One-Pot Synthesis of Core-Expanded Naphthalene Diimides: Enabling N-Substituent Modulation for Diverse n-Type Organic Materials

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ABSTRACT

A mild and versatile one-pot synthesis of core-expanded naphthalene diimides has been developed, which undergoes a nucleophilic aromatic substitution reaction and then an imidization reaction, allowing an easy and low-cost access to diverse n-type organic materials. Some newly synthesized compounds by this one-pot operation exhibited high electron mobility of up to 0.70 cm² V⁻¹ s⁻¹ in ambient conditions.

Naphthalene diimides (NDIs), an important class of π-functional materials, have been widely used in supramolecular chemistry, DNA sensors, artificial photosystems, anion transport, and organic transistors.¹ The development of new NDI-based materials depends on the modification of the NDI core and/or the N-substituent. The core substituents can be used to significantly tune the molecular electronic structures of NDIs.¹b Some core-substituted NDIs that possess excellent electron-transporting (n-type) properties were developed by introducing electron-withdrawing groups (such as CN and halogen atoms)² or electron-donating moieties (such as thiophenes)³ onto the NDI core.

Recently, core-expanded naphthalene diimides fused with two 2-(1,3-dithiol-2-ylidene)malononitrile moieties (NDI-DTYM2) were successfully developed.⁴ The solution-processed n-channel organic thin film transistors (OTFTs) based on these compounds exhibited high electron mobility (0.19–1.2 cm² V⁻¹ s⁻¹) and excellent air/operating stability,⁴,⁵ demonstrating that the π-core of

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NDI-DTYM2 is a perfect building block for air-stable electron transport. For rylene and related diimides, \( N \)-substituent modulation does not substantially affect the molecular electronic structure\(^6\) but allows for tuning solubility, molecular aggregation behavior, and molecular packing in the solid state.\(^7\) Therefore, the \( N \)-substituent modulation will play an important role in using the \( \pi \)-core of NDI-DTYM2 to achieve superior n-type organic materials. This will greatly contribute to the development of organic electronics, where one of the biggest challenges is the distinct lack of high-performance, ambient-stable, n-type organic materials.\(^8\) Moreover, new properties and applications of NDI-DTYM2 derivatives could also be accomplished by \( N \)-substituent modulation. Given the significance of \( N \)-substituent modulation for NDI-DTYM2 derivatives, an efficient synthetic strategy is highly desirable.

As shown in Scheme 1 (method A), the previously reported synthetic method for symmetrically \( N \)-substituted NDI-DTYM2 derivatives that attach the swallow-tail alkyl chains suffers from the complex multistep reactions with the low total yields (9–20\%), the use of a harsh solvent/reagent (acetic acid/phosphorus tribromide), and a relatively high reaction temperature.\(^4\) Furthermore, method A could only afford limited types of symmetrically \( N \)-substituted NDI-DTYM2 derivatives and was not efficient for synthesizing unsymmetrically \( N \)-substituted molecules. To overcome these drawbacks and to pursue promising low-cost high-performance n-type organic materials, a mild and straightforward synthetic strategy for diverse NDI-DTYM2 derivatives is highly desirable.

Herein, we report a versatile one-pot synthesis of NDI-DTYM2 derivatives, which allows for efficient \( N \)-substituent modulation. This one-pot operation possesses some noteworthy virtues, such as the efficiency for synthesizing both symmetrically and unsymmetrically \( N \)-substituted compounds, a fast and straightforward procedure (one-pot synthesis, no catalyst used, and no additional reagents required), mildness (reactions can be run between room temperature and 50 °C with DMF as solvent), and wide functional group tolerance (e.g., alkyl, aryl, benzyl, and other functionalized \( N \)-groups).

