Naphthalene diimide (NDI) compounds can be functionalized with tin reagent to provide a useful, versatile synthetic tool. One embodiment provides, for example, a composition comprising at least one NDI compound comprising at least one stannyl substituent bonded to the naphthalene moiety of the NDI compound. Applications include organic electronic devices including OLED, OPV, OPET, and sensing devices.

19 Claims, No Drawings
STANNYL DERIVATIVES OF NAPHTHALENE DIIMIDES AND RELATED COMPOSITIONS AND METHODS

This application is a U.S. national phase entry under 35 U.S.C. §371 of International Application No. PCT/US2012/033598, filed on Apr. 13, 2012, which claims priority to U.S. Provisional Application No. 61/475,888, filed on Apr. 15, 2011; U.S. Provisional Application No. 61/579,608, filed on Dec. 22, 2011; and U.S. Provisional Application No. 61/591,767, filed on Jan. 27, 2012, the entirety of all of which is being incorporated herein by reference for all purposes.

BACKGROUND

Organic electronics is an important area for commercial development including, for example, advanced transistors, displays, lighting, photovoltaic, and sensing devices. The broad diversity of organic compounds and materials provides advantages for organic electronics. In but one example of the versatile chemistry and material science available for organic electronics, tetracarboxylic diimide derivatives of polyenes, particularly of naphthalene and perylene (NDIs and PDIs, respectively), represent one of the most extensively studied classes of functional materials in the field of organic electronics. The thermal, chemical, and photochemical stability as well as their high electron affinities and charge-carrier mobilities render these materials attractive for applications in organic field-effect transistors (OFETs) and organic photovoltaic cells (OPVs). They have also been widely used as acceptors in transient absorption studies of photoinduced electron-transfer, again due to their redox potentials, and to the stability and distinctive absorption spectra of the corresponding radical anions.

The N,N'-substituents of PDIs and NDIs generally only have minimal influence on the optical and electronic properties of isolated molecules, although they can be used to control solubility, aggregation, and intermolecular packing in the solid-state. In contrast, core substitution of these species typically has a much more significant effect on the redox potentials (enabling, in some cases, the electron affinities to be brought within a range in which air-stable OFFET operation can be achieved) and optical spectra of these species. Moreover, core substitution can be used as a means of constructing more elaborate architectures such as conjugated oligomers or polymers and donor or acceptor functionalized products.

Functionalized NDIs are most effectively obtained through the selective bromination of naphthalene-1,4:5,8-tetracarboxylic dianhydride (NDA) with dibromoisocyanuric acid (DBI) in concentrated sulfuric acid or oleum, followed by imidization with the primary amine of choice in refluxing acetic anhydride. NDA can also be brominated using Br₂ in concentrated sulfuric acid or oleum. The brominated NDI can then serve as an intermediate for further functionalization through either nucleophilic substitution to afford amino, thiol or alkyl or alkox substituted derivatives, or through palladium-catalyzed coupling reactions to yield cyano, phenyl, alkynyl and thienyl functionalized products. However, the range of conjugated species that can be obtained by palladium-catalyzed methods is determined by the availability of appropriate candidate coupling partners. In particular, metalled reagents such as stannanes can be difficult to obtain for electron-poor (acceptor) building blocks.

Additionally, monobrominated NDI, which is useful for a full range of NDI derived compounds, generally can only be obtained by manipulating the equivalents of brominating reagents and/or by manipulating reaction conditions; however, a difficult to separate mixture of non-brominated, mono-brominated, and dibrominated results, which makes large scale production impractical.

Accordingly, both mono- and di-metallated NDI species would be valuable building blocks for new types of conjugated NDI derivatives in which acceptor groups are directly conjugated to the NDI core.

SUMMARY

Embodiments described herein include compositions and compounds, as well as methods of making, methods of using, inks, and devices comprising these compositions and compounds.

One embodiment provides a naphthalene diimide (NDI) compound comprising at least one stannyl substituent bonded to the naphthalene core of the NDI compound.

Another embodiment provides the compound which is represented by the structure:

wherein R¹ and R⁴ are independently selected from a C₁₋C₃₀ normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyl-aryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups; R², R³, and R⁴ are independently selected from hydrogen, halide, or a C₁₋C₃₀ organic group independently selected from cyano, normal, branched, or cyclic alkyl, fluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups, or one or more of R⁵, R⁶, and R⁷ are optionally Sn(Rs)₃; and R⁸ is an alkyl or aryl group.

In another embodiment, R², R³, and R⁴ are independently selected from hydrogen, fluoro and cyano; and R⁸ is independently selected from hydrogen, halide, or a C₁₋C₃₀ organic group independently selected from cyano, normal, branched, or cyclic alkyl, perfluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups and Sn(Rs)₃, wherein R² is as previously defined.
Another embodiment provides a compound which is a mono-stannyl NDI compound represented by the structure:

wherein

a) $R^1$ and $R^1'$ are independently selected from a $C_{1-30}$ normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyldiaryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups,

b) $R^2$, $R^3$, and $R^4$ are independently selected from hydrogen, halide, or a $C_{1-30}$ organic group independently selected from cyano, normal, branched, or cyclic alkyl, perfluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups; and

c) $R^5$ is an alkyl or aryl group.

Another embodiment provides compounds as described herein but which exclude one or more mono-stannyl NDI compounds represented by the structure:

wherein

da) $R^1$ and $R^1'$ are independently selected from a $C_{1-30}$ normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyldiaryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups,

e) $R^2$, $R^3$, and $R^4$ are independently selected from hydrogen, halide, or a $C_{1-30}$ organic group independently selected from cyano, normal, branched, or cyclic alkyl, perfluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups; and

f) $R^5$ is an alkyl or aryl group.

Another embodiment provides the compound which is a bis-stannyl NDI compound represented by the structure:

wherein

a) $R^1$ and $R^1'$ are independently selected from a $C_{1-30}$ normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyldiaryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups,

b) $R^2$ and $R^4$ are independently selected from hydrogen, halide, or a $C_{1-30}$ organic group independently selected from cyano, normal, branched, or cyclic alkyl, perfluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups; and

c) $R^5$ is an alkyl or aryl group.

