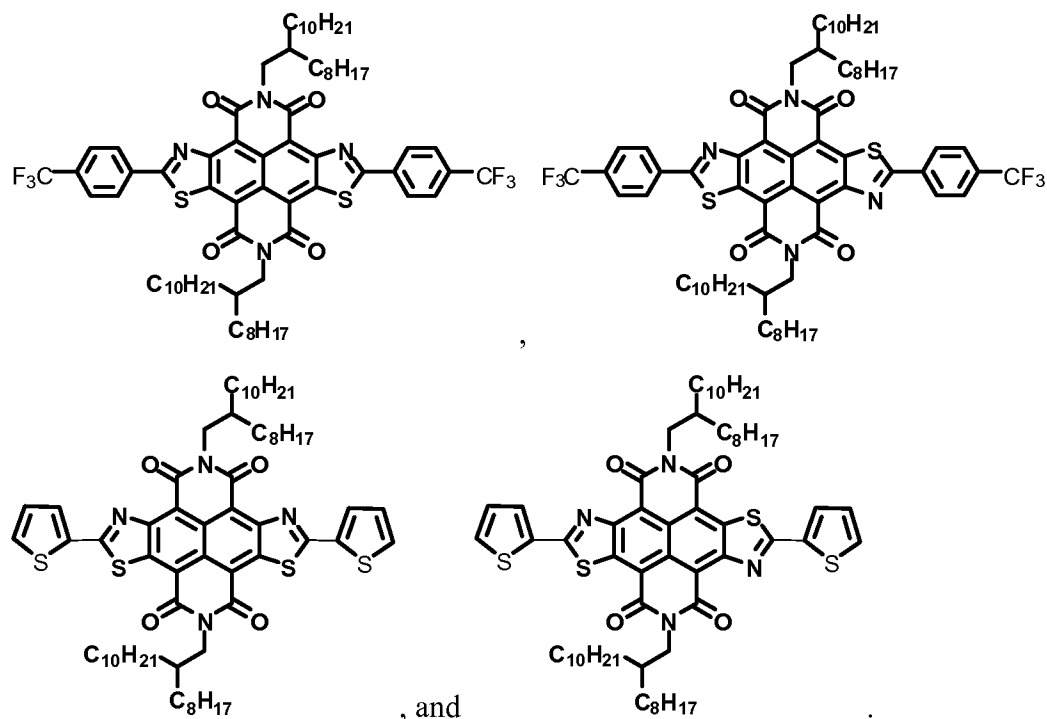
Additional embodiments include those wherein the compound of Formula (I) or Formula (II) is represented by formulae (IX), (X), (XI) or (XII):



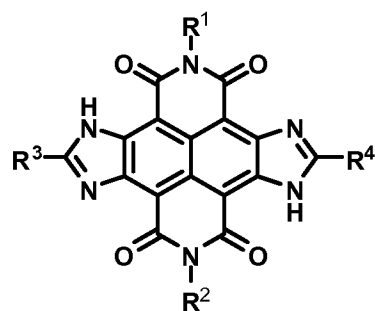
wherein R^{12} , R^{13} , R^{14} , R^{15} , R^{16} and R^{17} are independently selected from hydrogen, halogen, cyano, nitro, acyl, linear or branched alkyl group, linear or branched fluoroalkyl group, and linear or branched heteroalkyl group.

In other embodiments, the compound of Formula (I) or Formula (II) is selected from



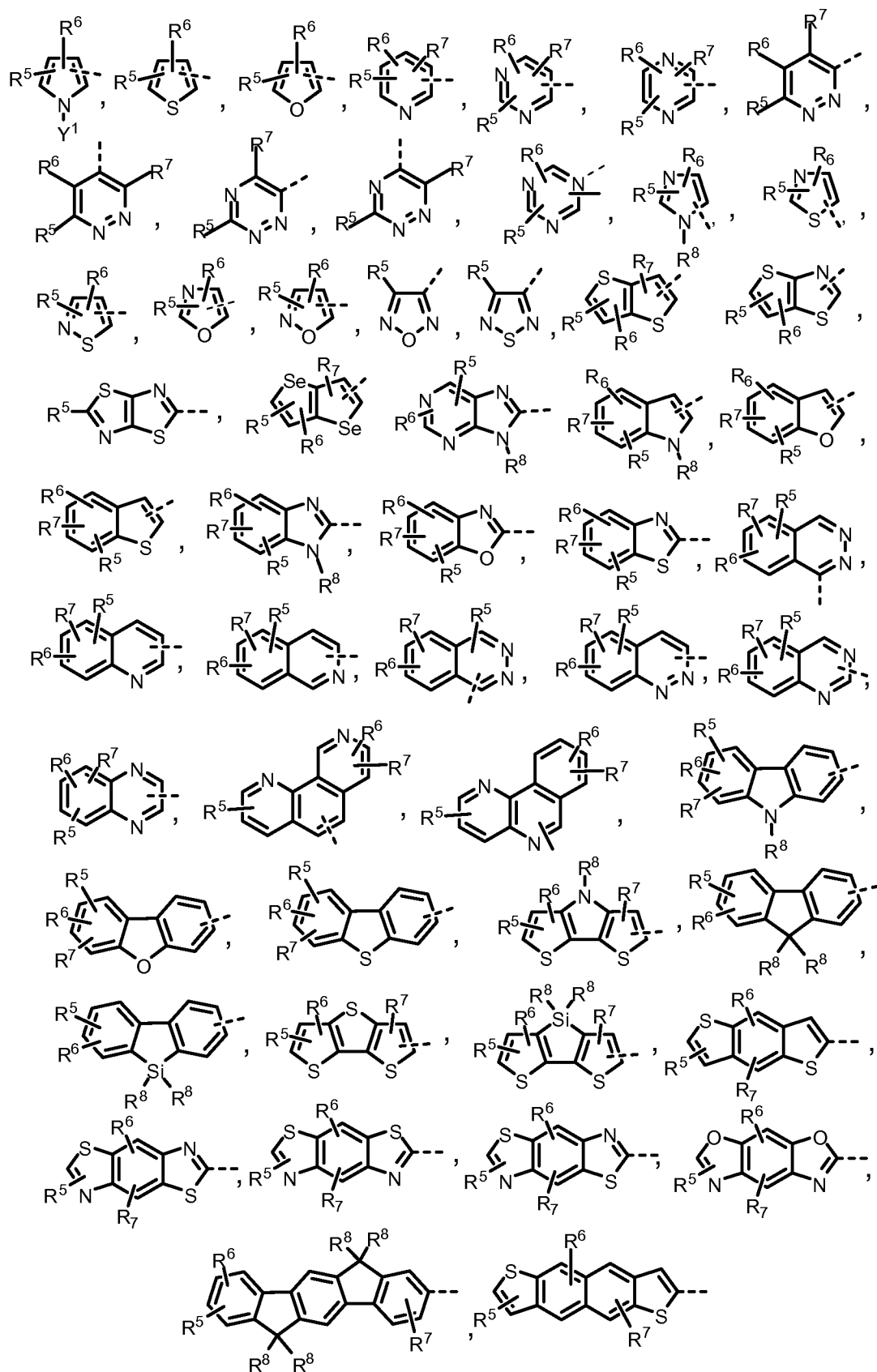


Another embodiment is a compound represented by formula (XIII)



(XIII); wherein R^1 and R^2 are independently selected from

optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group; wherein R^3 and R^4 are independently selected from:



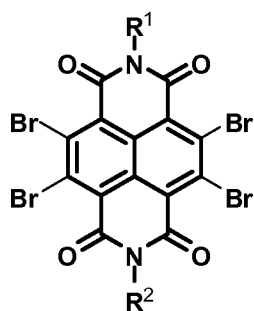
wherein R⁵, R⁶ and R⁷ are selected from hydrogen, halogen, hydroxyl, cyano, nitro, amine, silyl, siloxanyl, and optionally substituted linear, branched or cyclic C₁-C₃₀ organic

group, wherein optionally two or more of adjacent R^5 , R^6 and R^7 form a ring; and

wherein R^8 is selected from hydrogen, optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group.

Compositions are also provided. For example, one embodiment is a composition comprising at least one of the compounds of the Formulae described herein including Formulae (I) and (II). One embodiment is a composition comprising at least one compound represented by Formula (I) and at least one compound represented by Formula (II).

Methods of making are also provided for each of the compounds, compositions, and devices described herein. For example, one embodiment is a method for making the compounds as described herein or the compositions as described herein, comprising reacting a first compound represented by



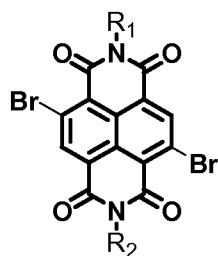
with a second compound represented by



wherein X is S, O or –

NH.

In another embodiment, a method is provided for making a single compound of Formula I, comprising reacting a compound represented by



with a compound represented by



wherein X is S, O or –NH.

Devices and uses of compounds and compositions in and for making devices are also provided. For example, one embodiment provides for an electronic device comprising at least one of the compounds or compositions, as described herein, or the compounds or compositions made by the methods described herein. In one embodiment, an n-channel transistor is provided comprising a layer comprising at least one of the compounds described herein or at least one composition described herein, or at least one compound or composition made by the methods

described herein, wherein said layer is obtained by solution processing and annealing a composition as described herein, wherein said composition comprises at least one solvent and at least one of the compounds described herein or made by the methods described herein.

The compounds having Formula I and II have a conjugated structure with rigid polycyclic backbone having electronic structures (particularly in their conjugated π orbital systems) that can result in absorption of ultraviolet, visible, and/or near-infrared light, tunable HOMO/LUMO energy levels, as well as physical structures and morphological properties that encourage intermolecular facial π -stacking interactions and/or crystallinity, which can promote a high mobility of current carriers such as electrons. Moreover, for at least some embodiments, the compounds of Formula I or II have been found to possess unexpectedly high melting points and thermal and oxidative stability.

Furthermore, the naphthobisazole compounds of Formula (I and II) typically can have good solubility in common organic solvents that allows them to be processed to form thin films, and therefore can be readily employed in solution processes for making organic electronic devices, such as for example transistors, solar cells, and/or organic light emitting diodes (OLEDs).

Furthermore, the compounds of Formula (I and II) typically can have reasonable to high electron affinity (> 4 eV) and ionization potential (> 6 eV) that allows them to be good electron transport materials under ambient conditions in organic electronic devices such as for example transistors, solar cells, and/or organic light emitting diodes (OLEDs).

In summary, compounds as described and claimed herein can be based on naphthobisazole diimides or derivatives thereof comprising naphthalene diimides fused by twoazole units. The advantages of fusing azole into NDI core can include, for example: (i) to enhance planar π -conjugation by expanding the polycyclic ring size from naphthalene to naphthobisazole ring which can promote enhanced rigidity and intermolecular π - π stacking; (ii) to achieve low lying LUMO energies (about 4.0 eV) via a large-degree of π -electron deficiency, which is vital for realizing good electron injection and ambient air-stability; (iii) to increase thermal oxidative stability and ambient air durability of the organic semiconductors; and (iv) to allow further synthetic manipulation of the HOMO/LUMO energy levels, charge transport, and optical properties by linking appropriate electron donating/withdrawing groups.

In addition, it was found that OFET devices, which contain naphthobisazole diimides as disclosed herein for n-channel semiconductors, can show good mobility and on/off ratio values, and can be easily prepared using solution deposited techniques.

Other advantages for one or more embodiments include high electron affinity (e.g., >4.0 eV), oxidative stability (e.g., >6.0 eV), and/or tunable optical band gaps (e.g., 1.0-2.2 eV).

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 discloses absorption spectra of NBTDI-1T in CHCl_3 and as a thin film. See Example 3.

Figure 2 discloses cyclic voltammogram of NBTDI-1T on a platinum electrode in 0.1 mole/L Bu_4NPF_6 , benzene:acetonitrile (10:3) solution. (a) Oxidation and (b) reduction scans. See Example 3.

Figure 3 discloses absorption spectra of *syn*-NBTDI-1T in CHCl_3 and as a thin film.

Figure 4 discloses reduction cyclic voltammograms of *syn*-NBTDI-1T on a platinum electrode in 0.1 mole/L Bu_4NPF_6 , benzene:acetonitrile (10:3) solution.

Figure 5 discloses (A) TGA thermograms of *syn*-NBTDI-1T in nitrogen obtained at a $10^\circ\text{C}/\text{min}$ heating rate; (B) the second heating and cooling DSC scans of *syn*-NBTDI-1T.

Figure 6 discloses absorption spectra of *anti*-NBTDI-1T in CHCl_3 and as a thin film.

Figure 7 discloses reduction cyclic voltammograms of *anti*-NBTDI-1T on a platinum electrode in 0.1 mole/L Bu_4NPF_6 , benzene:acetonitrile (10:3) solution.

Figure 8 discloses (A) TGA thermograms of *anti*-NBTDI-1T in nitrogen obtained at a $10^\circ\text{C}/\text{min}$ heating rate; (B) the second heating and cooling DSC scans of *anti*-NBTDI-1T.

Figure 9 discloses optical absorption spectra of PNBTDIT in dilute CHCl_3 and as thin films.

Figure 10 discloses cyclic voltammograms of poly(naphthobisthiazole diimide) copolymer thin films in 0.1 M Bu_4NPF_6 solution in acetonitrile at a scan rate of 40 mV/s.

Figure 11 discloses XRD reflections and d-spacing of naphthobisthiazole diimide copolymer PNBTDIT.

Figure 12 discloses representative output curves and transfer characteristics of a PNBTDIT FETs.

Figure 13 discloses optical absorption spectra of PNBIDI-PT in dilute CHCl_3 and as thin films.

Figure 14 discloses cyclic voltammograms of PNBIDI-PT copolymer thin films in 0.1 M Bu_4NPF_6 solution in acetonitrile at a scan rate of 40-50 mV/s: (A) Oxidation waves and (B) oxidation and reduction waves.

DETAILED DESCRIPTION

INTRODUCTION

All references cited herein are incorporated herein by reference in their entirety.

The term “halogen” can include fluorine, chlorine, bromine, and iodine.

If a group or moiety is optionally substituted, this means that the group or moiety is either unsubstituted or substituted with at least one monovalent group. Examples of monovalent groups are not particularly limited and include, for example, halogen, pseudohalogen, alkyl, heteroalkyl, aryl, heteroaryl, alkenyl, alkynyl, acyl, dicyanovinylene, amide, amine, ester, and the like, as known in the art. Organic groups which can be unsubstituted or optionally substituted are well-known in the art and include, for example C₁-C₅₀ groups, C₁-C₂₅ groups, and C₆-C₂₅ groups.

As used herein, an alkyl group can be typically linear or branched and can be, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethylpropyl, n-hexyl, n-heptyl, n-octyl, 1,1,3,3-tetramethylbutyl and 2-ethylhexyl, n-nonyl, decyl, undecyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, eicosyl, heneicosyl, docosyl, tetracosyl or pentacosyl, preferably C₁-C₈ alkyl such as methyl, ethyl, n-propyl, n-hexyl, n-heptyl, n-octyl, 1,1,3,3-tetramethylbutyl and 2-ethylhexyl, more preferably C₁-C₄ alkyl such as typically methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert. butyl. C₁-C₂₅ alkyl groups are commonly preferred. Cyclic alkyl groups can be included. An alkyl group can be optionally substituted.

As used herein, heteroalkyl can be, for example, an alkyl group wherein one or more of the carbon atoms are replaced with a heteroatom such as oxygen or nitrogen or sulfur. Examples include amino, alkoxy, and alkylthio groups. Examples of alkoxy include C₁-C₈ alkoxy such as methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, isobutoxy, tert-butoxy, n-pentoxo, 2-pentoxo, 2,2-dimethylpropoxy, n-hexoxy, n-heptoxy, n-octoxy, 1,1,3,3-tetramethylbutoxy, preferably C₁-C₄ alkoxy such as typically methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, isobutoxy, tert-butoxy. The term “alkylthio group” means the same group as the alkoxy groups, except that the oxygen atom of ether linkage is replaced by a sulfur atom. A heteroalkyl group can be optionally substituted. Amino groups can be, for example, primary or secondary or tertiary or quaternized amino groups including alkylamine.

As used herein, the term “aryl group” is typically C₆-C₂₄ aryl, such as phenyl, 1-naphthyl, 2-naphthyl, 4-biphenyl, phenanthryl, terphenyl, pyrenyl, 2- or 9-fluorenyl or anthracenyl,

preferably C₆-C₁₂ aryl, such as phenyl, 1-naphthyl, 4-biphenyl, which may be unsubstituted or substituted. An aryl group can be optionally substituted.

The term “heteroaryl or heterocyclic group” is a ring with five to seven ring atoms, wherein nitrogen, oxygen or sulfur are possible hetero atoms, and is typically an unsaturated heterocyclic radical with five to 18 atoms having at least six conjugated π -electrons such as thienyl, benzo[b]thienyl, dibenzo[b,d]thienyl, thianthrenyl, furyl, furfuryl, 2H-pyranyl, benzofuranyl, isobenzofuranyl, dibenzofuranyl, phenoxythienyl, pyrrolyl, imidazolyl, pyrazolyl, pyridyl, bipyridyl, trazinyl, pyrimidinyl, pyrazinyl, pyridazinyl, indoliziny, isoindolyl, indolyl, indazolyl, purinyl, quinoxinyl, chinolyl, isochinolyl, phthalazinyl, naphthridinyl, chinoxaliny, chinazoliny, cinnoliny, pteridinyl, carbazolyl, carboliny, benzotriazolyl, benzoxazolyl, phenanthridinyl, acridinyl, perimidinyl, phenanthroliny, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl or phenoxazinyl, preferably the above-mentioned mono-or bicyclic heterocyclic radicals.

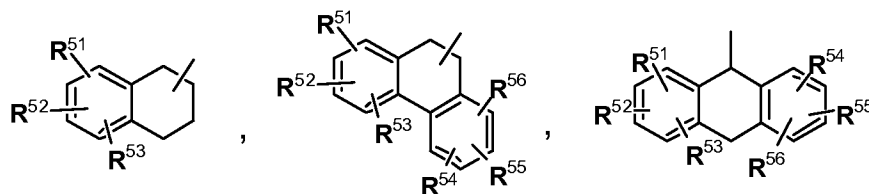
The term “aralkyl group” is typically C₇-C₂₄ aralkyl, such as benzyl, 2-benzyl-2-propyl, β -phenyl-ethyl, α , α -dimethylbenzyl, ω -phenyl-butyl, ω , ω -dimethyl- ω -phenyl-butyl, ω -phenyl-dodecyl, ω -phenyl-octadecyl, ω -phenyl-eicosyl or ω -phenyl-docosyl, preferably C₇-C₁₈ aralkyl such as benzyl, 2-benzyl-2-propyl, β -phenyl-ethyl, α , α -dimethylbenzyl, ω -phenyl-butyl, ω , ω -dimethyl- ω -phenyl-butyl, ω -phenyl-octadecyl, ω -phenyl-eicosyl or ω -phenyl-docosyl, in which both the aliphatic hydrocarbon group and aromatic hydrocarbon group may be unsubstituted or substituted.

The term “aryl ether group” is typically a C₆₋₂₄ aryloxy group that is to say O-C₆₋₂₄ aryl, such as for example, phenoxy or 4-methoxyphenyl. The term “arylthioether group” is typically a C₆₋₂₄ arylthio group that is to say S-C₆₋₂₄ aryl, such as, for example, phenylthio or 4-methoxyphenylthio. The term “carbomyl group” is typically a C₁₋₈ cabamoyl radical, preferably C₁₋₈ cabamoyl radical which may be unsubstituted such as for example, carbamoyl, methylcarbamoyl, ethylcarbamoyl, n-butylcarbamoyl, tert-butylcarbamoyl, dimethylcarbamoyloxy, morpholinocarbamoyl or pyrrolidinocarbamoyl.

The term “cycloalkyl group” is typically C₅-C₁₂cycloalkyl, such as cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl, cyclododecyl, preferably cyclopentyl, cyclohexyl, cycloheptyl, or cyclooctyl, which may be unsubstituted or substituted. The term “cycloalkenyl group” means an unsaturated alicyclic hydrocarbon group containing one or more double bonds, such as cyclopentenyl, cyclopentadienyl, cyclohexenyl and the like, which may be unsubstituted or substituted. The cycloalkyl group, in particular a

cyclohexyl group, can be condensed one or two times by phenyl which can be substituted one to three times with C₁-C₄-alkyl, halogen and cyano.

Examples of such condensed cyclohexyl groups are:



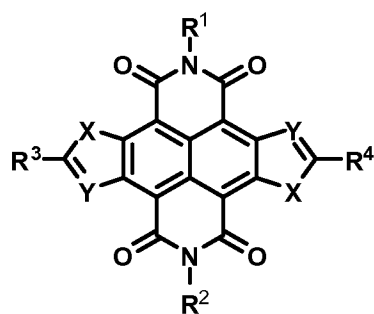
wherein R⁵¹, R⁵², R⁵³, R⁵⁴, R⁵⁵ and R⁵⁶ are independently of each other C₁-C₈-alkyl, C₁-C₈-alkoxy, halogen and cyano, in particular hydrogen.

The wording “a group comprising a five-membered heterocyclic ring, containing one to three heteroatoms selected from the group of nitrogen, oxygen and sulfur” means a single five-membered heterocyclic ring, such as thienyl, furyl, furfuryl, 2H-pyranyl, pyrrolyl, imidazolyl, or pyrazolyl, or a five membered heterocyclic ring which is part of a fused ring system, which is formed by the five-membered heterocyclic ring with aryl, heteroaryl and/or cycloalkyl groups, which can optionally be substituted. Examples of such groups are contained in the list of groups for R³ and R⁴ as well as in the definition of heteroaryl or heterocyclic groups.

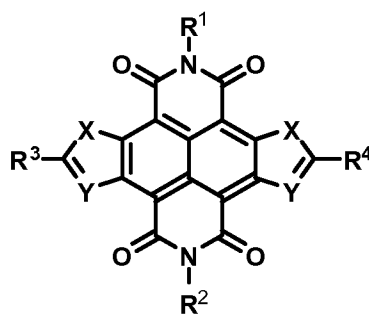
The wording “a group comprising a six-membered heterocyclic ring, containing one to three heteroatoms selected from the group of nitrogen, oxygen and sulfur” means a single six-membered heterocyclic ring, such as pyridyl, triazinyl, pyrimidinyl, pyrazinyl, pyridazinyl, or a six-membered heterocyclic ring which is part of a fused ring system, which is formed by the six-membered heterocyclic ring with aryl, heteroaryl and or/cycloalkyl groups, which can optionally be substituted. Examples of such groups are contained in the list of groups for R³ and R⁴ as well as in the definition of heteroaryl or heterocyclic group.

CORE FORMULA

One embodiment provides for a compound represented by formulae (I) or (II):



(I)



(II)

wherein:

- (i) wherein X is O, S, Se, Te, or NR; and Y is N; wherein R independently is H, alkyl, heteroalkyl, aryl, or heteroaryl; wherein X and Y are different;
- (ii) R^1 and R^2 are independently selected from optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group;
- (iii) R^3 and R^4 are independently selected from hydrogen, halogen, optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group.

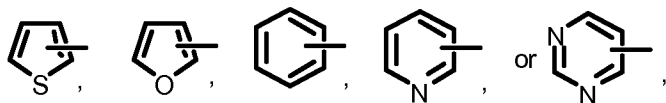
Formulae (I) and (II) represent isomers (e.g., anti versus syn, respectively). One embodiment provides for a composition comprising a mixture of (I) and (II). In another embodiment, the compounds (I) and (II) are in purified and relatively pure form (e.g., compound represented by (I) is free or substantially free of compound represented by (II), and vice-versa). For example, a composition or compound can comprise at least 90 wt.%, or at least 95 wt.%, or at least 99 wt.% of a compound per Formula (I). Alternatively, a composition or compound can comprise at least 90 wt.%, or at least 95 wt.%, or at least 99 wt.% of a compound per Formula (II).

The Y group in particular can be N, for example. The X group in particular can be O or S.

The R^1 and R^2 groups, independently, can be the same or different and are not particularly limited but can be, for example, an organic group such as optionally substituted branched alkyl designed to enhance solubility for the compound. In other embodiments, R^1 and R^2 are independently selected from optionally substituted C_1 - C_{25} alkyl group and optionally substituted C_1 - C_{25} heteroalkyl group. In other embodiments, R^1 and R^2 are independently selected from linear, mono- or pluri-cyclic, or branched alkyl group; linear, mono- or pluri-cyclic, or branched fluoroalkyl group; and linear, mono- or pluri-cyclic, or branched heteroalkyl group. Other examples include, for example, an aryl group (e.g., phenyl, Ph), or a C_7 - C_{24} aralkyl group (e.g., CH_2 -Ph), or an aryloxy group (e.g., $-C_6H_4OR$, including para-substituted aryloxy), or a C_6 - C_{24} arylthio group (e.g., $-C_6H_4SR$, including para-substituted $-SR$), or a heteroaryl group (e.g., pyrrole).

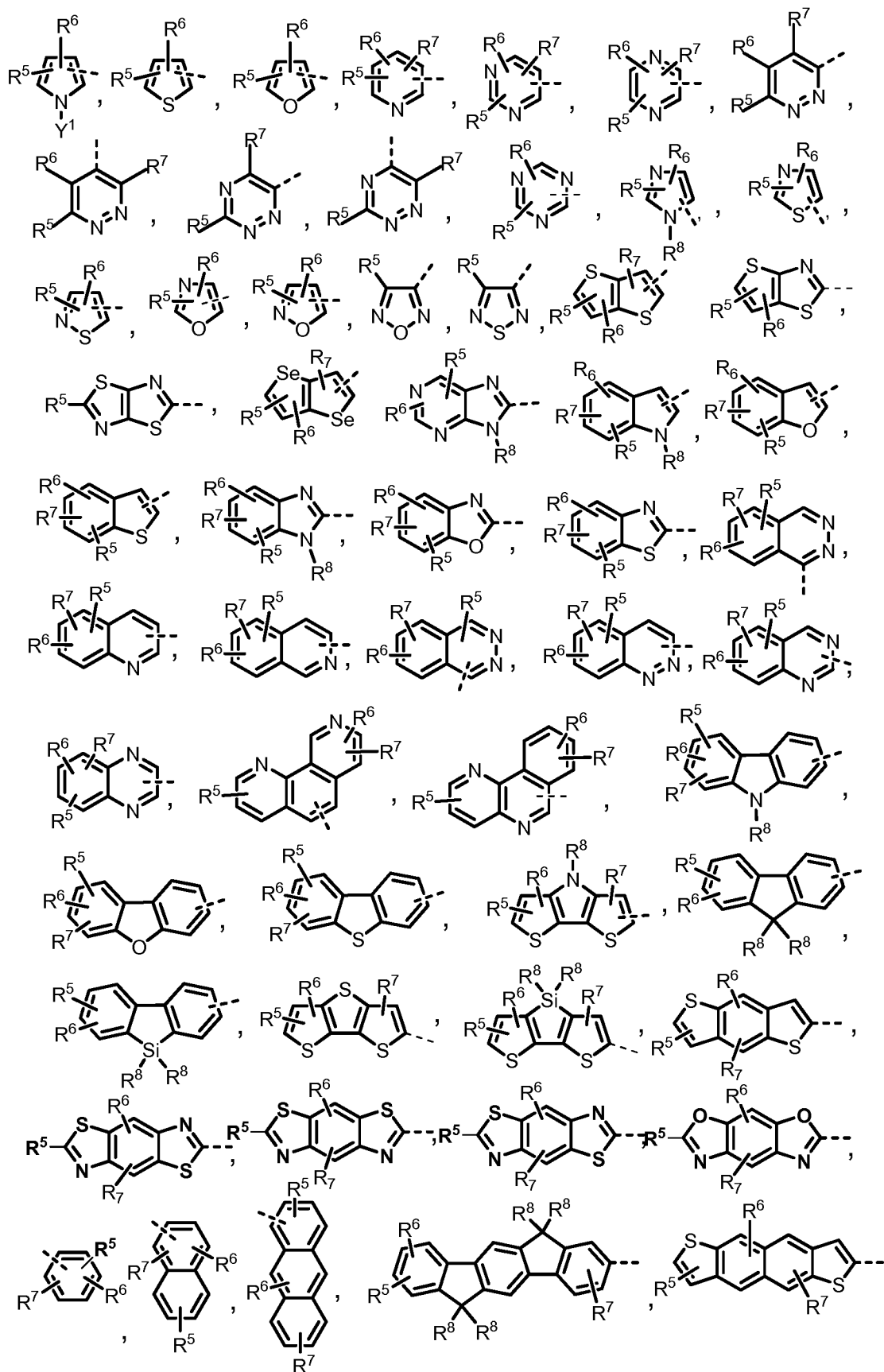
The R^3 and R^4 groups, independently, can be the same or different and can be optionally substituted aryl or heteroaryl rings, including five- and six-membered rings, which can be conjugated with the rest of the compound structure. The R^3 and R^4 groups can be, for

example, independently from each other represent a hydrogen or a halogen or a substituted or unsubstituted alkyl, cycloalkyl or aryl group, substituted fluoroalkyls, a five membered heterocyclic ring, containing one to three heteroatoms selected from the group of nitrogen, oxygen and sulfur, or a six membered cyclic ring, containing one to three heteroatoms selected from the group of nitrogen, oxygen and sulfur, wherein R^3 and R^4 are a single five or six membered cyclic ring of formulae such as



said heterocyclic ring is substituted by at least a group selected from a hydrogen atom, a C_1 - C_{25} alkyl group, a cycloalkyl group, an aralkyl group, an alkenyl group, a cycloalkenyl group, an alkynyl group, a hydroxyl group, a mercapto group, an alkoxy group, an alkythio group, an aryl ether group, an aryl thioether group, an aryl group, a heterocyclic group, a halogen atom, a haloalkyl group, a haloalkenyl group, a haloalkynyl group, a cyano group, an aldehyde group, a carboxyl group, an ester group, a carbomyl group, a nitro group, a silyl group, siloxanyl group, a substituted or unsubstituted vinyl group, a group NR^8R^9 , wherein R^8 and R^9 independently of each other stand for a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group, a heteroaryl group, a heterocyclic group, an aralkyl group, or R^8 and R^9 together with the nitrogen atom to which they are bonded form a five or six membered heterocyclic ring, which can be condensed by one or two optionally substituted phenyl groups, wherein, the heterocyclic ring is directly bonded to the naphthobisazole diimide (NBADI) unit.

