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N,N′-Unsubstituted Naphthodithiophene Diimide: Synthesis and Derivatization via *N*-Alkylation and -Arylation

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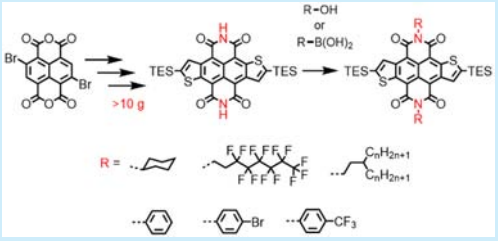
Supporting Information

ABSTRACT: An efficient and scalable method for the synthesis of *N,N′*-unsubstituted naphtho[2,3-*b*:6,7-*b′*]dithiophene-4,5,9,10-tetracarboxylic diimide (NDTI) was newly developed, and the compound was utilized in the Mitsunobu reaction and copper-catalyzed coupling reaction with phenyl boronic acids to synthesize a range of *N*-alkyl- and phenyl-substituted NDTI derivatives. The new synthetic protocol to NDTI derivatives is advantageous over the previously reported one in terms of the amenability to large-scale synthesis and compatibility with the synthesis of a wide range of *N*-alkyl and phenyl derivatives, which can in turn pave the way to wide application of NDTI derivatives into electronic materials.



Rylene diimides, represented by naphthalene diimide and perylene diimide (NDI and PDI, Figure 1a), have been intensively investigated as dyestuff, pigments, and opto/electronic materials in the past few decades.[1] The electronic structure of the system can be largely tuned by the central rylene moiety, and it has been demonstrated that the vertical extension of the rylene core, i.e., increasing the number of the naphthalene moiety, can drastically alter the optical property.[2] On the other hand, the lateral extension of the π-conjugation system based on NDI has also been examined with fused aromatic rings, such as benzene,[3] thiophene,[4] thiazole,[5] benzo[*b*]thiophene,[6] benzo[*b*]pyrrole,[7] quinoxaline,[8] and so on (Figure 1b). The latter approach, in contrast to the former vertical π-extension, is an interesting way to control the electronic structure of the resulting core-extended NDI derivatives; the lowest unoccupied molecular orbital (LUMO) of the system tends to localize on the NDI skeleton, i.e., the vertical molecular axis, whereas the highest molecular orbital (HOMO) tends to delocalize in the lateral direction through the naphthalene 2-, 3-, 6-, and 7-carbon atoms. This in turn affords an opportunity to finely tune the HOMO with keeping the LUMO almost intact or only slightly altered.[7a]

Among these laterally extended NDIs, we have focused on a thiophene-annulated one, naphtho[2,3-*b*:6,7-*b′*]dithiophene-4,5,9,10-tetracarboxylic diimide (NDTI, Figure 1c),[9] for the following reasons: (i) less steric-demanding fused-thiophene rings without the β-substituents allow the NDTI core to keep planar structures, giving the efficiently π-extended systems with slightly lower energy levels of LUMO (E_{LUMO}s: ∼−4.0 eV) and smaller HOMO−LUMO gaps than those of the corresponding NDI derivatives; (ii) the thiophene α-position can be utilized in chemical modifications, leading various conjugated oligomers and polymers, which can act as n-type and ambipolar organic semiconductors in organic field-effect transistors and organic photovoltaic cells.[9]

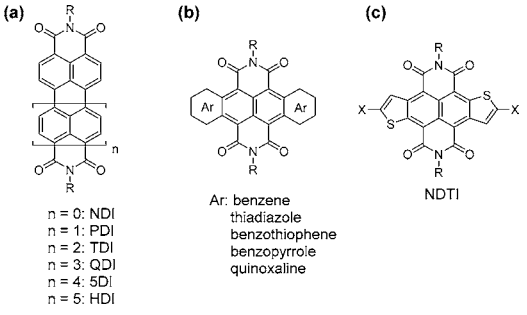


Figure 1. Chemical structure of a series of rylene diimide (a), π-extended NDIs (b), and NDTI (c).

The key chemistry in the synthesis of NDTI is the nucleophilic hydrogen substitution (S_NH) reaction of sodium sulfide[10] on 2,6-bis((trimethylsilyl)ethynyl)-NDI derivatives (**2**),[11] which are readily derived from 2,6-dibromo-1,4,5,8-naphthalene tetracarboxylic anhydride (**1**, Scheme 1, upper route). The method for the synthesis of NDTI derivatives, however, has several drawbacks, which may hinder the further development of NDTI-based materials: (i) Introduction of *N*-alkyl or phenyl groups on the imide nitrogen atoms was carried out at the first step of the synthesis before the annulation of the fused-thiophene rings. This means that the synthesis of NDTI derivatives with different groups on the imide nitrogen atoms

