

Orthogonally Functionalized Naphthodithiophenes: Selective Protection and Borylation

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ABSTRACT



Selective functionalization protocols of naphtho[1,2-*b*;5,6-*b'*]dithiophene (NDT3) by combining protection of the thiophene α -positions and direct borylation on the naphthalene core are described, which allows synthesizing a number of new NDT3-based building blocks with various substituents and isomeric NDT3-based polymers with different main chain structures. The same protocol is applicable to other isomeric naphthodithiophenes (NDTs), which affords a set of key building blocks for the development of elaborated functional π -materials.

Acenedithiophenes (AcDTs), two thiophene rings fused at both ends of acene cores, have been utilized as key build-

ing blocks in the development of superior organic semiconductors,¹ as exemplified by high-performance OFETs^{2,3} and organic photovoltaics (OPVs)^{4,5} based on benzo[1,2-*b*;4,5-*b'*]dithiophene (BDT)^{2,4} and anthra[2,3-*b*;6,7(7,6)-*b'*]dithiophene (ADT)^{3,5} derivatives (Figure 1). Although naphthalene-based AcDTs, naphthodithiophenes (NDTs), were scarcely studied owing to their synthetic difficulty,⁶ we have recently established selective syntheses of a series of NDTs (Figure 1)⁷ and found that, among isomeric NDTs,

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naphtho[1,2-*b*;5,6-*b'*]dithiophene (NDT3) is the most useful building block for developing semiconducting polymers: Poly(NDT3-bithiophene) (PNDT3-BT) afforded high-performance solution-processed OFETs with mobilities as high as $0.77 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^{8,9} The NDT3 core was utilized not only in polymers for OFETs but also in oligomers and polymers combined with electron-deficient units, which functioned as the electron donor in bulk heterojunction solar cells to show decent photoconversion efficiencies.¹⁰

To further utilize NDT3 as an ingredient for optoelectronic materials, we have been interested in functionalization on the naphthalene part, i.e., 5- and 10- positions, for the following reasons. First, π -extended NDT3-based materials generally have poor solubility, in particular, when incorporated into polymers and large oligomers, and therefore functionalization on the naphthalene part with solubilizing groups can allow the development of soluble NDT3-based materials. Second, introduction of substituents also provides a chance to tune the electronic structure of the core, i.e., the energy level of HOMO and LUMO, which is a very important factor in developing optoelectronic materials, in particular, materials for solar cell applications. Third, functionalization at the 5- and 10-positions can minimize the steric hindrance between neighboring units connected at the thiophene α -positions. Fourth, π -extension from the naphthalene part will give a new material class from the one extended from the conventional thiophene α -positions.

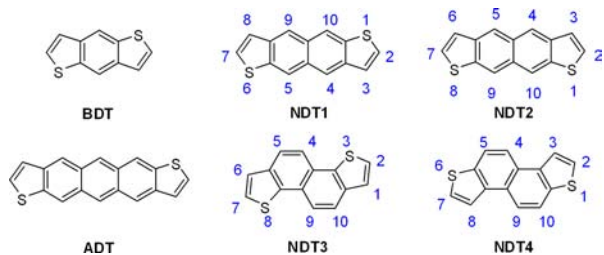


Figure 1. Molecular structures of BDT, ADT, and four isomeric NDTs.⁹

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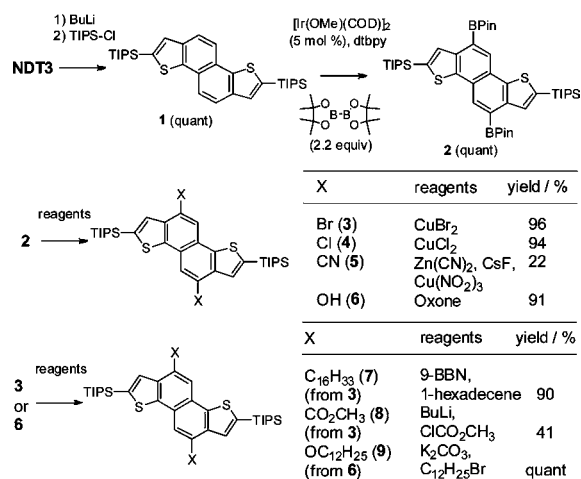
(9) The present numbering of NDT isomers, i.e., NDT1 for naphtho[2,3-*b*;6,7-*b'*]dithiophene, NDT2 for naphtho[2,3-*b*;7,6-*b'*]dithiophene, NDT3 for naphtho[1,2-*b*;5,6-*b'*]dithiophene, and NDT4 for naphtho[2,1-*b*;6,5-*b'*]dithiophene, is just for convenience without any scientific significance, which follows our recent publications (refs 7b and 8b).