In other embodiments, R^3 and R^4 are each an optionally substituted aryl group or an optionally substituted heteroaryl group selected from:



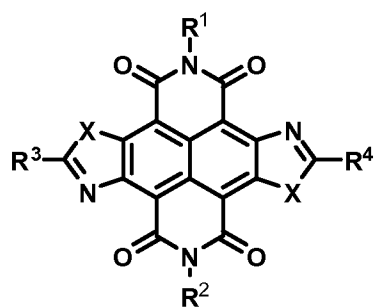
wherein R^5 , R^6 and R^7 are selected from hydrogen, halogen, hydroxyl, cyano, nitro, amine, silyl, siloxanyl, and optionally substituted linear, branched, or cyclic C_1 - C_{30} organic group, wherein optionally two or more of adjacent R^5 , R^6 and R^7 form a ring; and

wherein R^8 is selected from hydrogen, optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group.

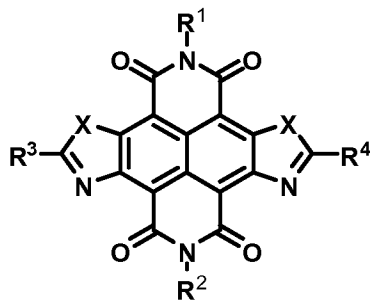
In other embodiments, R^3 and R^4 are independently selected from optionally substituted thiophenyl, optionally substituted furanyl, optionally substituted phenyl, optionally substituted pyridinyl, optionally substituted pyrimidinyl, optionally substituted pyridazinyl, optionally substituted pyrazinyl, 1,2,4-triazinyl, 1,3,5-triazinyl, and 1,2,4,5-tetrazinyl.

In one embodiment, one or more of the groups R^1 , R^2 , R^3 , and/or R^4 can be, for example, a group comprising a five or six membered heterocyclic ring.

In other embodiments, the compound is represented by formulae (III) or (IV) and X is O, S, Se:

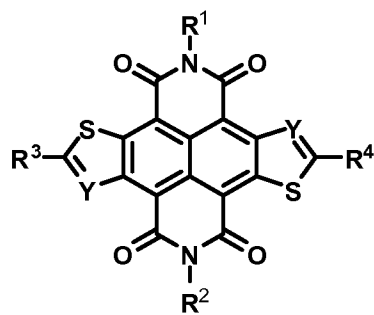


(III)

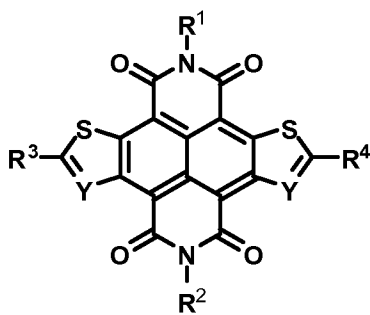


(IV).

In other embodiments, the compound is represented by formulae (V) or (VI) as X is S:

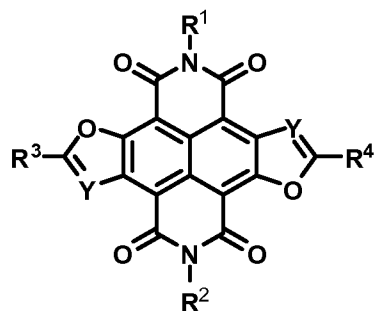


(V)

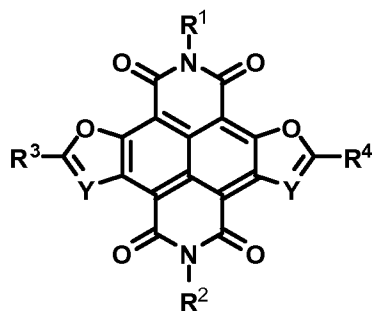


(VI).

In other embodiments, the compound is represented by formulae (VII) or (VIII) as X is O:

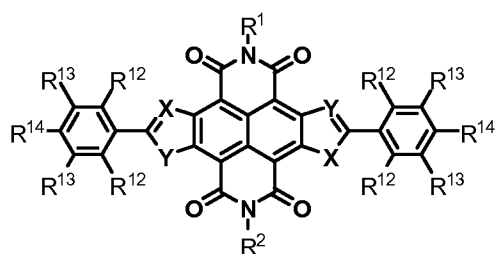


(VII)

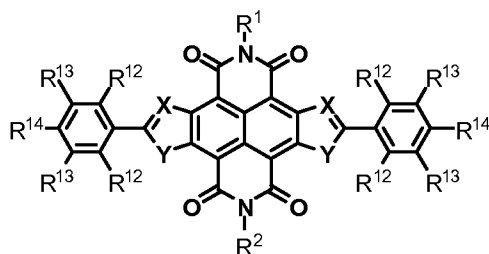


(VIII).

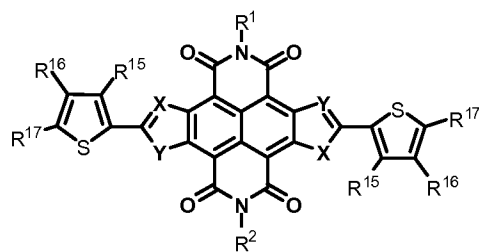
In other embodiments, the compound is represented by formulae (IX), (X), (XI) or (XII):



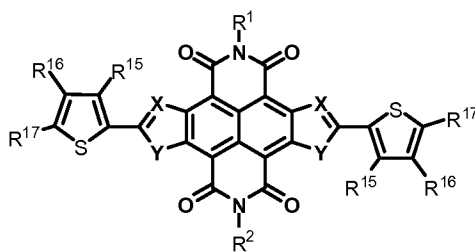
(IX)



(X)



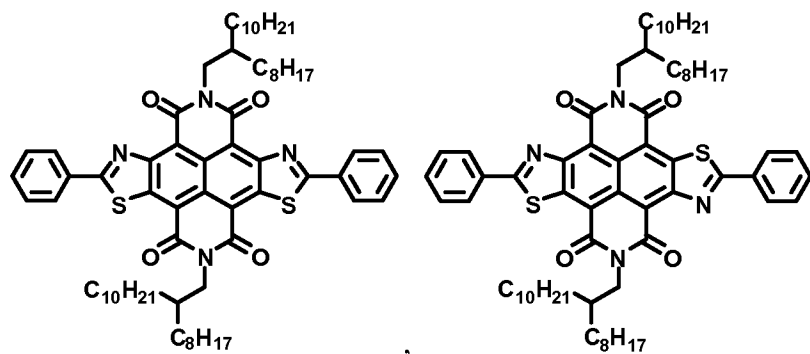
(XI)

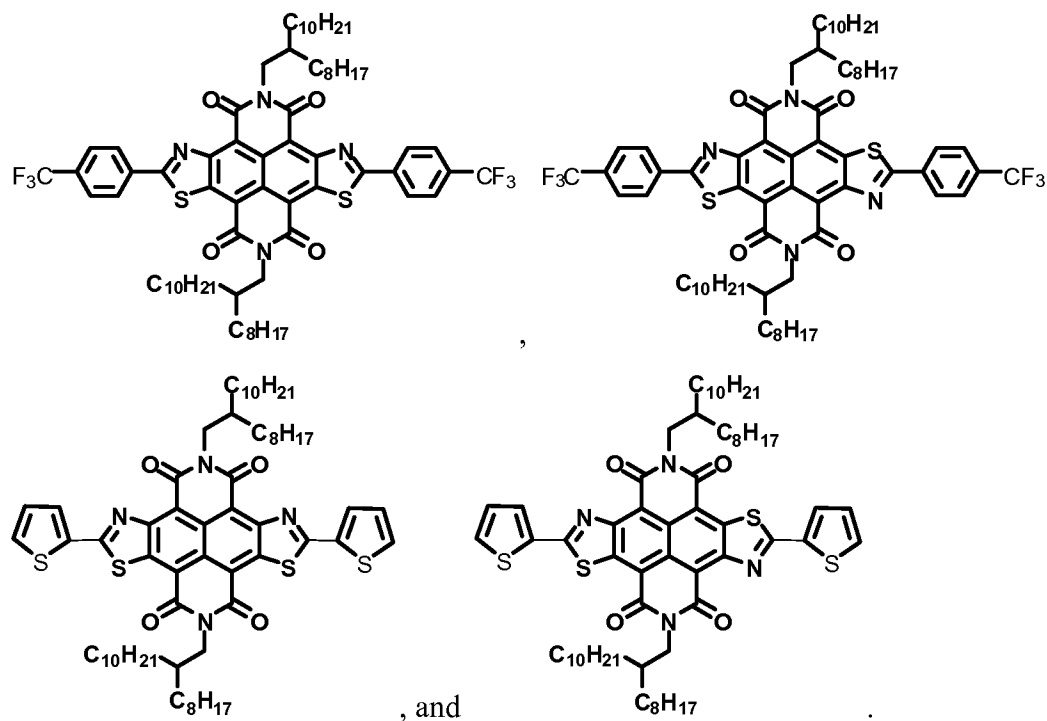


(XII)

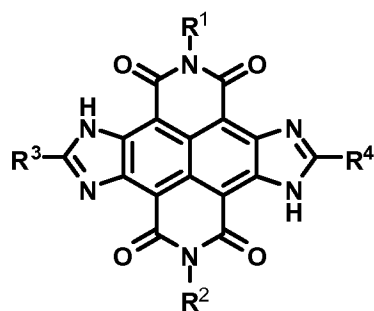
wherein R^{12} , R^{13} , R^{14} , R^{15} , R^{16} and R^{17} are independently selected from hydrogen, halogen, cyano, nitro, acyl, linear or branched alkyl group, linear or branched fluoroalkyl group, and linear or branched heteroalkyl group.

In other embodiments, the compound is selected from



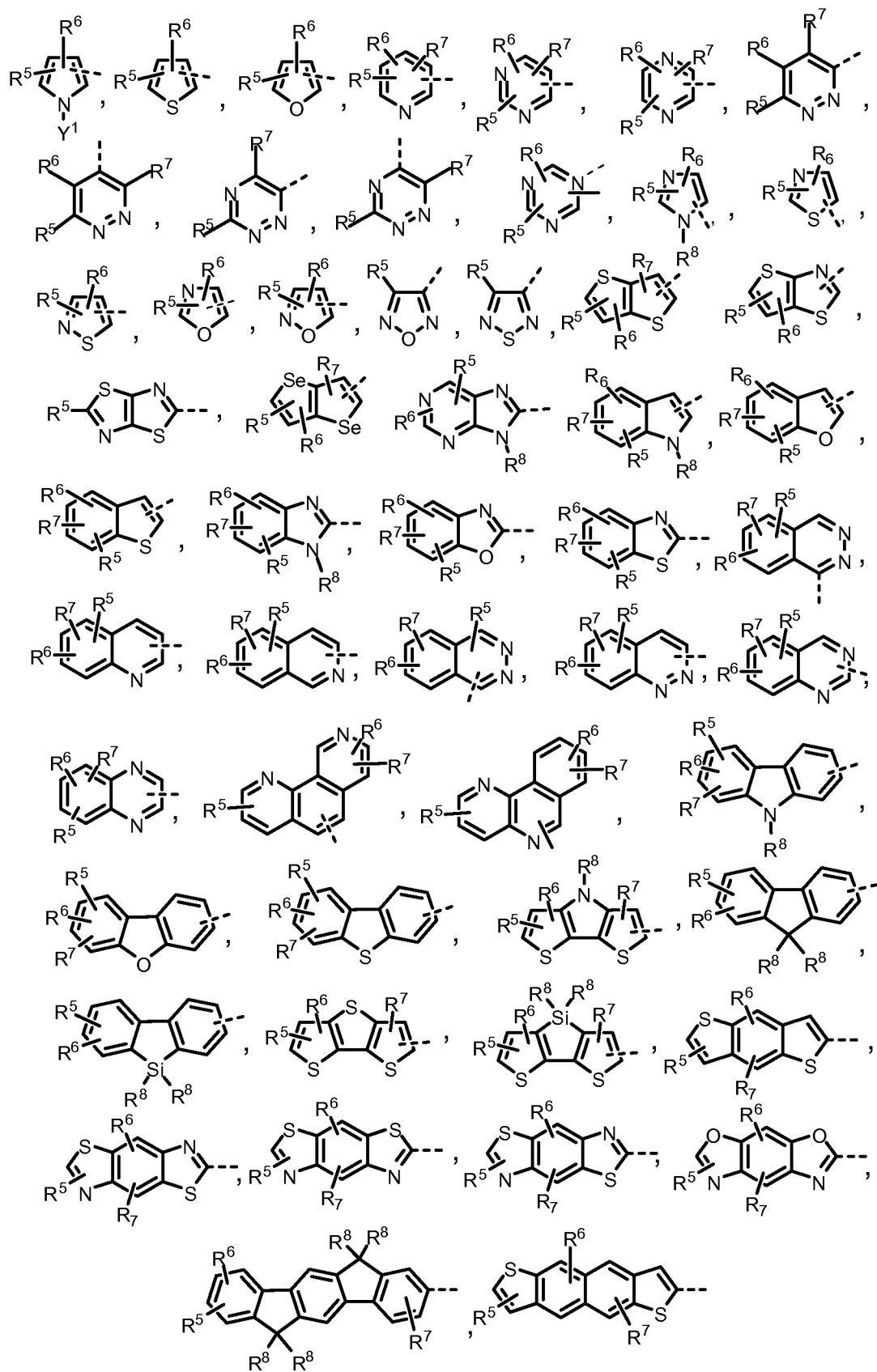


In other embodiments, the compound represented by formula (XIII)



(XIII); wherein R¹ and R² are independently selected from

optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group; wherein R³ and R⁴ are independently selected from



wherein R⁵, R⁶ and R⁷ are selected from hydrogen, halogen, hydroxyl, cyano, nitro, amine, silyl, siloxanyl, and optionally substituted linear, branched or cyclic C₁-C₃₀ organic

group, wherein optionally two or more of adjacent R^5 , R^6 and R^7 form a ring; and

wherein R^8 is selected from hydrogen, optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group.

In many embodiments of the Formulas (I and II), the optional substituents on "X" can be varied to modify the electronic and physical properties of the conjugated diimides, so as to produce and/or differentiate subunits having "weak" or "strong" electron acceptor properties.

The combinations of elements in Formulae (I) and (II) result in tunable "charge transfer", absorption bands in the UV or UV-visible or infra red region, HOMO/LUMO energy levels and charge carrier mobilities. It is also possible to "tune" the identity of the compounds and their optional substituents of aliphatic/aromatic R^3 and R^4 as described above, so as to modulate the optical and physical properties of the compounds in the solid state (π - π stacking and crystallinity), which promotes a high mobility of current carriers such as electrons.

The embodiments described herein relate to the compounds comprising of naphthobisthiazole- or naphthobisoxazole- diimides or its related compounds are of several advantages compare to naphthalene diimides (NDIs). The lateral fusion of thiazole or oxazole units, for example, into NDI enhances i) electron accepting property ii) rigidity and conjugation; iii) electron affinity (> 4 eV); iv) thermal and oxidative stability (IP > 6.0 eV) and durability; v) intermolecular π - π stacking; and vi) electron transport.

In many embodiments, the R^3 and/or R^4 subunits typically comprise one or more conjugated aryl or heteroaryl rings having delocalized HOMO orbitals of relatively high energy that tend to impart electron acceptor characteristics such as a low ionization potential or a low electrochemical oxidation potential (See for example, Y. Shirota and H. Kageyama, *Chem. Rev.* 2007, 107, 953-1010 and V. D. Parker, *J. Am. Chem. Soc.* 1976, 98, 98-103).

COMPOSITIONS

Additional embodiments include compositions comprising one or more compounds as described herein, or as made as described herein. The compounds described herein related to Formula (I) and/or (II) can be used as pure compounds or formulated with other materials to form compositions are useful for making devices such as, for example, organic thin film transistors.

For example, ink composition can be provided wherein one or more of the semiconductor compounds as described herein is mixed with one or more solvents. Organic solvents can be polar or non-polar, aromatic or aliphatic, and halogenated or non-halogenated.

In addition, compositions can comprise a mixture of a compound according to Formula (I) and a compound according to Formula (II). The amounts of each component in the composition can vary widely so that, for example, the amount of the compound according to Formula (I) can be about 1 wt.% to about 99 wt.%, or about 20 wt.% to about 80 wt.% of the total composition. The molar ratio of Formula (I) compound to Formula (II) compounds can be, for example, about 2:1 to about 0.5:1, or about 1:1.

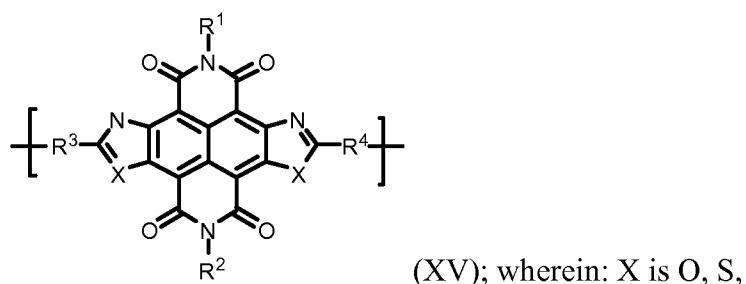
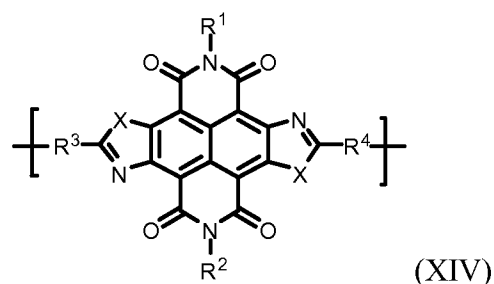
POLYMERS AND OLIGOMERS

The compounds described herein can be adapted for coupling reactions to serve as oligomerization or polymerization monomers, forming oligomers or polymers. Polymerization can be, for example, through the R1 and R2 groups, or through the R3 and R4 groups, as shown in Formulae (I) and (II). For example, halogen substituents can be the site for an oligomerization or polymerization reaction. The oligomers and polymers can be purified. Weight average molecular weights can be, for example, 200 to 1,000,000, or 1,000 to 100,000.

Hence, one embodiment provides for an oligomer or polymer prepared by the polymerization of a compound according to Formulae (I) or (II). In one embodiment, an oligomer is formed which has a weight average molecular weight of about 5,000 or less, or about 3,000 or less, or about 2,000 or less, or about 1,000 or less. In another embodiment, a polymer is formed which has a weight average molecular weight of about 3,000 or more, or about 5,000 or more, or about 10,000 or more, or about 30,000 or more, or about 50,000 or more.

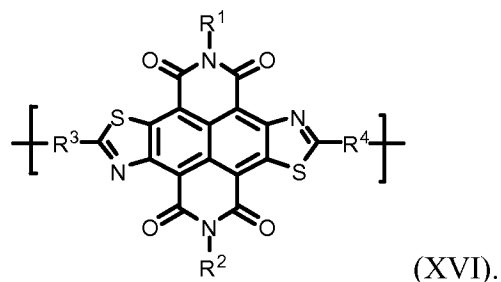
Copolymers and co-oligomers can be prepared including use of monomers that do not fall within the structures of Formulae (I) and (II).

For example, many embodiments described herein relate to a polymer or oligomer comprising at least one first repeating unit RU1, wherein RU1 is represented by formula (XIV) or (XV):

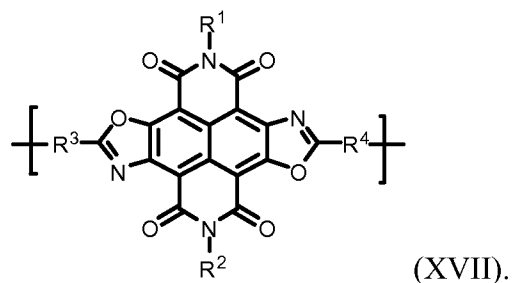


Se, or NH; R^1 and R^2 have the same definitions as previously described; and R^3 and R^4 are same or different and are each an optionally substituted aryl or heteroaryl group as previously described.

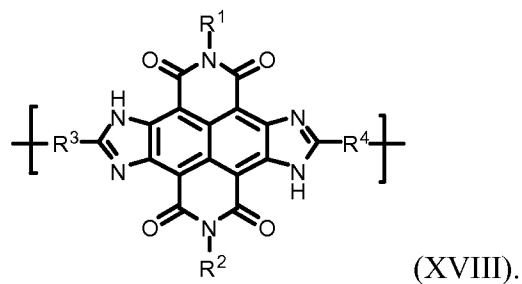
In some embodiments, X is S, and RU1 is represented by formula (XVI)



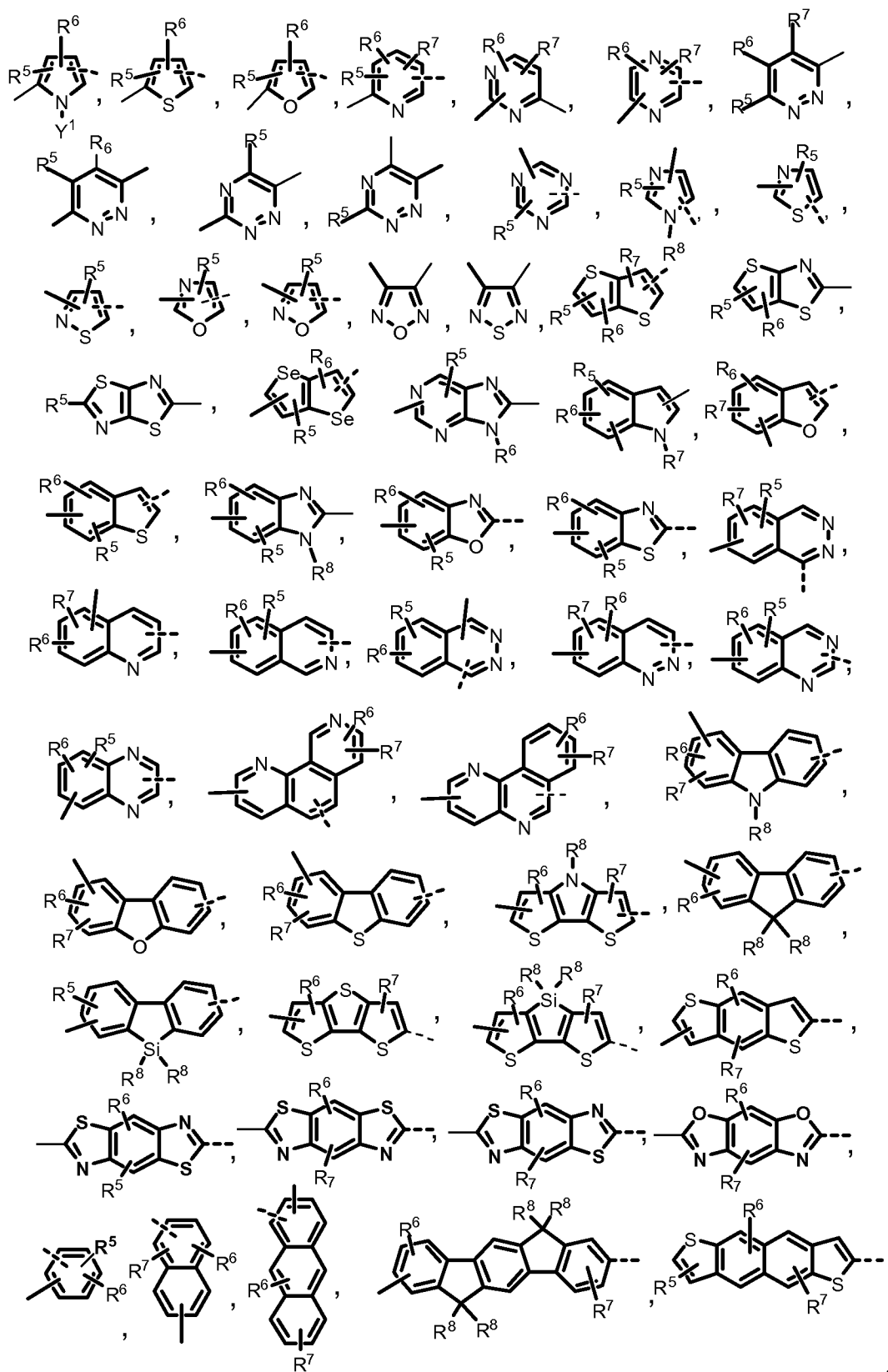
In some embodiments, X is O, and RU1 is represented by formula (XVII)



In some embodiments, X is NH, and RU1 is represented by formula (XVIII)



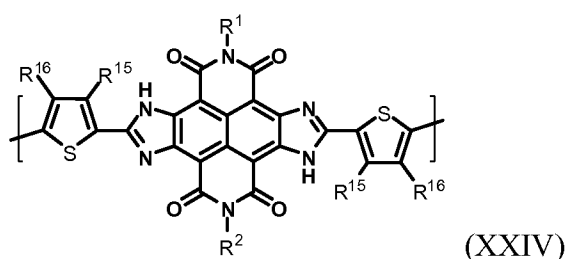
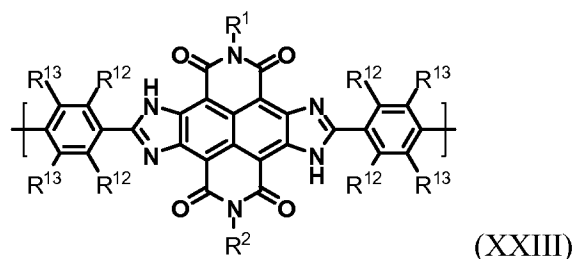
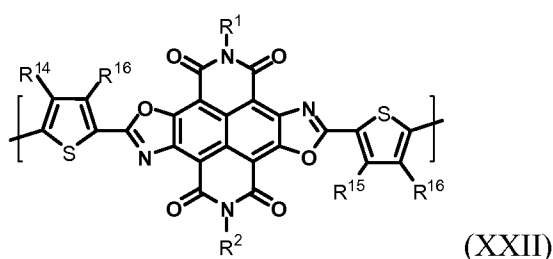
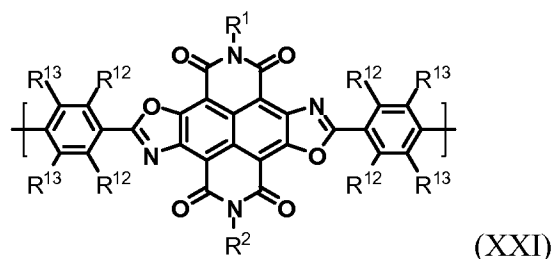
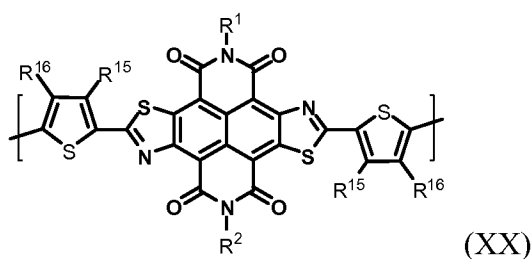
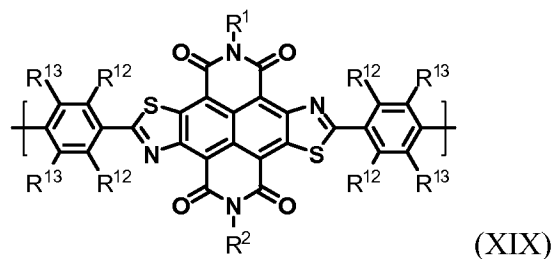
In some embodiments, R^3 and R^4 are each independently selected from



wherein R^5 , R^6 , R^7 and R^8 have the same definitions as previously described.