Another embodiment provides a composition comprising at least one naphthalene diimide (NDI) compound as defined in various embodiments described herein.

An embodiment for a method comprises a method comprising: reacting at least one first naphthalene diimide (NDI) precursor compound with at least one tin reagent to form at least one first NDI reaction product compound comprising at least one stannyl substituent bonded to the naphthalene core of the NDI compound.

In one embodiment, the tin reagent is an organotin reagent.

In another embodiment, the tin reagent is one or more of a hexaalkylltin reagent, or a hexaaryl tin reagent.

In another embodiment, the tin reagent is not a halogenated tin reagent.

In another embodiment, in the reacting step, only one NDI precursor compound is reacted with at least one tin reagent.

In another embodiment, the first NDI reaction product compound comprises one or two stannyl substituents.

In another embodiment, the first NDI reaction product comprises the structure:
wherein \( X \) is \( H, R^3 \) or a stannyl substituent \( Sn(R^3)\_3 \); wherein each \( R^1, R^1', R^2, R^3, R^4 \) and \( R^5 \) are as previously defined.

In another embodiment, the first NDI reaction product comprises a mixture of the following structures:

![Diagram 1](image1.png)

wherein \( X \) is \( H \) or \( R^3 \);

and:

![Diagram 2](image2.png)

wherein \( X \) is \( Sn(R^3)\_3 \).

In another embodiment, the reacting step is carried out in the presence of at least one metal catalyst.

Another embodiment further comprises the separation of the stannyl NDI reaction products via chromatography.

Another embodiment provides a method, said method being a method for making the compounds as described herein or the compositions as described herein, said method comprising the steps of:

(a) providing or obtaining a monomeric naphthalene diimide precursor compound represented by the structure:

![Diagram 3](image3.png)

wherein \( LG \) is a halogen;

(b) reacting the monomeric naphthalene diimide precursor compound with a compound having the structure \((R^5)\_3Sn.Sn(R^5)\_3\), in the presence of a catalyst, wherein

\[ R^5 \] is an alkyl or aryl group, to form at least some of the naphthalene diimide organotin compound, wherein \( R^1 \) and \( R^1' \) are previously defined.

\[ R^2, R^3, \text{ and } R^4 \] are independently selected from hydrogen, halide, or a \( C_1-C_{30} \) organic group independently selected from cyano, normal, branched, or cyclic alkyl, fluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups.

Another embodiment provides for use of the organotin compounds as described herein or of the compositions as described herein or compounds or compositions made by the methods described herein, wherein the use is to form an oligomer or polymer.

Another embodiment is use of the oligomer of polymer formed as described herein as a semiconducting oligomer or polymer in an organic electronic device, including, for example, OLED, OPV, OFET, or sensing device.

One embodiment provides a composition comprising at least one naphthalene diimide (NDI) compound comprising at least one stannyl substituent bonded to the naphthalene moiety of the NDI compound, wherein in one embodiment, the compound has one stannyl substituent. In another embodiment, the compound has two stannyl substituents.

In one embodiment, the stannyl substituent is \( -SnR'\_3 \) wherein the \( R' \) groups, independently, are alkyl or aryl.

In one embodiment, the NDI compound comprises at least one NDI moiety. In another embodiment, the NDI compound comprises at least two NDI moieties.

In one embodiment, the molecular weight of the compound is about 2,000 g/mol or less. In another embodiment, the molecular weight of the compound is about 1,000 g/mol or less. In another embodiment, the molecular weight of the compound is about 750 g/mol or less.

One embodiment provides for naphthalene diimide organotin compounds having the structure (I):

![Diagram 4](image4.png)

wherein \( R^1 \) and \( R^1' \) are independently selected from a \( C_1-C_{30} \) normal, branched, or cyclic alkyl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups; \( R^2, R^3, \text{ and } R^4 \) are independently selected from hydrogen, halide, or a \( C_1-C_{30} \) organic group independently selected from cyano, normal, branched, or cyclic alkyl, perfluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups or one or more of \( R^2, R^3, \text{ and } R^4 \) are optionally Sn \( (R^5)\_3 \); and \( R^5 \) is an alkyl or aryl group.

In one embodiment, \( R^2 \) and \( R^3 \) are independently a \( C_1-C_{30} \) normal or branched alkyl or fluoroalkyl group. In another embodiment, \( R^2, R^3, \text{ and } R^4 \) are independently selected from
Another embodiment provides for naphthalene diimide organotin compounds having the structure (I'):

wherein $R'$ and $R''$ are independently selected from a $C_1$-$C_{30}$ normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyl-aryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups; $R^2$ and $R^4$ are independently selected from hydrogen, halide, or a $C_1$-$C_{30}$ organic group independently selected from cyano, normal, branched, or cyclic alkyl, or perfluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, or alkoxy groups.

Another embodiment provides for naphthalene diimide organotin compounds having the structure (II):

wherein X is H or a stannyl substituent; wherein each R is independently a $C_1$-$C_{30}$ normal, branched, or cyclic alkyl, aryl, heteroaryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups; and wherein each of the $R'$ moieties is independently an alkyl or aryl moiety. In one embodiment, each R is independently an optionally substituted $C_1$-$C_{30}$ alkyl moiety and each of the $R'$ moieties is independently a $C_1$-$C_{20}$ alkyl moiety.

Another embodiment provides for naphthalene diimide organotin compounds having the structure (III):

wherein each R is independently a $C_1$-$C_{30}$ normal, branched, or cyclic alkyl, aryl, heteroaryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups; and wherein each of the $R'$ moieties is independently an alkyl or aryl moiety. In one embodiment, each R is independently an optionally substituted $C_1$-$C_{30}$ alkyl moiety and each of the $R'$ moieties is independently a $C_1$-$C_{20}$ alkyl moiety.

