ORGANIC LETTERS

2012
Vol. 14, No. 1
292–295

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

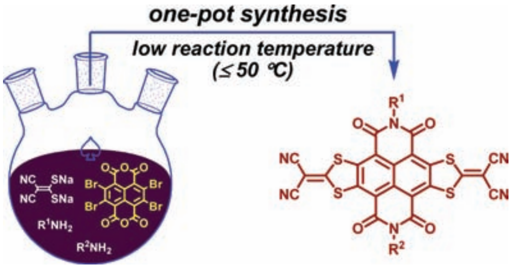
Yunbin Hu,[†] Yunke Qin,[†] Xike Gao,[*,†] Fengjiao Zhang,[‡] Chong-an Di,[*,‡] Zheng Zhao,[†] Hongxiang Li,[†] and Daoben Zhu[*,†,‡]

Laboratory of Materials Science, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences (CAS), 345 Lingling Road, Shanghai 200032, China, and Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, CAS, Beijing 100190, China

gaoxk@mail.sioc.ac.cn; dicha@iccas.ac.cn; zhudb@iccas.ac.cn

Received November 14, 2011

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 $\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ 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 $\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$) and excellent air/operating stability,[4,5] demonstrating that the π-core of

---

[†] Shanghai Institute of Organic Chemistry.

[‡] Institute of Chemistry.

(1) (a) Bhosale, S. V.; Jani, C. H.; Langford, S. J. *Chem. Soc. Rev.* **2008**, *37*, 331. (b) Sakai, N.; Mareda, J.; Vauthey, E.; Matile, S. *Chem. Commun.* **2010**, *46*, 4225. (c) Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. *Adv. Mater.* **2011**, *23*, 268. (d) Jung, B. J.; Tremblay, N. J.; Yeh, M.-L.; Katz, H. E. *Chem. Mater.* **2011**, *23*, 568. (e) Würthner, F.; Stolte, M. *Chem. Commun.* **2011**, *47*, 5109.

(2) (a) Jones, B. A.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Chem. Mater.* **2007**, *19*, 2703. (b) Oh, J. H.; Suraru, S.-L.; Lee, W.-Y.; Könemann, M.; Höffken, H. W.; Röger, C.; Schmidt, R.; Chung, Y.; Chen, W.-C.; Würthner, F.; Bao, Z. *Adv. Funct. Mater.* **2010**, *20*, 2148.

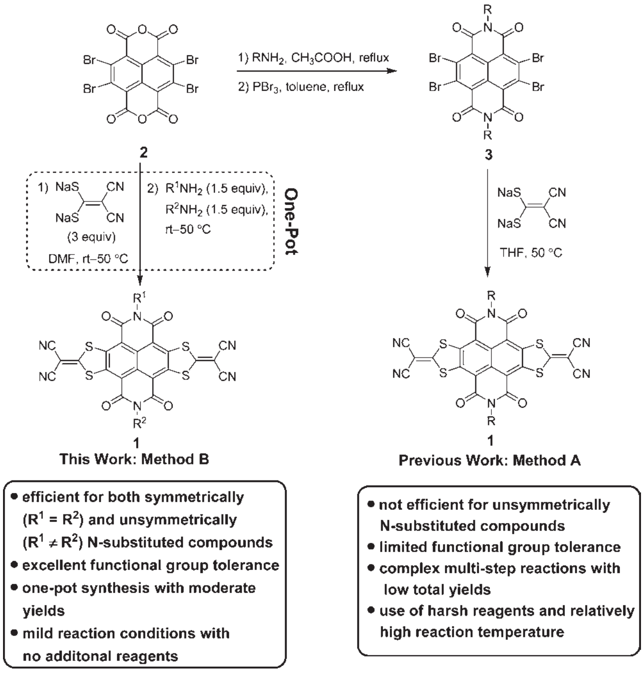
(3) (a) Yan, H.; Chen, Z.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dötz, F.; Kastler, M.; Facchetti, A. *Nature* **2009**, *457*, 679. (b) Polander, L. E.; Tiwari, S. P.; Pandey, L.; Seifried, B. M.; Zhang, Q.; Barlow, S.; Risko, C.; Brédas, J.-L.; Kippelen, B.; Marder, S. R. *Chem. Mater.* **2011**, *23*, 3408.

(4) (a) Gao, X.; Di, C.; Hu, Y.; Yang, X.; Fan, H.; Zhang, F.; Liu, Y.; Li, H.; Zhu, D. *J. Am. Chem. Soc.* **2010**, *132*, 3697. (b) Hu, Y.; Gao, X.; Di, C.; Yang, X.; Zhang, F.; Liu, Y.; Li, H.; Zhu, D. *Chem. Mater.* **2011**, *23*, 1204.

(5) Zhao, Y.; Di, C.; Gao, X.; Hu, Y.; Guo, Y.; Zhang, L.; Liu, Y.; Wang, J.; Hu, W.; Zhu, D. *Adv. Mater.* **2011**, *23*, 2448.

