

Stannyl Derivatives of Naphthalene Diimides and Their Use in Oligomer Synthesis

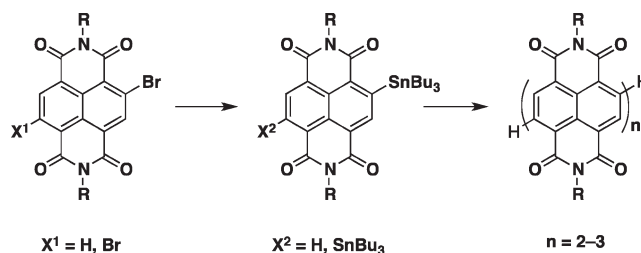
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ABSTRACT



2-Stannyl and 2,6-distannyl naphthalene diimides (NDIs) can be synthesized through the palladium-catalyzed reaction of the appropriate bromo derivatives with hexabutyltin. The utility of these precursors in palladium catalyzed cross-coupling reactions is demonstrated by the synthesis of bi- and ter-NDI derivatives, UV–vis, cyclic voltammetry, and n-channel organic field-effect transistor data for which are compared to those of the monomeric parent NDI.

Tetracarboxylic diimide derivatives of rylenes, particularly of naphthalene and perylene (NDIs and PDIs, respectively), are extensively studied for organic electronics.^{1,2} Their thermal, chemical, and photochemical stability, high electron affinities (EAs), and large charge-carrier mobility

values render these materials attractive for applications in field-effect transistors (OFETs)^{3–15} and photovoltaic cells (OPVs).^{12,16–20} They have also been widely used as acceptors in transient absorption studies of photoinduced electron transfer, again due to their redox potentials and to

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the stability and distinctive absorption spectra of the corresponding radical anions,^{21–24} and as ligands in nucleic acid studies of telomerase inhibition in metastatic cancer cells, due to their selective recognition of G-quadruplex oligonucleotides.^{25–28}

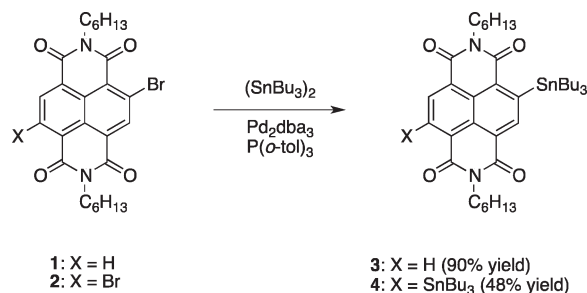
The *N,N'*-substituents of PDIs and NDIs generally have only minimal influence on the optical and electronic properties of isolated molecules, although they can be used to control solubility, aggregation, and intermolecular packing in the solid state. Core substitution of these species typically has a much more significant effect on the redox potentials (enabling air-stable OFET operation in some cases^{5,13,29}) and optical spectra. Moreover, core substitution can be used as a means of constructing more elaborate architectures such as conjugated polymers^{7,11,20,30,31} and donor- or acceptor-functionalized products.^{13,14,32–36}

Functionalized NDIs are most effectively obtained through the selective bromination of naphthalene-1,4:5,8-tetracarboxylic dianhydride (NDA) with dibromoisocyanuric acid (DBI) in conc. H₂SO₄ or oleum, followed by

imidization with a primary amine in refluxing HOAc.^{5,31,36} NDA can also be brominated using Br₂ in conc. H₂SO₄ or oleum.^{5,37} The brominated NDI can then serve as an intermediate for use in either nucleophilic substitutions, to afford amino, thiol, or alkoxy derivatives,^{35,36} or Pd-catalyzed coupling reactions, to yield cyano,^{5,33} phenyl,^{32,33} alkynyl,³³ and thienyl^{11,14,32} products. However, the range of conjugated species that can be obtained by Pd-catalyzed methods is limited by the availability of appropriate candidate coupling partners. In particular, metalated reagents such as stannanes and boronates can be difficult to obtain for electron-poor (acceptor) building blocks. Accordingly, metalated 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.