Another embodiment provides for naphthalene diimide organotin compounds having the structure (IV):

wherein each R is independently a $C_1$-$C_{30}$ normal, branched, or cyclic alkyl, aryl, heteroaryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups; and wherein each of the $R'$ moieties is independently an alkyl or aryl moiety. In one embodiment, each R is independently an optionally substituted $C_1$-$C_{30}$ alkyl moiety and each of the $R'$ moieties is independently a $C_1$-$C_{20}$ alkyl moiety.
Another embodiment provides a method for making the compounds of these embodiments, comprising the steps of:

(a) providing or obtaining a monomeric naphthalene diimide compound having the structure (V):

\[
\begin{align*}
\text{(V)} \quad & R_1 - \text{O} - \text{N} - \text{O} - \text{Sn} - \text{LG} \\
& \text{R}_2 - \text{N} - \text{O} - \text{Sn} - \text{LG} \\
& \text{R}_3 - \text{O} - \text{N} - \text{O} - \text{Sn} - \text{LG} \\
& \text{R}_4 - \text{N} - \text{O} - \text{Sn} - \text{LG}
\end{align*}
\]

wherein R1, R2, and R3 are independently selected from a C1-C30 normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyl-aryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups; R7 is an alkyl or aryl group, to form at least some of the naphthalene diimide organotin compound. In another embodiment, R5 of the monomeric naphthalene diimide compound of Step (a) is also LG.

(b) reacting the monomeric naphthalene diimide compound with a compound having the structure \((R')_3\text{Sn-Sn}(R')_3\) in the presence of a catalyst, wherein R' is an alkyl or aryl group, to form at least some of the naphthalene diimide organotin compound. In another embodiment, R5 of the monomeric naphthalene diimide compound of Step (a) is also LG.

Another embodiment provides for a method comprising: reacting at least one first naphthalene diimide (NDI) precursor compound with at least one tin reagent to form at least one first NDI compound comprising at least one stannyl substituent bonded to the naphthalene moiety of the NDI compound.

Another embodiment provides that the tin reagent is an organotin reagent. In one embodiment, the tin reagent is a ditin reagent. In one embodiment, the tin reagent is an alkyltin reagent. In another embodiment, the tin reagent is a hexabutylditin reagent. In one embodiment, the tin reagent is not a halogenated tin reagent.

In one embodiment, in the reacting step, only the one NDI precursor compound is reacted with the at least one tin reagent.

In one embodiment, the reacting step, a mixture of two different NDI precursor compounds is reacted with the at least one tin reagent to form at least one first NDI reaction product compound and also at least one second different NDI reaction product compound, wherein each of the first and second NDI reaction product compounds comprise at least one stannyl substituent bonded to the naphthalene moiety of the first and second NDI compounds.

In one embodiment, the first naphthalene diimide (NDI) precursor compound has zero, one, or two halogen moieties. In one embodiment, the first naphthalene diimide (NDI) precursor compound has one or two halogen moieties.

In one embodiment, the first NDI reaction product compound comprises one stannyl substituent and the second NDI reaction product compound comprises two stannyl substituents.
March's Advanced Organic Chemistry, methoxy, ethoxy, propoxy (e.g., n-propoxy and isopropoxy), "haloalkyl". Examples of haloalkyl include methyl (Me), ethyl (Et), propyl (e.g., n-propyl and iso-propyl), butyl (e.g., n-buty1, iso-butyl, sec-butyl, tert-butyl), pentyl groups (e.g., n-pentyl, iso-pentyl, neopentyl), and the like. In various embodiments, an alkyl group can have 1 to 6 carbon atoms, and can be substituted with halogen atoms (e.g., perfluoroalkyl groups such as CF3, CF2Cl, CH2F, CCl3, CHCl2, CH2Cl, C2Cl3, and the like. Perhaloalkyl groups, i.e., alkyl groups where all of the hydrogen atoms are replaced with halogen atoms (e.g., perfluoroalkyl groups such as CF3 and C2F5), are included within the definition of "haloalkyl."

As used herein, "alkoxy" can refer to alkyl group having one or more halogen substituents. At various embodiments, a haloalkyl group can have 1 to 20 carbon atoms, and can be substituted with 1-5 R1 groups, and R1 is as defined herein. As used herein, "alkoxy" can refer to —O—alkyl group. Examples of alkoxy groups include, but are not limited to, methoxy, ethoxy, propoxy (e.g., n-propoxy and isopropoxy), t-butoxy groups, and the like. The alkyl group in the —O—alkyl group can be substituted with 1-5 R1 groups and R1 is as defined herein.

As used herein, "heteroatom" can refer to an atom of any element other than carbon or hydrogen and includes, for example, nitrogen, oxygen, silicon, sulfur, phosphorus, and selenium.

As used herein, "heteroaryl" can refer to an aromatic monocyclic ring system containing at least one ring heteroatom selected from oxygen (O), nitrogen (N), sulfur (S), silicon (Si), and selenium (Se), or a polycyclic ring system wherein at least one of the rings present in the ring system is aromatic and contains at least one ring heteroatom. A heteroaryl group, as a whole, can have, for example, from 5 to 16 ring atoms and contain 1-5 ring heteroatoms (i.e., 5-16-membered heteroaryl group). In some embodiments, heteroaryl groups can be substituted with one or more terminal R1 groups, where R1 is as defined herein. Both substituted and unsubstituted heteroaryl groups described herein can comprise between 1-30, or 1-20 carbon atoms, including the R1 substituents.

As used herein, "aryl" can refer to a broad variety of unsaturated cyclic groups which can provide conjugation and delocalization and can be fused and can be optionally substituted, as known in the art. Aryl groups with C6 to C40, or C6 to C30 in carbon number can be used, for example.

**NDI-Sn Compositions**

One embodiment provides, for example, a composition comprising at least one naphthalene diimide (NDI) compound comprising at least one stannyl substituent bonded to the naphthalene moiety of the NDI compound.