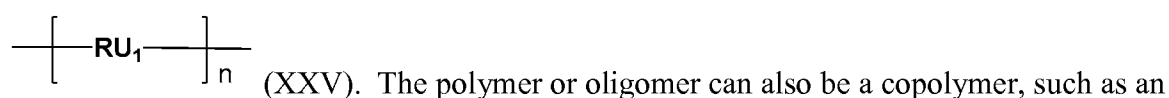
In some embodiments, R^3 and R^4 are each independently selected from phenyl, thiophene, furan, pyrrole, thiazole, oxazole, imidazole, benzothiazole, benzoxazole, selenophene, pyridine, pyrimidine, pyrazine, pyridazine, 1,2,4-triazine, 1,3,5-triazine, and 1,2,4,5-tetrazine, wherein each of the aryl or heteroaryl group can be optionally substituted. In some embodiments, R^3 and R^4 are each independently selected from phenyl and thiophene.

In some embodiments, the first repeating unit RU1 is represented by formulae (XIX) to (XIV):



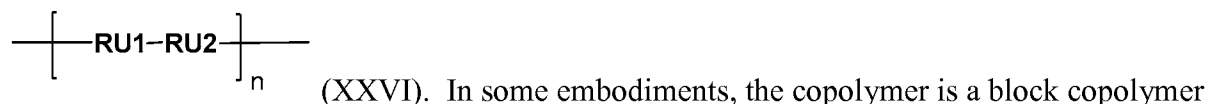
wherein R^{12} , R^{13} , R^{15} , and R^{16} have the same definitions as previously described.

The polymer or oligomer can be a homopolymer represented by



The polymer or oligomer can also be a copolymer, such as an alternating copolymer or a block copolymer, that comprises at least one second repeating unit RU2 having the same definitions as R^3 and R^4 as described in the foregoing paragraphs.

In some embodiments, the copolymer is an alternating copolymer represented by



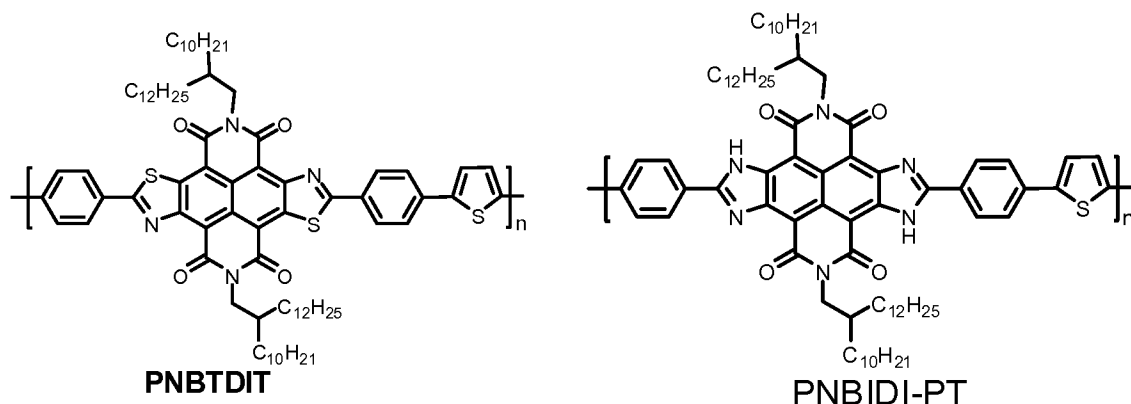
In some embodiments, the copolymer is a block copolymer

represented by $\text{---}(\text{RU1})_m(\text{RU2})_n\text{---}$ (XXVII). The copolymer can comprise, for example, at least two different RU1 repeating units.

RU2 can be the same as or different from R^3 and can be the same as or different from R^4 . In some embodiments, RU2 is selected from phenyl, thiophene, furan, pyrrole, thiazole, oxazole, imidazole, benzothiazole, benzoxazole, selenophene, pyridine, pyrimidine, pyrazine, pyridazine, 1,2,4-triazine, 1,3,5-triazine, and 1,2,4,5-tetrazine, wherein each of the aryl or heteroaryl group can be optionally substituted. In some embodiments, RU2 is selected from phenyl and thiophene.

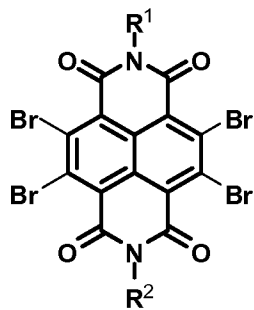
In some embodiments, the copolymer is an alternating copolymer, with the alternating section comprising at least one RU1 repeating unit and at least one RU2 repeating unit. In some embodiments, the copolymer is an alternating copolymer, with the alternating section comprising at least one RU1 repeating unit and at least two RU2 repeating units, said at least two RU2 units can be same or different. In some embodiments, the copolymer is an alternating copolymer, with the alternating section comprising at least one RU1 repeating unit and at least three RU2 repeating units, said at least three RU2 units can be same or different. In some embodiments, the copolymer is an alternating copolymer, with the alternating section comprising at least two RU1 repeating units, said at least two RU1 units can be same or different.

Particular examples of the copolymer described herein include the following:



METHODS OF MAKING

Also provided are methods of making the compounds described herein. For example, one method comprises reacting a first compound represented by:

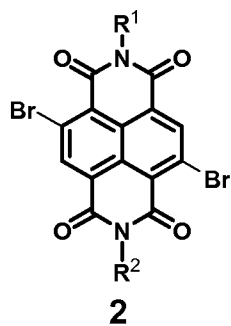


(1) with a second compound represented by



Se, or -NH.

A second method comprises reacting a compound **2** represented by:

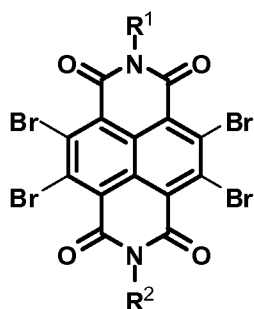


with a compound represented by

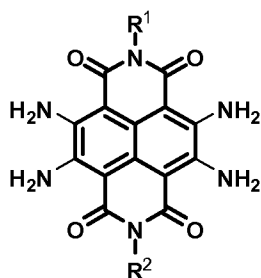


wherein X is S, O, Se or -NH.

A third method comprises (A) reacting a compound represented by



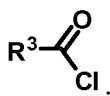
with hydrazine to obtain a naphthalene diimide tetramine represented by



formula (XXII)

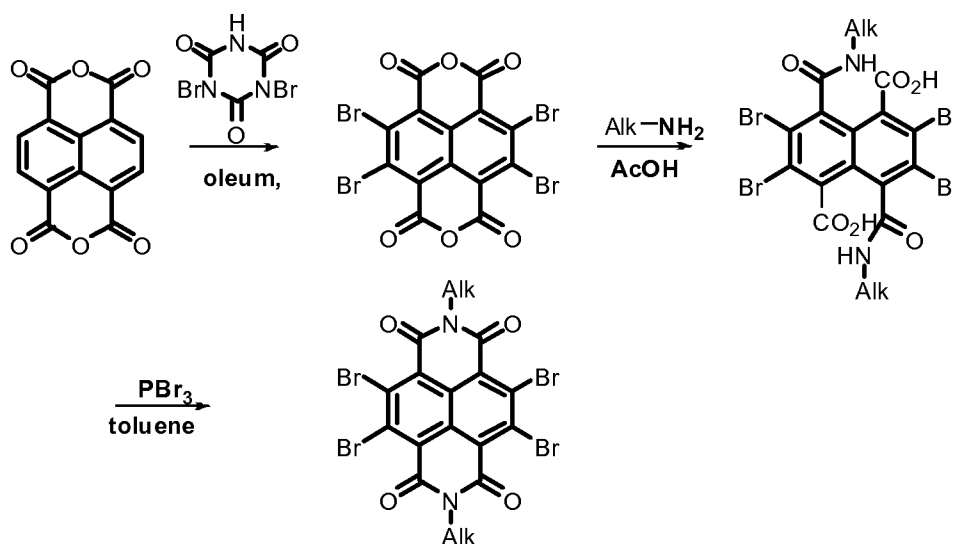
(XXII); and (B) reacting the naphthalene diimide tetramine

with a compound represented by



Generic synthetic schemes for making starting materials required to synthesize the compounds as described herein are presented below, and specific examples of such generic synthetic methods are also provided below in the “Working Examples.”

Synthesis of N-alkyl-tetrabromo naphthalene tetracarboxylic diimides

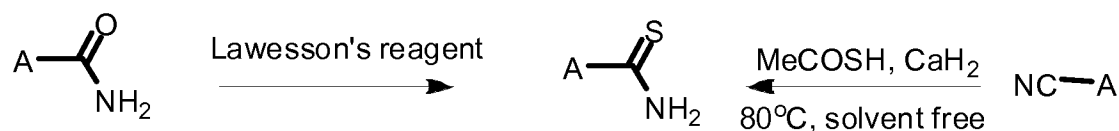


Zhu, et al. *Org. Lett.* **2007**, 9, 3917-3920

The references cited above in connection with the synthetic schemes are hereby incorporated by reference herein for their disclosures relating to methods of synthesis of the starting materials referenced above.

Applicants have also invented methods for making other starting materials useful for making the naphthobisazole compounds comprising aromatic "A" (A₁ and A₂) subunits described herein, as illustrated below and in the Examples.

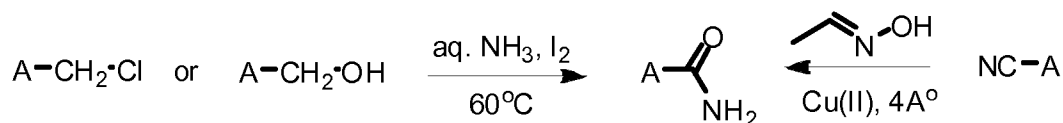
Synthesis of N-aryl thioamides



Dembinski *et al. Org. Lett.* 2006, 8, 1625-1628.

Arunachalam *et al Synlett* 2009, 14, 2338-2340.

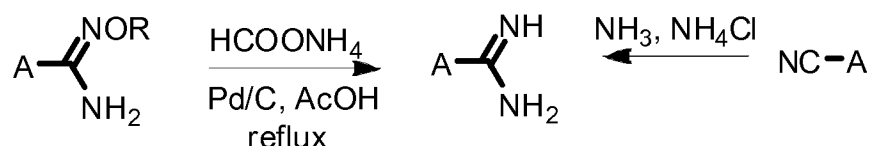
Synthesis of N-aryl carboxamides



Hell *et al Tetrahedron Lett.* 2011, 52, 6021-6023.

Togo *et al Tetrahedron Lett.* 2010, 51, 4378-4381.

Synthesis of N-aryl carboxamidines



Mariappan et al *Synthesis* 2003, 16, 2467-2469.

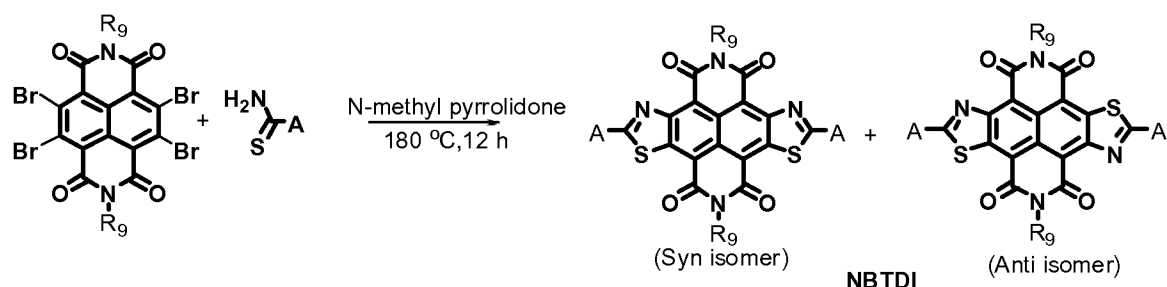
Krapacho et al *J. Org. Chem.* 1962, 27, 1255-58.

The references cited above in connection with the synthetic schemes are hereby incorporated by reference herein for their disclosures relating to methods of synthesis of the starting materials referenced above.

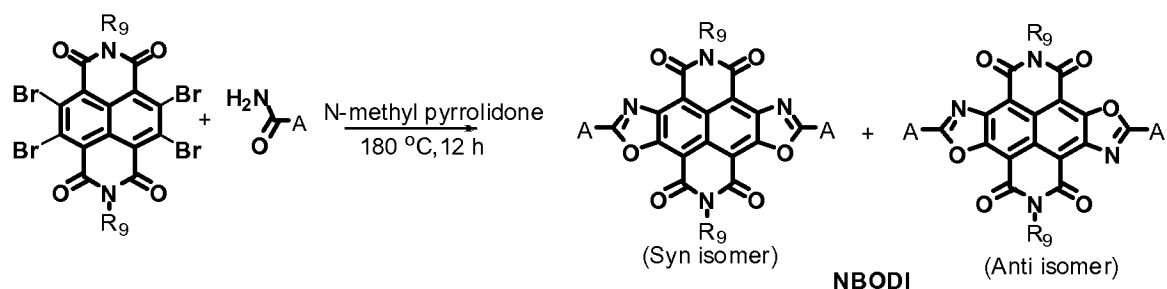
Synthesis of Naphthobisazole Diimides (NBADI)

The generic reaction schemes shown below illustrate synthesis of the naphthobisazole compounds and or/ co-oligomers. Specific examples of such methods are provided in the Examples section of the disclosure below.

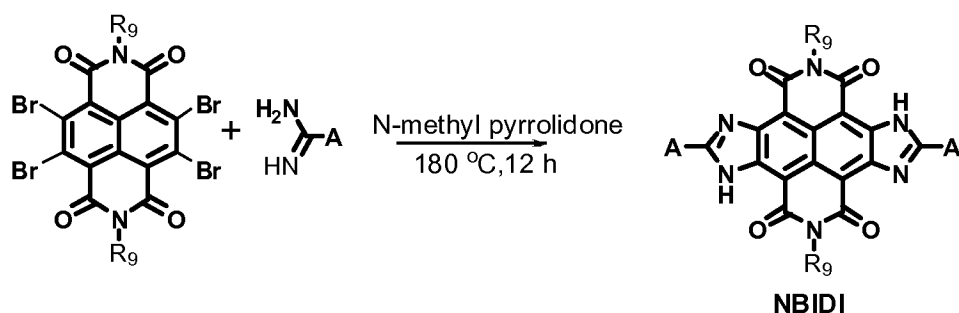
General Synthetic Methods to Produce Naphthobisthiazole diimides (NBTDIs)



General Synthetic Methods to Produce Naphthobisoxazole diimides (NBODIs)



General Synthetic Methods to Produce Naphthobisimidazole diimides (NBIDIs)



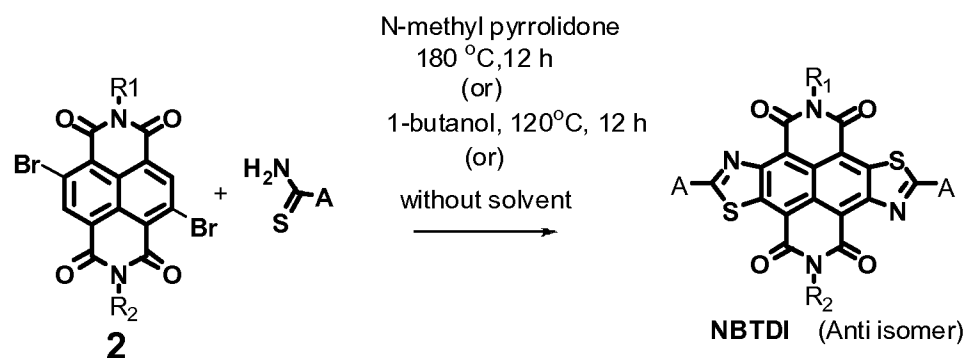
As shown in the generic scheme above, the naphthobisazole diimide (NBADI) can be obtained from a simple, one pot synthesis of tetrabromo naphthalenediimide and thioamide/carboxamide/carboxamidine. N-methyl pyrrolidone, acts both as a solvent and a base. For an example, syn- and anti-isomer of naphthobisthiazole diimide (NBTDI) was obtained from the nucleophilic substitution of tetrabromide and in *situ* ring closing reaction with arylthioamide.

Similarly, the oxazole derivative (NBODI) was obtained from the corresponding carboxamide. However, only one isomer will be anticipated in the case of naphthobisimidazole diimide (NBIDI).

SYNTHESIS OF ENRICHED ISOMERS

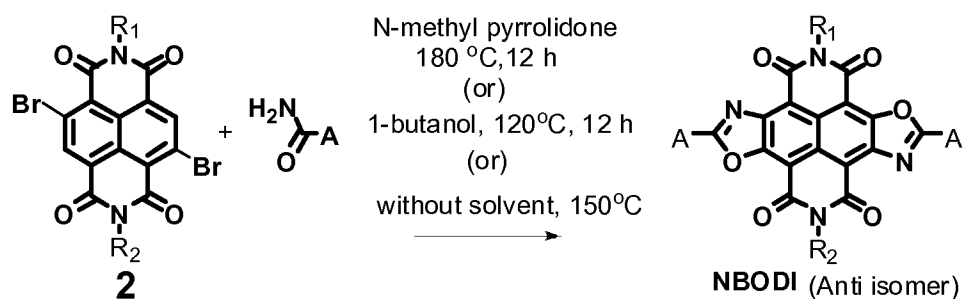
Applicants have also invented an alternate method for making single (anti) isomer of naphthobisazole compounds (NBADI) from dibromo naphthalene diimide (**2**). The reaction was carried out by using N-methylpyrrolidone at 180 °C for 12h, or any alkyl alcohol (1-butanol) at 120 °C for 12 h, or without any solvents at 150 °C. The generic reaction schemes shown below illustrate synthesis of naphthobisazole compounds and or/ co-oligomers. Specific examples of such methods are provided in the Examples section of the disclosure below.

General Synthetic Methods to Produce Naphthobisthiazole diimides (NBTDIs)



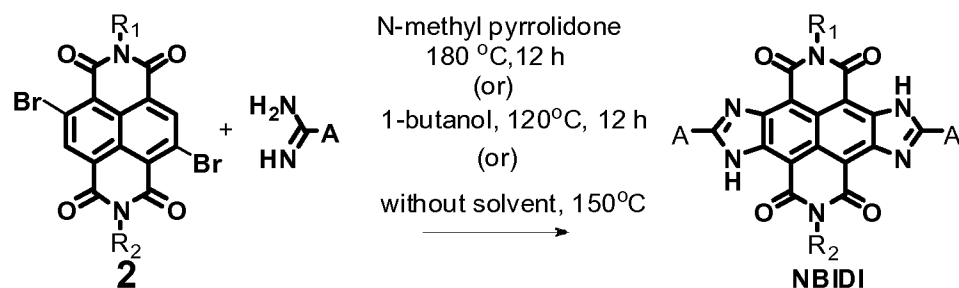
Accordingly, one embodiment described herein is an anti-isomer composition of NBTDI.

General Synthetic Methods to Produce Naphthobisoxazole diimides (NBODIs)



Accordingly, one embodiment described herein is an anti-isomer composition of NBODI.

General Synthetic Methods to Produce Naphthobisimidazole diimides (NBIDIs)

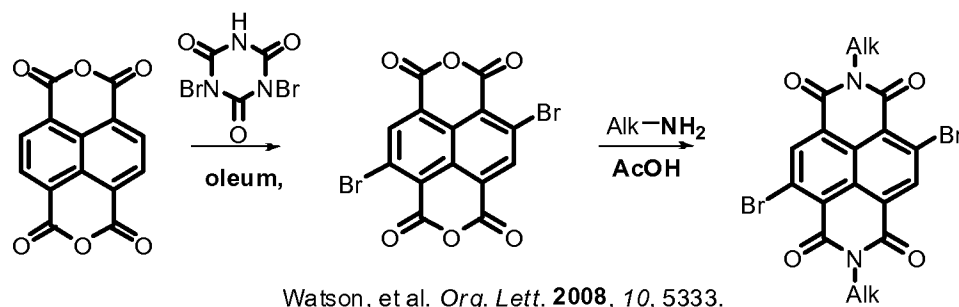


SEPARATION OF ISOMER MIXTURES

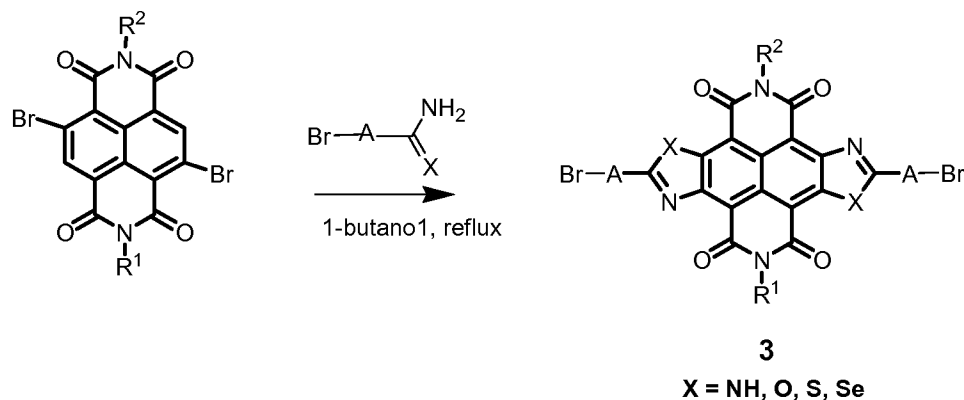
The syn and anti isomer mixtures of compounds described herein can be separated by using one of the purification techniques such as column chromatography, semi preparative high performance liquid chromatography, preparative thin layer chromatography, sublimation, and recrystallization.

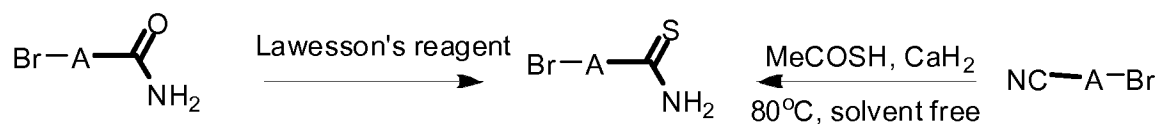
SYNTHESIS OF COPOLYMER

Synthesis of N-alkyl-dibromo naphthalene tetracarboxylic diimides

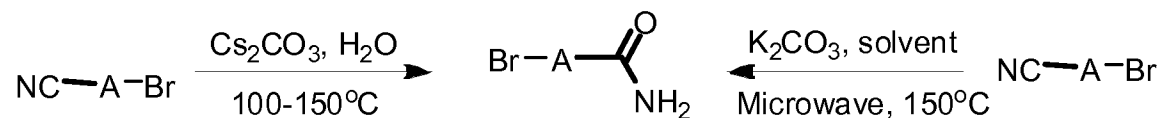


Synthesis of dibromo naphthobisthiazole diimides

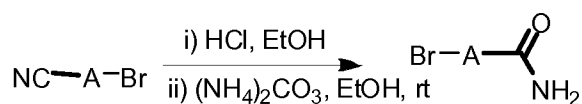


Synthesis of bromo-N-aryl thioamides

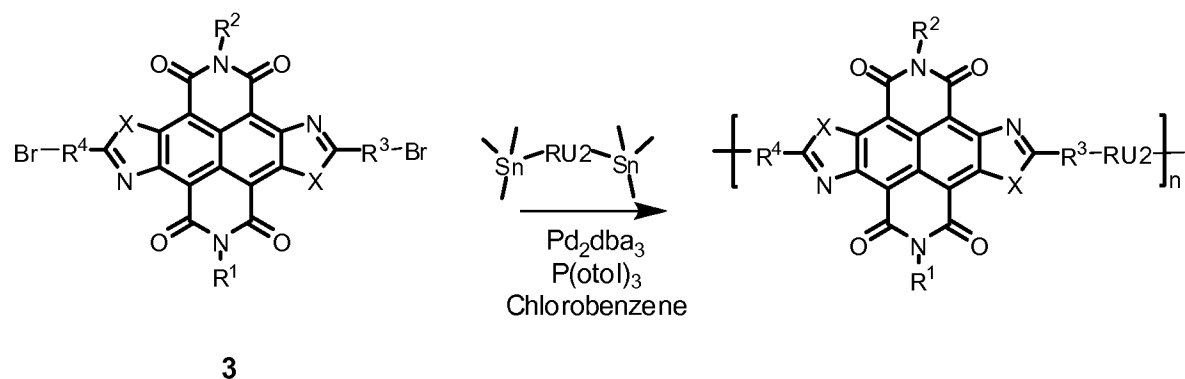
Dembinski et al. *Org. Lett.* **2006**, 8, 1625-1628.

Synthesis of bromo-N-aryl carboxamides

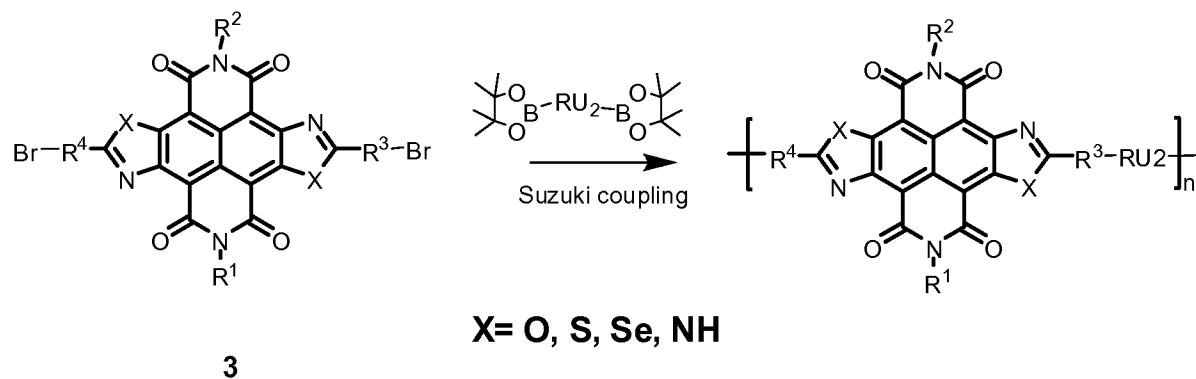
Tu et al. *Green Chemistry* **2012**, 14, 921-924.

Synthesis of bromo-N-aryl-carboxamidines

Negora et al. *Bioorganic & Medicinal Chemistry* **2012**, 20, 2369-2375.

General Synthetic Methods to Produce Naphthobisazole Diimide Copolymers

X= O, S, Se, NH



X= O, S, Se, NH

ORGANIC ELECTRONIC DEVICES

Some embodiments relate to novel organic electronic devices comprising the compounds described herein, including, for example, organic light emitting diodes (OLEDs), transistors, and solar cells. Each of those end use applications typically requires the formation of a film of the compounds on a substrate. Organic films of the compounds described herein can be prepared by known methods such as, for example, spin coating methods, casting methods, dip coating methods, inkjet methods, doctor blade coating methods, screen printing methods, and spray coating methods. By using such methods, it becomes possible to prepare organic films having good properties such as mechanical strength, toughness, and/or durability without forming cracks in the films. Therefore, the organic films can be preferably used for organic electronic devices such as photovoltaic cells, FET elements, and light emitting elements.