Here we report the synthesis, using Pd-catalyzed coupling^{38,39} of brominated NDIs and Sn₂Bu₆, of the first stannyl derivatives of NDIs and their use in Stille reactions to obtain bi- and ter-NDIs.

Scheme 1. Preparation of Stannyl NDI Derivatives



N,N'-Di-(*n*-hexyl)-2-tri(*n*-butyl)stannyl naphthalene-1,4,5,8-bis(dicarboximide), **3**, and *N,N'*-di(*n*-hexyl)-2,6-bis(tri(*n*-butyl)stannyl)naphthalene-1,4,5,8-bis(dicarboximide), **4**, were obtained in good to moderate yields, respectively, according to Scheme 1: a mixture of the appropriate mono- or dibromo derivative, **1** or **2**, and Sn₂Bu₆ (1 equiv per Br) was heated in toluene in the presence of Pd₂dba₃ (0.05 equiv per Br) and P(*o*-tol)₃ (0.2 equiv per Br). Purification of the products by silica gel chromatography and recrystallization from MeOH 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 crystallography (Figure 1; see Supporting Information (SI) for details).⁴⁰ The ability to isolate and thoroughly purify the distannyl derivative is important for potential applications in conjugated-polymer syntheses, where the ability to obtain

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(40) Under identical conditions, the monobrominated PDI derivative undergoes homocoupling to yield the bi-PDI product and the corresponding stannyl PDI intermediate cannot be isolated.

high-molecular-weight material is critically dependent on precise control of monomer stoichiometry.

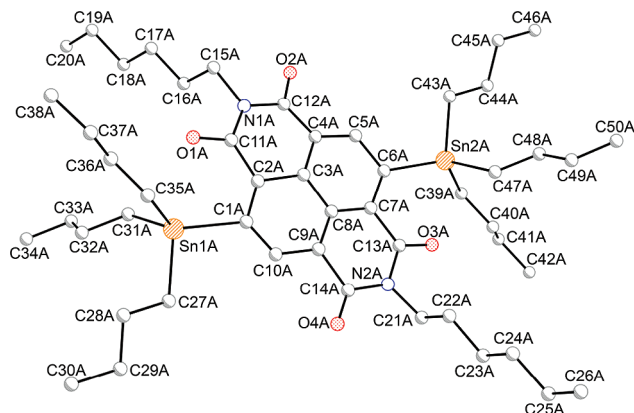
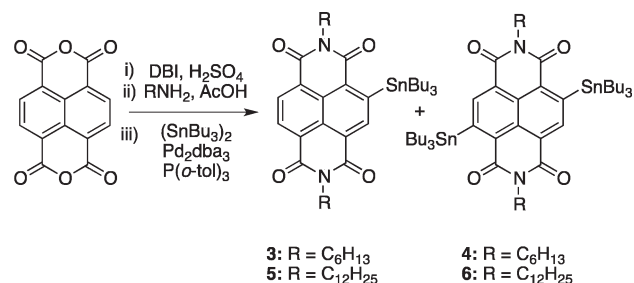


Figure 1. One of the independent molecules of compound **4** found in its crystal structure. Atoms are shown as spheres of arbitrary size.

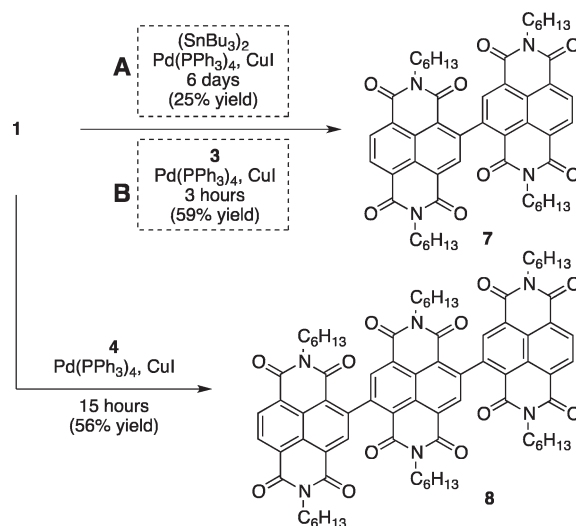
Moreover, the different chromatographic behavior of **3** ($R_f = 0.3$ on silica, eluting with 1:1 $\text{CH}_2\text{Cl}_2/\text{hexanes}$) and **4** ($R_f = 0.3$, silica, 1:10 $\text{CH}_2\text{Cl}_2/\text{hexanes}$) suggested to us the possibility of carrying out this reaction using a mixture of mono- 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 (using 1 equiv of DBI as the brominating agent).⁴¹ As shown in Scheme 2, N,N' -bis(*n*-dodecyl) analogues **5** and **6** have also been obtained in the same way in similar isolated yields. The facile separation of the highly soluble mono- and distannyl NDI products via column chromatography is an attractive alternative to the more difficult separation 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 R_f (0.4 and 0.3 for **1** and **2**, silica, CH_2Cl_2). Thus, a two-step process involving 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.