One representation of an NDI structure is as follows, showing the core naphthalene group and the two imide groups:

![NDI Structure](image_url)
example, the compound can have one stannyl substituent, or it can have two stannyl substituents.

In one embodiment, the NDI compound comprises at least one NDI moiety, whereas in another embodiment, the NDI compound comprises at least two NDI moieties, or at least three NDI moieties. Hence, for example, oligomers of NDI can be derivatized with one or more stannyl moieties.

In one embodiment, the molecular weight of the NDI-Sn compound is about 2,000 g/mol or less, or about 1,000 g/mol or less, or about 750 g/mol or less.

In one embodiment, the Applicants have unexpectedly discovered a ready and practical method for making naphthalene diimide organotin compounds (NDI-tin compounds) represented by the structure (I):

![Diagram](image)

wherein R¹ and R' are independently selected from a C₁-C₃₀ normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyl-aryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups; R², R³, and R⁴ are independently selected from hydrogen, halide, or a C₁-C₃₀ organic group independently selected from cyano, normal, branched, or cyclic alkyl, perfluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups or one or more of R², R³, and R⁴ are optionally Sn(X)₃ or R⁴ is an alkyl or aryl group. In one embodiment, R², R³, and R⁴ are independently selected from hydrogen, halide, or a C₁-C₃₀ organic group independently selected from cyano, normal, branched, or cyclic alkyl, perfluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups. In another embodiment, R², R³, and R⁴ are independently selected from hydrogen, fluoro and cyano. In another embodiment, R³ is a C₁-C₁₅ alkyl group.

In another embodiment, the NDI-tin compound is represented by the structure (I'):
aryl, heteroaryl, alkyl-aryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups; and wherein each of the R' moieties is independently an alkyl or aryl moiety. In another embodiment, each R is independently an optionally substituted C₁₋₃₀ alkyl moiety and each of the R' moieties is independently a C₁₋₂₀ alkyl moiety.

In another embodiment, the compound is represented by the structure (III):

![Structure (III)](image)

wherein each R is independently a C₁₋₃₀ normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyl-aryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups; and wherein each of the R' moieties is independently an alkyl or aryl moiety. In another embodiment, each R is independently an optionally substituted C₁₋₃₀ alkyl and each of the R' moieties is independently a C₁₋₂₀ alkyl moiety.

In another embodiment, the compound is represented by the structure (IV):

![Structure (IV)](image)

wherein each R is independently a C₁₋₃₀ normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyl-aryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups; and wherein each of the R' moieties is independently an alkyl or aryl moiety. In another embodiment, each R is independently an optionally substituted C₁₋₃₀ alkyl and each of the R' moieties is independently a C₁₋₂₀ alkyl moiety.

Methods of Making NDI-Sn Compounds

Also described herein are methods of making the compounds described supra. For example, another embodiment provides for a method comprising: reacting at least one first naphthalene diimide (NDI) precursor compound with at least one tin reagent to form at least one first NDI compound comprising at least one stannyl substituent bonded to the naphthalene moiety of the NDI compound. Precursor compounds are described further below.

Tin reagents and organotin reagents are known in the art. For example, the tin reagent can be an alkyltin or aryltin reagent and preferably, an alkyltin reagent. The tin reagent can provide the tin moiety in the NDI compounds described supra, including formulas I, II, III and IV. The tin reagent can comprise two tin atoms per molecule (a “ditin” compound) such as, for example, R'₃Sn—SnR'₃, wherein R’ is independently alkyl or aryl, and preferably alkyl. In one embodiment, the R’ alkyl group are independently selected from a C₁₋₃₀ normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyl-aryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups. The R’ alkyl group can be, for example, a C₁₋₂₀ alkyl group including, for example, methyl or butyl (including n-butyl). In one example, the tin reagent is a hexabutylditin reagent.

In one embodiment, the tin reagent is not a halogen tin reagent. For example, tin reagents are known which can be represented by X-SnR’₃, wherein X is a halogen. However, such reagents can be excluded.

For one embodiment, in the reacting step, only one NDI precursor compound is reacted with the at least one tin reagent. However, mixtures of different NDI precursor compounds can be subjected to reaction with tin reagent, and this use of mixtures can provide important advantages. In another embodiment, in the reacting step, a mixture of two different NDI precursor compounds is reacted with the at least one tin reagent to form the at least one first NDI reaction product compound and also at least one second different NDI reaction product compound, wherein each of the first and second NDI compounds comprise at least one stannyl substituent bonded to the naphthalene moiety of the first and second NDI compounds.

In one embodiment, for example, the first NDI compound comprises one stannyl substituent and the second NDI compound comprises two stannyl substituents.

In one embodiment, the reacting step produces a mixture of the first and second different NDI reaction product compounds and the mixture is subjected to a separation procedure to separate the first and second NDI reaction product compounds (e.g. chromatography).

In these reactions, as described in supra, the first NDI compound can be represented by a compound of Formulas (I)-(IV).

In addition, the below Scheme A illustrates a synthetic method starting from NDA precursor.
In Scheme A, the three arrows can represent, schematically, reaction steps which are needed to form the desired target: (i) halogenation of one or both of the naphthalene phenyl rings in compound A to allow introduction of the tin substituents to the naphthalene core, (ii) conversion of the two anhydride moieties in compound A (NDA) to the imide, and (iii) introduction of the tin moiety to the phenyl ring (replacing the halogen or halogens introduced in (i)). Starting from a single precursor compound A, the two tin reaction products, B and C, can be produced as a mixture and then separated by methods known in the art, such as chromatography as illustrated in the Working Examples, below. In Scheme A, the imide R and tin R' groups in B and C can be as described above, independently of each other. Purification steps can be carried out after any or each of the three steps (i), (ii), and (iii), including only after step (iii). Compounds B and C can be further substituted as described in Formulas (I)-(IV), and the compound A can, in some instances, contain corresponding substituents.

