First Synthesis of 2,3,6,7-Tetrabromonaphthalene Diimide
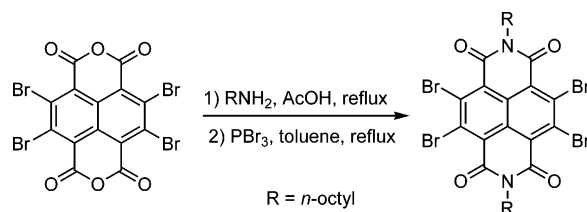
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Received June 29, 2007

ABSTRACT

N,N′-Bis(n-octyl)-2,3,6,7-tetrabromonaphthalene diimide (TBNDI) was synthesized by a new imidization reaction and characterized by HRMS, ¹H NMR, ¹³C NMR, elemental analyses, FT-IR, UV−vis, and single-crystal X-ray analysis. The TBNDIs are the key precursors for the synthesis of core-tetrasubstituted-naphthalene diimides.

Naphthalene diimides (NDIs) are an important class of organic species. They have been extensively used in supramolecular chemistry,[1] electron-transfer systems,[2] DNA sensors,[3] electrically conductive aggregates,[4] and n-type organic field effect transistors (OFETs).[5] Two different methods were used to achieve the chemical modification of NDIs. One is to introduce substituents at N atoms of imide groups, and the other is to functionalize the naphthalene core of NDIs. The synthesis of the latter mostly uses 2,6-

dichloronaphthalene dianhydride (DCNDA) or 2,6-bromonaphthalene dianhydride (DBNDA) as precursors. Würthner et al.[6] reported core-substituted NDI dyes by introducing one or two alkyl amines to the naphthalene core; these NDI dyes exhibit intensive fluorescence with high quantum yields. More excitingly, some of these chromophores have been successfully used in artificial photosynthesis.[7] Marks and Wasielewski attached two cyano groups to the naphthalene core of NDI and obtained air-stable, flexible, and optically

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transparent *n*-type OFETs.[8] However, up to now, core-tetrasubstituted NDIs have not been available in the literature owing to synthetic difficulty. In fact, 2,3,6,7-tetrabromonaphthalene diimides (TBNDIs) are the key precursors for the synthesis of core-tetrasubstituted NDIs, using nucleophilic aromatic substitution (S_NAr),[6,7,9] nucleophilic halogen exchange reaction,[8,10] and the Suzuki or Stille cross-coupling reaction.[11,2e] Herein, we report the first synthesis of TBNDIs, *N*,*N*′-bis(*n*-octyl)-2,3,6,7-tetrabromonaphthalene diimide (Scheme 1, **5**).

Scheme 1. Synthesis of TBNDIs (**5**)
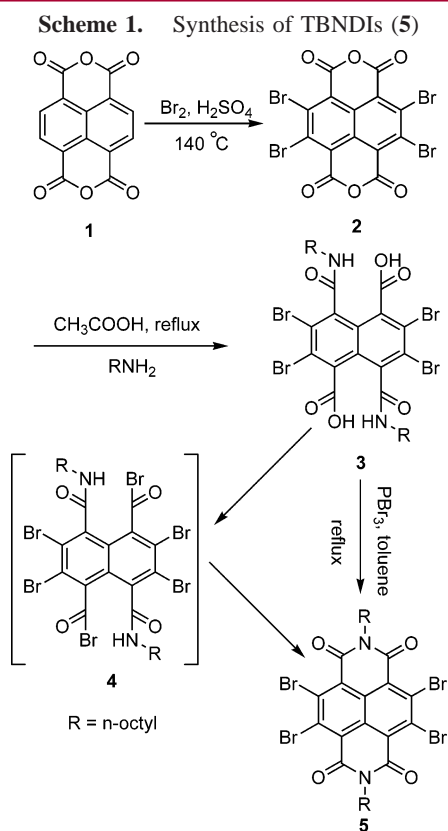
2,3,6,7-Tetrabromonaphthalene dianhydride (TBNDA, **2**) is an ideal synthon for the synthesis of TBNDIs. **2** has been reported as a small quantity of byproducts by brominating NDA (**1**) with Br_2 in sulfuric acid,[12] but this protocol could not be reproduced even for the synthesis of DBNDA.[6b] We recently discovered that 1,6,7,12-tetrabromoperylene dian-

hydride (TBPDA) could be obtained by brominating PDA with Br_2 in the mixture of sulfuric acid and oleum.[11] By the modification of the synthesis of TBPDA and as shown in Scheme 1, **2** was synthesized by treatment of **1** and 5.3 equiv of Br_2 in the mixture of sulfuric acid and oleum (V:V = 4:1) at 140 °C for 4 weeks. High-purity **2** was obtained with a high yield of 96%, which was characterized by elemental analyses, HRMS, and FT-IR. To avoid the aforementioned S_NAr reactions, the synthesis of **5** was performed in acetic acid, where most amino functions are protonated, and the reactivity of the amines is sufficiently low.[6b] However, our results showed that for an elongated reaction time (>30 min), the reaction of **2** and 4 equiv of *n*-octylamines in refluxing acetic acid could lead to more and more core-(*n*-octylamino)-substituted compounds, with deep red color. The reaction with a shortened reaction time (≤30 min) also failed to afford **5**. A yellow solid-state crude product was instead obtained, which is difficult to purify further or to isolate. The MALDI-TOF-MS indicated that 2,3,6,7-tetrabromo-4,8-bis(octylcarbamoyl)naphthalene-1,5-dicarboxylic acid (**3**) was contained in the yellow solid.

