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Synthesis and Properties of Naphthobisbenzothiophene Diimides

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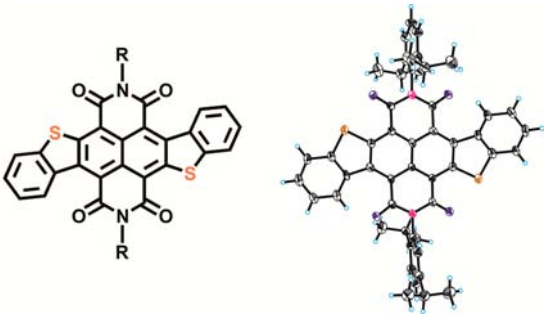
ABSTRACT



Laterally extended naphthalene diimides composed of naphthobisbenzothiophene skeleton and two imide groups were synthesized, which exhibit interesting packing arrangements and optoelectrical properties.

Over the past decade, the design and synthesis of polycyclic aromatic hydrocarbons (PAHs) with rigid, fused-ring structures have received a great deal of attention due to their potential application in various optoelectronic devices, such as organic field-effect transistors (OFETs), light-emitting diodes (LEDs), and organic photovoltaics (OPVs).[1] Among all the one-dimensional organic π-conjugated materials, oligoacenes, particularly pentacene and their derivatives, are of great interest owing to their exceptional optical and electrochemical properties and have been considered as the benchmark materials for OFETs due to their appropriate molecular arrangement in the solid state, which is decisive for efficient charge-carrier transport.[2] However, the linear expansion of the acene system will lead to a high highest occupied molecular orbital (HOMO). Pentacene and higher acenes usually exhibit poor stability in ambient conditions.[3] To improve the stability of acenes, the introduction of sulfur atoms into the aromatic system is considered one of the most effective strategies.[4]

Linearly thiophene-fused heteroarenes, in particular, acenebisbenzothiophenes (**1**, Figure 1) have been attracting a great deal of interest because of their ability to not

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(1) (a) Li, C.; Liu, M.; Pschirer, N. G.; Baumgarten, M.; Müllen, K. *Chem. Rev.* **2010**, *110*, 6817. (b) Figueira-Duarte, T. M.; Müllen, K. *Chem. Rev.* **2011**, *111*, 7260. (c) Gsänger, M.; Oh, J. H.; Könemann, M.; Höffken, H. W.; Krause, A.-M.; Bao, Z.; Würthner, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 740. (d) Schmidt, R.; Oh, J. H.; Sun, Y.-S.; Deppisch, M.; Krause, A.-M.; Radacki, K.; Braunschweig, H.; Könemann, M.; Erk, P.; Bao, Z.; Würthner, F. *J. Am. Chem. Soc.* **2009**, *131*, 6215. (e) Cao, X.-Y.; Zhang, W.-B.; Wang, J.-L.; Zhou, X.-H.; Lu, H.; Pei, J. *J. Am. Chem. Soc.* **2003**, *125*, 12430. (f) Luo, J.; Zhou, Y.; Niu, Z.-Q.; Zhou, Q.-F.; Ma, Y.; Pei, J. *J. Am. Chem. Soc.* **2007**, *129*, 11314. (g) Mao, J.; He, N.; Ning, Z.; Zhang, Q.; Guo, F.; Chen, L.; Wu, W.; Hua, J.; Tian, H. *Angew. Chem., Int. Ed.* **2012**, *51*, 9873. (h) Cho, D. M.; Parkin, S. R.; Watson, M. D. *Org. Lett.* **2005**, *7*, 1067.

(2) (a) Lin, Y.-Y.; Gundlach, D. J.; Nelson, S. F.; Jackson, T. N. *IEEE Electron Device Lett.* **1997**, *18*, 606. (b) Klauk, H.; Halik, M.; Zschieschang, U.; Schmid, G.; Radlik, W.; Weber, W. *J. Appl. Phys.* **2002**, *92*, 5259. (c) Holmes, D.; Kumaraswamy, S.; Matzger, A. J.; Vollhardt, K. P. C. *Chem.—Eur. J.* **1999**, *5*, 3399.