In additional embodiments, NDI-organotin compounds can be made by a method comprising the steps of (a) providing or obtaining a monomeric naphthalene diimide compound substituted with a leaving group L,G, and represented by the structure (V);

![Diagram of structure (V)](image)

wherein R', R'' are independently selected from a C₁⁻C₃₀ normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyl-aryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups; R₁, R₂, and R₃ are independently selected from hydrogen, halide, or a C₁⁻C₃₀ organic group independently selected from cyano, normal, branched, or cyclic alkyl, perfluoralkyl, aryl, heteroaryl, alkylaryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups; and L,G is a halogen, such as Br or I; and (b) reacting the monomeric naphthalene diimide compound with a compound having the structure (R₃)₂Sn—Sn(R₃)₂ in the presence of a catalyst (typically soluble palladium compounds, such as the Stille coupling catalysts, e.g. Pd₂(dba)₃ and P(O-tol)₃ ligand), and wherein R₃ is an alkyl or aryl group, to form at least some of the naphthalene diimide organotin compounds. In another embodiment, R₃ of the monomeric naphthalene diimide compound of Step(a) is also L,G.

This method for making isolatable quantities of the naphthalene diimide organotin compounds is unexpected. Without wishing to be bound by theory, it was expected that under such "Stille Coupling" conditions, the naphthalene diimide organotin compounds would be formed as a reaction intermediate, but would cross couple in situ in a "Stille Coupling" with another molecule of the leaving-group substituted NDI, to generate an NDI-NDI dimer with directly coupled NDI groups. Unexpectedly, (especially in view of differing results with related perylenediimide and moieties known in the "dimerization" coupling reaction of bromide substituted NDI compounds did not proceed at a significant rate, but as a result the NDI organotin compounds can be isolated in good yield and used as synthetic intermediates to make other NDI-based materials. The nucleophilic NDI organotin compounds isolated from these unexpected reactions can however be readily coupled (in the presence of various appropriate palladium coupling catalysts well known to those of ordinary skill in the art) with other (less sterically hindered) bromide-substituted heteroaryl compounds, even if the brominated heteroaryl compounds are highly electron withdrawing, and enable the practical synthesis of NDI-hAr-NDI oligomers with electron withdrawing hAr bridging groups or other compounds, such as those described herein.

For introducing the tin substituents, the reacting step can be carried out under reaction conditions known in the art and illustrated by the working examples herein. For example, purification, temperature, pressure, atmosphere, solvent, reaction time, catalyst, and other reaction parameters can be controlled for a particular synthesis. Reaction temperature can be, for example, 50°C to 150°C. and reflux conditions can be used. Reaction time can be, for example, 3 h to 72 h. One or more organic solvents can be used such as an aromatic solvent like toluene. The catalyst materials can be introduced in one or more than one steps. Reaction yields can be, for example, at least 10%, at least 25%, or at least 50%.

Again, while methods related to NDI compounds are a preferred embodiment herein, higher rylene compounds such as PDI and related perylene compounds can be also functionalized with tin substituents and reacted to form additional compounds for use in, for example, organic electronic devices. Rylene compounds and moieties are known in the art. See, for example, Zhan et al., Adv. Mater., 2011, 23, 268-284. Besides NDI and PDI, other known rylene compounds include TDI, QDI, 5DI, and HDI, for example.

Use of Stannylated Compounds

As disclosed above, the NDI-organotin compounds of the present invention are highly useful as "nucleophilic" compounds in well known palladium catalyzed coupling reactions, which afford access to a number of different types of compounds, which can be utilized as a semiconducting oligomer or polymer in an organic electronic device such as, for example, an OLED, OPV, OFET, or sensing device.

The following compounds are representative compounds that can be accessed utilizing the NDI-organotin compounds embodied herein. For example, certain compounds of this invention can be further reacted to form NDI-hAr-NDI oligomers of the generic structure:
wherein \( h\text{Ar} \) is a heteroaryl that bridges the two NDI group and the NDI compounds are substituted as defined in Formulas (I)-(IV). See, for example, U.S. provisional application 61/475,888 filed Apr. 15, 2011 to Polander et al., which is cited above and incorporated by reference. See also U.S. provisional application 61/591,767 filed Jan. 27, 2012 cited above.

If needed, these compounds can be further manipulated to achieve the resulting compound for use as a semiconducting oligomer or polymer in an OLED, OPV, OFET, or sensing device.

WORKING EXAMPLES

1. Materials and General Methods

Materials.

Starting materials were reagent grade and were used without further purification unless otherwise indicated. Solvents were dried by passing through columns of activated alumina (toluene, \( \text{CH}_2\text{Cl}_2 \)), by distillation from \( \text{Na}/\text{benzophenone} \) (THF), or were obtained as anhydrous grade from Acros Organics. For reference, \( \text{N,N'-(n-hexyl)naphthalene-1,4,5,8-bis(dicarboximide)} \), was synthesized according to the literature: (1) Rademacher, A.; Märkle, S.; Langhals, H. \textit{Chem. Ber.} 1982, 115, 2927. (2) G. Hamilton, D.; Prodi, L.; Feeder, N.; K. M. Sanders, J. J. \textit{Chem. Soc., Perkin Trans. 1} 1999, 1057. (3) Reczek, J. J.; Villazor, K. R.; Lynch, V.; Swager, T. M.; Iverson, B. L. \textit{J. Am. Chem. Soc.} 2006, 128, 7995.

Hexabutyltin was obtained from Sigma-Aldrich.

Characterization.

Chromatographic separations were performed using standard flash column chromatography methods using silica gel purchased from Solvent Technologies (60 A, 32-63 \( \mu \)m). \( ^1H \) and \( ^13C\{^1H\} \) NMR spectra were obtained on a Bruker AMX 400 MHz Spectrometer with chemical shifts referenced using the \( ^1H \) resonance of residual \( \text{CHCl}_3 \) or the \( ^13C \) resonance of \( \text{CDCl}_3 \) unless otherwise indicated. Mass spectra were recorded on an Applied Biosystems 4700 Proteomics Analyzer by the Georgia Tech Mass Spectrometry Facility. Elemental analyses were performed by Atlantic Microlabs.