### Scheme 1. Synthesis of NDI-DTYM2 Derivatives (1) from 2,3,6,7-Tetrabromonaphthalene Dianhydride (2) via Methods A and B with Different Key Features

<table>
<thead>
<tr>
<th>entry</th>
<th>( R^1, R^2 )</th>
<th>yield of 1 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( R^1 = R^2 )</td>
<td>1a (18)/28</td>
</tr>
<tr>
<td>2</td>
<td>( R^1 = R^2 )</td>
<td>1b (11)/29</td>
</tr>
<tr>
<td>3</td>
<td>( R^1 = \text{aromatic} )</td>
<td>1c (48)</td>
</tr>
<tr>
<td>4</td>
<td>( R^1 = \text{aromatic} )</td>
<td>1d (trace)</td>
</tr>
<tr>
<td>5</td>
<td>( R^1 = \text{aromatic} )</td>
<td>1e (0)/42</td>
</tr>
<tr>
<td>6</td>
<td>( R^1 = \text{aromatic} )</td>
<td>1f (0)/13</td>
</tr>
<tr>
<td>7</td>
<td>( R^1 = \text{alkyl} )</td>
<td>1g (trace)</td>
</tr>
<tr>
<td>8</td>
<td>( R^1 = \text{alkyl} )</td>
<td>1h (trace)</td>
</tr>
<tr>
<td>9</td>
<td>( R^1 = \text{alkyl} )</td>
<td>1i (trace)</td>
</tr>
</tbody>
</table>

*Isolated total yields achieved by method A. *Isolated yields achieved by method B at 50 °C; the reaction can also be performed at room temperature, but the yield is relatively lower. *Complex mixture of nonseparable products.

\( a \) Isolated total yields achieved by method A.

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As shown in Scheme 1 (method B, 50 °C was chosen as an optimized reaction temperature for this study), the one-pot synthesis involves two stages from the starting material 2,3,6,7-tetram bromonaphthalene dianhydride (2).9 First the reaction of 2 with 3 equiv of Na3(i-mnt)10 (i-mnt = 1,1-dicyanoethene-2,2-dithiolate) was performed in DMF at 50 °C for 1 h, and then one (R1′NH2 and R2′NH2, R1 = R2, 3 equiv vs 2) or two types of amines (R1′NH2 and R2′NH2, R1 ≠ R2, 1:5:1.5 equiv vs 2) were added to the above solution and further stirred for 6 h at 50 °C, affording the target NDI-DTYM2 derivatives.

Compounds 1a–i (Table 1) not only highlight the efficiency and excellent functional group tolerance of the one-pot synthesis (method B) but also provide promising n-type organic materials. Compound 1a has been reported previously,4a and its optimum OTFT devices exhibited electron mobilities as high as 0.55–1.2 cm2 V−1 s−1 in ambient.5 NDI-DTYM2 derivatives 1b–i are newly developed compounds. As shown in Table 1 (entries 1 and 2), both methods A and B are applicable to the synthesis of symmetrically N-substituted compounds 1a and 1b that bear the N-alkyl chains and N-benzyl groups, respectively, but the yield achieved by method B is much higher than that obtained by method A (28% vs 18%4a for 1a, and 29% vs 11% for 1b). Compound 1c, bearing two N-(2-aminoethyl)-3,4,5-tris (dodecylxoyl)benzamide moieties, could not be obtained by method A due to the complex reactions involved (entry 3). The implementation of method A for the synthesis of 1d (a symmetrically N-substituted compound with 4-ter-butylnaphenyl N-groups) is also unsuccessful, giving only a trace amount of product (entry 4). Compounds 1e and 1f could not be prepared by method A due to their acid-sensitive N-substituents (entries 5 and 6). Similar to 1f, when trying to synthesize other unsymmetrically N-substituted compounds by method A, the results were so disappointing that we obtained only a trace of the target compounds (Table 1, entries 7–9, 1g–i). Fortunately, the one-pot synthetic method B is very efficient for the synthesis of both symmetrically N-substituted NDI-DTYM2 derivatives (Table 1, entries 1–5, 1a–e, R1 = R2) and unsymmetrically N-substituted ones (Table 1, entries 6–9, 1f–i, R1 ≠ R2) with moderate yields of 28–55% and 13–21%, respectively.