Films of the compounds described herein are typically prepared by coating a coating liquid, which is prepared by dissolving the compound in a solvent such as, for example, dichloromethane, tetrahydrofuran, chloroform, toluene, chlorobenzene, dichlorobenzene, or xylene, on a substrate. Specific examples of the coating methods include spray coating methods, spin coating methods, blade coating methods, dip coating methods, cast coating methods, roll coating methods, bar coating methods, die coating methods, ink jet methods, dispense methods, etc. In this regard, a proper method and a proper solvent are selected in consideration of the properties of the molecules used. Suitable materials for use as the substrate on which a film of the compound of the present invention is formed include inorganic substrates such as glass plates, silicon plates, ITO plates, and FTO plates, and organic substrates such as plastic plates (e.g., PET films, polyimide films, and polystyrene films), which can be optionally subjected to a surface treatment. It is preferable that the substrate has a smooth surface.

The thickness of the organic film and the organic semiconductor layer of the organic thin film transistor are not particularly limited. However, the thickness is determined such that the resultant film or layer is a uniform thin layer (the film or layer does not include gaps or holes adversely affecting the carrier transport property thereof). The thickness of the organic semiconductor layer is generally not greater than 1 micron, and preferably, for example, from about 5 nm to about 200 nm.

In sum, embodiments include an electronic device comprising at least one of the compounds as described herein, or made by a method as described herein, or at least one composition as described herein.

TRANSISTORS

The organic thin film transistors of the present invention typically have a configuration such that an organic semiconductor layer including the naphthobisazole diimides (NBADIs) as described herein is formed therein while also contacting the source electrode, drain electrode and insulating layer of the transistor.

The organic thin film transistor prepared above is typically thermally annealed. Annealing can be performed while the film is set on a substrate, and is believed (without wishing to be bound by theory) to allow for at least partial self-ordering and/or π -stacking of the molecules to occur in the solid state. The annealing temperature is determined depending on the property of the compounds/ or molecules, but is preferably from room temperature (about 25 °C) to 300 °C, and more preferably from 50 to 300 °C. In many embodiments, thermal annealing is carried out at at least 150 °C, or preferably above 170 °C, or above 200 °C. When the annealing temperature is too low, the organic solvent remaining in the organic film may not be well removed therefrom. In contrast, when the annealing temperature is too high, the organic film can be thermally decomposed. Annealing is preferably performed in a vacuum, or under nitrogen, argon or air atmosphere. In some embodiments annealing is performed in an atmosphere including a vapor of an organic solvent capable of dissolving the polymer so that the molecular motion of the molecule is accelerated, and thereby a good organic thin film can be prepared. The annealing time is properly determined depending on the aggregation speed of the polymer.

An insulating (dielectric) layer can be used in the organic thin film transistors comprising the compounds/ or molecules of the present invention, situated between the gate electrode and the organic thin film comprising the compounds. Various insulating materials can be used for the insulating layer. Specific examples of the insulating materials include inorganic insulating materials such as, for example, silicon oxide, silicon nitride, aluminum oxide, aluminum nitride, titanium oxide, tantalum oxide, tin oxide, vanadium oxide, barium strontium titanate, barium zirconate titanate, lead zirconium titanate, lead lanthanum titanate, strontium titanate, barium titanate, barium magnesium fluoride, bismuth tantalate niobate, hafnium oxide, and trioxide yttrium; organic insulating materials such as, for example, polymer materials, e.g., polyimide, polyvinyl alcohol, polyvinyl phenol, polystyrene, polyester, polyethylene, polyphenylene sulfide, unsubstituted or halogen-atom substituted polyparaxylylene, polyacrylonitrile, and cyanoethylpullulan; etc. These materials can be used alone or in combination. Among these materials, materials having a high dielectric constant and a low conductivity are preferably used.

Suitable methods for forming such an insulating layer include dry processes such as, for example, CVD methods, plasma CVD methods, plasma polymerization methods, and vapor deposition methods; wet processes such as spray coating methods, spin coating methods, dipcoating methods, inkjet coating methods, castcoating methods, blade coating methods, and bar coating methods; etc.

In order to improve the adhesion between the insulating layer and organic semiconductor layer, to promote charge transport, and to reduce the gate voltage and leak current, an organic thin film (intermediate layer) can be employed between the insulating layer and organic semiconductor layer. The materials for use in the intermediate layer are not particularly limited as long as the materials do not chemically affect the properties of the organic semiconductor layer, and for example, molecular films of organic materials, and thin films of polymers can be used therefor. Specific examples of the materials for use in preparing the molecular films include coupling agents such as octadecyltrichlorosilane, octyltrichlorosilane, octyltrimethoxysilane, hexamethyldisilazane (HMDS), and octadecylphosphonic acid. Specific examples of the polymers for use in preparing the films of the compounds include the polymers mentioned above for use in the insulating layer. Such polymer films can serve as the insulating layer as well as the intermediate layer.

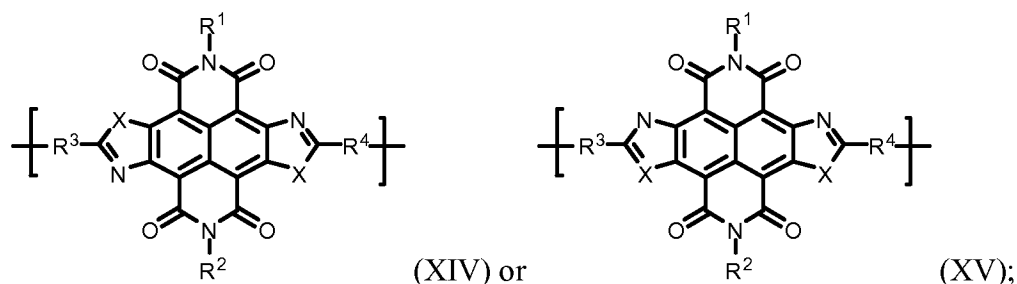
The materials of the electrodes (such as gate electrodes, source electrodes and drain electrodes) of the organic thin film transistor as described herein are not particularly limited as long as the materials are electrically conductive. Specific examples of the materials include metals such as platinum, gold, silver, nickel, chromium, copper, iron, tin, antimony, lead, tantalum, indium, aluminum, zinc, tungsten, titanium, calcium, and magnesium; alloys of these metals; electrically conductive metal oxides such as indium tin oxide (ITO); inorganic or organic semiconductors, whose electroconductivity is improved by doping or the like, such as silicon single crystal, polysilicon, amorphous silicon, germanium, graphite, carbon nanotube, polyacetylene, polyparaphenylene, polythiophene, polypyrrole, polyaniline, polythienylenevinylene, polyparaphenylenevinylene, and complexes of polyethylenedioxythiophene (PEDOT) and polystyrene sulfonic acid.

In sum, embodiments described herein include an n-channel transistor comprising a layer comprising at least one of the compounds as described herein, said layer is obtained by solution processing, and annealing a composition, said composition comprising at least one solvent and at least one of the compounds as described herein or made by a method as described herein.

Additional embodiments are providing for in the following non-limiting working examples.

ADDITIONAL EMBODIMENTS

Embodiment 1 – A polymer or oligomer comprising at least one first repeating unit RU1 represented by:



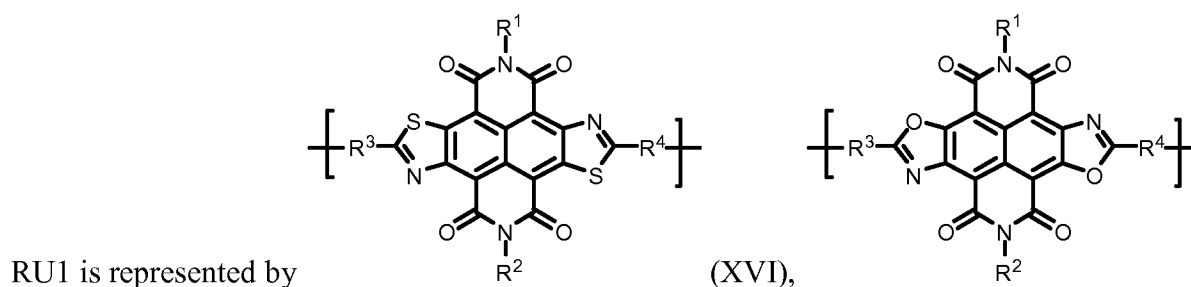
wherein:

- (i) wherein X is O, S, Se, or NH;
- (ii) R^1 and R^2 are each independently selected from optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group;
- (iii) R^3 and R^4 are each independently selected from optionally substituted aryl group and optionally substituted heteroaryl group.

Embodiment 2 – The polymer or oligomer of Embodiment 1, wherein the first repeating unit RU1 is represented by formula (XIV).

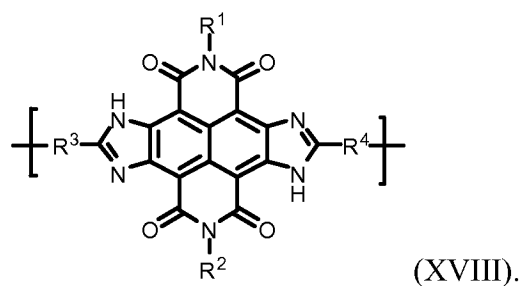
Embodiment 3 – The polymer or oligomer of Embodiment 1, wherein the first repeating unit RU1 is represented by formula (XV).

Embodiment 4 – The polymer or oligomer of Embodiment 1, wherein the first repeating unit



RU1 is represented by

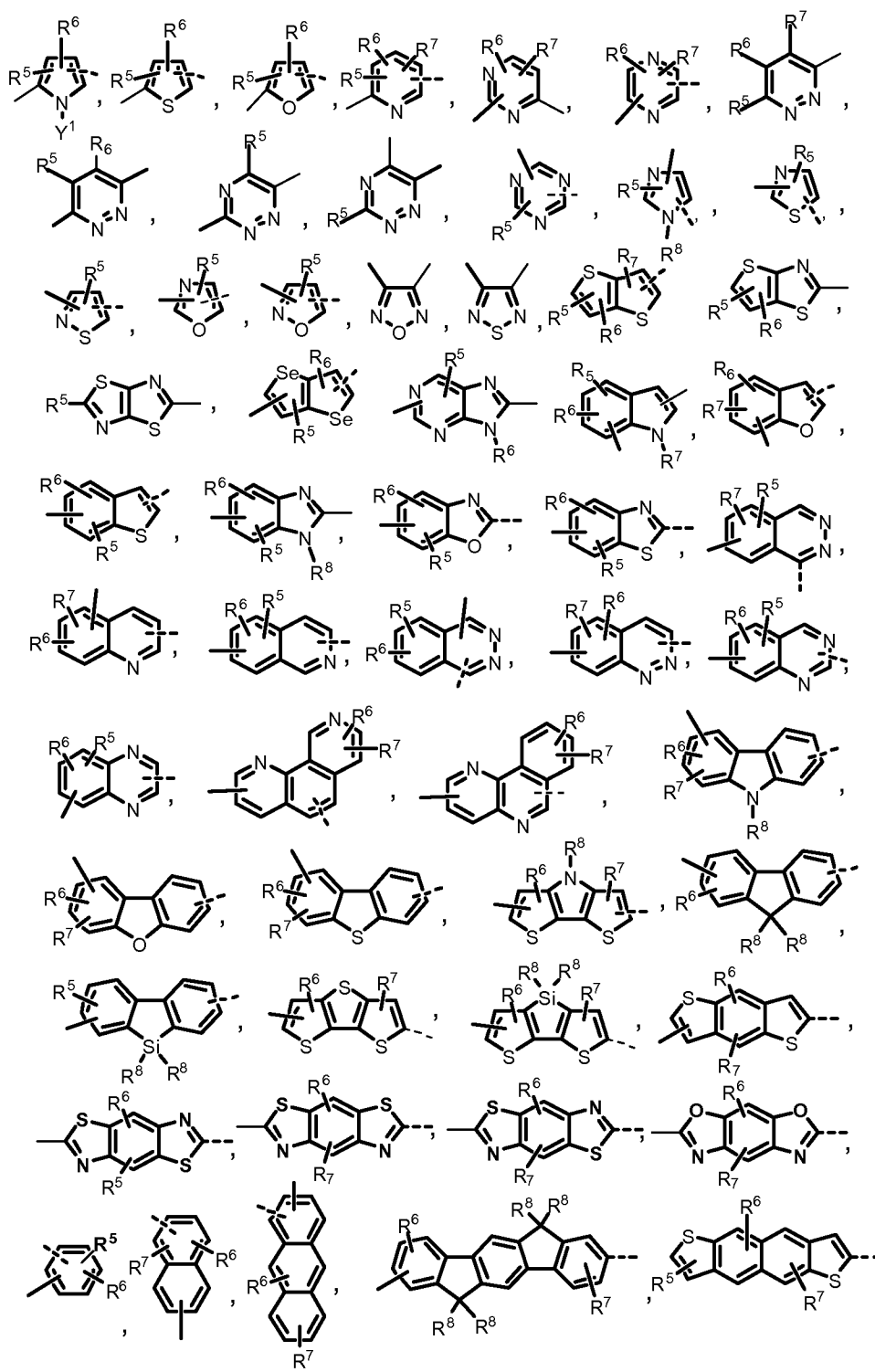
(XVII), or



Embodiment 5 – The polymer or oligomer of any of Embodiments 1-4, wherein R^1 and R^2 are each independently selected from optionally substituted C_1 - C_{25} alkyl group and optionally substituted C_1 - C_{25} heteroalkyl group.

Embodiment 6 – The polymer or oligomer of any of Embodiments 1-5, wherein R^1 and R^2 are each independently selected from linear, mono- or pluri-cyclic, or branched alkyl group, linear, mono- or pluri-cyclic, or branched fluoroalkyl group, and linear, mono- or pluri-cyclic, or branched heteroalkyl group.

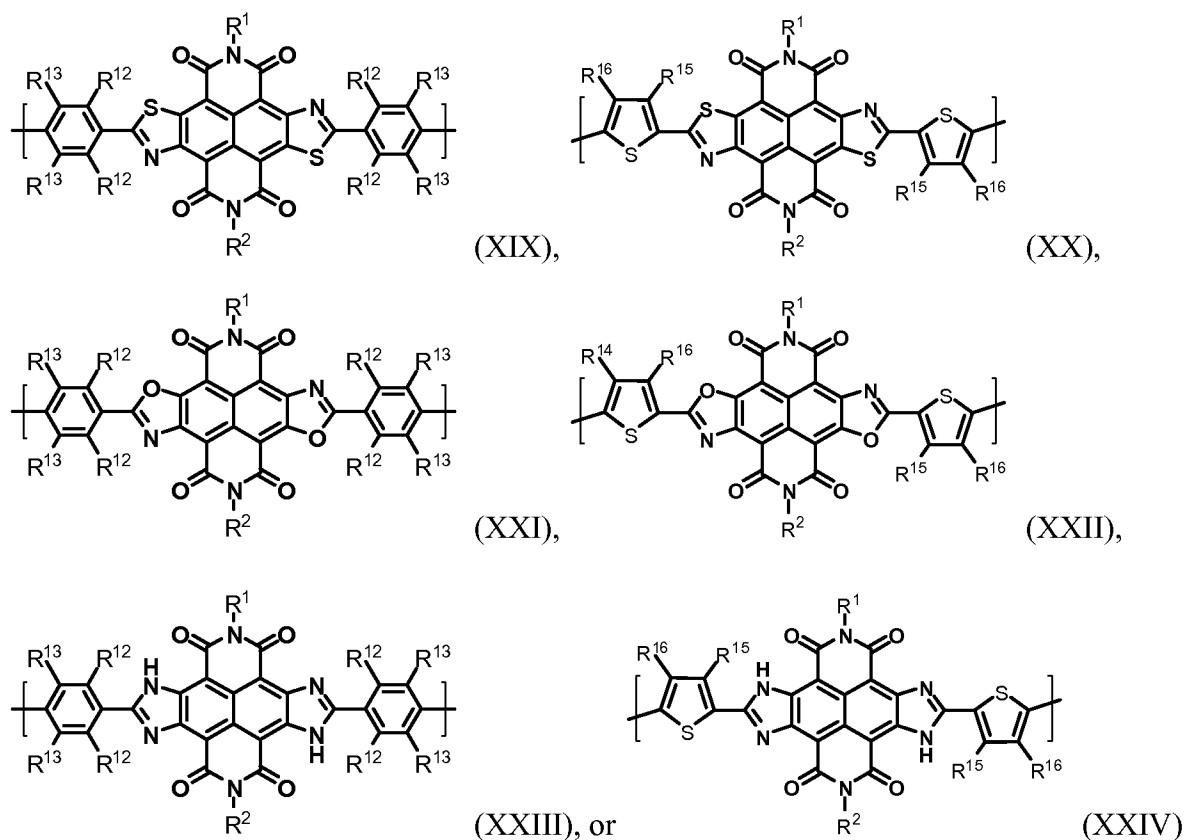
Embodiment 7 – The polymer or oligomer of any of Embodiments 1-6, wherein R^3 and R^4 are each independently selected from



wherein R⁵, R⁶ and R⁷ are each hydrogen or an optionally substituted linear, branched, or cyclic C₁-C₃₀ organic group, wherein optionally two or more of adjacent R⁵, R⁶ and R⁷ form a ring; and wherein R⁸ is selected from hydrogen, optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group.

Embodiment 8 – The polymer or oligomer of any of Embodiments 1-7, wherein R^3 and R^4 are independently selected from optionally substituted phenyl, optionally substituted thiophenyl, optionally substituted furanyl, optionally substituted pyridinyl, optionally substituted pyrimidinyl, optionally substituted pyridazinyl, optionally substituted pyrazinyl, optionally substituted 1,2,4-triazine, optionally substituted 1,3,5-triazine, and optionally substituted 1,2,4,5-tetrazine.

Embodiment 9 – The polymer or oligomer of any of Embodiments 1-8, wherein the first repeating unit RU1 is represented by:



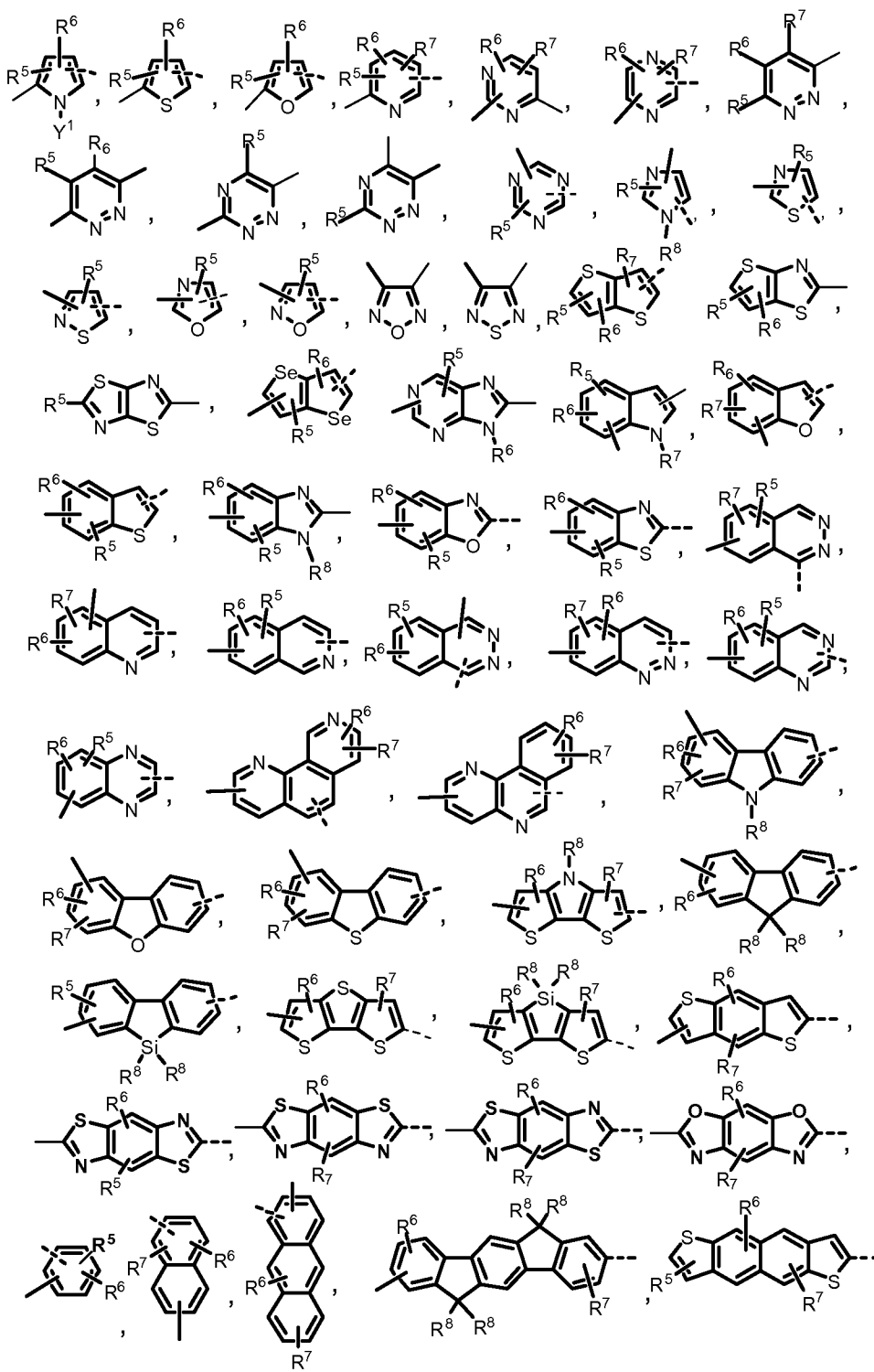
wherein R^{12} , R^{13} , R^{15} , and R^{16} are independently selected from hydrogen, linear or branched alkyl group, linear or branched fluoroalkyl group, and linear or branched heteroalkyl group.

Embodiment 10 – The polymer or oligomer of any of Embodiments 1-9, selected from

- (i) a homopolymer represented by $\left[\text{RU}_1 \right]_n$ (XXV),
- (ii) an alternating copolymer represented by $\left[\text{RU}_1\text{-RU}_2 \right]_n$ (XXVI), and

(iii) a block copolymer represented by $\text{---}(\text{RU1})_m(\text{RU2})_n\text{---}$ (XXVII), wherein RU2 represents a second repeating unit.

Embodiment 11 – The polymer or oligomer of any of Embodiments 1-10, comprising a second repeating unit RU2 selected from

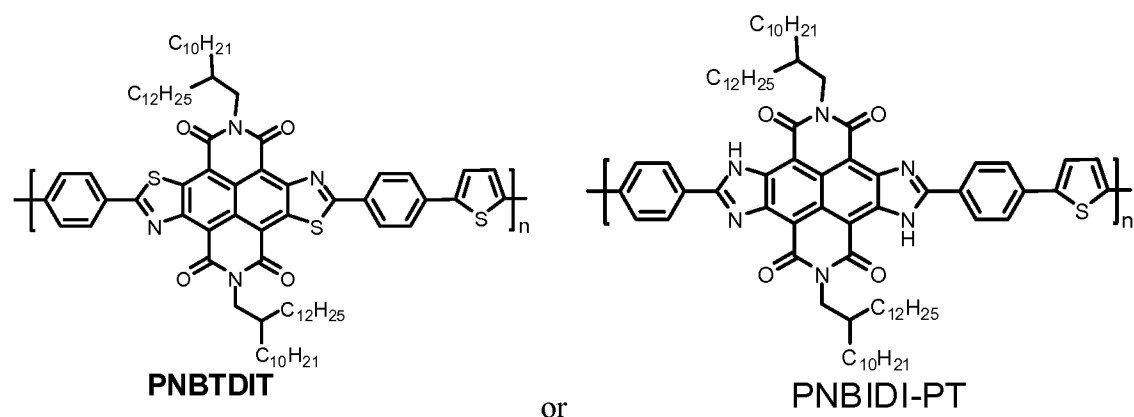


wherein R⁵, R⁶ and R⁷ are each hydrogen or an optionally substituted linear, branched, or

cyclic C₁-C₃₀ organic group, wherein optionally two or more of adjacent R⁵, R⁶ and R⁷ form a ring; and wherein R⁸ is selected from hydrogen, optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group.

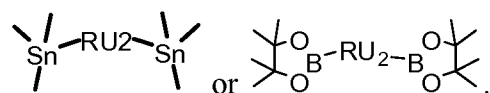
Embodiment 12 – The polymer or oligomer of any of Embodiments 1-10, comprising a second repeating unit RU2 selected from optionally substituted phenyl, optionally substituted thiophenyl, optionally substituted furanyl, optionally substituted pyridinyl, optionally substituted pyrimidinyl, optionally substituted pyridazinyl, optionally substituted pyrazinyl, optionally substituted 1,2,4-triazine, optionally substituted 1,3,5-triazine, and optionally substituted 1,2,4,5-tetrazine.

Embodiment 13 – The polymer or oligomer of Embodiment 1, represented by:



Embodiment 14 – A polymer or oligomer obtained by reacting a polymerizable derivative of the first repeating unit RU1 as described in any of Embodiments 1-9 with a polymerizable derivative of the second repeating unit RU2 as described in any of Embodiments 11-12.

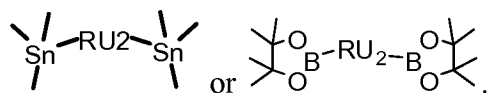
Embodiment 15 – The polymer or oligomer of Embodiment 14, which is obtained by reacting a halogenated derivative of the first repeating unit RU1, such as wherein R³ and R⁴ are each derivatized with Br, with a polymerizable derivative of the second repeating unit RU2 represented by



Embodiment 16 – A composition comprising at least one of the polymer or oligomer of any of Embodiments 1-15.

Embodiment 17 – A method for making the polymer or oligomer of any of Embodiments 1-15 or the composition of Embodiment 16, comprising reacting a halogenated derivative of the first

repeating unit RU1, such as wherein R³ and R⁴ are each derivatized with Br, with a polymerizable derivative of the second repeating unit RU2 represented by



Embodiment 18 – An electronic device comprising the polymer or oligomer of any of Embodiments 1-15 or the composition of Embodiment 16, or the polymer or oligomer or composition made by the method of Embodiment 17.

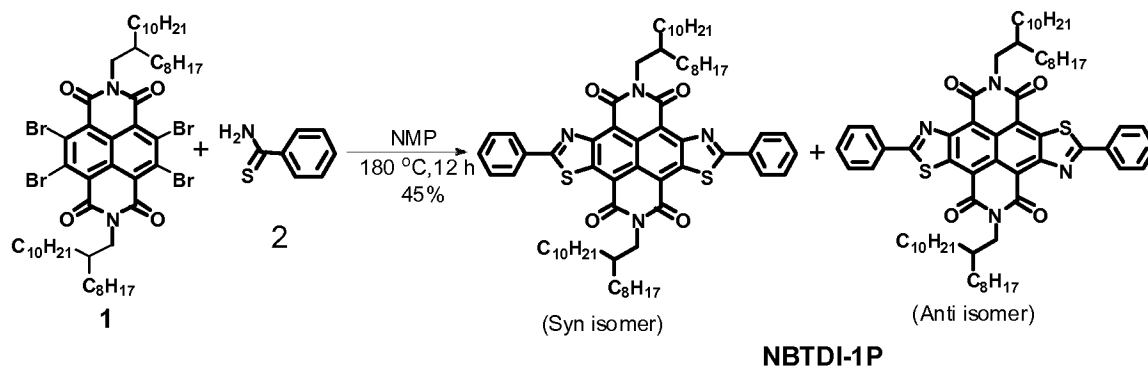
Embodiment 19 – An n-channel transistor comprising a layer obtained by solution processing and annealing the composition of Embodiment 16.

WORKING EXAMPLES

Materials. All commercially available reagents were purchased from Sigma-Aldrich, Across, Alfa-Aesar and TCI America, Laboratory of Chemicals.