(3) (a) Pannemann, C.; Diekmann, T.; Hilleringmann, U. *J. Mater. Res.* **2004**, *19*, 1999. (b) Maliakal, A.; Raghavachari, K.; Katz, H.; Chandross, E.; Siegrist, T. *Chem. Mater.* **2004**, *16*, 4980.

(4) (a) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891. (b) Minemawari, H.; Yamada, T.; Matsui, H.; Tsutsumi, J.; Haas, S.; Chiba, R.; Kumai, R.; Hasegawa, T. *Nature* **2011**, *475*, 364. (c) Takimiya, K.; Shinamura, S.; Osaka, I.; Miyazaki, E. *Adv. Mater.* **2011**, *23*, 4347. (d) Shinamura, S.; Osaka, I.; Miyazaki, E.; Nakao, A.; Yamagishi, M.; Takeya, J.; Takimiya, K. *J. Am. Chem. Soc.* **2011**, *133*, 5024. (e) Mamada, M.; Minamiki, T.; Katagiri, H.; Tokito, S. *Org. Lett.* **2012**, *14*, 4062.

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only successfully lower the HOMO levels together with higher air stability compared to pentacene but also preserve the close crystal packing arrangements similar to that of pentacene showing promising semiconducting properties.[5] For example, benzo[1,2-*b*:4,5-*b*′]bis[*b*]benzothiophene, which is an analogue of pentacene, has a herringbone π-stacking motif in which the plane-to-plane distance is ca. 3.52 Å,[6] whereas highly fluorinated benzobisbenzothiophenes exhibit a brickstone arrangement with an average face-to-face distance of 3.34 Å.[7] Naphthobisbenzothiophene and *i*-Pr_3Si-substituted anthrabisbenzothiophene show highly ordered herringbone and brickstone structures in single crystals, respectively. Field effect transistors based on the anthrabisbenzothiophene derivatives also exhibit high charge-carrier mobilities.[8]

Laterally extended naphthalene tetracarboxylic diimides (NDIs), especially heterocyclic naphthalene diimides, have recently gained great attention due to their easily tunable optical and electrical properties and potential application as high performance organic semiconductors. For example, core-expanded NDIs fused with 2-(1,3-dithiol-2-ylidene)malonitrile groups exhibit excellent ambient stability and high electron mobilities,[9] whereas NDIs fused with indole rings show ambipolar transport properties with a large hole mobility.[10]

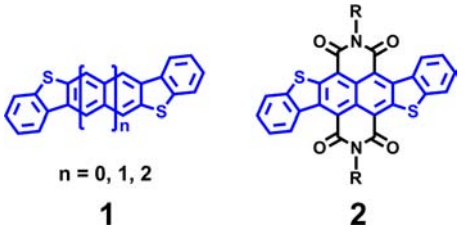
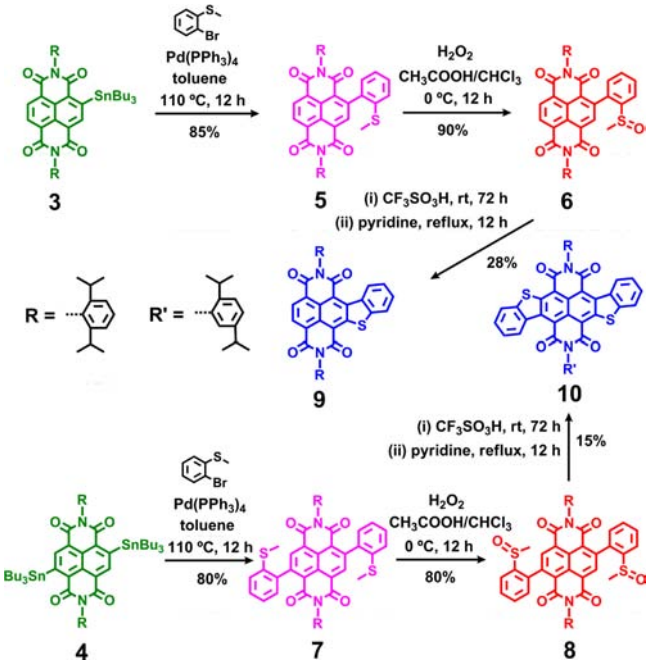


Figure 1. Acenebisbenzothiophenes (**1**) and laterally extended naphthalene diimides (**2**).