Obviously, the dehydration reaction of **3** could lead to the formation of **5**. Scheme 2 shows our attempts to prepare **5**

Scheme 2. Attempts to Prepare **5** from **3**
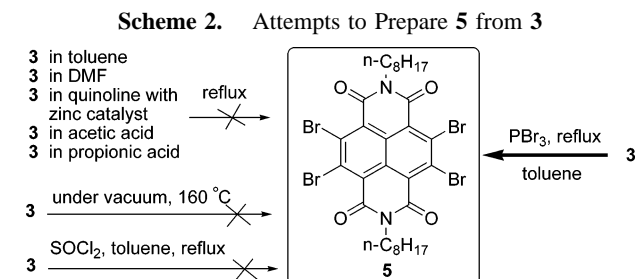
from **3**. First, we tried the dehydration reaction of **3** in refluxing organic solvents such as toluene, DMF, quinoline with zinc acetate catalyst, and organic acids, but we failed. Then, we carried out the dehydration reaction of **3** under vacuum at 160 °C for several hours, which also gave no hint of the formation of **5**. This failure might be ascribed to the strong electron-withdrawing ability of four Br atoms, which makes **3** a strong organic acid and might form the internal salt. Thus, the exploration of conceptually new methodology is a compelling subject in aromatic bisimides chemistry. It is well-known that the reactivity of acyl halide is very high. As shown in Schemes 1 and 2, we tried new ways to synthesize **5**.[13] Fortunately, the reaction of **3** with excess PBr_3 in refluxing toluene for 12 h afforded **5** in 31.4% overall yield calculated from **1**. The first TBNDIs, **5**, was characterized by HRMS, ^{1}H NMR, ^{13}C NMR, elemental analyses, FT-IR, UV−vis, and single-crystal X-ray analysis. As displayed in Scheme 1, the synthesis of **5** from **3** might

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(13) $SOCl_2$ could also lead to the imidization reaction of **3** in refluxing toluene and afforded the core-tetrasubstituted NDIs. But the unexpected nucleophilic halogen exchange reactions occurred, affording various core-tetrahalogenate NDIs with one or two Br atoms being replaced by Cl atoms.

involve two reaction steps: the first step is the formation of 2,3,6,7-tetrabromo-4,8-bis(octylcarbamoyl)naphthalene-1,5-dicarbonyl dibromide (**4**), and the second one is the dehydrobromination reaction of **4**, which leads to the formation of **5**. In ^1H NMR spectrum of **5**, there are no signals in the aromatic region, indicating the core-tetrasubstituted behavior. Only four carbon signals appear in the aromatic region of the ^{13}C NMR spectrum of **5**, implying the symmetric core-tetrasubstituted feature. The NMR data together with the data of HRMS and elemental analyses demonstrate the accurate chemical structure of **5**.

Single crystals of **5** suitable for single-crystal X-ray analysis were obtained by slowly diffusing methanol into chloroform that contains **5**. The molecular structure of **5** is depicted in Figure 1. Unlike the core-unsubstituted NDIs,[14]
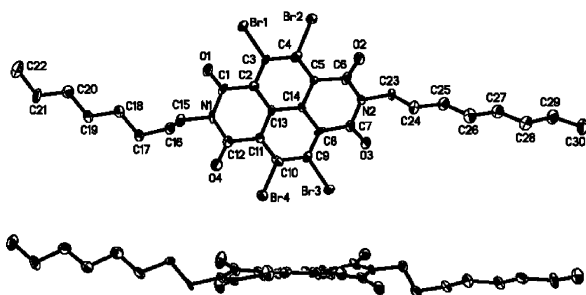

Figure 1. ORTEP drawings of **5** (50% probability for thermal ellipsoids): a face-on view (top) and a side view (bottom).

steric crowding of Br atoms and adjacent O atoms results in a slightly unsymmeric molecular structure of **5** in crystal. The naphthalene core together with four Br atoms are coplanar with the mean atom deviation of 0.043 Å from the plane. However, the two six-membered imide rings are twisted because of the interatomic steric crowding. The mean atom deviations from the N1 imide ring and the N2 imide ring are 0.084 and 0.076 Å, respectively.