Mass spectra were recorded on a Bruker Esquire LC/ Ion Trap Mass spectrometer and a Jeol HX-110 FAB Mass spectrometer. ¹H-NMR spectra were recorded on a Bruker AV300/AV500 at 300 MHz/500 MHz respectively using CDCl₃ or C₆D₄Cl₂ or CF₃COOD or C₂D₄Cl₄ as the solvents. Cyclic voltammetry was done on an EG&G Princeton Applied Research Potentiostat/Galvanostat 273A. A three-electrode cell was used, using platinum wire electrodes as both counter and working electrode. Silver/silver ion (Ag in 0.1 M AgNO₃ solution, Bioanalytical System, Inc.) was used as a reference electrode. Ferrocene/ferrocenium (Fc/Fc⁺) was used as an internal standard. The potential values obtained in reference to Ag/Ag⁺ were converted to the saturated calomel electrode (SCE) scale. Cyclic voltammetry was performed in benzene:acetonitrile (10:3) containing 0.1M TBAPF₆ solution. UV-vis absorption spectra were recorded on a Perkin-Elmer model Lambda 900 UV/vis/near-IR spectrophotometer.

Example 1 – 2,2'-Bis(phenyl)-N,N'-bis(2''-octyldodecyl)-Naphtho(2,3-d)bisthiazole tetracarboxylic diimide (NBTDI-1P):



2,3,6,7-Tetrabromo-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (1): The compound 1 was prepared as reported in the literature, see Gao, et al. *Org. Lett.* 2007, 9, 3917-3920 incorporated herein by reference for their disclosures of teachings related synthetic methods.

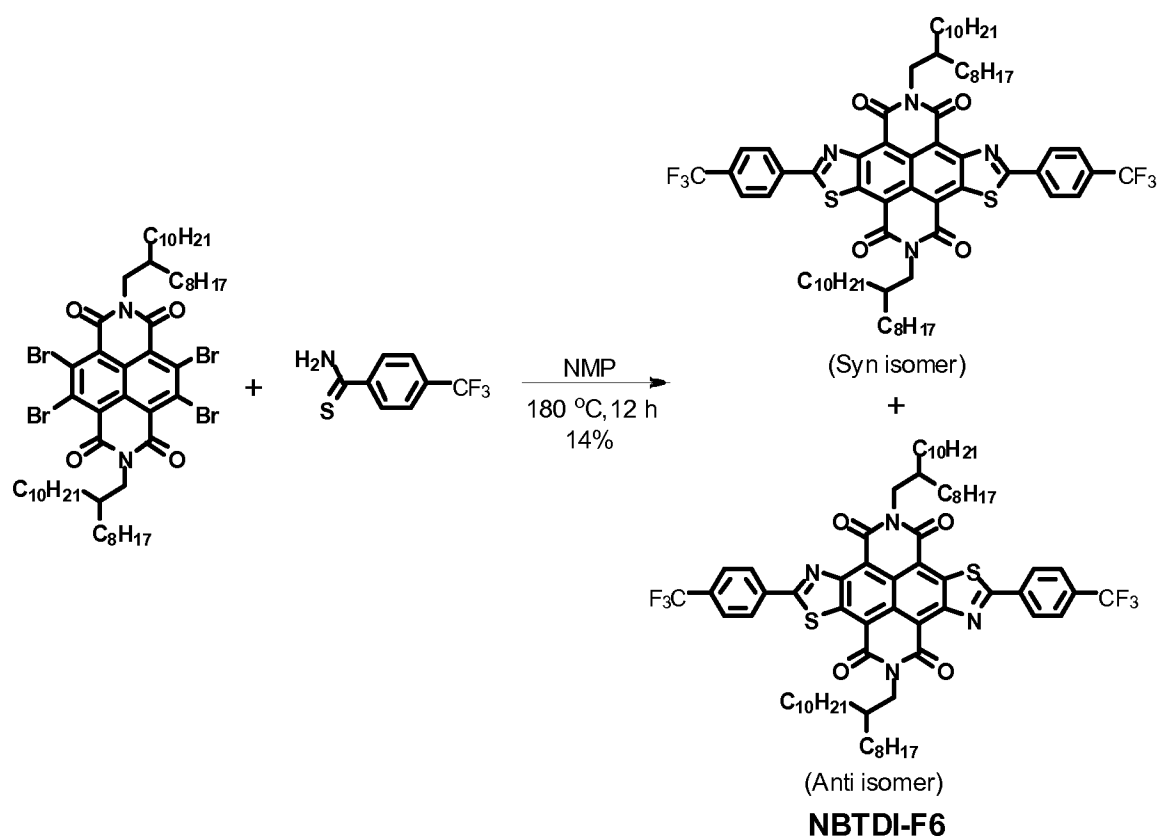
Thiobenzamide (2): The compound 2 can be purchased from Sigma Aldrich. The compounds 2 and its related derivatives can also be easily synthesized from the reported procedure, see (a) Kaleta, et al. *Org. Lett.* 2006, 8, 1625-1628. (b) Mahammed, et al., *Synlett* 2009, 14, 2338-2340 all hereby incorporated herein by reference for their disclosures of teachings related synthetic methods.

2,2'-Bis(phenyl)-N,N'-bis(2''-octyldodecyl)-Naphtho(2,3-d)bisthiazole tetracarboxylic diimide:(NBTDI-1P): A mixture of solution containing tetrabromo compound 1 (0.15 g, 0.13 mmol) and thiobenzamide (0.038 g, 0.28 mmol) in dry N-methyl pyrrolidone (3 mL) under Argon was stirred for 12 h at 180 °C. After completion of the reaction, NMP was evaporated under reduced pressure and then poured into water (100 mL). Using chloroform (2 x 50 mL) to extract the product, the combined organic layer was separated and evaporated under vacuum. The crude product was purified by using hexane/CHCl₃ (1:9) as a solvent afforded mixture of syn and anti isomer of NBTDI-1P (1:1 molar ratio) as red flakes. ¹H NMR (CDCl₃, 300 MHz, ppm): 8.44 (d, 4H, *J* = 6.0 Hz), 7.62-7.59 (m, 6H), 4.37-4.34 (m, 4H), 2.27-2.10 (m, 2H), 1.44-1.26 (m, 64 H), 0.84-0.82 (m, 12H). (FAB-MS): Found *M*+1, 1094.7 requires 1093.61.

NBTDI-1P is very soluble in common organic solvents such as chloroform, chlorobenzene and dichlorobenzene at room temperature. The absorption spectra of NBTDI-1P in dilute chloroform (~10⁻⁶M) and as a thin film were measured. In solution, the absorption spectrum has a vibronic structure with the peaks at 493 and 465 nm which correspond to *0-0* and *0-1* transitions. The thin film absorption spectrum also has no vibronic structure and a absorption peak maximum at 473 nm. The optical band gap determined from the absorption edge of the thin film is 2.14 eV.

The HOMO and LUMO energy level of NBTDI-1P was estimated from solution cyclic voltammetry (CV) results. NBTDI-1P has irreversible oxidation and reversible reduction waves and the areas and close proximity of the anodic and cathodic peaks were inspected. The onset oxidation potential and onset reduction potential of NBTDI-1P are 2.01 and -0.30 V (vs SCE), respectively, from which we estimate an ionization potential (IP, HOMO level) of 6.41 eV ($IP = E_{ox}^{onset} + 4.4$), an electron affinity (EA, LUMO level) of 4.10 eV ($EA = E_{red}^{onset} + 4.4$) and an electrochemical bandgap of 2.31 eV ($E_g^{el} = IP - EA$).

Example 2 – 2,2'-Bis(4-trifluoromethylphenyl)-N,N'-bis(2''-octyldodecyl) Naphtho(2,3-d)bisthiazole tetracarboxylic diimide (NBTDI-F6):



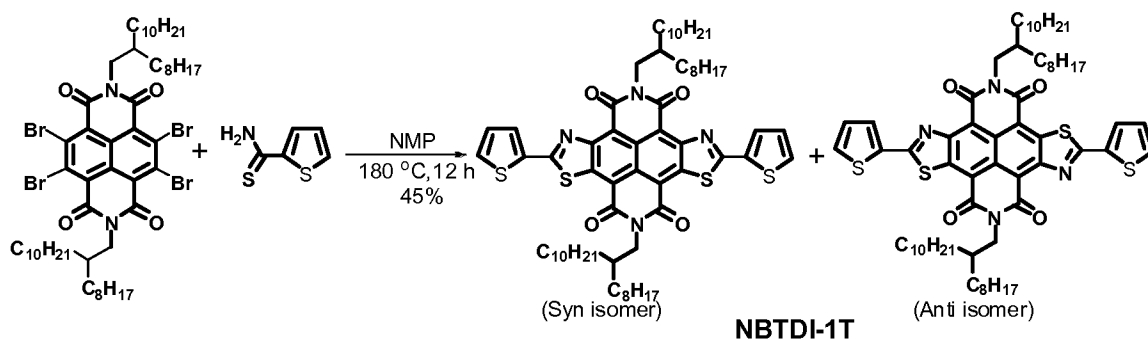
2,2'-Bis(4-trifluoromethylphenyl)-N,N'-bis(2''-octyldodecyl)-Naphtho(2,3-d)bisthiazole tetracarboxylic diimide (NBTDI-F6): A mixture of tetrabromide 1 (0.5 g, 0.44 mmol), and 4-trifluoromethyl-thiobenzamide (0.19 g, 0.92 mmol) in anhydrous NMP (9 mL) was stirred at 180 °C for 12 h under Argon. The reaction mixture was then allowed to cool at room temperature and poured into ice water (200 mL) and extracted with CH₂Cl₂ (2 x 50 mL). The organic layer was washed with water (2 x 50 mL) and dried over anhydrous Na₂SO₄. The crude product obtained after the removal of solvent under reduced pressure was subjected to column chromatography over SiO₂ using hexane/ethylacetate (3:1) as eluant to give mixture of syn and anti isomer (1:1

molar ratio) of NBTDI-F6 in 25% yield (80 mg) as red solid; ^1H NMR (CDCl_3 , 300 MHz, ppm): ^1H NMR (CDCl_3 , 300 MHz, ppm): 8.53 (d, 4H, $J = 7.8$ Hz), 7.85 (d, 4H, $J = 7.8$ Hz), 4.38 (d, 2H, $J = 7.5$ Hz), 4.34 (d = 2H, $J = 7.5$ Hz), 2.24 (m, 2H), 1.55-1.42 (m, 64 H), 0.84-0.82 (m, 12H). (FAB-MS): Found $M+1$, 1230.2, requires 1229.61.

NBTDI-F6 is very soluble in common organic solvents such as chloroform, chlorobenzene and dichlorobenzene at room temperature. The absorption spectra of NBTDI-F6 was measured in dilute chloroform solution ($\sim 10^{-6}\text{M}$) and as a thin film. In solution, the absorption spectrum has a vibronic structure with the peaks at 481 and 458 nm which correspond to 0-0 and 0-1 transitions. The thin film absorption spectrum has also vibronic structure with the broad absorption peak at 461 and 533 nm. The optical band gap determined from the absorption edge of the thin film is 2.18 eV.

The HOMO and LUMO energy level of NBTDI-F6 was estimated from solution cyclic voltammetry (CV) results. CVs showed NBTDI-F6 has irreversible oxidation and reversible reduction as evident from the areas and close proximity of the anodic and cathodic peaks. The onset oxidation potential and onset reduction potential of NBTDI-F6 are 1.75 and -0.12 V (vs SCE), respectively, from which we estimate an ionization potential (IP, HOMO level) of 6.15 eV ($\text{IP} = E_{\text{ox}}^{\text{onset}} + 4.4$), an electron affinity (EA, LUMO level) of 4.28 eV ($\text{EA} = E_{\text{red}}^{\text{onset}} + 4.4$) and an electrochemical bandgap of 1.87 eV ($E_g^{\text{el}} = \text{IP} - \text{EA}$).

Example 3- 2,2'-Bis(thiophen-2-yl)-N,N'-bis(2''-octyldodecyl)-Naphtho(2,3-d) bisthiazole tetracarboxylic diimide (NBTDI-1T):



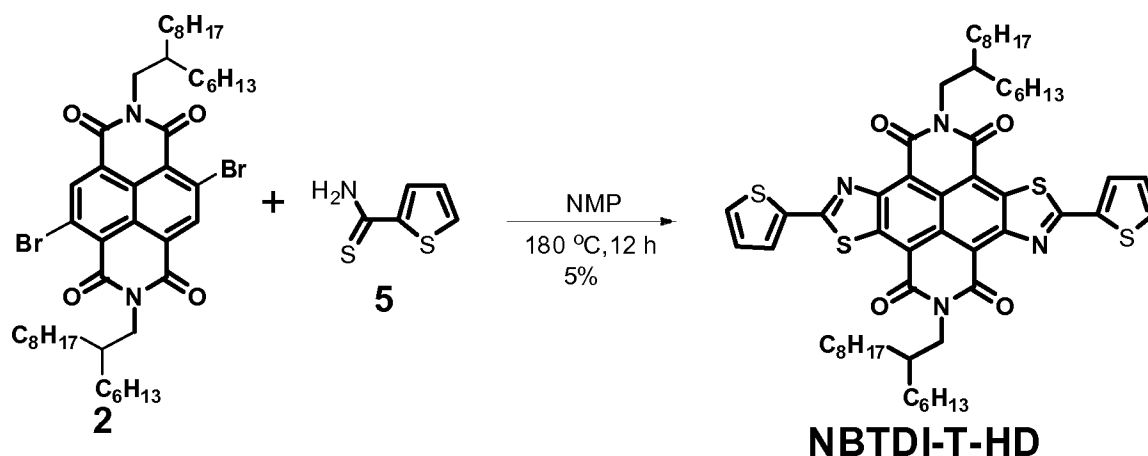
2,2'-Bis(thiophen-2-yl)-N,N'-bis(2''-octyldodecyl)-Naphtho(2,3-d)bisthiazole tetracarboxylic diimide (NBTDI-1T): A mixture of solution containing tetrabromo compound 1 (0.15 g, 0.13 mmol) and thiophene-2-thiocarboxamide (0.04 g, 0.28 mmol) in dry NMP (3 mL) under Argon was stirred for 12 h at 180 °C. Then NMP was evaporated under reduced pressure and then poured into water. Using chloroform (2 x 50 mL) to extract the product, the combined organic layer was separated and evaporated under vacuum. The crude

product was purified by using hexane/ethylacetate (5:1) as a solvent afforded mixture of syn and anti isomer (1:1 molar ratio) of NBTDI-1T as purple solid. ^1H NMR (CDCl_3 , 300 MHz, ppm): 8.05-8.03 (m, 2H), 7.77-7.76 (m, 2H), 7.29-7.26 (m, 2H), 4.37-4.30 (m, 4H) 2.15-2.50 (m, 2H), 1.40-1.11 (m, 64 H), 0.84-0.87 (m, 12H). (EI-MS): Found M^+ , 1105.7 requires 1105.67.

NBTDI-1T is very soluble in common organic solvents such as chloroform, chlorobenzene and dichlorobenzene at room temperature. Figure 1 shows the absorption spectra of NBTDI-1T in dilute chloroform ($\sim 10^{-6}\text{M}$) and as a thin film. In solution, the absorption spectrum has a vibronic structure with the peaks at 524 and 494 nm which correspond to $0-0$ and $0-1$ transitions. The thin film absorption spectrum has no vibronic structure with a absorption peak at 509 nm. The optical band gap determined from the absorption edge of the thin film is 2.01 eV.

The HOMO and LUMO energy level of NBTDI-1T was estimated from solution cyclic voltammetry (CV) results (Figure 2a & 2b). NBTDI-1T has irreversible oxidation and reversible reduction as evident from the areas and close proximity of the anodic and cathodic peaks as shown in the figure 2a & 2b. The onset oxidation potential and onset reduction potential of NBTDI-1T are 2.09 and -0.29 V (vs SCE), respectively, from which we estimate an ionization potential (IP, HOMO level) of 6.49 eV ($\text{IP} = \text{E}_{\text{oxonset}} + 4.4$), an electron affinity (EA, LUMO level) of 4.11 eV ($\text{EA} = \text{E}_{\text{red onset}} + 4.4$) and an electrochemical bandgap of 2.38 eV ($\text{E}_{\text{gel}} = \text{IP} - \text{EA}$).

Example 4 - 2,2'-Bis(thiophen-2-yl)-N,N'-bis(2''-octyldodecyl)-Naphtho(2,3-d) bisthiazole tetracarboxylic diimide (NBTDI-T-HD):



2,6-Dibromo-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (2): The compound 1 was prepared as reported in the literature, see Guo, et al. *Org. Lett.* 2008, 10, 5333-5336 incorporated herein by reference for their disclosures of teachings related synthetic methods.

2,2'-Bis(thiophen-2-yl)-N,N'-bis(2''-hexyldecyl)-Naphtho(2,3-d) bisthiazole tetracarboxylic diimide (NBTDI-T-HD): A mixture of dibromide **2** (0.15 g, 0.17 mmol), and thiophene-2-thiocarboxamide **5** (0.051 g, 0.36 mmol) in anhydrous NMP (3 mL) was stirred at 180 °C for 12 h under Argon. The reaction mixture was then allowed to cool at room temperature and poured into ice water (200 mL) and extracted with CH₂Cl₂ (2 x 50 mL). The organic layer was washed with water (2 x 50 mL) and dried over anhydrous Na₂SO₄. The crude product obtained after the removal of solvent under reduced pressure was subjected to column chromatography over SiO₂ using hexane/ethylacetate (3:1) as eluant to give NBTDI-T-HD in 5% yield (8 mg) as purple solid; ¹H NMR (CDCl₃, 300 MHz, ppm): ¹H NMR (C₂D₄Cl₂, 300 MHz, ppm): 8.03 (d, 2H, *J* = 4.2 Hz), 7.81 (d, 2H, *J* = 4.5 Hz), 7.29 (t, 2H, *J* = 4.0 Hz) 4.27 (d, 4H, *J* = 7.0 Hz), 2.14-2.15 (m, 2H), 1.59-1.23 (m, 48 H), 0.85-0.83 (m, 12H). (FAB-MS): Found *M*+1, 994.3, requires 993.46.

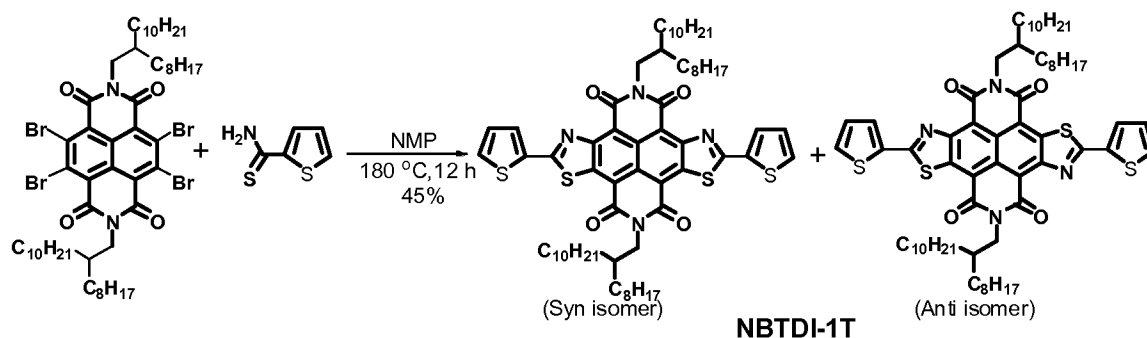
Example 5 – Transistors Employing the Naphthobisazole Diimides

Preparation of the Transistors - Thin film transistors comprising naphthobisthiazole diimide molecules or compounds of Examples 1 and 3 were fabricated and tested to evaluate charge carrier mobility and other electrical parameters. Thin film transistors were fabricated in conventional bottom-contact, bottom-gate geometry. Gold electrodes with a thin chromium adhesive layer were patterned on top of heavily-doped silicon with silicon dioxide (*t*_{ox}=200 or 300 nm) substrates. The channel widths of the devices were 400 or 800 μm and lengths were 20 or 40 μm. The surface of the silicon dioxide was cleaned and treated with octyltrichlorosilane (OTS8). Molecules were spun onto hydrophobically modified oxide from solutions in chloroform. Thin films were then annealed at 150 °C for 10 min under inert atmosphere. Devices were initially tested in nitrogen-filled dry box. For stability test, devices were stored and tested in air. Electrical parameters were calculated by using the standard equation for metal-oxide-semiconductor field-effect transistors in saturation region: $I_{ds}=(\mu C_o W/2L)(V_g-V_t)^2$.

Both NBTDI-1P and NBTDI-1T showed unipolar electron transport properties. The average electron mobility of $7.7 \times 10^{-4} \text{ cm}^2/\text{Vs}$ was obtained from solution-deposited thin films of NBTDI-1P. When the benzene unit was changed to thiophene unit in NBTDI-1P, the electron mobility decreased to $4.8 \times 10^{-7} \text{ cm}^2/\text{Vs}$. The current on/off ratios was $>10^1$ to 10^4 .

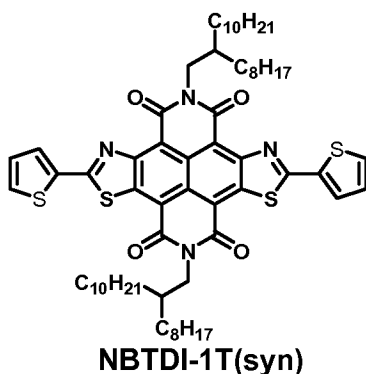
The average threshold voltage of NBTDI-1P and NBTDI-1T was 44.7 V and 23.5 V, respectively.

Example 6 – 2,2'-Bis(thiophen-2-yl)-N,N'-bis(2''-octyldodecyl)-Naphtho(2,3-d) bisthiazole tetracarboxylic diimide (NBTDI-1T):



2,2'-Bis(thiophen-2-yl)-N,N'-bis(2''-octyldodecyl)-Naphtho(2,3-d)bisthiazoletetracarboxylic diimide (NBTDI-1T): A mixture of solution containing tetrabromo compound 1 (0.15 g, 0.13 mmol) and thiophene-2-thiocarboxamide (0.04 g, 0.28 mmol) in dry N-methyl pyrrolidone (3 mL) under Argon was stirred for 12 h at 180 °C. Then NMP was evaporated under reduced pressure and then poured into water. Using chloroform (2 x 50 mL) to extract the product, the combined organic layer was separated and evaporated under vacuum. The crude product was purified by using hexane/ethylacetate (5:1) as a solvent afforded mixture of syn and anti isomer (1:1 molar ratio) of NBTDI-1T as purple solid. The mixture of *syn*- and *anti*- isomers of NBTDI-1T was separated and purified by column chromatography using hexane/chloroform (1:5). Further purification was carried out by using preparative thin layer column chromatography yields 30% of pure *syn*-2,2'-Bis(thiophen-2-yl)-N,N'-bis(2''-octyldodecyl)-Naphtho(2,3-d) bisthiazole tetracarboxylic diimide (*syn*-NBTDI-1T) and *anti*-2,2'-Bis(thiophen-2-yl)-N,N'-bis(2''-octyldodecyl)-Naphtho(2,3-d) bisthiazole tetracarboxylic diimide (*anti*-NBTDI-1T) and 35% of pure *anti*-NBTDI-1T.

Syn-2,2'-Bis(thiophen-2-yl)-N,N'-bis(2''-octyldodecyl)-Naphtho(2,3-d) bisthiazole tetracarboxylic diimide (*syn*-NBTDI-1T)



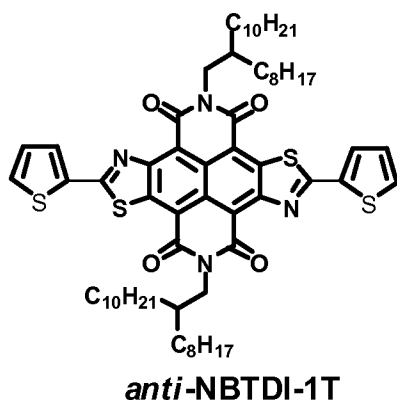
¹H NMR (CDCl₃, 500 MHz, ppm): 7.79 (d, 2H, *J* = 4.5 Hz), 7.66 (d, 2H, *J* = 4.5 Hz), 7.13 (t, 2H, *J* = 4.5 Hz), 4.38 (d, 2H, *J* = 7.5 Hz), 4.32 (d, 2H, *J* = 7.5 Hz), 2.29-2.18 (m, 2H),

1.48-1.23 (m, 64 H), 0.88-0.87 (m, 12H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): 171.35, 162.68, 160.91, 154.72, 141.59, 136.80, 133.37, 131.99, 128.80, 126.20, 121.20, 116.88, 116.73, 45.85, 45.40, 36.64, 36.27, 31.97, 31.94, 31.69, 31.60, 30.38, 30.26, 29.82, 29.81, 29.78, 29.72, 29.70, 29.67, 29.46, 29.41, 26.59, 26.42, 22.70, 14.13; (EI-MS): Found M^+ , 1105.8 requires 1105.67.

syn-NBTDI-1T is soluble in organic solvents such as chloroform, chlorobenzene and dichlorobenzene at room temperature. Figure 3 shows the absorption spectra of *syn*-NBTDI-1T in dilute chloroform ($\sim 10^{-6}\text{M}$) and as a thin film. In solution, the absorption spectrum has a vibronic structure with the peaks at 525 and 490 nm which correspond to *0-0* and *0-1* transitions. The thin film absorption spectrum has no vibronic structure with a absorption peak at 509 nm. The optical band gap determined from the absorption edge of the thin film is 2.1 eV.

Solution cyclic voltammetry was used to investigate the HOMO/LUMO energy level of *syn*-NBTDI-1T in benzene:acetonitrile (1:3) solution. Figure 4 shows that the *syn*-NBTDI-1T has two reversible reduction waves. Based on the first reduction potential onset ($E_{\text{oxs}}^{\text{onset}} = -0.17\text{ V}$), the LUMO energy level of *syn*-NBTDI-1T was calculated to be 4.2 eV (EA, LUMO = $E_{\text{red}}^{\text{onset}} + 4.4\text{ eV}$). No obvious oxidation peaks are observed and therefore the HOMO energy level of *syn*-NBTDI-1T was calculated from the optical band gap ($E_{\text{HOMO}} = E_{\text{g}}^{\text{opt}} + E_{\text{LUMO}}$) to be -6.33 eV. The thermal behavior of *syn*-NBTDI-1T was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). *syn*-NBTDI-1T showed onset thermal decomposition temperature (T_d) at 405°C under nitrogen (Figure 5A), and DSC scans of *syn*-NBTDI-1T showed melting transition at 270 °C (Figure 5B) indicating good thermal stability.

2,2'-Bis(thiophen-2-yl)-N,N'-bis(2''-octyldodecyl)-Naphtho(2,3-d) bisthiazole tetracarboxylic diimide (*anti*-NBTDI-1T):



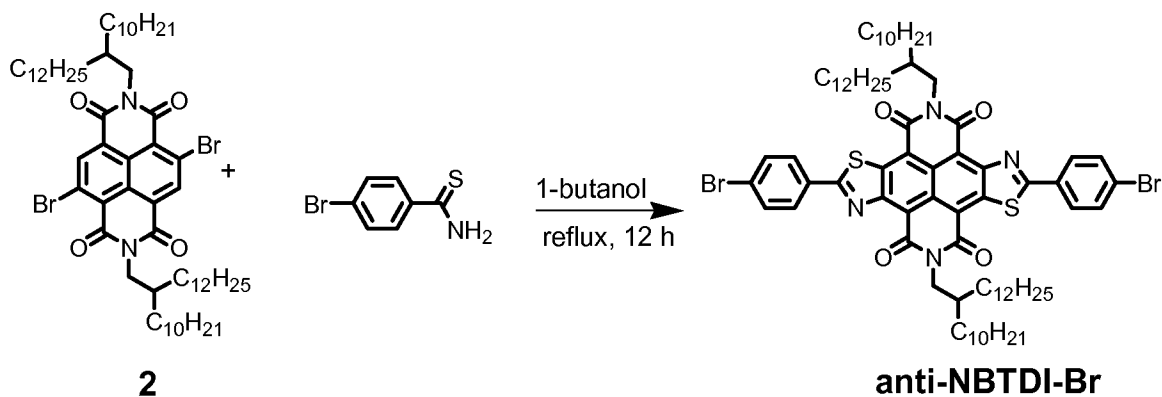
^1H NMR (CDCl_3 , 500 MHz, ppm): 7.99 (d, 2H, $J = 4.5\text{ Hz}$), 7.70 (d, 2H, $J = 4.5\text{ Hz}$), 7.26 (t, 2H, $J = 4.5\text{ Hz}$), 4.36 (d, 4H, $J = 7.5\text{ Hz}$), 2.25 (bs, 2H), 1.48-1.24 (m, 64 H), 0.89-0.85 (m, 12H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): 171.68, 161.96, 159.87, 153.83, 140.9, 135.85,

132.57, 131.20, 127.89, 122.93, 117.68, 113.89, 44.63, 35.35, 30.88, 30.58, 29.44, 29.20, 28.69, 28.63, 28.34, 25.42, 21.62, 13.08. (EI-MS): Found M^+ , 1105.7 requires 1105.7.

anti-NBTDI-1T is soluble in organic solvents such as chloroform, chlorobenzene and dichlorobenzene at room temperature. Figure 6 shows the absorption spectra of *anti*-NBTDI-1T in dilute chloroform ($\sim 10^{-6}$ M) and as a thin film. In solution, the absorption spectrum has a vibronic structure with the peaks at 531 and 495 nm which correspond to *0-0* and *0-1* transitions. The thin film absorption spectrum has no vibronic structure with a absorption peak at 509 nm. The optical band gap determined from the absorption edge of the thin film is 2.0 eV.

