ORGANIC LETTERS
2012
Vol. 14, No. 11
2706–2709

Reactions of Brominated Naphthalene Diimide with Bis(tributylstannyl)acetylene: A Simple Approach for Conjugated Polymers and Versatile Coupling Intermediates

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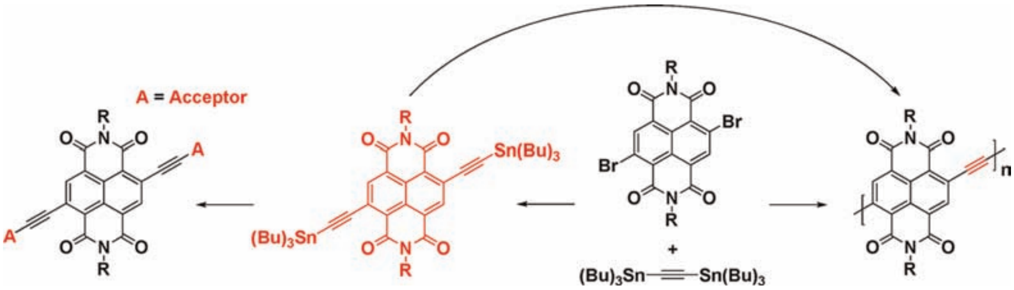
Received April 6, 2012

ABSTRACT



A new synthetic approach to 1,4,5,8-naphthalenetetracarboxylic diimide (NDI) containing materials and conjugates is described. A simple one-step Stille coupling procedure is used to create either novel alkyne-linked NDI polymers or a new stannylated diyne synthetic building block that provides a flexible approach to new NDI conjugates and polymers.

1,4,5,8-Naphthalenetetracarboxylic diimide (NDI) has proven useful in a number of contexts ranging from highly ordered organic architectures and molecular recognition[1] to DNA intercalation.[2] NDI has now become a promising material for organic electronics[1,3] due to its respectable charge-carrier mobility,[4] electron deficient core and low lying, tunable LUMO,[3b,5] tunable absorption spectrum,[6] and stable radical anion.[3c]

The widely used 2,6-dibromo NDI **1**[7] has been assimiliated into many conjugated small molecules and polymers by standard Stille coupling protocols.[8] For example, conjugated NDI-containing donor−acceptor polymers and

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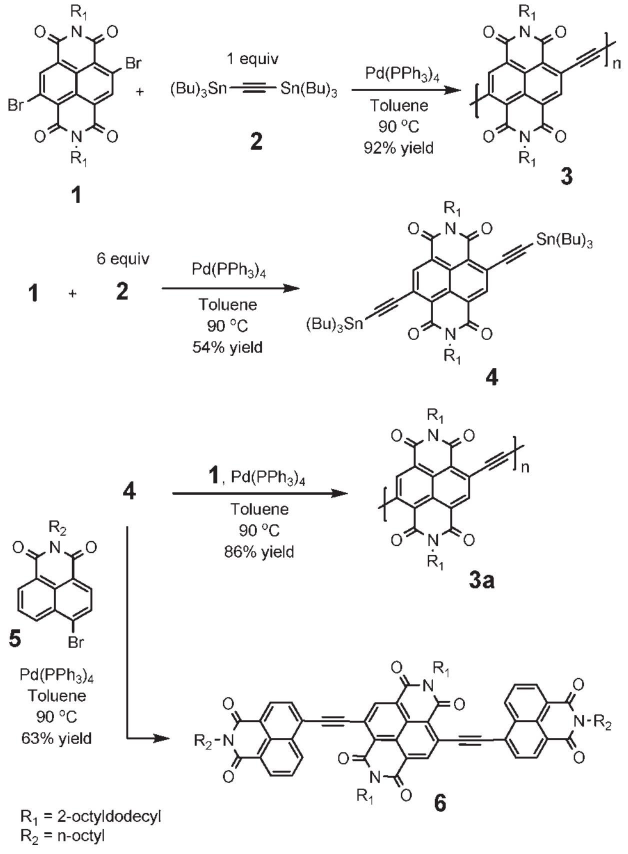
small molecules are an important class of n-type materials that have exhibited efficiencies of 1.5% when paired with poly(3-hexylthiophene) as the p-type material in photovoltaic devices.[9]