2. Synthetic Details

Example 1

Preparation of Compounds 1, 2

A solution of naphthalene-1,4,5,8-tetracarboxydianhydride (10.0 g, 59.5 mmol) in concentrated sulfuric acid (600 mL) was heated to 85° C. After 30 min, potassium dibromosuccinurate (19.3 g, 59.5 mmol) was added portionwise and the mixture was allowed to stir at 85° C. for 20 h. The mixture was poured into ice water (1.5 L) and allowed to stir for 2 h, while allowing to warm to room temperature. The resulting yellow precipitate was collected by filtration, washed with methanol, and dried under vacuum (16.6 g). The yellow solid was transferred to a flask with glacial acetic acid (600 mL) and n-hexylamine (19.4 g, 0.191 mol). The reaction mixture was refluxed for 20 min, allowed to cool overnight, and poured into methanol (1.5 L). The resulting precipitate was collected by filtration, washed with methanol, and dried under vacuum. The crude product was purified by column chromatography (silica, 3:2 dichloromethane/hexanes). During column packing, a portion of a poorly soluble yellow solid was isolated and found to be 2 (3.91 g, 6.60 mmol, 18%). The first band from the column afforded additional 2 as a yellow solid (0.650 g, 1.10 mmol, 21% overall yield). The second band gave 1 as a white solid (1.35 g, 2.63 mmol, 7%).
m/z calcd for C_{26}H_{28}Br_{2}N_{2} tylditin (1 eq per bromo substituent) was heated in toluene in the presence of Pd(II)(C5H5)2 and P(o-tol)3 were obtained in good to moderate yields, respectively, butyl)stannyl)naphthalene-1,4,5,8-bis(dicarboximide according to the following general scheme. A mixture of the appropriate mono- or dibromo derivative, 1 or 2, and hexabutyldistannane (1.64 mmol, 2.82 mmol), and tri-o-tolylphosphine (0.172 g, 0.565 mmol) in dry toluene (30 mL) was deoxygenated with nitrogen for 5 min. Tris(dibenzylideneacetone)di-palladium (0.129 g, 0.141 mmol) was added and the reaction mixture was precipitated in methanol (10 mL), the solid was removed via filtration, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica, dichloromethane) to yield the bi-PDI product and the stannyl PDI intermediate could not be isolated.

The ability to isolate and thoroughly purify the distannyl derivative is important for applications in conjugated-polymer syntheses, where the ability to obtain high-molecular-weight material is critically dependent on precise control of monomer stoichiometry.

Example 3

Preparation of Compound 3 from Compound 1

A solution of 1 (1.45 g, 2.82 mmol), 1,1,1,2,2,2-hexabutyldistannane (1.64 g, 2.82 mmol), and tri-o-tolylphosphine (0.172 g, 0.565 mmol) in dry toluene (30 mL) was deoxygenated with nitrogen for 5 min. Tris(dibenzylideneacetone)di-palladium (0.129 g, 0.141 mmol) was added and the reaction mixture was precipitated in methanol (10 mL), the solid was removed via filtration, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica, dichloromethane) to yield a yellow solid (1.53 g, 2.11 mmol, 75%). 1H NMR (400 MHz, CDCl3) δ 8.94 (s, 1H), 8.70 (d, J = 7.6 Hz, 1H), 8.67 (d, J = 7.6 Hz, 1H), 4.18 (t, J = 7.6 Hz, 2H), 4.16 (t, J = 8.0 Hz, 2H), 1.75-1.64 (m, 4H), 1.55-1.45 (m, 6H), 1.40-1.23 (m, 16H), 1.19 (t, J = 8.2 Hz, 6H), 0.90-0.80 (m, 15H), 13C{1H} NMR (100 MHz, CDCl3) δ 164.91, 163.62, 163.12, 163.04, 156.00, 138.65, 131.67, 130.24, 130.13, 126.84, 126.72, 126.70, 125.98, 123.64, 53.40, 41.00, 40.91, 31.50, 29.20, 28.25, 28.07, 28.02, 27.39, 26.76, 26.65, 22.54, 22.48, 17.27, 14.02, 13.69, 13.58, 11.58. HRMS (MALDI) m/z calcd for C_{35}H_{28}N_{2}O_{8}Sn (0.2 eq per bromo). Purification of the reaction products by silica gel chromatography and recrystallization from methanol afforded the mono- and distannyl derivatives as long yellow needles; these compounds were characterized by NMR spectroscopy, mass spectrometry, elemental analysis, and, in the case of 4, X-ray crystal structure.
Example 4

Preparation of Compound 4 from Compound 2

A solution of 2 (0.500 g, 0.844 mmol), 1,1,1,2,2,2-hexabutyldistannane (1.00 g, 1.73 mmol), and tri-o-tolylphosphine (0.051 g, 0.169 mmol) in dry toluene (10 mL) was deoxygenated with nitrogen for 5 min. Tris(dibenzylideneacetone)dipalladium (0.039 g, 0.042 mmol) was added and the reaction was heated to 90° C. for 24 h. Additional portions of tri-o-tolylphosphine (0.051 g, 0.169 mmol) and tris(dibenzylideneacetone)dipalladium (0.039 g, 0.042 mmol) were added and the reaction was stirred at 90° C. for an additional 2 d. After cooling, the reaction mixture was filtered through a plug of silica gel eluting with chloroform/hexanes (1:1) and the solvent was removed under reduced pressure. The crude product was recrystallized from methanol to yield a yellow solid (0.407 g, 0.402 mmol, 48%).

\[ \text{Example 4} \]

**Example 5**

Synthesis of 3-6 from NDA

\[ \text{i) DBI, H}_2\text{SO}_4 \]
\[ \text{ii) RNH}_2, \text{AcOH} \]
\[ \text{iii) (SnBu}_3\text{)}_3 \text{Pd}_2\text{dba}_3 \text{P(o-tol)}_3 \]