Solution cyclic voltammetry was used to investigate the HOMO/LUMO energy level of *syn*-NBTDI-1T in benzene:acetonitrile (1:3) solution. Figure 7 shows that the *syn*-NBTDI-1T has two reversible reduction waves. Based on the first reduction potential onset ($E_{\text{oxs}}^{\text{onset}} = -0.12$ V), the LUMO energy level of *anti*-NBTDI-1T was calculated to be 4.3 eV (EA, LUMO = $E_{\text{red}}^{\text{onset}} + 4.4$ eV). No obvious oxidation peaks are observed and therefore the HOMO energy level of *syn*-NBTDI-1T was calculated from the optical band gap ($E_{\text{HOMO}} = E_{\text{g}}^{\text{opt}} + E_{\text{LUMO}}$) to be -6.28 eV. The thermal behavior of *anti*-NBTDI-1T was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). *anti*-NBTDI-1T showed onset thermal decomposition temperature (T_d) at 400 °C under nitrogen (Figure 8A), and DSC scans of *anti*-NBTDI-1T showed melting transition at 290 °C (Figure 8B) indicating good thermal stability.

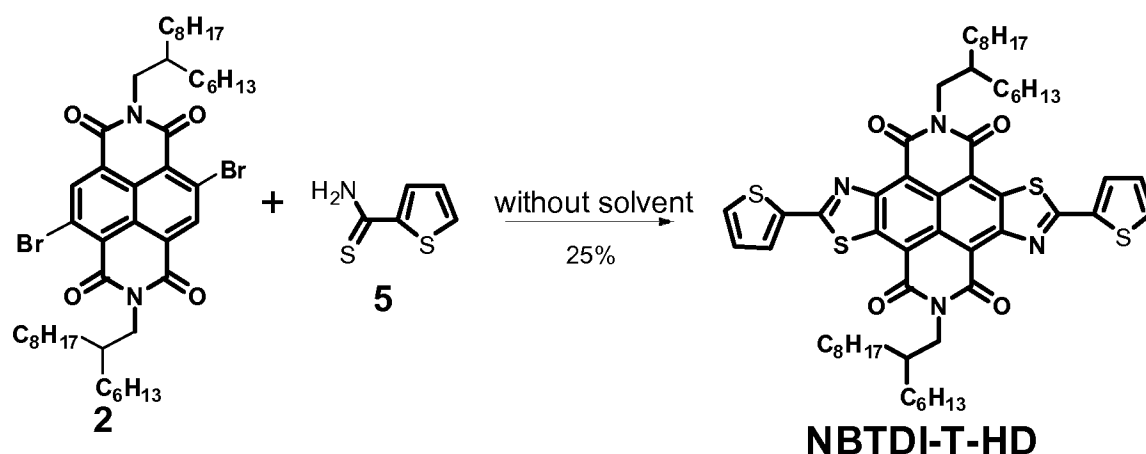
Example 7 – N,N'-bis(2''-decyltetradecyl)-2,2'-bis-(4-bromophenyl)1,4,5,8-naphtho(2,3-d)bisthiazole tetracarboxylic diimide (*anti*-NBTDI-Br):



A mixture of solution containing NDI dibromide **2** (1 g, 0.13 mmol) and 4-bromothiobenzamide (0.038 g, 0.28 mmol) in 1-butanol (6 mL) was stirred at 120 °C for 12 h. After completion of the reaction, 1-butanol was evaporated under reduced pressure and then poured into water (50 mL). Extract the reaction mixture using chloroform solvents (2 x 50 mL),

and the combined organic layer was separated and evaporated under vacuum. The crude product was purified by column chromatography using hexane/ CHCl_3 (1:9) as a solvent afforded dibromide **3** as red solid in 30% yield. ^1H NMR (CDCl_3 , 300 MHz, ppm): 8.24 (d, 4H, $J = 8.4$ Hz), 7.71 (d, 4H, $J = 8.4$ Hz), 4.35 (d, 4H), 2.15 (bs, 2H), 1.20-1.54 (m, 80H), 0.82-0.86 (m, 12H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) 178.3, 162.5, 160.5, 154.4, 141.2, 132.6, 131.0, 130.0, 128.5, 123.5, 118.8, 115.2, 45.7, 36.5, 31.9, 31.7, 30.33, 29.8, 29.7, 29.4, 26.5, 22.7, 14.1. (FAB-MS): Found $M+1$, 1364.63 requires 1363.62.

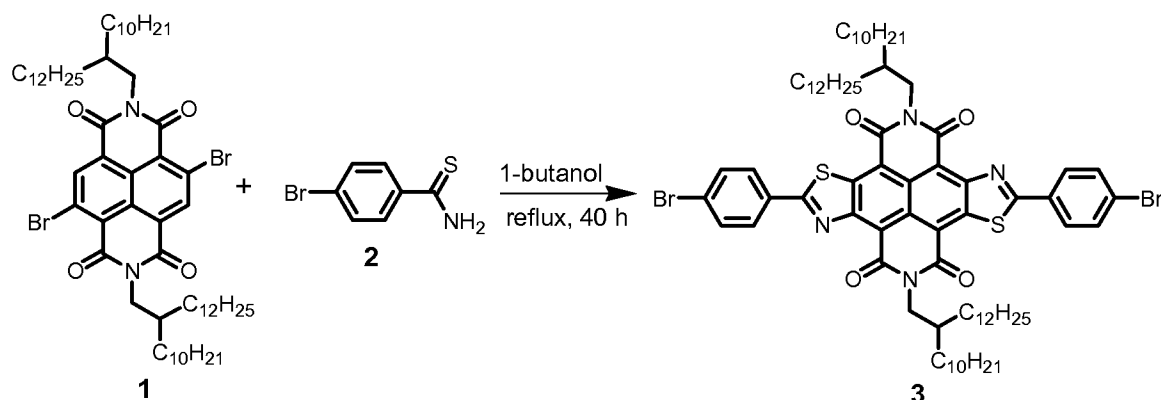
Example 8 – 2,2'-Bis(thiophen-2-yl)-N,N'-bis(2''-octyldodecyl)-Naphtho(2,3-d) bisthiazole tetracarboxylic diimide (NBTDI-T-HD):



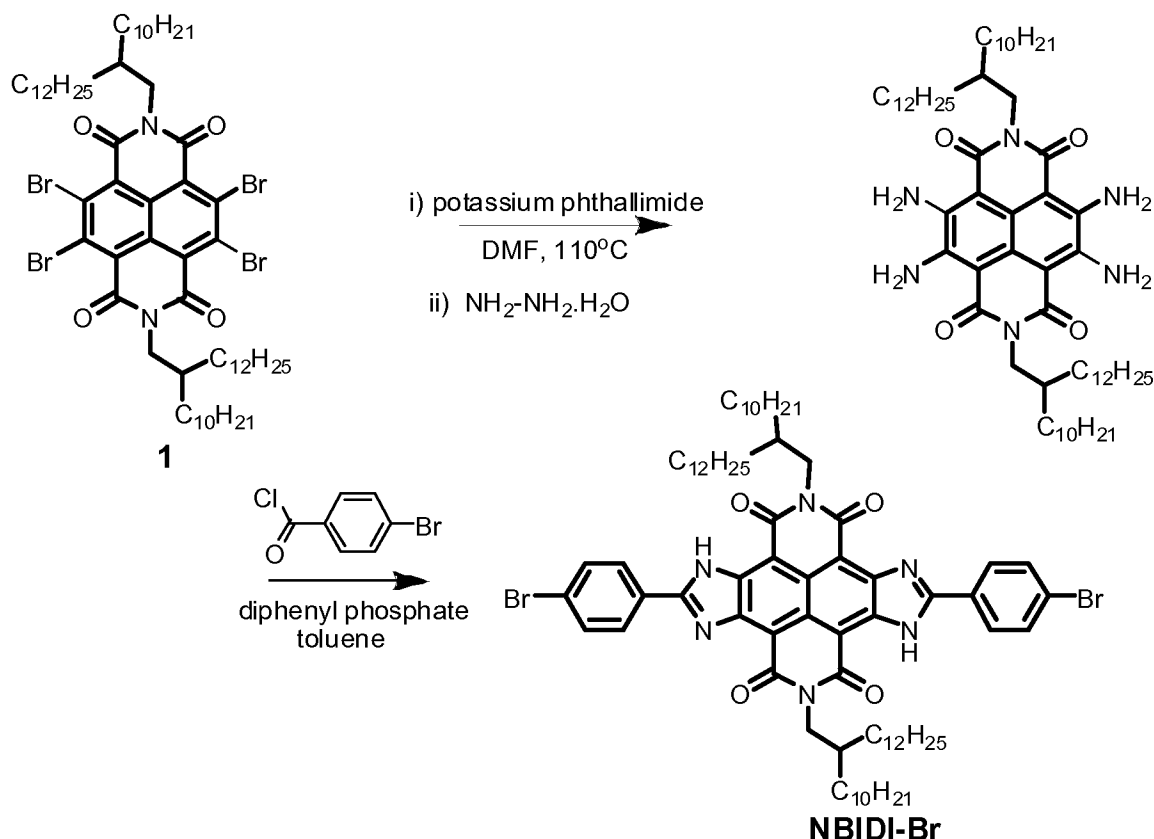
A mixture of NDI dibromide (**2**) and thiophene-thiocarboxamide was taken in to 10 mL vial with a stir bar inside. The reaction mixture was heated up to 150°C and kept stirring for 12 h. Then the reaction mixture was directly purified by column chromatography gave 35% of NBTDI-T-HD in 25% yield.

Example 9 – Synthesis of Polymerizable Compounds

Synthesis of dibromo naphthobisthiazole diimides



Synthesis of dibromo naphthobisimidazole diimides



Synthesis of tetramino naphthalene diimide

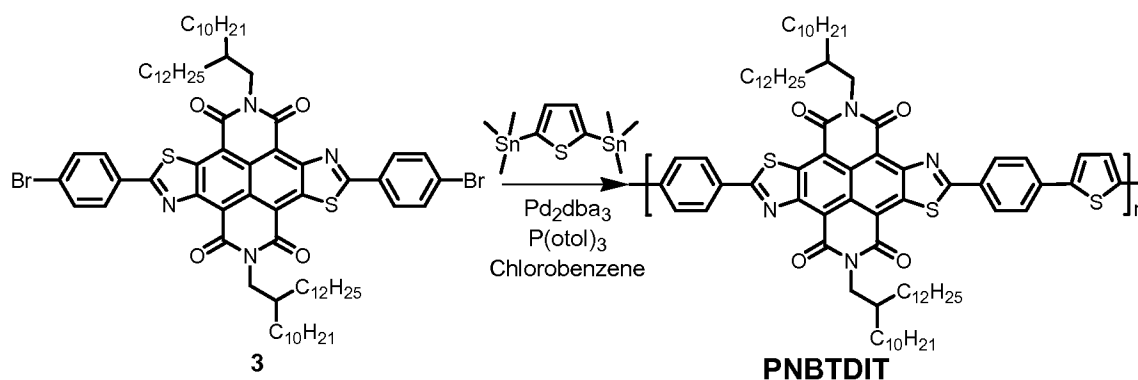
Potassium phthalimide (0.21 g, 1.15 mmol) was added to a solution of NDI-tetrabromide (0.3 g, 0.26 mol) in 10 ml dry DMF. The reaction was stirred for 16 hours at 90 °C. After cooling to room temperature, the reaction mixture was poured into 150 ml water and extracted with dichloromethane (3 x 100 ml). The combined organic layers were washed with 200 ml of 0.2 N KOH, water, saturated ammonium chloride, dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The crude product was purified by column chromatography to give tetrasubstituted phthalimide derivative.

Tetrasubstituted phthalimide (0.14 g, 0.1mmol), hydrazine hydrate (hydrazine, 51 %) (0.6 ml, 0.065 mol) and 100 ml methanol were stirred at 95 °C for 24 h. Then the methanol was evaporated under reduced pressure, the residue diluted with 100ml dichloromethane and washed with 10 % KOH (2 x 50 ml). Aqueous layers were combined and extracted with dichloromethane (3 x 20 mL). The combined organic layers were washed with brine (2 x 50 ml) and dried over MgSO_4 . The removal of dichloromethane afforded NDI-tetramine as a stable purple solid.

N,N'-bis(2''-octyldodecyl)-2,2'-bis-(4-bromophenyl)-1,4,5,8-naphtho(2,3-d)bisimidazole tetracarboxylic diimide (NBIDI-Br):

A mixture of NDI-tetramine (0.5 g, 0.56 mmol), 4-bromobenzoyl chloride (0.27 g, 1.23 mmol) and diphenyl phosphate (0.5 g) in toluene at 110°C was stirred under argon atmosphere for 24 h. Then the reaction mixture was cooled to room temperature. The solvent was evaporated under vacuum. The crude product was purified by column chromatography to give NBIDI-Br as a pure compound.

Example 10 – Poly[(N,N'-bis(2''-decyltetradecyl)-2,2'-diphenyl)-1,4,5,8-naphtho(2,3-d)bisthiazole tetracarboxylic diimide)-alt-2,2'-thiophene] (PNBTDIT):



A mixture of N,N'-bis(2''-decyltetradecyl)-2,2'-bis-(4-bromophenyl)-1,4,5,8-naphtho(2,3-d)bisthiazole tetracarboxylic diimide (**2**) (134 mg, 0.098 mmol), 2,5-bis(trimethylstannyl)thiophene (40 mg, 0.098 mmol), tri-*o*-tolylphosphine, (2.4 mg, 0.008 mmol) and tris(dibenzylideneacetone)dipalladium (0), (2 mg, 0.002 mmol) in 7 mL chlorobenzene was refluxed for 3 days, under argon atmosphere. Then the reaction solution was poured into beaker containing 200 mL of 5% hydrochloric acid/methanol solution and stirred for 4 h. The filtered solid was subjected to soxhlet extraction of methanol and hexane for 8 h each. The product was dried in vacuum oven for 10 h and collected as a shiny dark blue solid (114 mg, 91%) GPC: M_n = 163.7 kDa, M_w = 349.9 kDa, PDI = 2.14. ^1H NMR (CDCl_3 , 300 MHz, ppm): 7.30-6.30 (bm, 10H), 4.38 (bs, 4H), 2.20-0.61 (m, 94 H).

The number-average molecular weight (M_n), and the polydispersity index (PDI) was estimated to be 31.5 kDa and 3.5, respectively by performing Gel permeation chromatography (GPC) in chlorobenzene at 60 °C using polystyrene as standard. PNBTDIT is readily soluble in almost all organic solvents such as dichloromethane, chloroform and chlorobenzene at room temperature. Figure 9 shows normalized optical absorption spectra of PNBTDI in dilute chloroform ($\sim 10^{-6}\text{M}$) and as thin films. Both solution and thin film spectra showed two characteristic bands: (i) an absorption at shorter wavelength (320-420 nm) correspond to π - π^* transitions and (ii) a relatively broad and intense absorption at longer wavelength (480-680 nm)

corresponds to intramolecular charge transfer (ICT) between strong electron accepting naphthobisthiazole diimide and aromatic subunits. In solution, PNBTDIT had a peak maximum at 600nm and the shape of the absorption spectra is identical to that of thin film spectrum. The thin film absorption spectrum of PNBTDI has a vibronic structure with a high energy shoulder at 600 nm and a peak maximum at 620 nm, resulting in an absorption edge optical band gap (E_g^{opt}) of 1.77 eV.

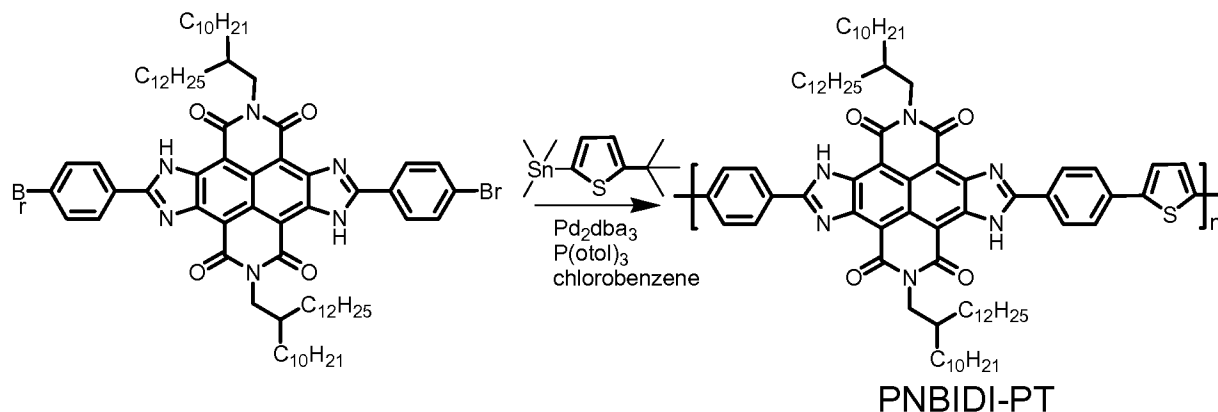
The electronic energy levels, highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) energy levels of new copolymer PNBTDIT films was estimated by cyclic voltammetry (Figure 10). Cyclic voltammograms of PNBTDIT showed an irreversible oxidation peak with oxidation potential onset ($E_{\text{ox}}^{\text{onset}}$) of 1.4 eV, from which the HOMO energy level was estimated to be -5.8 eV ($E_{\text{HOMO}} = E_{\text{ox}}^{\text{onset}} + 4.4$ eV). In contrast, the copolymer PNBTDI showed two reversible reduction peaks with the first reduction potential onset ($E_{\text{red}}^{\text{onset}}$) of -0.45 eV, from which the LUMO energy level was estimated to be -3.95 eV ($E_{\text{LUMO}} = E_{\text{red}}^{\text{onset}} + 4.4$ eV).

To investigate the solid state morphology/crystallinity of naphthobisthiazole diimide copolymer PNBTDIT, X-ray diffraction (XRD) measurements were conducted on solution drop-casted films on to a glass substrate at 200 °C for 20 min. Figure 11 shows XRD patterns of PNBTDIT films. A strong diffraction peak corresponding to a d -spacing of 2.5 nm due to the lamellar reflections (100) are observed for the copolymer PNBTDIT indicating that high crystallinity in thin films. Interestingly, the interlayer d_{100} -spacing of PNBTDI was found to be significantly shorter than that of expected alkyl chain length of 4.3 nm ($2 \times C_{14}$) suggesting that there is strong interdigitation of alkyl sides between the polymer backbone. It is noteworthy to mention that, similar trend was obtained in previous studies related to NDI-selenophene copolymers. On the other hand, a weak and broad diffraction peak with a d -spacing of 0.35 nm due to π - π reflections (010) was observed for PNBTDIT. The difference in the observation of 1-2 orders of magnitude shorter π - π stacking distance (0.3-0.9 nm) of PNBTDI relative to the previously studied PNDI copolymer can be accounted for by the larger ring size and planarity of naphthobisthiazole moiety, suggests that this could be beneficial to charge transport and optoelectronic properties of the materials.

Output and transfer characteristics of the FETs showed clear current modulation and saturation with unipolar n-type field-effect charge transport as shown in Figure 12. The on/off current ratios were in the range of 10^4 – 10^5 with threshold voltage of 25 V as calculated from extrapolating square root of drain current. The field-effect electron mobility calculated from the

saturation region of transfer characteristics ($V_{gs}V_s I_{ds}$) at V_{ds} of 80 V showed mobility of 0.001 cm^2/Vs .

Example 11 – Poly[(N,N'-bis(2''-octyldodecyl)-2,2'-diphenyl)-1,4,5,8-naphtho(2,3-d)bisimidazole tetracarboxylic diimide)-alt-2,2'-thiophene] (PNBIDI-PT):



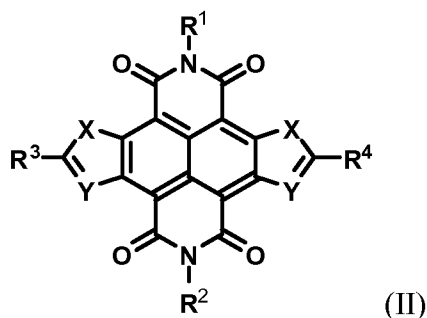
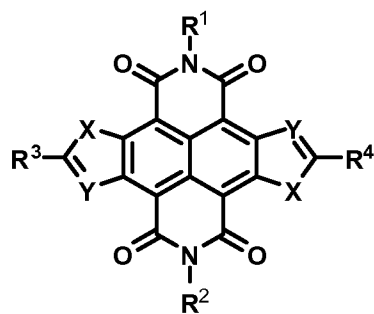
A mixture of N,N'-bis(2''-octyldodecyl)-2,2'-bis-(4-bromophenyl)-1,4,5,8-naphtho(2,3-d)bisimidazole tetracarboxylic diimide (200 mg, 0.164 mmol), 2,5-bis(trimethylstannyl)thiophene (109 mg, 0.164 mmol), tri-*o*-tolylphosphine, (4 mg, 0.012 mmol) and tris(dibenzylideneacetone)dipalladium (0), (3 mg, 0.003 mmol) in 5 mL chlorobenzene was refluxed for 3 days, under argon atmosphere. Then the reaction solution was poured into beaker containing 200 mL of 5% hydrochloric acid/methanol solution and stirred for 4 h. The filtered solid was subjected to soxhlet extraction of methanol and hexane for 8 h each. The product was dried in vacuum oven for 10 h and collected as a shiny dark blue solid (80%).

Gel permeation chromatography (GPC) of PNBIDI-PT showed a number- averaged molecular weight (M_n) of 11.1 kg/mol with a polydispersity index (PDI) of 12.64. PNBIDI-PT is well soluble in all common organic solvents such as chloroform, chlorobenzene and dichlorobenzene at room temperature. Figure 13 shows the absorption spectra of PNBIDI-PT in dilute chloroform (10^{-6} M) solution and as a thin film. The absorption maximum in solution was found to be 597 nm. Absorption spectra of thin films are slightly red shifted and showed absorption maximum at 601 nm. The optical band gap determined from the absorption edge of the thin film is 1.74 eV. The HOMO and LUMO level of PNBIDI-PT was estimated from cyclic voltammetry (CV) results (Figure 14A-14B). The onset of the oxidation and reduction peaks was 1.58 V and -0.67 V (versus SCE) respectively, from which the HOMO and LUMO level of the polymer are calculated to be 5.98 and 3.73 eV. The electrochemical band gap was calculated to be 1.95 eV.

Polymer	Mobility(μ_e) (cm^2/Vs)	$V_{th}(\text{V})$	I_{on}/I_{off}
PNBIDI-PT	5.2×10^{-5}	30	10^2

WHAT IS CLAIMED IS:

1. A compound represented by formulae (I) or (II):



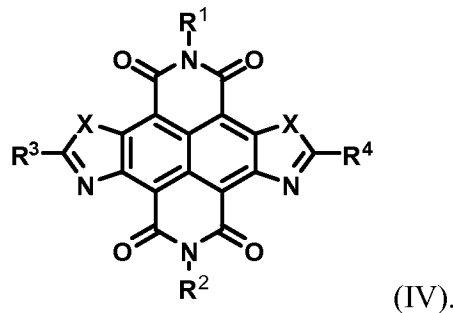
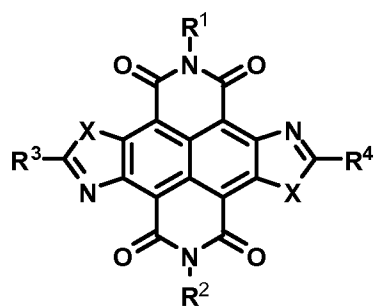
wherein:

- (i) wherein X is O, S, Se, Te, or NR; and Y is N; wherein R is independently H, alkyl, heteroalkyl, aryl, or heteroaryl; wherein X and Y are different;
- (ii) R^1 and R^2 are independently selected from optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group;
- (iii) R^3 and R^4 are independently selected from hydrogen, halogen, optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group.

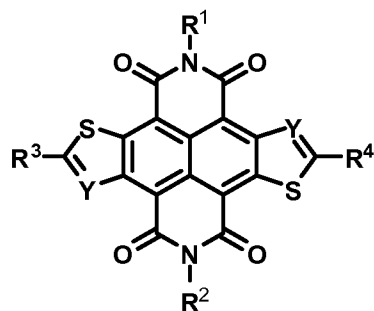
2. The compound of claim 1, wherein the compound is represented by formula (I).

3. The compound of claim 1, wherein the compound is represented by formula (II).

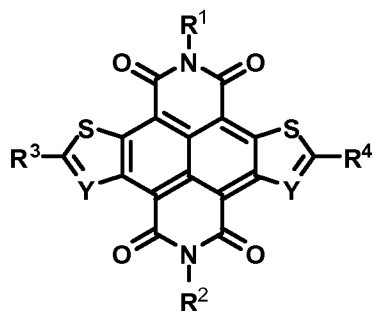
4. The compound of claim 1, wherein the compound is represented by formulae (III) or (IV) and X is O, S, Se:



5. The compound of claim 1, wherein X is S and Y is N, and the compound is represented by formulae (V) or (VI):

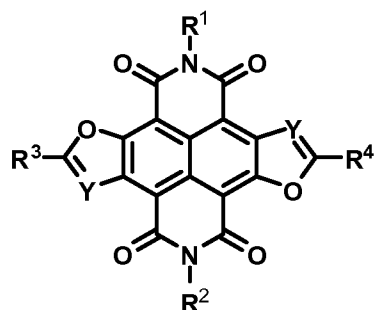


(V)

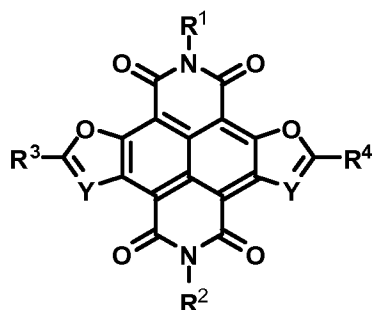


(VI).