Current research now focuses on new methods to synthesize conjugated NDI-based materials. For instance, Wang et al. constructed conjugated butadiynylene-NDI oligomers through an oxidative coupling of 1,6-di((trimethylsilyl)ethynyl)-NDI monomers.[10] The Marder group was the first to append tributylstannyl groups directly onto the aromatic core of NDI using a Pd-catalyzed reaction between brominated NDI and Sn_2Bu_6. Their stannyl functionalized NDIs should broaden the scope of NDI used in Stille coupling reactions, and these workers demonstrated its ultility by making short NDI oligomers.[12]

We report here a simple method that utilizes the Stille coupling protocol and different substrate ratios for the synthesis of either alkyne-linked NDI containing polymers or the key stannyl functionalized diyne NDI monomer **4**. Compound **4** is a versatile building block that can be used to produce NDI conjugates as well as polymeric materials.

Scheme 1. NDI Polymer and Distannyl Intermediate Synthesis



Conjugated NDI polymers were rapidly synthesized through the copolymerization of 2,6-dibromo NDI (**1**) with commerically available bis(tributylstannyl)acetylene (**2**) using the Stille protocol as shown in Scheme 1. A 1:1 molar mixture of **2** and **1** with $Pd(PPh_3)_4$ was heated in toluene at 90 °C. The copolymerization was monitored by UV–vis spectroscopy and, upon reaching the maximum bathochromic shift (see Supporting Information), stopped by removing the solvent. Crude polymers were collected by precipitation from methanol. Further purification was accomplished by successive Soxhlet extractions with methanol, acetone, and dichloromethane. The dichloromethane fraction was reduced in volume, and polymer **3** was collected by precipitation from methanol.

Using a reaction time of 1 h provided polymers that were soluble in common organic solvents such as tetrahydrofuran, chloroform, and dichloromethane in 92% yield. Number average (M_n) and weight average (M_w) molecular weights were determined by gel permeation chromatography (GPC) against polystyrene standards in THF. Analysis using GPC yielded an M_n value of 4.5 kDa and an M_w value of 15.2 kDa with a polydispersity index (PDI) of 3.3 (Table 1).[13] Increasing the polymerization time resulted in lower yields presumably due to the decreased solubility of larger polymers. For instance, a 2 h reaction period produced polymers with an M_n of 5.7 kDa and an M_w of 19.6 kDa (PDI 3.4) in only 28% yield.

Table 1. A Summary of Polymer Molecular Weights and Optical Properties

polymer **3**						polymer **3a**					
rxn, h	yield, %	M_n, kDa	M_w, kDa	(PDI)	λ_{max}, nm	rxn, h	yield, %	M_n, kDa	M_w, kDa	(PDI)	λ_{max}, nm
1	92	4.5	15.2	3.3	557	1.5	86	4.3	14.0	3.2	557
2	28	5.7	19.6	3.4	557	2.5	36	4.5	13.5	3.0	557

Alternatively, an NDI polymer analogous to **3** was constructed through the copolymerization of **1** with distannyl NDI (**4**, vide infra) to make polymer **3a** (Scheme 1). The latter polymerization was carried out under the same reaction and purification conditions as those for **3** but required slightly longer reaction times (1.5 h) to adequately produce **3a** in 86% yield. Analysis by GPC yielded an M_n value of 4.3 kDa, an M_w of 14.0, and a PDI of 3.2 for this approach. Longer reaction times once again resulted in lower yields as 2.5 h provided similarly sized polymers but in only a 36% isolated yield (Table 1). Several factors may account for the different reaction times required to obtain similar yields and chain lengths for the synthesis of **3** and **3a**. In particular, it is reasonable to suspect that the initial