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To achieve these, we pursued methods for selective functionalization at the naphthalene part of NDT3 without interfering with the reactivity of thiophene α -positions and found that direct borylation at the naphthalene core catalyzed by Ir complexes in the presence of bis(pinacolato)-diboron¹¹ is a powerful tool for selective functionalization on NDT3. Here, we describe the synthesis of orthogonally functionalized NDT3 with α -silyl protecting groups and reactive boryl groups on the naphthalene core and its conversion to a range of substituted NDT3 derivatives including highly soluble ones.

Depicted in Scheme 1 is the synthesis of orthogonally functionalized NDT3 (**2**). Introduction of triisopropylsilyl (TIPS) groups can be readily done to protect the thiophene α -position (α -protection), and then the naphthalene core part is selectively borylated in quantitative yield. The molecular structure of **2** was determined by spectroscopic analyses and single crystal X-ray analysis, clearly showing the selective borylation takes place at the 5- and 10-positions that correspond to the sterically least hindered positions (Figure S1).

Scheme 1. Synthesis of Orthogonally Functionalized NDT3 (**2**) via α -Protection and Core Borylation, and Selective Functional Group (FG) Conversion of **2**



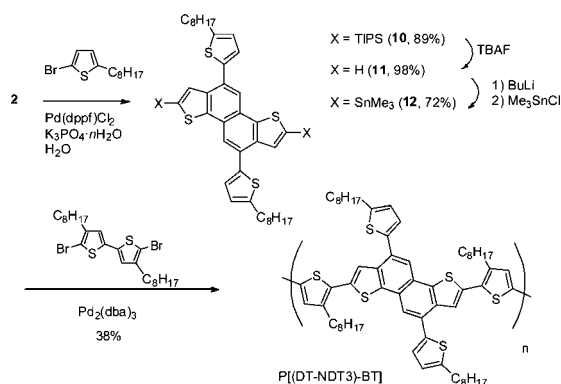
The boryl groups on **2** can be converted into various functional groups without interfering with the TIPS protection groups (*Functional group (FG) conversion*, Scheme 1). Treatment of **2** with CuBr₂ or CuCl₂ gave the corresponding 5,10-dibromo or -dichloro compounds (**3** or **4**) in good

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yields (>90%),^{11c,f,12} although a similar conversion into a 5,10-dicyano compound (**5**) was less effective (~22% isolated yield). Brominated NDT3 (**3**) can be further converted into alkyl (**7**) or ester derivatives (**8**) via the palladium-catalyzed coupling with 9-BBN-olefine¹³ or a Li–Br exchange reaction followed by treatment with methyl chloroformate, respectively. Moreover, treatment of **2** with Oxone gave the corresponding diol (**6**),^{11c,f,g} which was then alkylated to give an ether derivative (**9**). Among these derivatives, alkylated (**7**) and ether-modified NDT3s (**9**) are highly soluble and thus are useful intermediates for the synthesis of soluble NDT3-based materials. In addition, new NDT3 derivatives (**3–9**) are an interesting set of building blocks for developing new oligomeric/polymeric π -extended materials with finely tuned HOMO/LUMO energy levels. Summarized in Table S1 are the HOMO (or LUMO) energy levels that were electrochemically determined and optical energy gaps of **3–9**, which demonstrate that the HOMO energy levels are widely spread ranging from –5.2 to –5.9 eV or deeper (Figures S2–S3).

The boryl groups on **2** can, off course, act as the handle for functionalization via the Suzuki–Miyaura Ar–Ar coupling.¹⁴ For example, a typical Suzuki–Miyaura coupling reaction with 2-bromo-5-alkylthiophene afforded **10** (core functionalization), the α -TIPS groups of which were readily removed to give an α -unsubstituted intermediate (**11**). Functionalization of **11** at the thiophene α -position via the corresponding lithiated intermediate gave 5,10-disubstituted α -stannylated NDT3 (**12**) that was further employed in the synthesis of a new NDT3-BT polymer, P[(DT-NDT3)-BT] (α -deprotection–functionalization, Scheme 2).

Scheme 2. Synthesis of NDT3-Based Polymer via the α -Protection, Core Borylation–Functionalization, α -Deprotection–Functionalization Protocol