We are particularly interested in the design and synthesis of novel laterally extended naphthalene diimides with unique optical and electrical poperties and supramolecular self-assembly behavior. In previous work, we reported a facile one-pot synthesis of tetracene tetracarboxylic diimides based on the direct double ring extension of electron-dificient NDIs involving metallacyclopentadienes, which displays NIR absorption spectra and lower LUMO levels than those of NDIs and is a promising candidate for n-type semiconductors.[11] Quite recently, we also reported the effective synthesis of a series of six-membered heterocyclic acene diimides conducted by the condensation of *o*-phenylenediamine, 1,2-benzenedithiol, and 2-aminothiophenol with 4Br-NDI, which turned NDIs from potential n-type materials to promising p-type semiconductors.[12] Herein, we designed and synthesized novel laterally extended naphthalene diimides (**2**, Figure 1), the structures of which are composed of the naphthobisbenzothiophene skeleton and two imide groups. We also elucidate the molecular packing arrangement in single crystals and their unique optical and electrochemical properties.

Scheme 1. Synthesis of Laterally Extended Naphthalene Diimides



The synthesis of laterally extended naphthalene diimides **2** is shown in Scheme 1, and a monolaterally extended NDI composed of naphthobenzothiophene skeleton and two imides was also synthesized for comparison. The key starting materials 2-stannyl and 2,6-distannyl NDIs (**3** and **4**) were prepared according to a known procedure.[13] When 2-bromothioanisole was added to a toluene solution containing compound **3** in the presence of $Pd(PPh_3)_4$ and reacted at 110 °C for 12 h, compound **5** was obtained in high yield. Analogously, compound **7** was prepared via

(5) (a) Zhou, Y.; Liu, W.-J.; Ma, Y.; Wang, H.; Qi, L.; Cao, Y.; Wang, J.; Pei, J. *J. Am. Chem. Soc.* **2007**, *129*, 12386. (b) Gao, P.; Beckmann, D.; Tsao, H. N.; Feng, X.; Enkelmann, V.; Pisula, W.; Müllen, K. *Chem. Commun.* **2008**, *44*, 1548. (c) Gao, P.; Beckmann, D.; Tsao, H. N.; Feng, X.; Enkelmann, V.; Baumgarten, M.; Pisula, W.; Müllen, K. *Adv. Mater.* **2009**, *21*, 213.

(6) Ebata, H.; Miyazaki, E.; Yamamoto, T.; Takimiya, K. *Org. Lett.* **2007**, *9*, 4499.

(7) Wang, Y.; Parkin, S. R.; Gierschner, J.; Watson, M. D. *Org. Lett.* **2008**, *10*, 3307.

(8) (a) Yamamoto, K.; Katagiri, H.; Tairabune, H.; Yamaguchi, Y.; Pu, Y.-J.; Nakayama, K.-I.; Ohba, Y. *Tetrahedron Lett.* **2012**, *53*, 1786. (b) Lehnherr, D.; Hallani, R.; McDonald, R.; Anthony, J. E.; Tykwinski, R. R. *Org. Lett.* **2012**, *14*, 62.

(9) (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) 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) Suraru, S.-L.; Zschieschang, U.; Klauk, H.; Würthner, F. *Chem. Commun.* **2011**, *47*, 11504.

(11) Yue, W.; Gao, J.; Li, Y.; Jiang, W.; Di Motta, S.; Negri, F.; Wang, Z. *J. Am. Chem. Soc.* **2011**, *133*, 18054.

(12) Li, C.; Xiao, C.; Li, Y.; Wang, Z. *Org. Lett.* **2013**, *15*, 682.

(13) Polander, L. E.; Romanov, A. S.; Barlow, S.; Hwang, D. K.; Kippelen, B.; Timofeeva, T. V.; Marder, S. R. *Org. Lett.* **2012**, *14*, 918.