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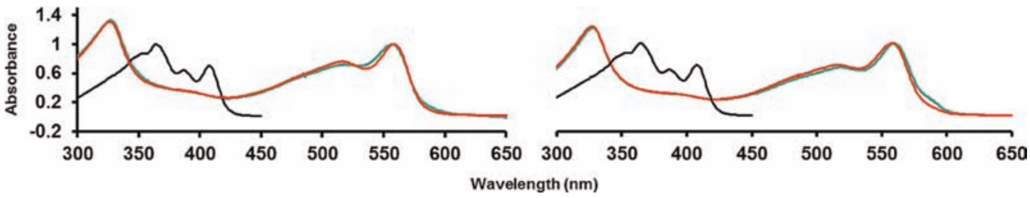

Figure 1. Left: Normalized UV−vis ($CHCl_3$) trace of monomer **1** (black) and polymer **3** after 1 h (red) and 2 h (green). Right: Normalized UV−vis ($CHCl_3$) trace of monomer **1** (black) and polymer **3a** after 1.5 h (red) and 2.5 h (green).

coupling to **1** will be faster with **2** than with **4** because **2** is expected to be the more electron rich of the two and an electron-rich organotin monomer typically facilitates the transmetalation step during a Stille coupling polymerization.[11] The nature of the polymerization intermediates will also be different for the two approaches and may influence overall polymerization rates.

Polymers were characterized by cyclic voltammetry (CV) and UV−vis spectroscopy. Structural characterization was accomplished with FT-IR, as a well resolved ^1H NMR spectrum was not obtained. An example of a typical ^1H NMR spectrum in toluene-d_8 at 100 °C is given in the Supporting Information. Given the less desirable PDI values, both **3** and **3a** exhibited the same CV and UV−vis characteristics, indicating a saturation effect in terms of chain length for their electronic properties. Two half-wave reduction potentials ($E_{1/2}$) at −0.96 and −1.61 V (referenced to Fc/Fc$^+$ at 0.0 V) were observed in the CV trace (see Supporting Information). These broad CV waves lack the distinct reduction peaks of individual NDI units, but onset and redox potentials closely resemble those reported for poly-NDI.[12] These two characteristic NDI reduction waves indicate initial radical anion and subsequent dianion formation. The UV−vis absorbance spectra in Figure 1 also show the strong bathochromic shift (λ_{max} of 557 nm) due to effective conjugation along the polymer backbone compared to monomer **1**.

A common route to append stannylactylene moieties onto a molecule of interest can require up to three steps: coupling an unsaturated organohalide to a protected terminal alkyne, deprotection, and stannylation of the alkyne. Initial work to couple 2,6-dibromo NDI with a silyl-protected acetylene and subsequential deprotection using TBAF were frustrated by what we suspect were competing reactions as reported by Saha et al.[14] Reaction mixtures quickly turned black and NMR core ^1H signals were lost, an indication that radical NDI anions were generated. To eliminate the deprotection step and any interfering anions, we sought to synthesize **4** in a single step using **2**. Initial attempts to synthesize **4** by slowly adding **1** to a solution containing $Pd(PPh_3)_4$ and an excess of **2** proved ineffective. TLC typically showed multiple products, and the reaction required extended periods of time or additional equivalents of **2** to reach completion, presumably due to homocoupling of the excess tin reagent.

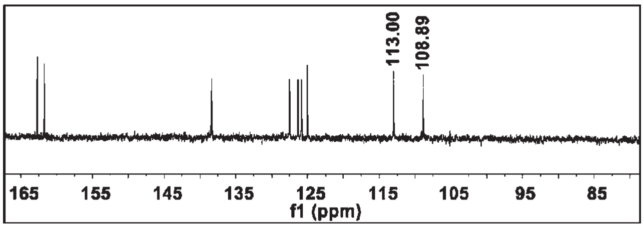

Figure 2. ^{13}C NMR ($CDCl_3$) spectrum of **4** showing the sp^2 and sp region.