6. The compound of claim 1, wherein X is O and Y is N, and the compound is represented by formulae (VII) or (VIII):



(VII)

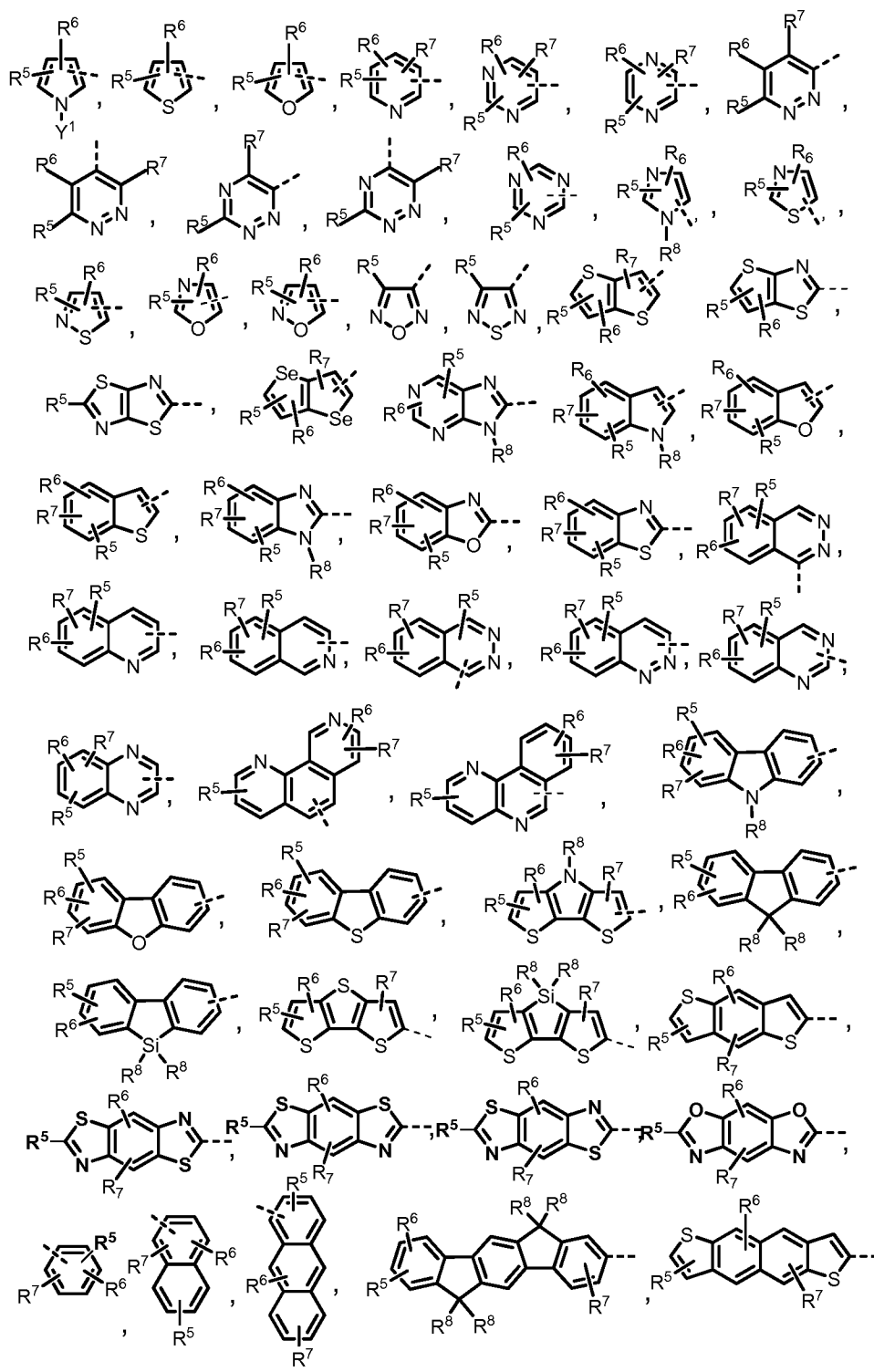


(VIII).

7. The compound of any of claims 1-6, wherein R¹ and R² are independently selected from optionally substituted C₁-C₂₅ alkyl group and optionally substituted C₁-C₂₅ heteroalkyl group.

8. The compound of any of claims 1-7, wherein R¹ and R² are independently selected from linear, mono- or pluri-cyclic, or branched alkyl group, linear, mono- or pluri-cyclic, or branched fluoroalkyl group, and linear, mono- or pluri-cyclic, or branched heteroalkyl group.

9. The compound of any of claims 1-8, wherein R³ and R⁴ are each an optionally substituted aryl group or an optionally substituted heteroaryl group selected from

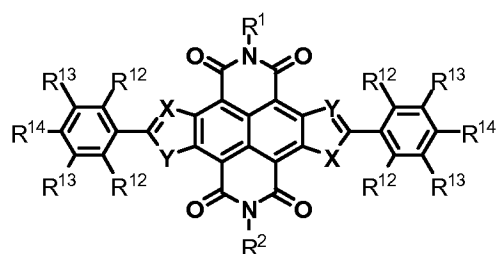


wherein R⁵, R⁶ and R⁷ are selected from hydrogen, halogen, hydroxyl, cyano, nitro, amine, silyl, siloxanyl, and optionally substituted linear, branched, or cyclic C₁-C₃₀ organic group, wherein optionally two or more of adjacent R⁵, R⁶ and R⁷ form a ring; and

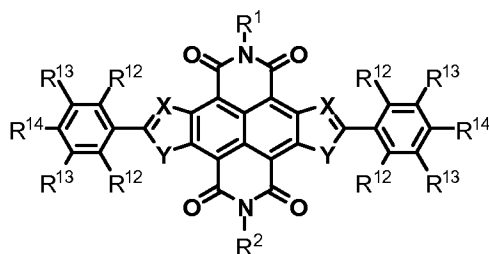
wherein R⁸ is selected from hydrogen, optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group.

10. The compound of any of claims 1-9, wherein R^3 and R^4 are independently selected from optionally substituted thiophenyl, optionally substituted furanyl, optionally substituted phenyl, optionally substituted pyridinyl, optionally substituted pyrimidinyl, optionally substituted pyridazinyl, optionally substituted pyrazinyl, optionally substituted 1,2,4-triazine, optionally substituted 1,3,5-triazine, optionally substituted 1,2,4,5-tetrazine.

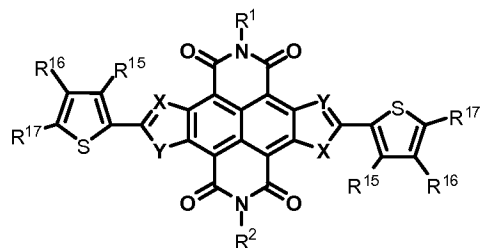
11. The compound of any of claims 1-10, wherein the compound of Formula (I) or Formula (II) is represented by formulae (IX), (X), (XI) or (XII):



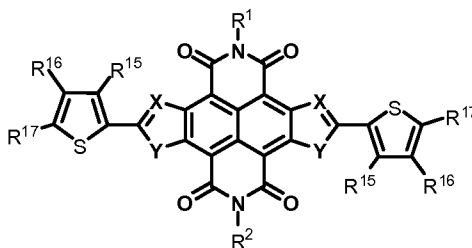
(IX)



(X)



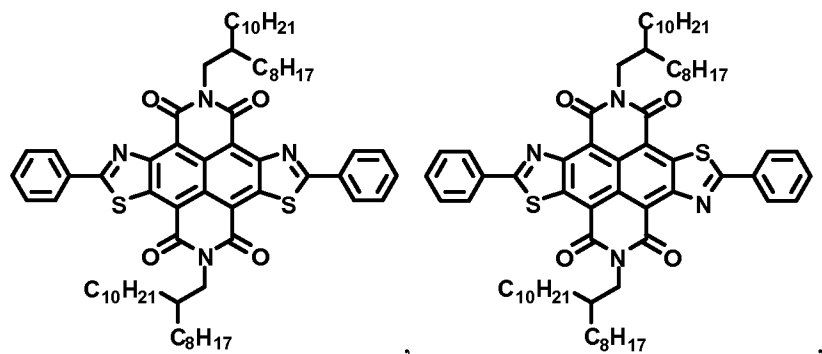
(XI)

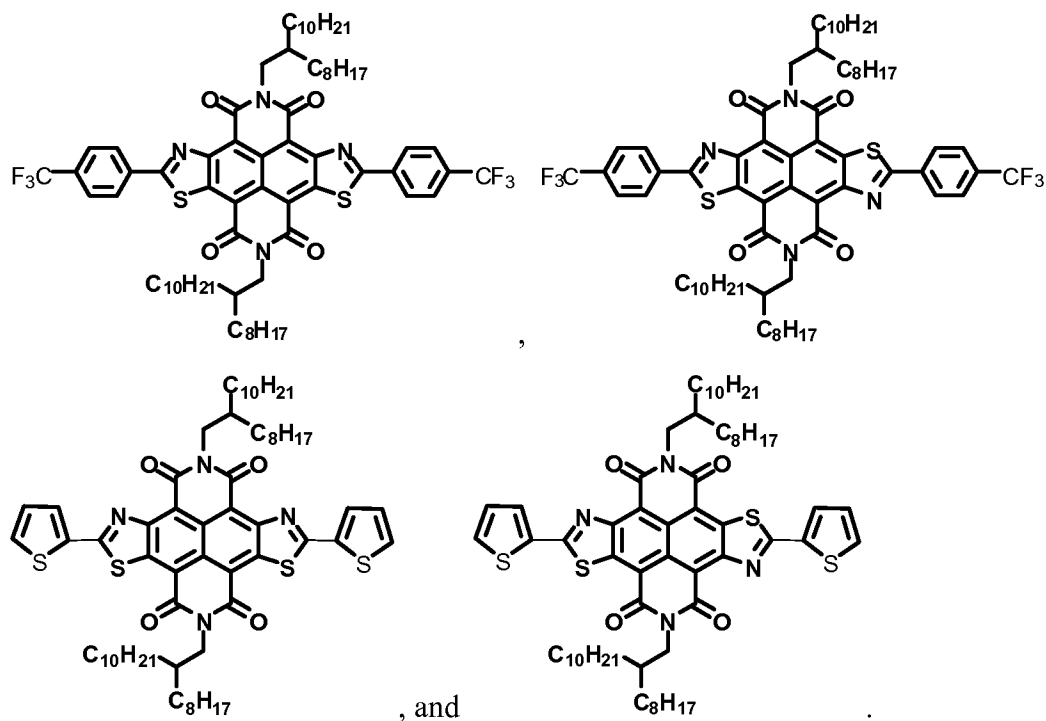


(XII)

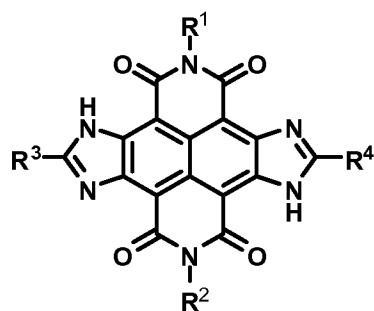
wherein R^{12} , R^{13} , R^{14} , R^{15} , R^{16} and R^{17} are independently selected from hydrogen, halogen, cyano, nitro, acyl, linear or branched alkyl group, linear or branched fluoroalkyl group, and linear or branched heteroalkyl group.

12. The compound of claim 1, wherein the compound of Formula (I) or Formula (II) is selected from



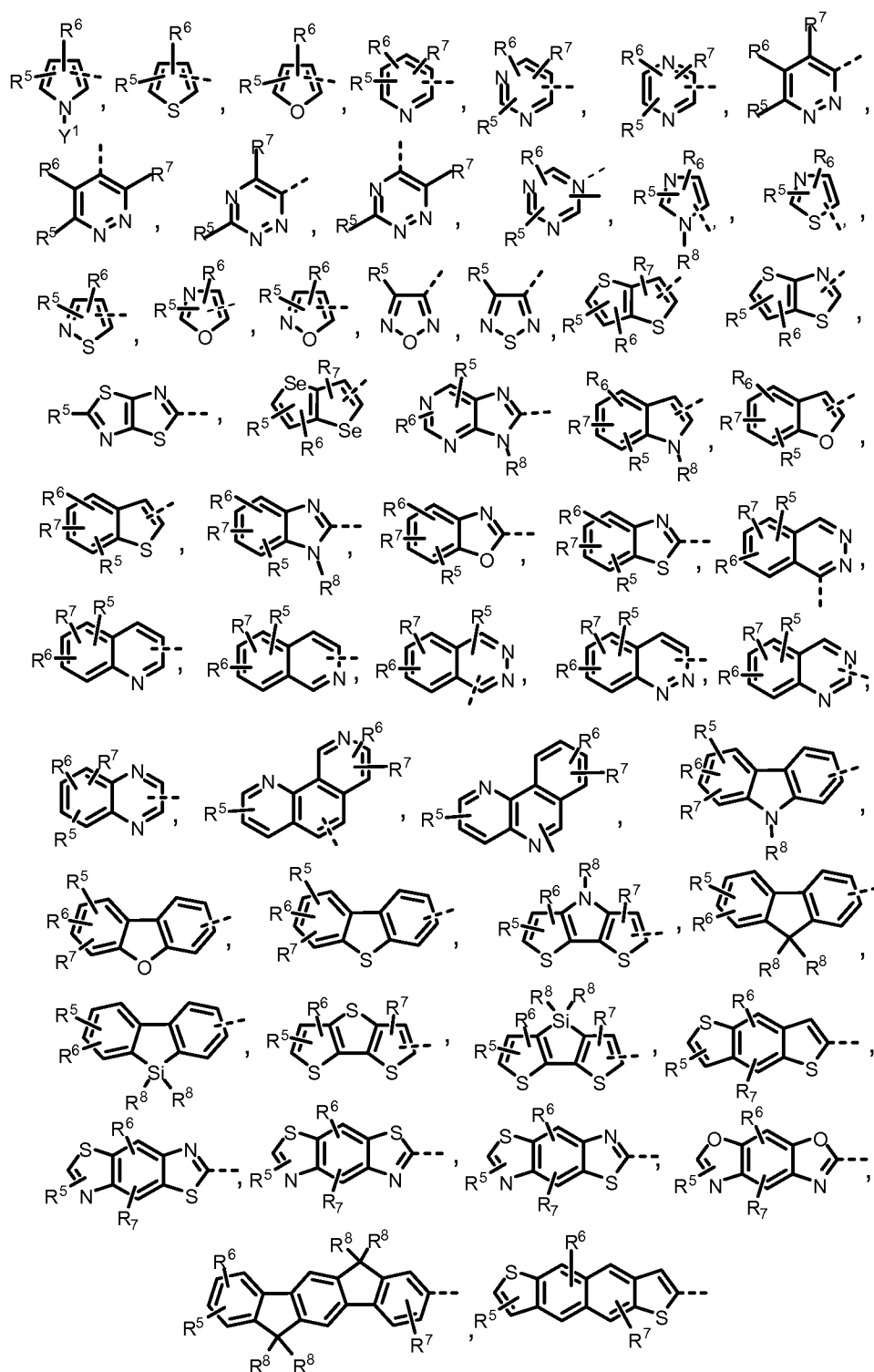


13. A compound represented by formula (XIII)



(XIII); wherein R¹ and R² are independently selected from

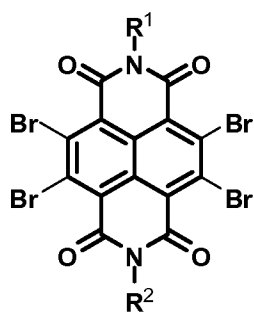
optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group; wherein R³ and R⁴ are independently selected from;



wherein R⁵, R⁶ and R⁷ are selected from hydrogen, halogen, hydroxyl, cyano, nitro, amine, silyl, siloxanyl, and optionally substituted linear, branched or cyclic C₁-C₃₀ organic group, wherein optionally two or more of adjacent R⁵, R⁶ and R⁷ form a ring; and

wherein R⁸ is selected from hydrogen, optionally substituted alkyl group, optionally substituted heteroalkyl group, optionally substituted aryl group and optionally substituted heteroaryl group.

14. A composition comprising at least one of the compounds of any of claims 1-13.
15. A composition comprising at least one compound represented by Formula (I) in claim 2 and at least one compound represented by Formula (II) in claim 3.
16. A method for making the compound of any of claims 1-13 or the composition of claims 14-15, comprising reacting a first compound represented by



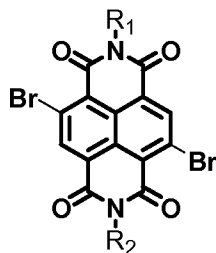
with a second compound represented by



NH_2 , wherein X is S, O or –

NH.

17. A method for making the single compound of Formula I in claim 2, comprising reacting a compound represented by



with a compound represented by NH_2 , wherein X is S, O or –NH.

18. An electronic device comprising at least one of the compounds of any of claims 1-13 or the compositions of claims 14-15, or the compounds or compositions made by the methods of claims 16-17.
19. An n-channel transistor comprising a layer comprising at least one of the compounds of any of claims 1-13 or at least one composition of claims 14-15, or at least one compound or composition made by the methods of claims 16-17, wherein said layer is obtained by solution processing and annealing a composition of claims 14-15, wherein said composition comprises at least one solvent and at least one of the compounds of any of claims 1-13 or made by the methods of claims 16-17.