Stille coupling between 2-bromothioanisole and compound **4**. Oxidation of **5** and **7** with hydrogen peroxide in a solution mixture of glacial acetic acid and chloroform (1:1) gave intermediate compounds **6** and **8**, respectively, both of which had poor stability in ambient conditions. Finally, the intramolecular ring closures of **6** and **8** were performed with trifluoromethanesulfonic acid in the presence of phosphorus pentoxide and reacted at room temperature for 72 h in the dark. The as-formed mixture was poured into ice/water followed by filtration, drying, and reflux in pyridine for 12 h. It should be noted that, in the solvent trifluoromethanesulfonic acid, the migration of alkyl groups around an aromatic ring usually occurs.[14] After the intramolecular ring-closure reaction, it was found that laterally extended NDIs had isomers. So we speculated that also 2,6-diisopropylbenzene groups may undergo a transalkylation reaction during the final ring-closure process. To verify our speculation, the regioisomerically pure compounds **9** and **10**, which are the main products and have good stability due to the introduction of two strong electron-withdrawing groups, were gained after purification by silica column chromatography and characterized by ^{1}H, ^{13}C NMR spectroscopy and HRMS. It was found that two sets of signals with the same integration in the ^{1}H NMR of **9** were observed in the region 3.0−2.7 ppm which was assigned to the protons of $-C\mathbf{H}(CH_3)_2$ in diisopropylphenyl groups, whereas two sets of signals with the integration of 1:3 in the same region together with unsymmetrical signals in the aromatic region were observed in the ^{1}H NMR of **10** (Supporting Information). So we speculated the migration of isopropyl groups in compound **10**.

To further confirm the structures of compounds **9** and **10** and study their arrangements in the solid state, attention was focused toward single-crystal growth. Crystals suitable for single-crystal X-ray analysis were obtained by slow evaporation of the dichloromethane/methanol solution of **9** and **10**, respectively, and the molecular structures and crystal packing arrangements are depicted in Figure 2. Four molecules of **9** and two molecules of **10** were found in the unit cell, respectively. As can be seen from Figure 2a, monolaterally extended NDI **9** has a slightly twisted skeleton. The torsional angle between the benzothiophene part and naphthalene plane is ~10.7°. The crystal packing arrangement of **9** is shown in Figure 2c, which reveals that the introduction of two strong electron-withdrawing imide groups to the thiophene-fused aromatics could cause the naphthobenzothiophene diimides to retain a herringbone-like arrangement along the *b*-axis, though the plane-to-plane distance is relatively large due to the steric encumbrance effect of diisopropylbenzene groups.

From Figure 2b we can see that laterally extended NDI **10** exhibits the migration of one isopropyl group which is