Encouraged by these results, we started to study the reaction process of the one-pot synthesis. As shown in Scheme 2, the one-pot operation is successful when we first carried out the reaction of 2 and Na2(i-mnt) in DMF, but it failed when the reaction of 2 with amine (R1′NH2 and R2′NH2) in DMF was first performed.11 A proposed mechanism for this one-pot synthesis is that the nucleophilic aromatic substitution (SNAr) reaction of 2 with Na2(i-mnt) in DMF affords the core-expanded naphthalene dianhydride (Scheme 2, 6).12 Then an imidization reaction of 6 and amine (R1′NH2 and R2′NH2) gives the target NDI-DTYM2 derivatives. This mild imidization reaction that can operate at low temperature (rt to 50 °C) is fairly scarce for the synthesis of rylene and related diimides.13

Compounds 1a–i obtained by the one-pot synthesis were characterized by mass spectroscopy,1H,13C NMR spectra, elemental analysis, and IR spectra. All compounds except 1d are well soluble in common organic solvents. Thermogravimetric analysis (TGA), UV–vis absorption spectra, and cyclic voltammetry (CV) were carried out to evaluate the thermal, optical, and electrochemical properties of the new compounds in detail.14 The good thermal stability of the new compounds largely depends on the feature of the N-substituent with the order of bis(N-phenyl) > N-phenyl, N’-alkyl > bis(N-alkyl). Compounds 1b–i showed similar absorption spectra and cyclic voltammograms with comparable peak values for their end absorptions and redox curves (Figures S3–5). This is due to the electronic decoupling of the NDI-DTYM2 core and the N-substituent.5 Compounds 1b–i have comparable low-lying LUMO levels of −4.29 to −4.36 eV calculated from the CV results using ferrocene (−4.8 eV to vacuum) as an internal standard (see Table S1 for details), and this is crucial for realizing electron carrier injection and conduction with ambient stability.14
Compound 1e is a highly soluble molecule, which, in addition to its acetal-containing flexible N-alkyl chains, makes 1e an easy solution-processable material. Compound 1i that bears one N-alkyl chain and one aromatic phenyl group is a representative molecule for unsymmetrically N-substituted NDI-DTYM2 derivatives. Herein, we study the electron-transporting properties of these two new compounds (1e and 1i) by fabricating and testing their solution-processed n-channel OTFTs (see Supporting Information, Table S2 for details). Thin films of 1e and 1i were spin-coated on octadecyltrichlorosilane (OTS)-treated SiO₂/Si substrates from their chloroform solution, affording a bottom-gate top-Au-contact device structure. All OTFT devices were measured in air. When annealed at 160 °C, a thin film of 1e gives a mobility of 0.12 cm² V⁻¹ s⁻¹, a threshold voltage of 13 V, and a current on/off ratio of 10⁶ (Figure S6 exhibits its output and transfer characteristics). As shown in Figure 1, OTFT devices based on 1i (annealed at 190 °C) show high electron mobilities up to 0.70 cm² V⁻¹ s⁻¹, with a threshold voltage of 7 V and a current on/off ratio of 10⁷. This is one of the best device performances reported so far for solution-processed, ambient-stable, n-type organic materials. Yet, there is still much room for improvement in the performance of 1i-based OTFTs, because the thin-film morphology of 1i is still insufficient (see Figures S7–9 for details).

In conclusion, a versatile one-pot synthesis of NDI-DTYM2 derivatives has been developed, which undergoes an SNAr reaction and then an imidization reaction, providing an easy and low-cost access to diverse n-type organic materials. Some newly developed compounds exhibited high electron mobilities up to 0.70 cm² V⁻¹ s⁻¹ in ambient conditions. More importantly, this one-pot synthetic method would afford a more diverse set of NDI-DTYM2 derivatives, which we foresee to have exciting applications in organic electronics.

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**Supporting Information Available.** General experimental methods, synthesis, and characterizations of compounds 1a–i, and OTFT device fabrication/characterization with semiconductors 1e and 1i. This material is available free of charge via the Internet at http://pubs.acs.org.