Scheme 2. Preparation of Stannyl NDI Derivatives from Commercially Available NDA



As an example of the utility of stannyl NDI derivatives as a reagent for cross-coupling with electron-poor moieties, we carried out stannyl-NDI/bromo-NDI cross-couplings to obtain N,N',N'',N''' -tetra(*n*-hexyl)-[2,2'-binaphthalene]-1,4:5,8:1',4':5',8'-tetra(dicarboximide), **7**, and N,N',N'',N''',N'''' -hexa(*n*-hexyl)-[2,2':6',2''-ternaphthalene]-1,4:5,8:1',4':5',8':1'',4'':5'',8''-hexa(dicarboximide) **8** (Scheme 3). In addition to using the cross-coupling of **1** and **3** (Scheme 3, B), **7** was also obtained by the one-pot homocoupling of **1** (Scheme 3, A) using 5.0 mol % of $\text{Pd}(\text{PPh}_3)_4$, 10 mol % of CuI , and 0.5 equiv of Sn_2Bu_6 in hot toluene over 6 d, a reaction that presumably involves the in situ generation and reaction of **3**. Purification of the reaction mixture by silica-gel chromatography and recrystallization from isopropanol afforded **7** in 25% yield. The cross-coupling of **1** and **3** was performed in the presence of 5.0 mol % of $\text{Pd}(\text{PPh}_3)_4$ and 10 mol % of CuI in hot toluene over only 3 h and afforded **7** in 59% yield after identical purification procedures.

Scheme 3. Preparation of Bi- and Ter-NDI Derivatives



8 was prepared by cross-coupling of **1** and **4** in the presence of 5.0 mol % of $\text{Pd}(\text{PPh}_3)_4$ and 10 mol % of CuI in hot toluene over 15 h. Purification of the reaction mixture by silica-gel chromatography and recrystallization from isopropanol afforded **8** in 56% yield.

The optical and electrochemical properties of **7** and **8** were compared to those of the corresponding monomeric parent NDI, N,N' -bis(*n*-hexyl)naphthalene-1,4:5,8-bis(dicarboximide), **9**. The UV-vis absorption spectra of **7** and **8** are similar in shape to that of **9** and the molar absorptivity, ϵ_{max} , increases with the number of NDI units, suggesting that each NDI subunit behaves largely independently of the other(s), consistent with inter-NDI steric interactions leading to significant deviation of the NDI subunits from coplanarity. However, the nonlinear

(41) The relative yields can be tuned somewhat with respect to the brominating agent, and yields of ca. 15–20% were obtained for both mono- and distannyl derivatives using 2 equiv of DBI.