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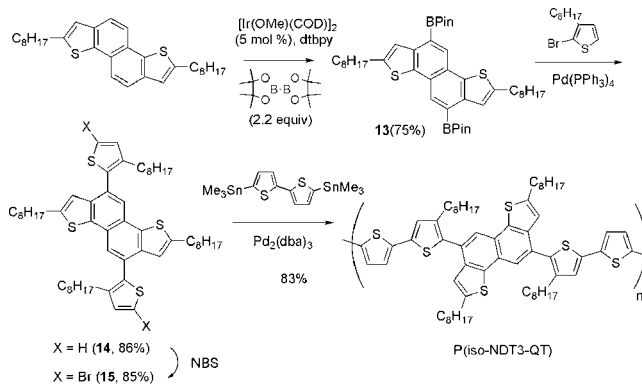
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On the other hand, α -functionalized NDT3 can also be borylated at the 5- and 10-positions: 2,7-dioctyl-NDT3, as the substrate, gave 2,7-dioctyl-5,10-bis[(pinacolato)boryl]-NDT3 (**13**) selectively (75% isolated yield, Scheme 3). **13** can be an interesting building block for the synthesis of a new type of NDT3-based polymers where the NDT3 units are connected at the naphthalene part. As demonstrated in Scheme 3, the Suzuki–Miyaura coupling with 2-bromo-3-alkylthiophene gave a new NDT3 derivative (**14**) with two thiophene moieties on the naphthalene core, which can act as a comonomer, after bromination (**15**), for polymerization with bis(trimethylstannyl)bithiophene to give P-(iso-NDT3-QT). These new polymers, P[(DT-NDT3)-BT] and P(iso-NDT3-QT), are in fact structural isomers to each other with markedly different electronic structures (Figure S4, Table S2), which thus well demonstrates that, by using these methodologies, various π -extended architectures based on the NDT3 core can be freely designed and selectively synthesized.

Similar orthogonal functionalization on isomeric NDTs, NDT1, NDT2, and NDT4 (Figure 1), therefore, should be very interesting, which can afford not only new NDT building blocks but also the scope and limitation of the present orthogonal functionalization chemistry, since the naphthalene parts of the NDT isomers have a different chemical environment, which would affect the efficiency of the direct borylation reaction.

Scheme 3. Synthesis of New Isomeric NDT3 Polymer via the α -Functionalization, Core Borylation–Functionalization Protocol



Regardless of the isomeric structures, the initial introduction of TIPS groups to the thiophene α -positions was straightforward giving the corresponding α -TIPS-protected intermediates. The following direct borylation was, however, largely affected by the isomeric structures of NDTs. The angular-shaped isomer, NDT4, possessing a similar molecular structure with that of NDT3, gave the corresponding α -TIPS, core-borylated derivative (**19**, Figure 2) in quantitative yield.¹⁵ Borylation on the linear

(15) The borylated site on **19** was confirmed by X-ray crystallographic analysis. See Figure S1.

shaped NDT1 core, on the other hand, proceeded quite slowly compared to the cases for NDT3 and NDT4, and the major product was the monoborylated NDT1 (**17**). The corresponding diborylated compound (**16**) can be obtained by a longer reaction time (~3 days) with additional reagents and a catalyst (42% isolated yield with **17** (57%)). The borylated sites on the NDT1 core were determined to be the 5- and 10-positions by NOESY (NOE correlated spectroscopy) spectra (Figure S5), where correlation peaks, i.e., nuclear Overhauser effect (NOE), between the singlets at approximately 7.6 and 9.4 ppm were clearly observed, indicating that these two protons exist in close proximity, within less than ca. 4.5 Å. The borylated sites on **16** are fairly crowded but seem to have sufficient room for the pinacoloboryl groups. Note that the borylation on linear-shaped acenes, such as naphthalene, anthracene, and tetracene, selectively occurs at the 2-, 6-/7- (naphthalene and anthracene), or 2-, 8-/9- (tetracene) positions and no borylation takes place at the peri-positions,^{11d-g} though on kinked chrysene¹⁶ or peri-condensed pyrene¹⁷ the borylation at the peri-position takes place. The different reactivity of NDT1 compared to the linear-shaped acenes could be explained by the steric effects of the thiophene rings that can take one neighboring hydrogen atom away at the borylation sites. On the other hand, the borylation on the NDT2 core was rather difficult: only a monoborylated product (**18**) was obtained, and no diborylated product was detected. This can be well explained by the steric effect originating from the substrate structure.

In summary, we have found that a direct borylation reaction on the naphthalene core part in NDT3 easily takes place, and the reaction gives new routes to the selective functionalization of NDT3 by combining the α -protection or functionalization of the thiophene moieties of NDT3. The orthogonally functionalized NDT3 (**2**) is thus a key intermediate for the *core functionalization*– α -*deprotection*/

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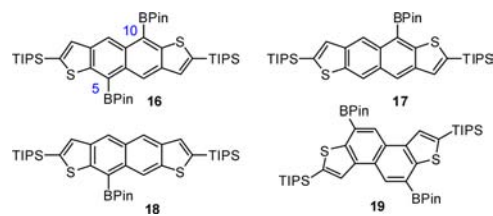


Figure 2. Orthogonally functionalized NDTs.

functionalization and the *FG conversion* of the boryl groups to give a series of NDT3 derivatives with finely tuned electronic properties. Furthermore, other orthogonally functionalized NDTs possessing α -TIPS and core boryl functionalities similar to those of **2** are readily prepared. With these new intermediates and methodologies, we hope that the materials development based on these NDT cores will be further accelerated in the near future.

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Supporting Information Available. Synthetic details, characterizations data, and NMR spectra of materials, characterization of polymers, crystallographic information files (CIF) for **2** and **19**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.