The different chromatographic behavior of 3 and 4 (3: \( R = \text{C}_6\text{H}_{13} \); 4: \( R = \text{C}_{12}\text{H}_{25} \)) suggested the possibility of carrying out this reaction using a mixture of mono- and dibromo species obtained from bromination and imidization of NDA, only purifying at the final stage. This transformation can indeed be carried out without separation of the mono- and difunctionalized intermediates to give isolated yields of mono- and distannyl derivatives of ca. 20% and 5%, respectively (when using 1 eq. DBI as the brominating agent). The relative yields can be somewhat tuned with respect to the brominating agent and after cooling, the reaction mixture was filtered through a plug of silica gel eluting with chloroform/hexanes (1:1) and the solvent was removed under reduced pressure. The crude product was recrystallized from methanol to yield a yellow solid (0.407 g, 0.402 mmol, 48%).
attractive alternative to the more difficult purification of that of the mono- and dibromo-NDI intermediates, such as 1 and 2, which are both less soluble in common organic solvents and less well-differentiated in Rf (0.4 and 0.3 for 1 and 2 on silica, eluting with dichloromethane). As such, a two-step isolation and purification of the brominated species followed by stannylation results in overall yields of ca. 9% and 2% for the mono- and distannyl NDI, respectively.

Example 6
Preparation of Compounds 3 and 4 from NDA

A solution of naphthalene-1,4,5,8-tetracarboxyldianhydride (NDA) (5.00 g, 18.6 mmol) in concentrated sulfuric acid (90 mL) while stirring at room temperature for 1 h. Once dissolved, the solution was added to the reaction flask and the mixture was allowed to stir at 85°C for 48 h. The mixture was poured into ice water (1 L) and allowed to stir for 2 h, while warming to room temperature. The resulting yellow precipitate was collected by filtration, washed with methanol, and dried under vacuum (4.51 g). The yellow solid was transferred to a flask with glacial acetic acid (100 mL) and n-hexylamine (7.2 g, 71.1 mmol). The reaction mixture was refluxed for 2 h, allowed to cool overnight, and poured into methanol (1 L). The resulting precipitate was collected by filtration, washed with methanol, and dried under vacuum (5.51 g). The orange solid was transferred to a dry Schlenk flask with 1,1,1,2,2,2-hexabutyldistannane (11.3 g, 19.5 mmol), tri-ortho-tolylphosphine (1.13 g, 3.71 mmol) and tris(dibenzylideneacetone)dipalladium (0.850 g, 0.930 mmol). The flask was pump-filled three times with nitrogen Anhydrous toluene (80 mL) was added and the reaction was heated to 100°C for 18 h. After cooling, the reaction mixture was diluted with hexanes (100 mL) and filtered through a plug of silica gel eluting with hexanes. Dichloromethane/hexanes (1:1) was used to elute the first yellow band (impure 4). The second yellow band was collected using dichloromethane as an eluent and was evaporated to give 3 as a yellow solid (2.60 g, 3.59 mmol, 19% overall yield from NDA). The first fraction was further purified by column chromatography (silica gel, 10:1 hexanes/dichloromethane) to yield 4 a yellow solid (0.780 g, 0.770 mmol, 4% from NDA). 1H NMR data were consistent with those obtained for 3 and 4 synthesized from 1 and 2, respectively.

Example 7
Preparation of Compounds 5 and 6 from NDA

A solution of naphthalene-1,4,5,8-tetracarboxyldianhydride (NDA) (5.00 g, 18.6 mmol) in concentrated sulfuric acid (180 mL) was heated to 55°C. In a separate flask, potassium dibromoisocyanurate (6.06 g, 18.6 mmol) was dis-
A solution of NDA (5.00 g, 18.6 mmol) in concentrated sulfuric acid (180 mL) was heated to 55°C. In a separate flask, potassium dibromoisocyanurate (6.06 g, 18.6 mmol) was dissolved in concentrated sulfuric acid (90 mL) while stirring at room temperature for 1 h. Once dissolved, the solution was added to the reaction flask and the mixture was allowed to stir at 85°C for 48 h. The mixture was poured into ice water (1 L) and stirred for 1 h, then allowed to stir at room temperature for 1 h. The solution was concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel): the first band was eluted with hexanes/dichloromethane (1:1) and was evaporated to a residue.

Data for 5: 1H NMR (400 MHz, CDCl3) δ 8.95 (s, 1H), 8.70 (d, J=7.6 Hz, 1H), 8.67 (d, J=7.7 Hz, 1H), 4.18 (m, 4H), 1.78-1.64 (m, 4H), 1.58-1.45 (m, 6H), 1.40-1.15 (m, 4H), 0.90-0.82 (m, 15H). 13C{1H} NMR (100 MHz, CDCl3) δ 164.90, 163.60, 163.09, 163.02, 155.98, 138.63, 131.65, 130.22, 130.12, 126.82, 126.71, 126.69, 125.96, 123.62, 40.98, 40.91, 31.89, 31.57, 28.61, 28.52, 29.48, 29.33, 29.20, 29.10, 28.12, 28.06, 27.39, 27.11, 26.99, 22.67, 14.09, 13.70, 11.57 (five aliphatic resonances not observed, presumably due to overlap). MS (MALDI) m/z 893.5 (7%, M+). 835.4 (100%, M+(C5H5)). Anal. Calcd. For C62H106N2S2: C, 67.33; H, 9.04; N, 3.14. Found: C, 67.40; H, 9.03; N, 3.13.

Data for 6: 1H NMR (300 MHz, CDCl3) δ 8.93 (s, 2H), 4.19 (t, J=7.2 Hz, 4H), 1.71 (quint., J=7.3 Hz, 4H), 1.53-1.46 (m, 12H), 1.57-1.42 (m, 12H), 1.42-1.02 (m, 24H). 13C{1H} NMR (75 MHz, CDCl3) δ 165.11, 163.11, 154.60, 153.84, 131.84, 126.89, 123.10, 40.93, 31.90, 29.64, 29.62, 29.50, 29.38, 29.34, 29.23, 28.12, 27.41, 27.04, 22.67, 14.10, 13.72, 11.52 (one aliphatic resonance not observed, presumably due to overlap). MS (MALDI) m/z 1066.4 (M-(C5H5)SnBu3). Anal. Calcd. For C62H50N2Sn8: C, 63.06; H, 9.05; N, 2.37. Found: C, 62.87; H, 9.09; N, 2.32.