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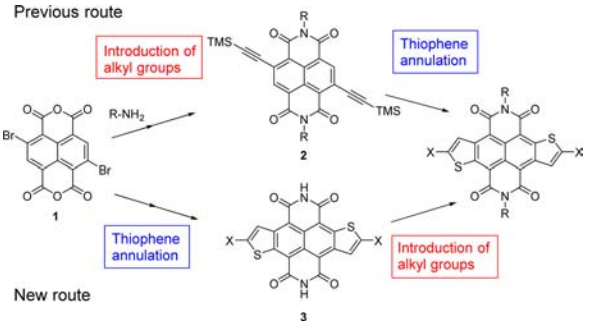
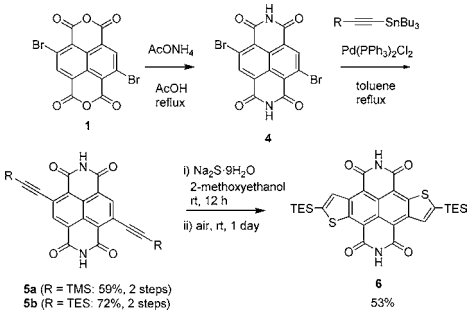
Scheme 1. Synthetic Strategy of NDTI Derivatives



should be restarted again from **1**. (ii) The imidation reaction on **1** required an excess amount of the corresponding amines, some of which are expensive or difficult to access. Moreover, alkylamines with strong nucleophilicity, such as cyclohexylamine, accelerated the nucleophilic aromatic substitution reaction at the bromine sites on the naphthalene core,[12] resulting in poor yields of the desired intermediates. (iii) Yields of the thiophene-annulation reaction were largely dependent on the solubility of precursors **2** in the alcoholic medium. In the case of poorly soluble precursors, e.g., ones with methyl or fluoroalkyl groups cannot be converted into the desired NDTI derivatives.

To overcome these drawbacks, we have redesigned the synthetic route to NDTI derivatives from **1** (Scheme 1, lower route). The key strategy is to construct *N,N′*-unsubstituted NDTI (**3**) followed by the introduction of *N,N′*-alkyl or phenyl groups, which solves the above first and second issues. Related to the third issue, a soluble precursor without *N,N′*-substituents in the alcoholic medium should be developed for the thiophene-annulation reaction. With these strategies, we first focused on *N,N′*-unsubstituted 2,6-dibromonaphthalene-1,4,5,8-tetracarbonic acid diimide (**4**), which can be readily prepared from the anhydride (**1**) in a good yield (Scheme 2).[13]

Scheme 2. Synthesis of *N,N′*-Unsubstituted NDTI Derivative



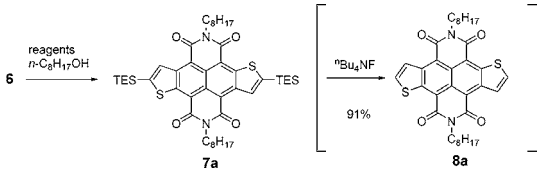
Subsequent Stille coupling reaction with stannylated (trimethylsilyl)acetylene gave 2,7-bis((trimetylsillyl)ethynyl)-naphthalene diimide (**5a**) in a 59% isolated yield (two steps). The thiophene-annulation reaction of **5a** mediated by sodium sulfide hydrate, however, did not proceed, and **5a** was recovered. As we anticipated, it is most likely that the poor solubility of **5a** disturbed the annulation reaction.

We then examined an alternative precursor, **5b**, with a triethylsilyl (TES) group instead of a trimethylsilyl (TMS) group. To our delight, **5b** with a better solubility can be converted into 2,7-bis(triethylsilyl)-NDTI (**6**) upon treatment with sodium sulfide as a maroon solid in moderate yields (around 50%). The structure of **6** was fully characterized by spectroscopic analysis. Its ^{1}H NMR spectrum shows two singlets assignable to the imide hydrogen (8.90 ppm) and thiophene *β*-hydrogen atoms (9.11 ppm), and the ^{13}C NMR spectrum yields nine peaks that are reasonably assigned to seven aromatic and two carbonyl carbon atoms. Both spectra were consistent with the C_{2h} symmetric structure of the NDTI core (see the Supporting Information).

It is noteworthy that the present thiophene-annulation reaction proceeded under rather mild conditions (rt, 12 h) in better yields (up to 53% isolated yield) than the previous synthesis of *N,N′*-dioctyl-2,7-bis(trimethylsiyl)-NDTI (60 °C, 12 h, 32% isolated yield).[9a] The different reactivity can be explained by the absence of electron-donating alkyl groups on the imide nitrogen atoms, which may enhance the electron density of the naphthalene core and then impede the S_NH reaction by the thiolate anion.[9a,10] It should be also mentioned that all of the experimental operations in the synthetic protocol for **6** were very simple: neither solvent extraction nor column chromatography in the workup are necessary, which makes the protocol amenable to the large-scale synthesis of **6**: in fact, we can synthesize **6** in 10-g, which is another merit of the new synthetic route.