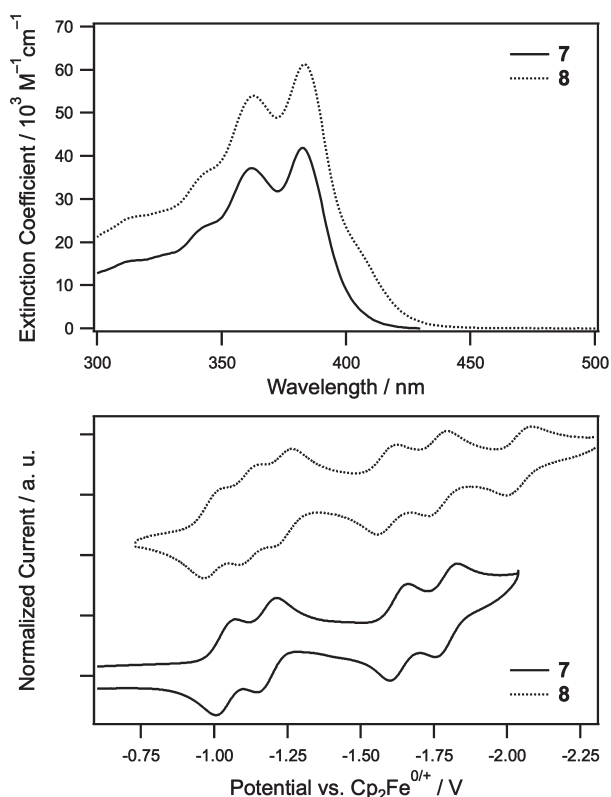


Figure 2. UV–vis spectra in CH_2Cl_2 (top) and cyclic voltammograms in $\text{CH}_2\text{Cl}_2/\text{}^n\text{Bu}_4\text{NPF}_6$ (bottom) of **7** and **8**.

increase of ϵ_{max} with the degree of oligomerization, some broadening seen in the spectra of **7** and **8**, and the appearance of a distinct shoulder on the low-energy side of the main absorption of **8** indicate that there are some interactions, possibly excitonic coupling, between the NDI subunits (differences in band shape are more clearly seen in normalized spectra of **7**, **8**, and **9**; see Figure S2).

Cyclic voltammetry showed four reversible reduction waves for **7** and six reversible reduction waves for **8** corresponding to the sequential reduction of each NDI to its radical anion and then to its dianion (Figure 2). No oxidation could be observed in the potential window investigated. The first halfwave reduction potentials are reported in Table 1. **7** and **8** are reduced at very a similar potential to one another and at only a marginally more anodic potential than the monomeric NDI, **9**, suggesting no significant delocalization of the charge between the NDIs, consistent with the picture of weakly interacting

NDIs indicated by the optical data. The slight anodic shift in the oligomeric species is perhaps attributable to the inductive electron-withdrawing effect of one NDI upon another, while the separation between the multiple reductions is likely to be due to electrostatic effects, given the close proximity of the multiple redox centers.

Table 1. Optical and Electrochemical Properties of Mono-, Bi-, and Ter-NDIs

compd	no. of NDI units	λ_{max}^a / nm	ϵ_{max}^a / $10^4 \text{ M}^{-1} \text{ cm}^{-1}$	$\lambda_{\text{max, solid}}^b$ / nm	$E_{1/2}^{0/-b}$ / V
9	1	380	2.76	393	−1.13
7	2	381	4.10	388	−1.03
8	3	383	6.09	389	−1.00

^a CH_2Cl_2 . ^b 0.1 M $\text{}^n\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ vs $\text{Fc}^+/0$.

Top-gate, bottom-contact geometry organic field-effect transistors were fabricated with a CYTOP (45 nm)/ Al_2O_3 (50 nm) bilayer gate dielectric, **7** or **8** as the active layer, and Au source and drain electrodes. The materials were spin-coated from 1,1,2,2-tetrachloroethane solutions to yield devices with n-channel characteristics with moderate electron mobility values, μ_e , of up to 0.34 and $0.014 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **7** and **8**, respectively (see SI). Although μ_e for **7** falls short of the state of the art for solution-processed n-channel devices ($1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),¹⁴ it is an order of magnitude higher than the highest value reported for solution-processed devices based on a simple *N,N'*-alkyl NDI without core substitution ($0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).³

To conclude, we have developed an efficient and straightforward synthesis of 2-stannyl and 2,6-distannyl NDIs. Their use in Pd-catalyzed coupling reactions was demonstrated by the synthesis of bi- and ter-NDI. These stannyl NDI derivatives may be useful building blocks for new small-molecule and polymeric NDIs and may facilitate structures that are otherwise difficult to obtain.

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Supporting Information Available. Full details of the synthesis and characterization of **1–8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.