What is claimed is:

1. A naphthalene diimide (NDI) compound comprising at least one stannyl substituent directly bonded to the naphthalene core of the NDI compound.

2. The compound of claim 1, which is represented by the structure:

What is claimed is:

1. A naphthalene diimide (NDI) compound comprising at least one stannyl substituent directly bonded to the naphthalene core of the NDI compound.

2. The compound of claim 1, which is represented by the structure:

wherein R1 and R1' are independently selected from a C1-C30 normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyl-aryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups;

R2, R3, and R4 are independently selected from hydrogen, halide, or a C1-C30 organic group independently selected from cyano, normal, branched, or cyclic alkyl, fluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups, or one or more of R2, R3, and R4 are optionally Sn(R3)3; and

R5 is an alkyl or aryl group.

3. The compound of claim 2, wherein R1', R2, and R4 are independently selected from hydrogen, fluoro and cyano; and

R3' is independently selected from hydrogen, halide, or a C1-C30 organic group independently selected from cyano, normal, branched, or cyclic alkyl, perfluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups,
optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups and Sn(R₅)₃ wherein R₅ is an alkyl or aryl group.

4. The compound of claim 1, which is a mono-stannyl NDI compound represented by the structure:

![Structure Image]

wherein

g) R¹ and R¹' are independently selected from a C₁-C₃₀ normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyl-aryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups,

h) R², R³, and R⁴ are independently selected from hydrogen, halide, or a C₁-C₃₀ organic group independently selected from cyano, normal, branched, or cyclic alkyl, perfluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups; and

i) R⁵ is an alkyl or aryl group.

5. The compound of claim 1, which is a bis-stannyl NDI compound represented by the structure:

![Structure Image]

wherein

d) R¹ and R¹' are independently selected from a C₁-C₃₀ normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyl-aryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups,

e) R² and R³ are independently selected from hydrogen, halide, or a C₁-C₃₀ organic group independently selected from cyano, normal, branched, or cyclic alkyl, perfluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups; and

f) R⁵ is an alkyl or aryl group.

6. A composition comprising at least one naphthalene diimide (NDI) compound as defined in claim 1.

7. A method comprising:

reacting at least one first naphthalene diimide (NDI) precursor compound with at least one tin reagent to form at least one first NDI reaction product compound comprising at least one stannyl substituent directly bonded to the naphthalene core of the NDI compound.

8. The method of claim 7, wherein the tin reagent is an organotin reagent.

9. The method of claim 7, wherein the tin reagent comprises one or more of a hexaalkyl ditin reagent, or a hexaaryl ditin reagent.

10. The method of claim 7, wherein the tin reagent is not a halogenated tin reagent.

11. The method of claim 7, wherein in the reacting step only one NDI precursor compound is reacted with the at least one tin reagent.

12. The method of claim 7, wherein the first NDI reaction product comprises one or two stannyl substituents.

13. The method of claim 7, wherein the first NDI reaction product comprises the structure:

![Structure Image]

wherein X is H, R³ or a stannyl substituent Sn(R₅)₃; wherein

R¹ and R¹' are independently selected from a C₁-C₃₀ normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyl-aryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups;

R², R³, and R⁴ are independently selected from hydrogen, halide, or a C₁-C₃₀ organic group independently selected from cyano, normal, branched, or cyclic alkyl, perfluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups; and

R⁵ is an alkyl or aryl group.
14. The method of claim 7, wherein the first NDI reaction product comprises a mixture of the following structures:

![Structure 1](image1)

wherein X is H or R^3, and:

![Structure 2](image2)

wherein X is Sn(R^3)_3.

R^1 and R^1' are independently selected from a C_1-C_{30} normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyl-aryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups;

R^2, R^3, and R^4 are independently selected from hydrogen, halide, or a C_1-C_{30} organic group independently selected from cyano, normal, branched, or cyclic alkyl, fluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups; and

R^5 is an alkyl or aryl group.

15. The method of claim 7, wherein the reacting step is carried out in the presence of at least one metal catalyst.

16. The method of claim 7 further comprising separating the stannyl NDI reaction products via chromatography.

17. The method of claim 7 wherein the at least one first naphthalene diimide (NDI) precursor compound is a monomeric naphthalene diimide precursor compound represented by the structure:

![Structure 3](image3)

wherein LG is a halogen;

R^1 and R^1' are independently selected from a C_1-C_{30} normal, branched, or cyclic alkyl, aryl, heteroaryl, alkyl-aryl, or alkyl-heteroaryl group optionally substituted with one or more halide, cyano, alkyl, or alkoxy groups;

R^2, R^3, and R^4 are independently selected from hydrogen, halide, or a C_1-C_{30} organic group independently selected from cyano, normal, branched, or cyclic alkyl, fluoroalkyl, aryl, heteroaryl, alkyl-aryl, and alkyl-heteroaryl groups, optionally substituted with one or more fluoro, cyano, alkyl, alkoxy groups;

and wherein the at least one tin reagent is a compound having the structure (R^5)_3Sn-Sn(R^5)_3, wherein R^5 is an alkyl or aryl group and wherein the reacting step is carried out in the presence of a catalyst.

18. A method for making an oligomer or polymer comprising reacting at least one naphthalene diimide (NDI) compound as defined in claim 1 with at least one bromide-substituted heteroaryl compound in the presence of a catalyst, thereby forming the oligomer or polymer.

19. A device comprising the oligomer or polymer of claim 18, wherein the device is an OLED, OPV, OPET, or sensing device.

* * * * *