Although the TES groups on **6** were readily cleaved off to afford parent NDTI without any substituents, the poor solubility hampered its purification and utilization to the alkylation/arylation reaction on the imide nitrogen atoms. Thus, the introduction of *N*-substituents should be done before the desilylation reaction, and for this purpose, we first examined Mitsunobu reaction on **6** with *n*-octanol as a test case for the alkylation (Table 1). Under typical reaction conditions for the

Table 1. Alkylation on 6 by Mitsunobu Reaction



run	reagents	solvent	temp (°C), time (h)	yield (%)
1	(i) PPh_3, n-$C_8H_{17}OH$, (ii) DEAD[a]	THF	rt, 16	43
2	(i) PBu_3, n-$C_8H_{17}OH$, (ii) TMAD[b]	toluene	rt, 16	
3	n-$C_8H_{17}OH$, CMBP[c]	toluene	100, 3	81
4	(i) n-$C_8H_{17}OH$, (ii) PPh_3, DEAD	THF	rt, 0.5	82

[a]DEAD: diethyl azodicarboxylate. [b]TMAD: *N,N,N′,N′*-tetramethylazodicarboxamide. [c]CMBP: cyanomethylenetributylphosphorane.

alkylation on the imide nitrogen atom mediated by diethyl azodicarboxylate (DEAD) and triphenylphosphine,[14] the desired *N,N′*-dioctyl-NDTI with two TES groups (**7a**) was obtained from a black tarry product (run 1). However, the isolated yield of **7a** was relatively low (~43%). To improve the yield, other reagents for Mitsunobu reaction were examined (runs 2 and 3). Although the combined reagents of *N,N,N′,N′*-tetramethylazodicarboxamide (TMAD)[15] and tributylphosphine did not afford the target product, cyanomethylenetributylphosphorane (CMBP)[16] afforded the desired product in an 81% isolated yield, indicating that the new route to *N,N′*-alkylated NDTIs (Scheme 1) is useful. CMBP, however, is less

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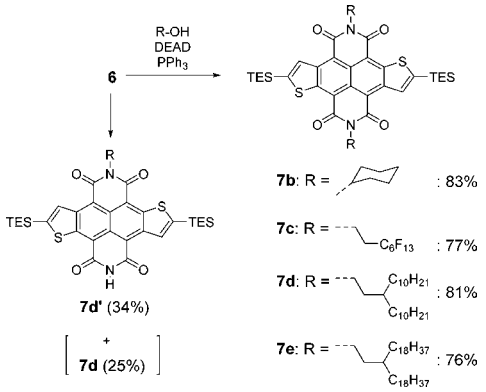
tractable (as it is oil with high viscosity at room temperature and easily oxidized by air) and expensive, though it is commercially available,[16] and for this reason, the alkylation procedure with CMBP cannot be acceptable as a practical method for the synthesis of NDTI-based electronic materials. We then again tested the DEAD/PPh_3 reagents, the standard for the Mitsunobu reaction. Inspired by the consideration that CMBP is a synthetic equivalent to the betaine intermediate in situ derived from DEAD/PPh_3,[16] we tested different orders of reagent addition (run 4); in run 1, PPh_3 was first mixed with **6** and the alcohol, and then the DEAD reagent was added, whereas in run 4, PPh_3 and DEAD were simultaneously added to the mixture of **6** and alcohol. This simple alteration in the procedure drastically improved the reaction, and **7a** was isolated in an 82% isolated yield. Furthermore, the TES groups on **7a** were easily cleaved off to *N*,*N*′-dioctyl-NDTI (**8a**) in a 91% isolated yield.

Using the optimized reaction conditions, NDTI derivatives with different alkyl groups, e.g., cyclohexyl (**7b**), 1*H*,1*H*,2*H*,2*H*-perfluorooctyl (**7c**), 3-decyltridecyl (**7d**), and 3-octadecylhenicosyl groups (**7e**), all of which are difficult to be synthesized by the previous method, were successfully obtained in good yields (76−83%, Scheme 3, right). In addition, by using a controlled

Scheme 3. Mitsunobu Reaction on the Imide Nitrogen of 6

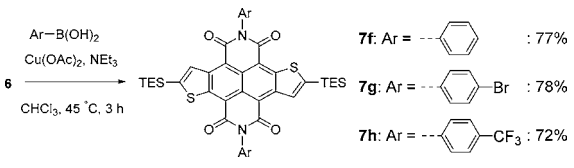


amount of the reagents, a mixture consisting of mono- (**7d′**, 34%), dialkylated (**7d**, 25%), and unsubstituted products (**6**, less than 10%) was obtained (Scheme 3, left), which were easily separated by column chromatography. Although the isolated yield was moderate, the present method was proven to be useful for the synthesis of monoalkylated NDTI derivatives.