10.1021/ol203059r

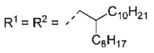
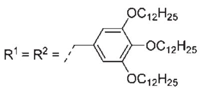
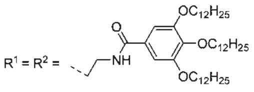
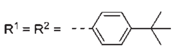
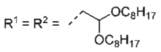
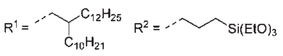
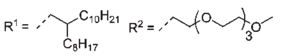
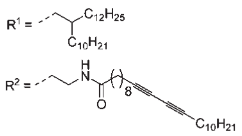
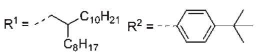
Scheme 1. Synthesis of NDI-DTYM2 Derivatives (**1**) from 2,3,6,7-Tetrabromonaphthalene Dianhydride (**2**) via Methods A and B with Different Key Features



- efficient for both symmetrically (R^1 = R^2) and unsymmetrically (R^1 ≠ R^2) N-substituted compounds
- excellent functional group tolerance
- one-pot synthesis with moderate yields
- mild reaction conditions with no additonal reagents

- not efficient for unsymmetrically N-substituted compounds
- limited functional group tolerance
- complex multi-step reactions with low total yields
- use of harsh reagents and relatively high reaction temperature

Table 1. Synthesis of NDI-DTYM2 Derivatives (**1a**–**i**) via Different Synthetic Methods (A and B)

entry	R^1, R^2	yield of **1** (%)
1		**1a** (18)[a]/(28)[b]
2		**1b** (11)[a]/(29)[b]
3		**1c** –[a,c]/(48)[b]
4		**1d** (trace)[a]/(55)[b]
5		**1e** (0)[a]/(42)[b]
6		**1f** (0)[a]/(13)[b]
7		**1g** (trace)[a]/(19)[b]
8		**1h** (trace)[a]/(21)[b]
9		**1i** (trace)[a]/(20)[b]

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

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 π-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.[4,9a] 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).

---

(6) (a) Langhals, H.; Demmig, S.; Huber, H. *Spectrochim. Acta A* **1988**, *44A*, 1189. (b) Wicklein, A.; Lang, A.; Muth, M.; Thelakkat, M. *J. Am. Chem. Soc.* **2009**, *131*, 14442.

(7) (a) Würthner, F. *Chem. Commun.* **2004**, 1564. (b) Huang, C.; Barlow, S.; Marder, S. R. *J. Org. Chem.* **2011**, *76*, 2386. (c) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Siegrist, T.; Li, W.; Lin, Y.-Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478. (d) Shukla, D.; Nelson, S. F.; Freeman, D. C.; Rajeswaran, M.; Ahearn, W. G.; Meyer, D. M.; Carey, J. T. *Chem. Mater.* **2008**, *20*, 7486. (e) Molla, M. R.; Ghosh, S. *Chem. Mater.* **2011**, *23*, 95.

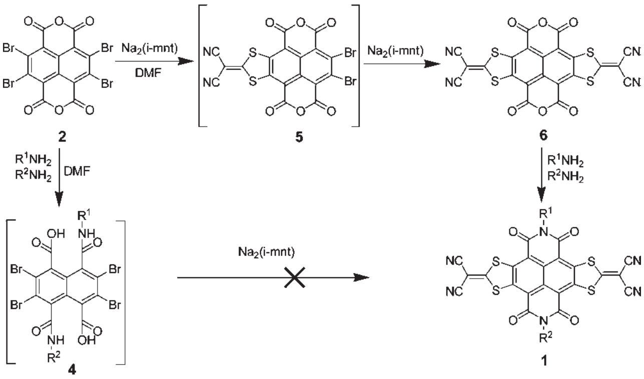
(8) (a) Newman, C. R.; Frisbie, C. D.; da Silva Filho, D. A.; Brédas, J.-L.; Ewbank, P .C.; Mann, K. R. *Chem. Mater.* **2004**, *16*, 4436. (b) Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. *Adv. Mater.* **2010**, *22*, 3876.

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-tetrabromonaphthalene dianhydride (**2**):[9] first the reaction of **2** with 3 equiv of Na$_2$(i-mnt)[10] (i-mnt = 1,1-dicyanoethene-2,2-dithiolate) was performed in DMF at 50 °C for 1 h, and then one (R^{1}NH$_2$ and R^{2}NH$_2$, R^1 = R^2, 3 equiv vs **2**) or two types of amines (R^{1}NH$_2$ and R^{2}NH$_2$, R^1 $\neq$ R^2, 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 cm^2 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 (dodecyloxy)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*-butylphenyl *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**, R^1 = R^2) and unsymmetrically *N*-substituted ones (Table 1, entries 6–9, **1f**–**i**, R^1 $\neq$ R^2) 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 Na$_2$(i-mnt) in DMF, but it failed when the reaction of **2** with amine (R^{1}NH$_2$ and R^{2}NH$_2$) in DMF was first performed.[11] A proposed mechanism for this one-pot synthesis is that the nucleophilic aromatic substitution (S$_N$Ar) reaction of **2** with Na$_2$(i-mnt) in DMF affords the core-expanded naphthalene dianhydride (Scheme 2, **6**),[12] and then an imidization reaction of **6** and amine (R^{1}NH$_2$ and R^{2}NH$_2$) gives the target NDI-DTYM2 derivatives (**1**). 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]