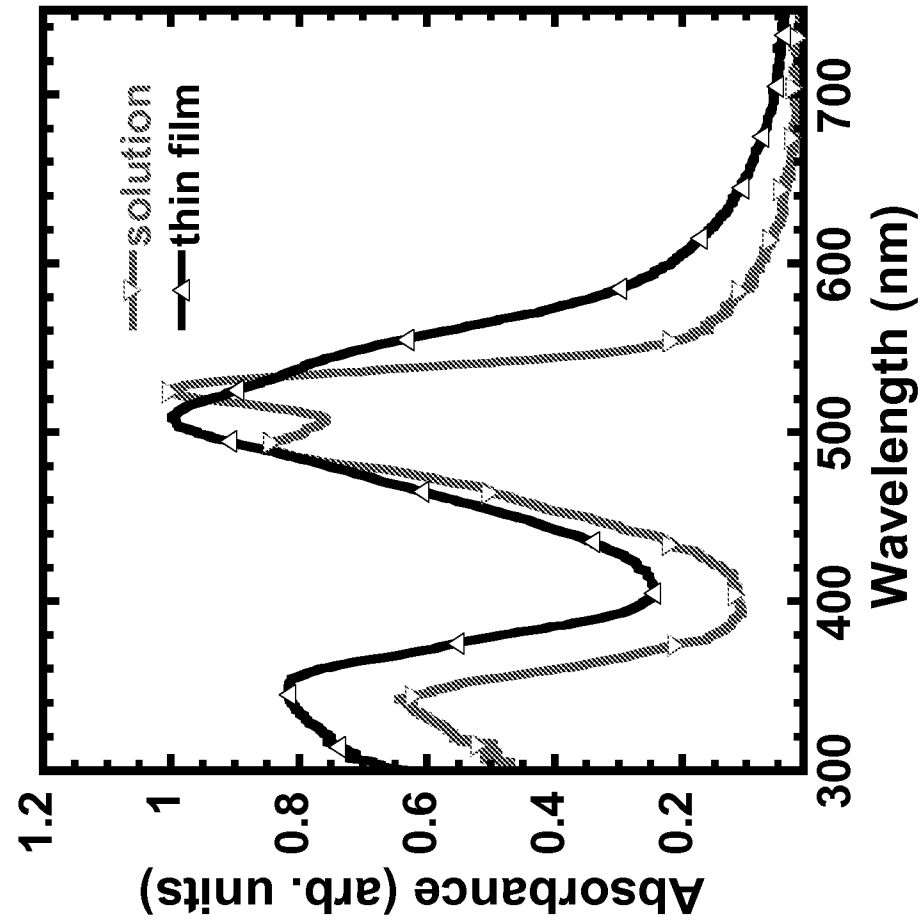


FIGURE 1

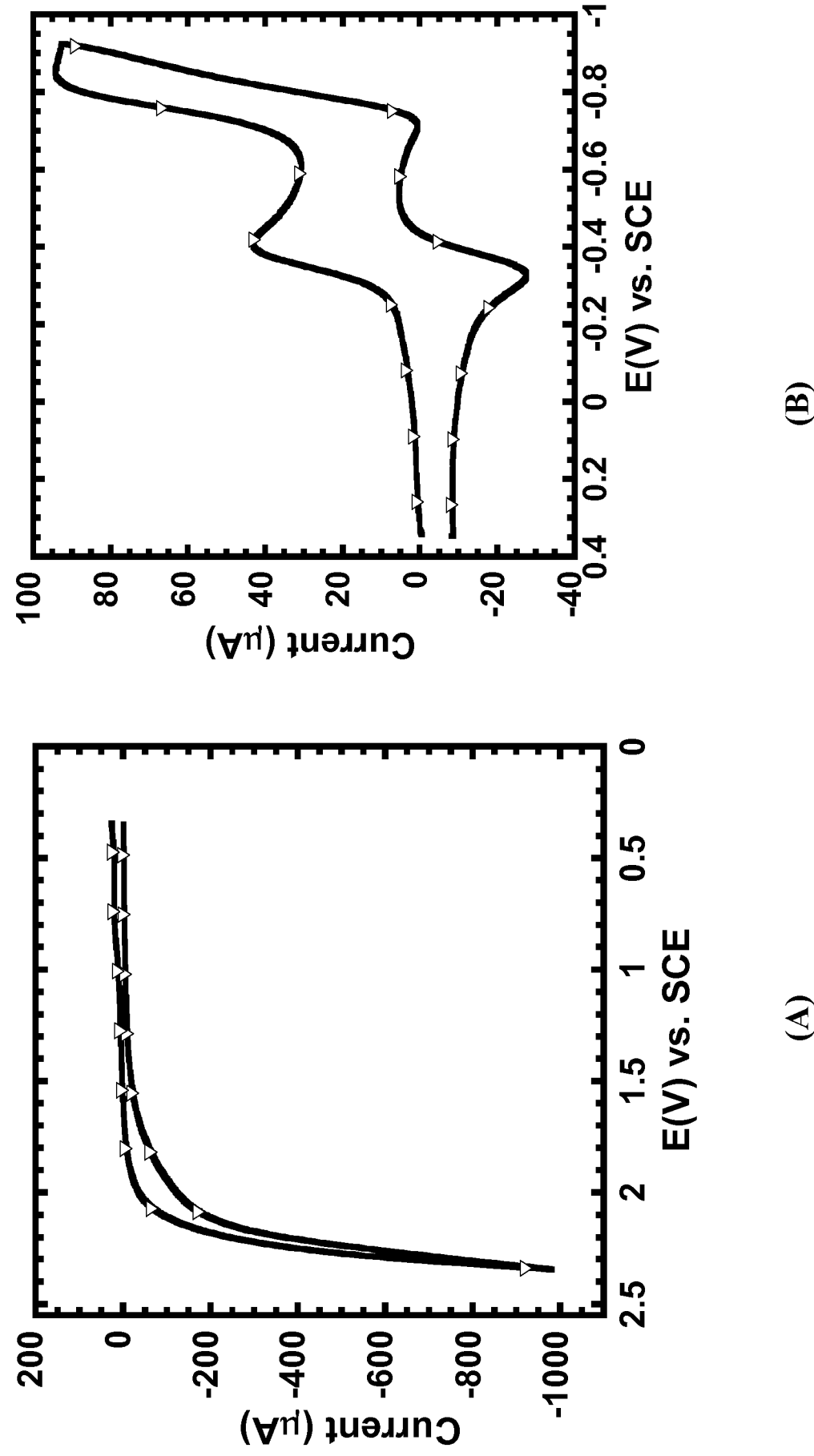


FIGURE 2

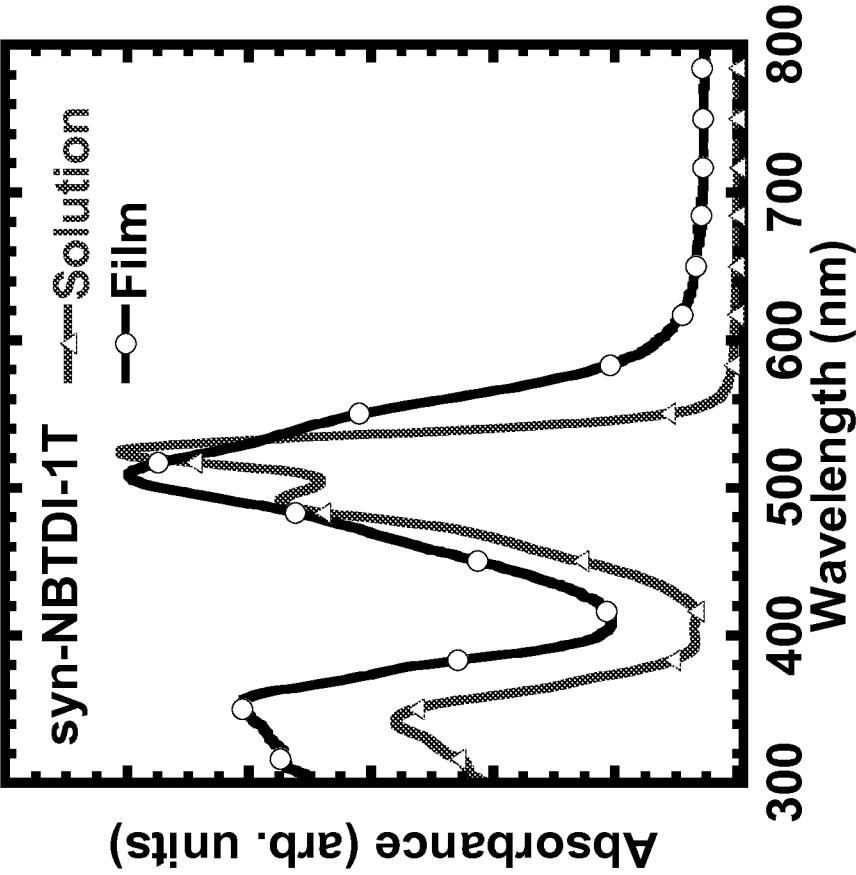


FIGURE 3

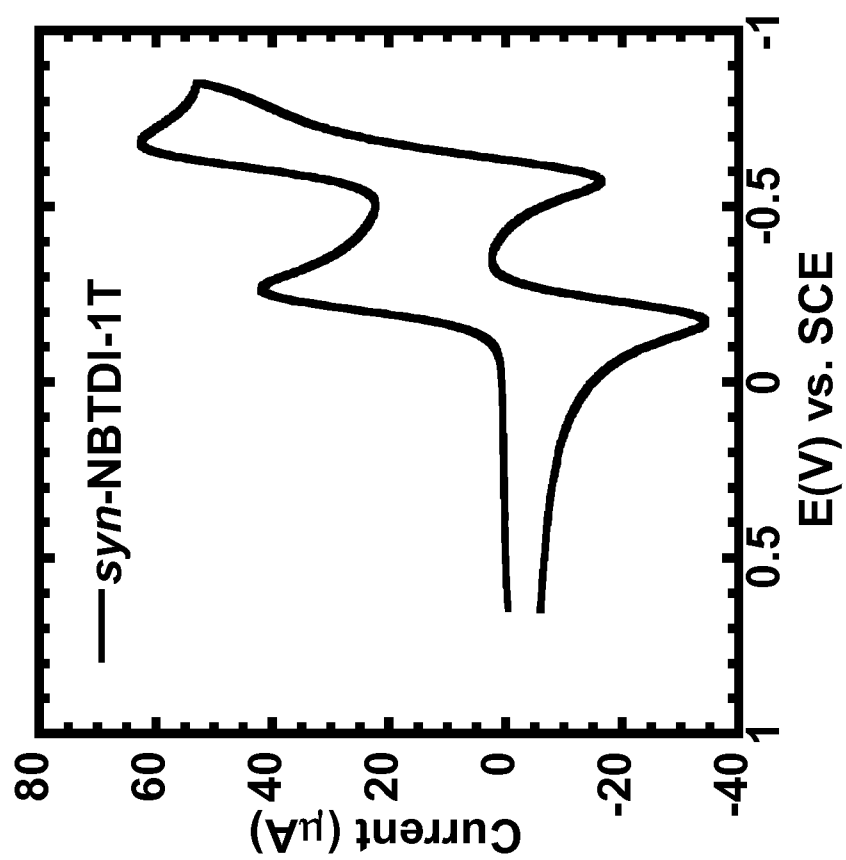


FIGURE 4

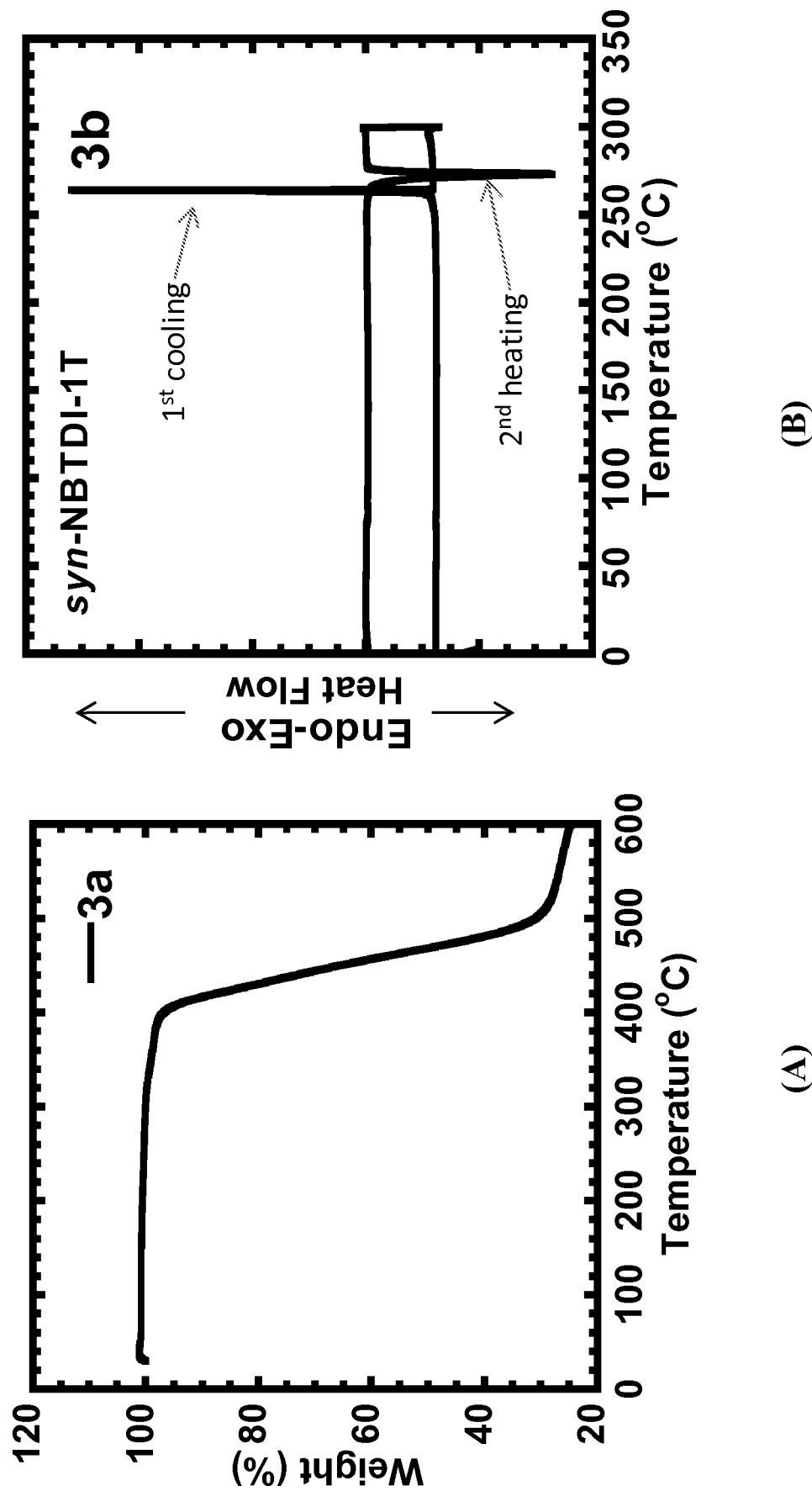


FIGURE 5

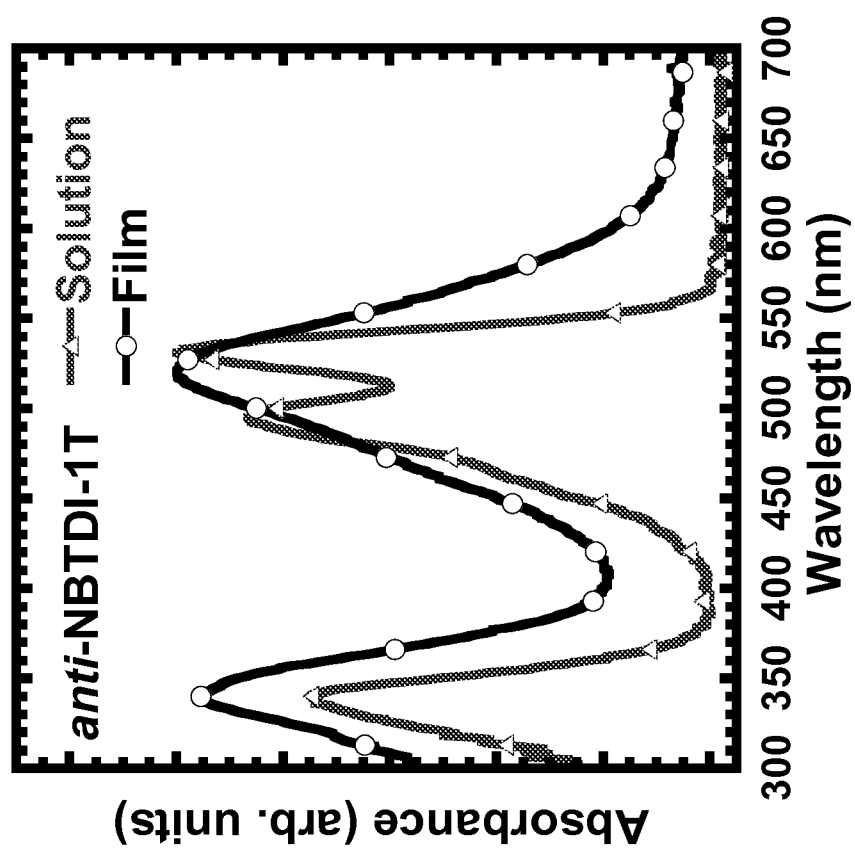


FIGURE 6

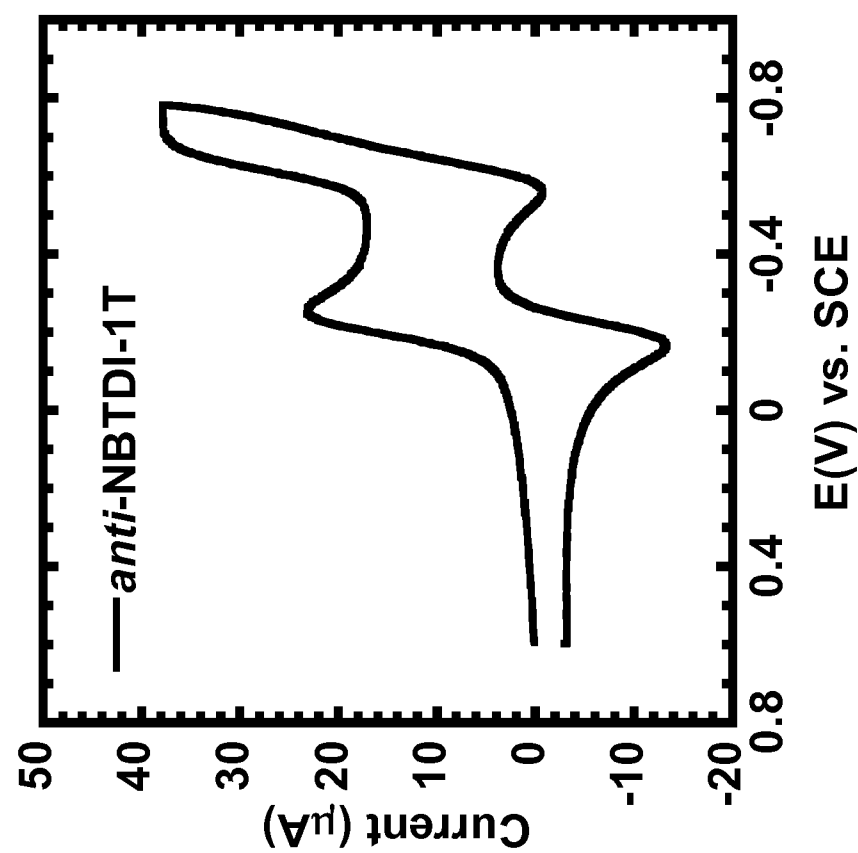


FIGURE 7

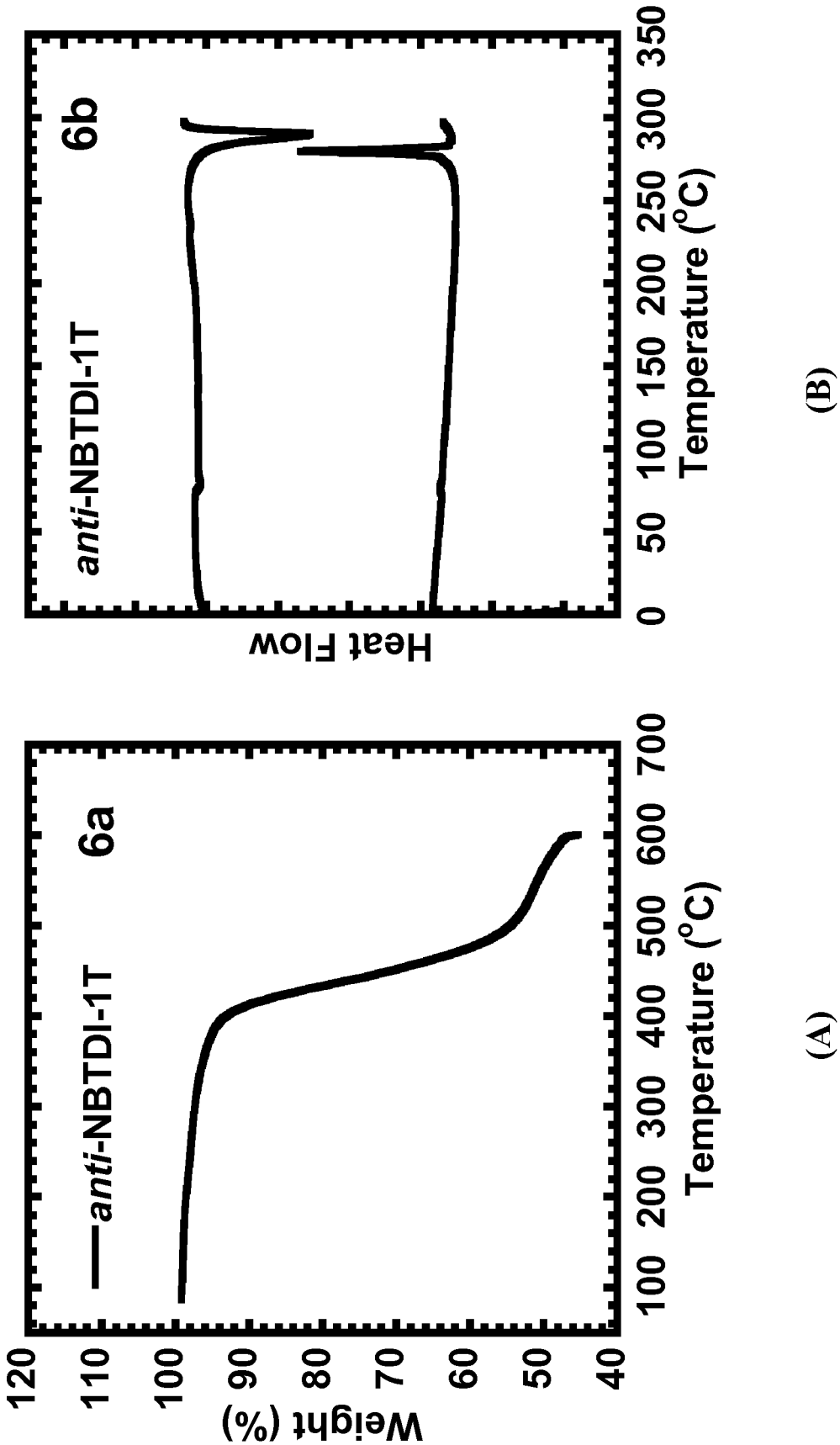


FIGURE 8

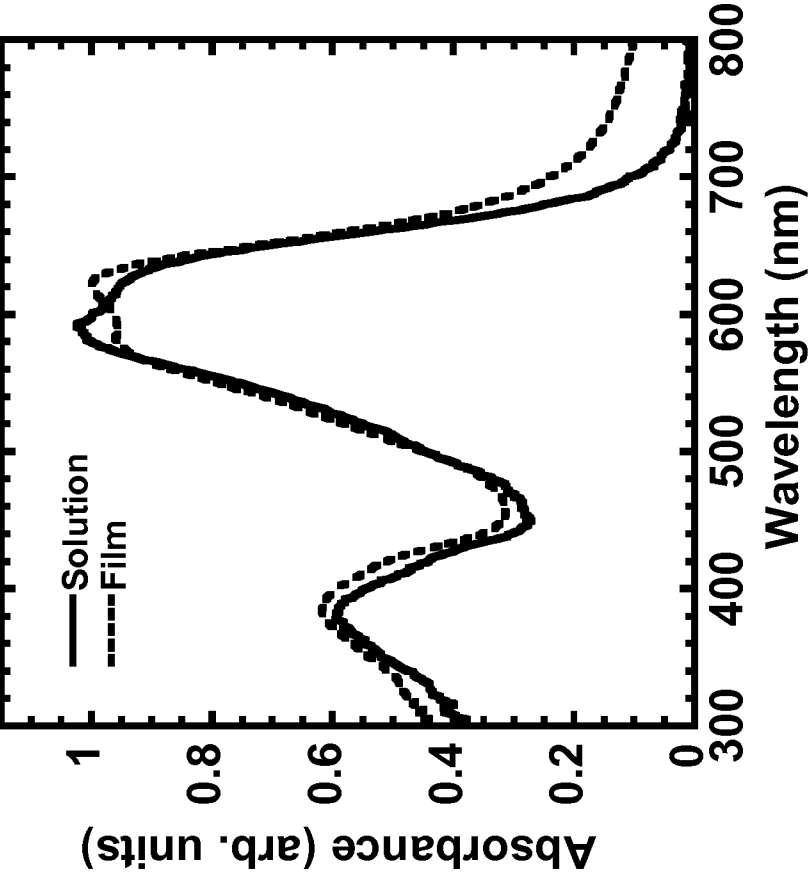


FIGURE 9

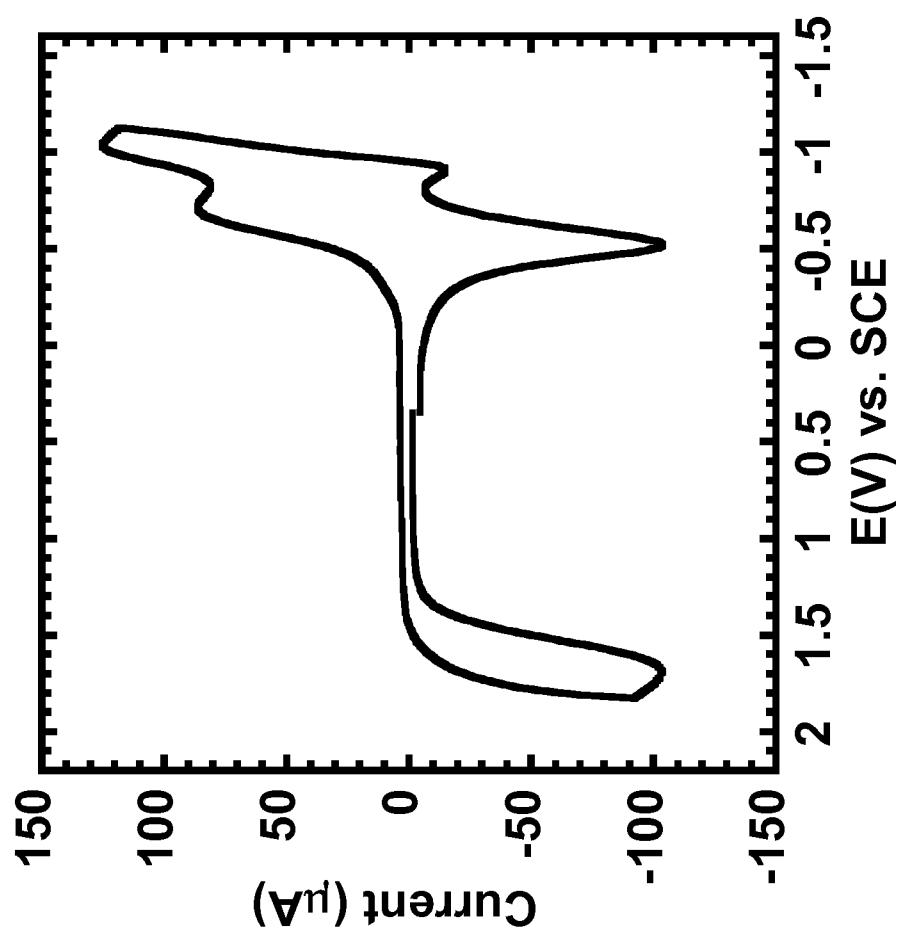


FIGURE 10

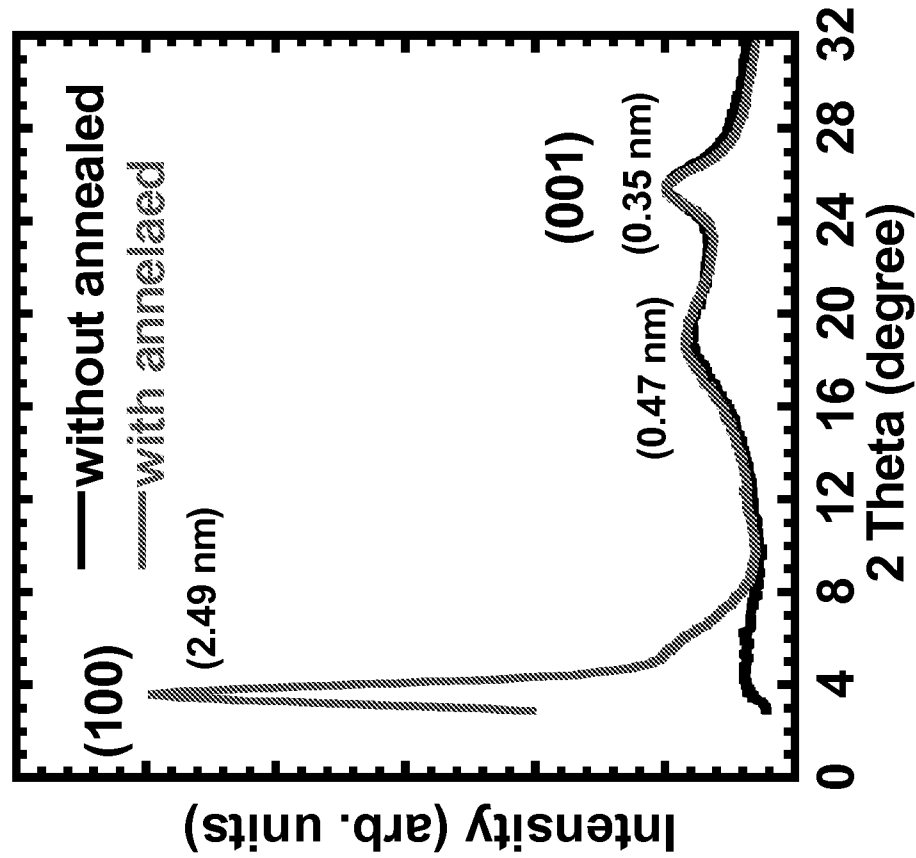


FIGURE 11

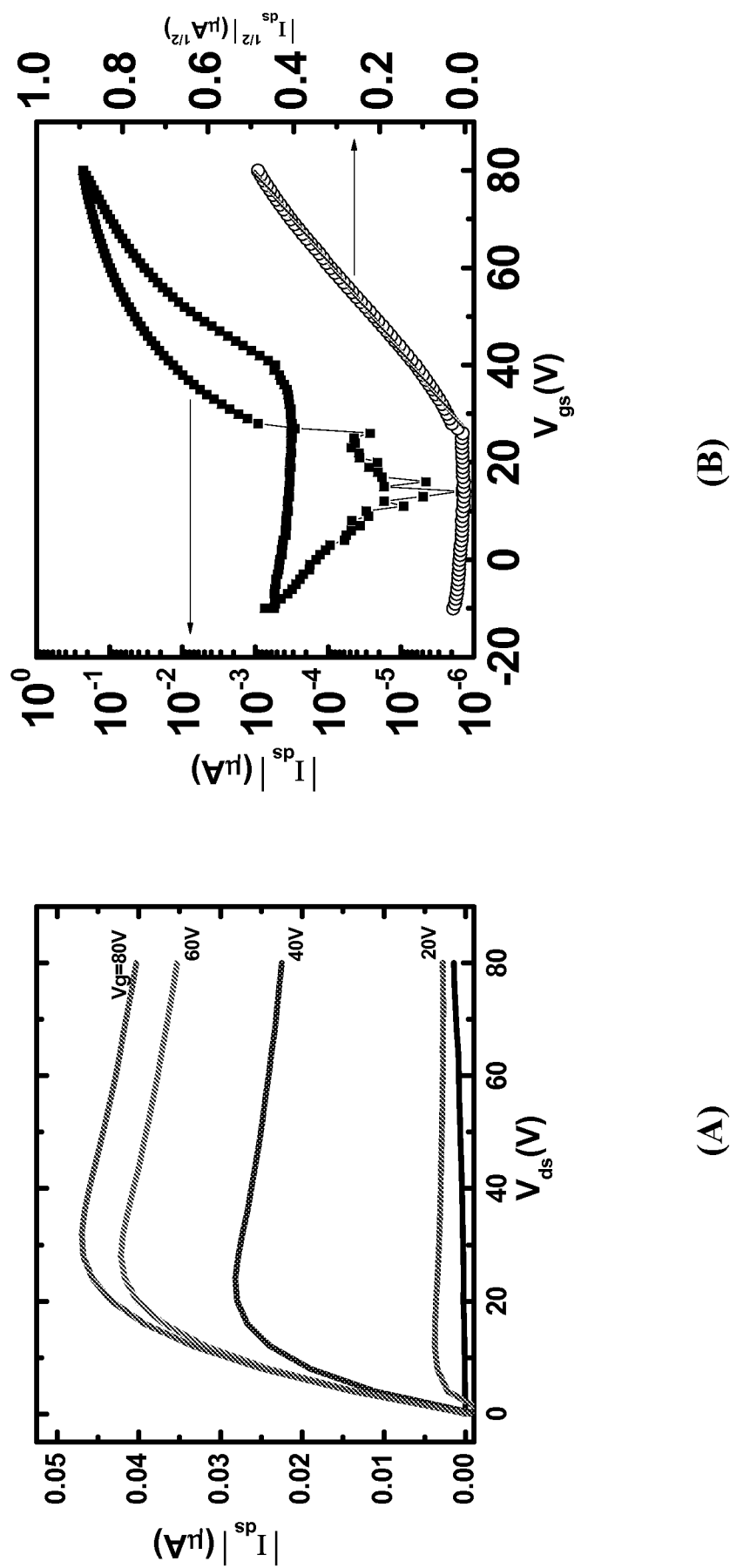


FIGURE 12

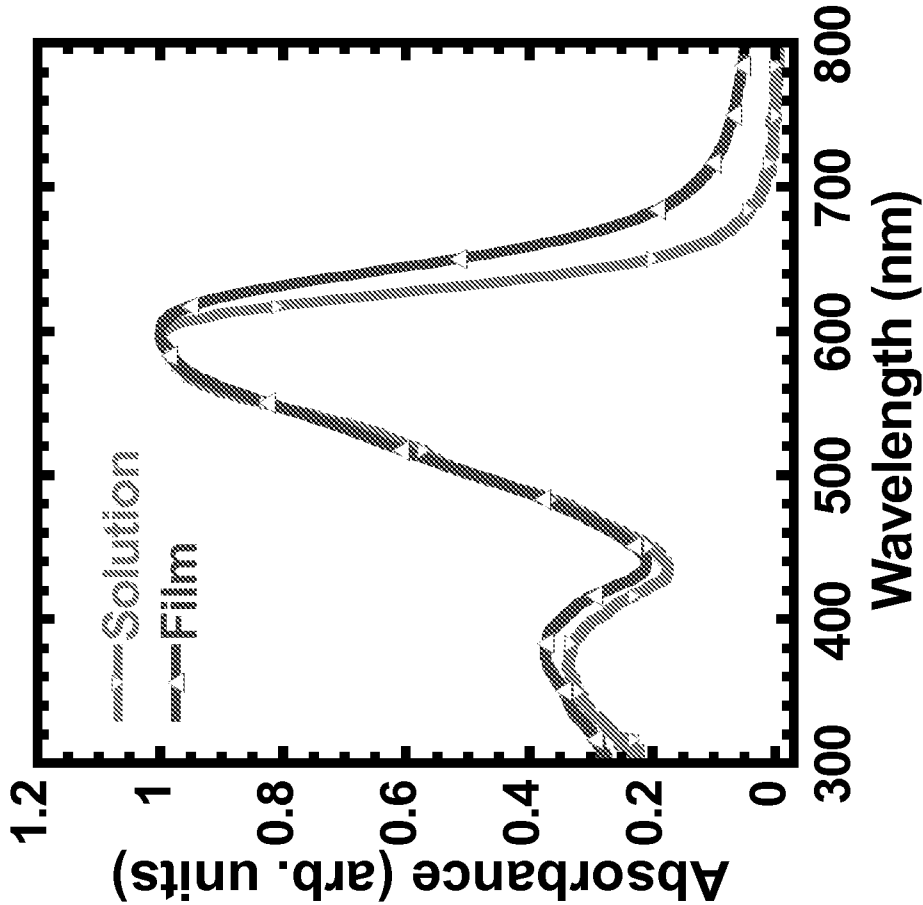


FIGURE 13

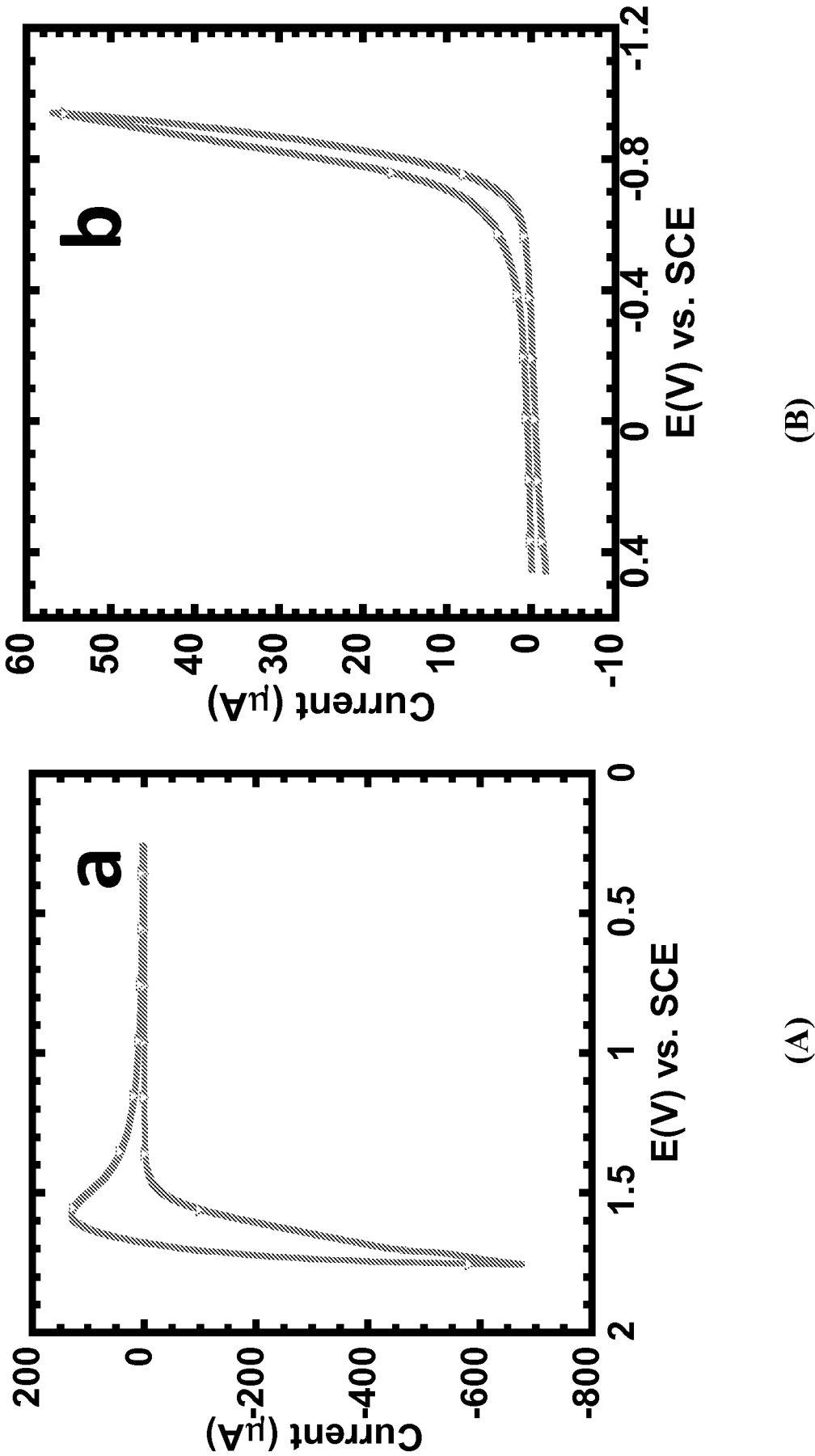


FIGURE 14