Introduction of phenyl groups on the imide nitrogen atoms was also examined by using boronic acids in the presence of copper acetate.[17] The reaction proceeded smoothly to afford phenyl (**7f**), 4-bromophenyl (**7g**), and 4-(trifluoromethyl)-phenyl (**7h**) derivatives in good yields (72−78% isolated yields, Scheme 4).

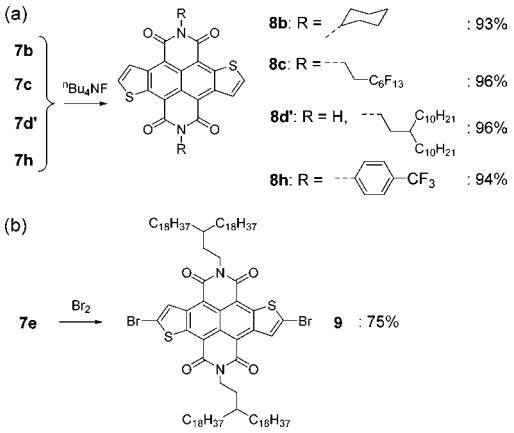
The TES groups in **7** were easily desilylated to afford the corresponding α-unsubstituted NDTI derivatives (**8b**,**c**,**h**,

Scheme 4. Introduction of *N*-Phenyl Substituents



Scheme 5), which can be used as n-channel organic semiconductors in OFET devices (vide infra) or converted

Scheme 5. Conversion of TES Groups: (a) Desilylation and (b) Bromination



into the bromine group (**9**, Scheme 5) for further derivatization into extended π-systems such as conjugated polymers and oligomers (Scheme S1). The desilylation of monoalkylated derivative (**7d′**) also afforded the corresponding α-unsubstituted NDTI (**8d′**), which is not accessible by the previous route.

The desilylated compounds can act as organic semiconductors for n-type OFET devices, and in particular, **8b**, **8c**, and **8h** seem to be interesting, as the NDI derivatives with cyclohexyl, fluoroalkyl, and (trifluolomethyl)phenyl groups at the imide nitrogen atoms were reported to show high electron mobilities or good air-stability.[18] Before testing them as the active n-type semiconducting materials in OFET devices, we evaluated their E_{LUMO}'s by cyclic voltammetry (see Supporting Information). Compounds **8b**, **8c**, and **8h** showed two sets of quasi-reversible reduction waves similar to those of *N*,*N*′-dioctyl-NDTI (**8a**, E_{LUMO}: 4.0 eV below the vacuum level). Interestingly, the redox potentials of **8b** were cathodically shifted by ca. 0.1 V, whereas those of **8c** and **8h** were anodically shifted by ca. 0.1 V. These reduction potentials correspond to E_{LUMO} of 3.9, 4.1, and 4.1 eV below the vacuum level for **8a**, **8b**, and **8h**, respectively (Figure S2). It is interesting to note that although the substituents on the imide nitrogen atoms do not participate to the π-conjugated system of the redox-active NDTI core, the inductive effects from the *N*-substituents are moderately large. As a result of upward shift of the E_{LUMO}, the OFETs fabricated with the vapor-deposited thin film of **8b** could not be operated under ambient conditions, though they showed decent FET characteristics under vacuum with a mobility of 1.2×10^{-2} cm^2 V^{-1} s^{-1} (Figure S3a,b).[19] On the other hand, the devices based on vapor-deposited thin films of **8c** and **8h** showed a typical n-channel transistor response under ambient conductions (Figure S3c−f). The extracted mobilities, up to 7.6×10^{-2} cm^2 V^{-1} s^{-1}, were higher than those of **8a**-based OFETs.

In summary, a new synthetic route to a range of NDTI derivatives via *N*,*N*′-unsubstituted 2,7-bis(triethylsilyl)-NDTI (**6**) have been established. The new route is advantageous over the previous one in many aspects: first, the key intermediate, **6**, can be prepared on a multigram scale (>10 g) without tedious workup and purification operations. Second, the NDTI derivatives with *N*,*N*′-cyclohexyl, fluoroalkyl, other elaborated

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alkyl groups, and phenyl groups, all of which cannot be synthesized or are very difficult to synthesize with the previous method, were easily synthesized. Third, *N*-monoalkylated NDTI can also be prepared, though the yield was relatively low. As demonstrated by these facile conversions of **6** into a range of derivatives, the present method for the synthesis can pave the way to tailored NDTI derivatives for various applications. Further studies on the design and synthesis of NDTI-based electronic materials are now underway in our group.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01785.

Experimental details, characterization data for the products, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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