Scheme 2. Proposed Reaction Process of the One-Pot Synthesis



Compounds **1a**–**i** obtained by the one-pot synthesis were characterized by mass spectroscopy, ^{1}H/^{13}C 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 **1b**–**i** (see Table S1 and Figures S2–5 for details). **1d** exhibits the highest onset decomposition temperature (T_d) of 476 °C, and **1i** shows the secondary T_d value of 399 °C, which are both higher than those of symmetrically *N*-substituted NDI-DTYM2 derivatives that bear swallow-tail *N*-alkyl chains (370–389 °C).[4] The results demonstrate that the thermal stability of NDI-DTYM2 derivatives 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.[6] 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]

---

(9) (a) Gao, X.; Qiu, W.; Yang, X.; Liu, Y.; Wang, Y.; Zhang, H.; Qi, T.; Liu, Y.; Lu, K.; Du, C.; Shuai, Z.; Yu, G.; Zhu, D. *Org. Lett.* **2007**, *9*, 3917. (b) Röger, C.; Würthner, F. *J. Org. Chem.* **2007**, *72*, 8070.

(10) Hatchard, W. R. *J. Org. Chem.* **1964**, *29*, 660.

(11) The reaction of **2** and amine (R^{1}NH$_2$ and R^{2}NH$_2$) in DMF generates 2,3,6,7-tetrabromo-4,8-*N*(R^1),*N*′(R^2)carbamoyl-naphthalene-1,5-diacarboxylic acid (Scheme 2, **4**; see ref 9a for details), which is difficult to further react with Na$_2$(i-mnt) in DMF even at a much elevated temperature due to its weak reactivity.

(12) Only bilateral core-expanded naphthalene dianhydride **6** was detected by mass spectrometry (Figure S1) during the S$_N$Ar reaction; the unilateral core-expanded compound **5** was not detected probably due to its much higher reactivity with Na$_2$(i-mnt) than **2**.

(13) (a) Zheng, Q.; Huang, J.; Sarjeant, A.; Katz, H. E. *J. Am. Chem. Soc.* **2008**, *130*, 14410. (b) Tambara, K.; Ponnuswamy, N.; Hennrich, G.; Pantos, G. D. *J. Org. Chem.* **2011**, *76*, 3338. (c) Yuan, Z.; Li, J.; Xiao, Y.; Li, Z.; Qian, X. *J. Org. Chem.* **2010**, *75*, 3007.

(14) (a) Jones, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 15259. (b) Usta, H.; Facchetti, A.; Marks, T. J. *Acc. Chem. Res.* **2011**, *44*, 501.

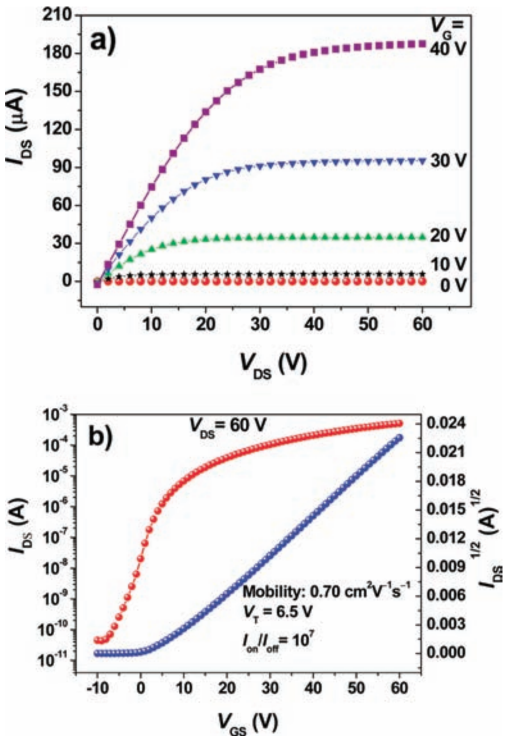


Figure 1. Output and transfer characteristics of an OTFT device based on **1i** (a, b), spin coated on OTS-treated SiO_2/Si substrate and annealed at 190 °C.

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 SiO_2/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 cm^2 V^{-1} s^{-1}, a threshold voltage of 13 V, and a current on/off ratio of 10^6 (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 cm^2 V^{-1} s^{-1}, with a threshold voltage of 7 V and a current on/off ratio of 10^7. 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 S_NAr 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 cm^2 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.

Acknowledgment. This work was supported by NSFC (20902105, 51173200, 60901050 and 61171055), MOST (2011CB932300), Shanghai Rising-Star Program (11QA 1408100), and Chinese Academy of Sciences. We thank Prof. S. M. Ma, Prof. S. L. You, and Prof. R. Hong at SIOC for helpful discussions.

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.