The more effective approach was to prepare **4** by saturating a toluene solution containing 5 mol % $Pd(PPh_3)_4$ and **1** at 90 °C with an excess of **2** in a single aliquot (Scheme 1). The solution was allowed to stir for 20 min before the reaction was stopped by removing the toluene. Monomer **4** was collected by reversed-phase (C-18) column chromatography[15] in a 54% yield, as tributyltin groups are often sensitive to silica gel and neutral alumina provided poorly resolved fractions.

The stability of **4** permitted full characterization by NMR and HRMS. The sp hybridized carbon peaks at 113.00 and 108.89 ppm presented in the ^{13}C spectrum (Figure 2) demonstrate that reversed-phase column chromatography cleanly yields **4** without contamination by acetylene-based side products. Obtaining a clean monomer is critcial because Stille coupling reactions are senstive to monomer stoichiometry and purity.[11] To further demonstrate its synthetic ultility, **4** was also coupled with 2 equiv of **5** to give **6** in 63% yield. **5** was chosen for its similarly electron deficient nature, and unlike the NDI polymers, the product **6** was readily characterized with ^1H and ^{13}C NMR spectroscopy. The UV−vis spectra in Figure 3 show that both the NDI and the naphthalene monoimide moieties of **6** are bathochromically shifted compared to the corresponding starting materials, **4** and **5**. Two reduction peaks were observed in the CV of **6** with $E_{1/2}$ values of −1.30

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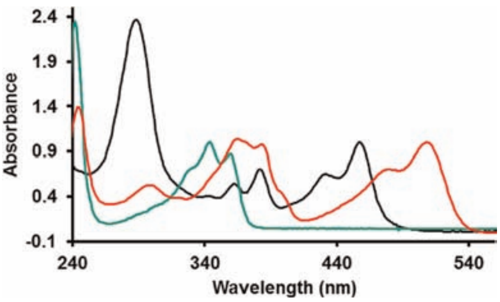

Figure 3. Normalized UV−vis ($CHCl_3$) trace of **4** (black), **5** (green), and **6** (red).

and −1.74 V. The cathodic shift of these potentials compared to those observed for **3** and **3a** may be due to fewer electron withdrawing moieties on the small molecule **6** or the fact that the naphthalene monoimide is a weaker electron withdrawing group than naphthalene diimide.

Stille coupling reactions are generally carried out with electron rich stannylated starting materials and relatively electron deficient unsaturated organohalides. Electron rich moieties are traditionally easier to stannylate, and electron deficient unsaturated organohalides facilitate the initial oxidative insertion step.[11] An advantage of using **4** is that different aryl halide monomers could be used in Stille coupling reactions to create a wide array of alkyne-linked, alternating polymer or small molecule architectures. For example, electron poor aromatic halides or electron rich units that are not readily stannylated could be combined with the relatively electron deficient NDI to create novel alkyne-linked alternating materials.

In summary, we have developed a very simple and versatile synthetic method that can be used either to directly produce alkyne-linked NDI-containing polymers or, by adjusting conditions and relative stoichiometries, to yield the key synthetic intermediate **4**. Compound **4** will enable the synthesis of new NDI-containing conjugates and alkyne-linked alternating polymers. It is worth noting that although the polymers accessible by this new approach do not have direct aryl−aryl linkages, an alkyne-linked NDI polymer maintains conjugation and may be of interest for applications that require more distance between aromatic units or would take advantage of alkyne chemistry.

Acknowledgment. This work was supported by the Robert A. Welch Foundation, Grant F1188 to B.L.I. We thank Dr. Bielawski and his group (University of Texas at Austin) for use of their GPC and CV.

Supporting Information Available. Synthesis and characterization, NMR spectra, UV−vis spectra, IR spectra, cyclic voltammograms, and GPC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.