To estimate the position of frontier orbitals of **5** and its counterpart compound (NDI-C8, a core-unsubstituted NDIs with two terminal *n*-octyl chains), Density Functional Theory (DFT) calculations were performed with Gaussian 03 at the B3LYP/6-31G(d) level. As shown in Figure 2 (top), the largest coefficients in the HOMO orbital of **5** are mainly located on the ambient heteroatoms of the π-skeleton, especially on four Br atoms, giving a polarized HOMO orbital. Whereas the HOMO orbital of NDI-C8 is mainly situated on the naphthalene core, for LUMO orbitals, both **5** and NDI-C8 have the strongest coefficients at aromatic carbon atoms along the molecular long axis (Figure 2, bottom). The energy values of HOMO and LUMO orbitals of **5** and NDI-C8 were also calculated by DFT (HOMO: −6.79 and −6.97 eV; LUMO: −3.61 and −3.35 eV; band gap: 3.18 and 3.62 eV for **5** and NDI-C8, respectively). The

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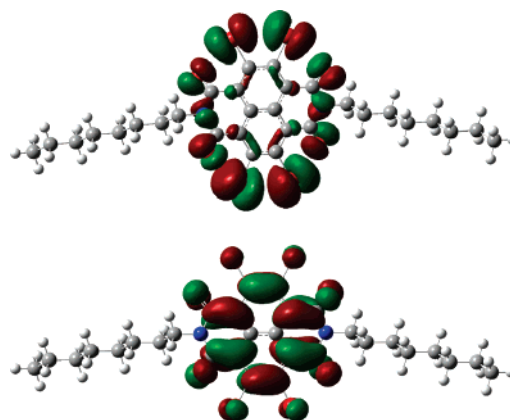
Figure 2. HOMO orbital (top) and LUMO orbital (bottom) of **5** obtained by DFT calculations.

DFT results show that **5** has a lower lying LUMO level and narrower band gap comparable to those of NDI-C8.
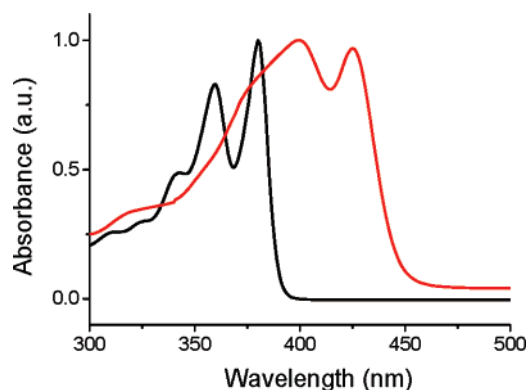
Figure 3. Normalized UV−vis absorption spectra of **5** (red line) and NDI-C8 (black line) in CH_2Cl_2.

As shown in Figure 3, the absorption spectrum of NDI-C8 exhibits the electronic S_0−S_1 absorption at 359 and 380 nm.[6b] However, the absorption of **5** showed much more red-shift than that of NDI-C8, with the bands at 400 and 425 nm. The results demonstrate that the introduction of four Br atoms to the naphthalene core greatly affects the electronic structure of NDIs. The optical band gaps of **5** and NDI-C8, estimated from the absorption edges, are 2.79 and 3.18 eV, respectively, implying the decreased band gaps when four Br atoms were introduced to the naphthalene skeleton. Similar results were obtained by the above DFT calculations. A thermogravimetric analysis (TGA) study reveals that **5** has excellent thermal stability with the onset decomposition temperature of 336 °C. According to its differential scanning calorimetry (DSC) measurement, a sharp melting endothermal peak was observed at 258 °C. The redox properties of **5** were investigated by cyclic voltammetry (CV) (see the Supporting Information for details). The first reversible NDI⁰/

NDI⁻ redox process was observed at −0.33 and −0.64 V vs Ag/AgCl for **5** and NDI-C8, respectively, indicating a 310 mV positive-shift when four electron-withdrawing Br atoms were attached to the naphthalene core of NDI. The LUMO levels of **5** and NDI-C8, estimated from the onset reduction potential relative to vacuum, are −4.12 and −3.84 eV, respectively. Although there is about 0.5 eV error, the values obtained by CV are basically consistent with the aforementioned DFT calculated LUMO energy levels (−3.61 and −3.35 eV, respectively), demonstrating the lower lying LUMO level of **5** relative to that of NDI-C8, which benefits the air-stable *n*-type OFETs.[8,10]

In summary, a hitherto unknown TBNDIs, **5**, was synthesized by a new imidization reaction. **5** has good thermal property and low-lying LUMO level, which makes it a promising *n*-type OFET material. More importantly, TBNDIs (**5** as one of its derivatives) can be widely used for the synthesis of core-tetrasubstituted NDIs. The core-tetrasubstituted NDIs would open up new opportunities in many applications, including organic dyes, organic field-effect transistors, and other new fields. We are currently exploring these avenues.

Supporting Information Available: General experimental methods; synthesis and characterizations of compounds **2**, **3**, and **5**; HRMS and FT-IR spectra of **2**; MALDI-TOF-MS spectrum of **3**; HRMS, ¹H NMR, ¹³C NMR, and FT-IR spectra of **5**; crystallographic data (CIF) of **5**; TGA-DTA and DSC images of **5**; CV and DPV plots of **5** and NDI-C8; and HOMO and LUMO orbitals of NDI-C8 obtained by DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

OL701539Z