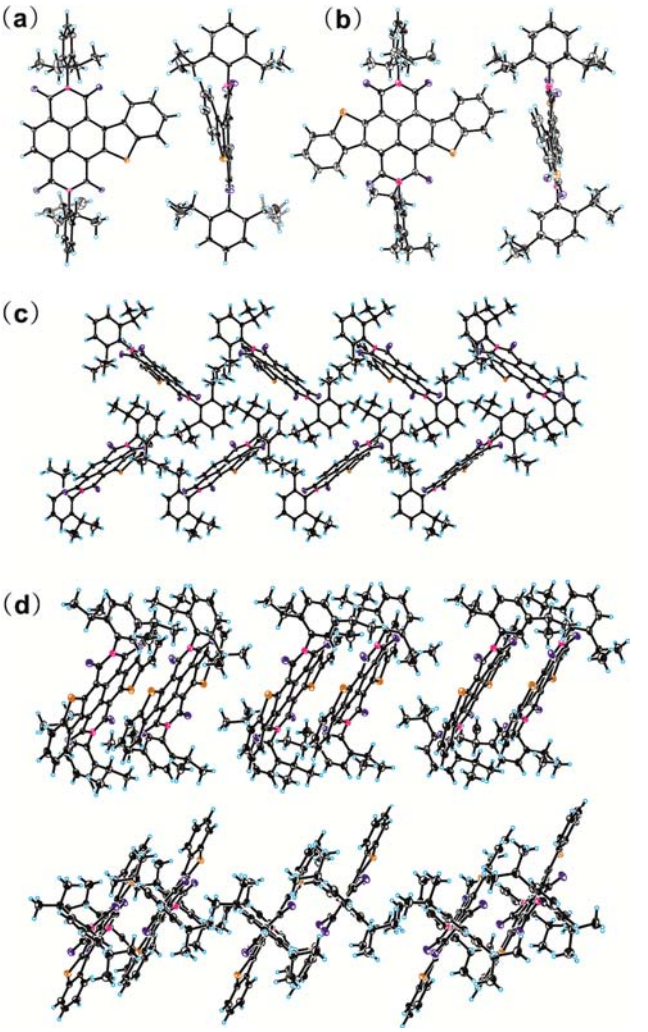


Figure 2. X-ray crystallographic structures of **9** (a) and **10** (b). Crystal packing of **9** (c) and **10** (d, side view and top view).

coincident with our conjecture based on the phenomenon in experiment and ^{1}H NMR. The introduction of two imide groups also makes the naphthobisbenzothiophene skeleton twist slightly. The unsymmetrical torsional angles between the benzothiophene part and naphthalene plane are approximately 15.1° and 6.8°. The crystal packing arrangement of **10** is shown in Figure 2d. Due to the strong $\pi-\pi$ interaction between the naphthobisbenzothiophene skeleton and the steric encumbrance effect of diisopropylbenzene groups, the molecules are arranged in stacks along the *b*-axis, in which dimers are packed tightly with a plane-to-plane distance of ca. 3.4 Å.

Figure 3 shows the comparison between the absorption and emission spectra of laterally extended NDIs **9** and **10** in $CHCl_3$, both of which have good solubility in common organic solvents. Compared with NDI (*N,N′*-di(2,6-diisopropylphenyl)-naphthalene-1,4,5,8-tetracarboxylic acid diimide),[15]

(14) (a) Roberts, R. M. G. *J. Org. Chem.* **1982**, *47*, 4050. (b) Bakoss, H. J.; Roberts, R. M. G.; Sadri, A. R. *J. Org. Chem.* **1982**, *47*, 4053. (c) Olah, G. A.; Farooq, O.; Farnia, S. M. F.; Olah, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 2560. (d) Sherman, S. C.; Iretskii, A. V.; White, M. G.; Gumienny, C.; Tolbert, L. M.; Schiraldi, D. A. *J. Org. Chem.* **2002**, *67*, 2034. (e) Ajaz, A.; McLaughlin, E. C.; Skraba, S. L.; Thamatam, R.; Johnson, R. P. *J. Org. Chem.* **2012**, *77*, 9487. (f) Lee, P. H.; Kang, D.; Choi, S.; Kim, S. *Org. Lett.* **2011**, *13*, 3470.

(15) Yue, W.; Zhen, Y.; Li, Y.; Jiang, W.; Lv, A.; Wang, Z. *Org. Lett.* **2010**, *12*, 3460.

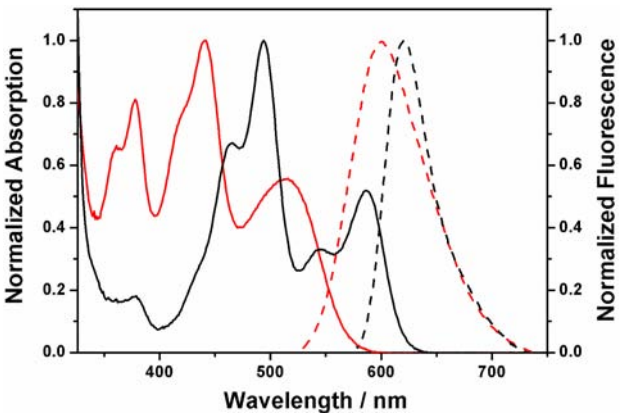


Figure 3. UV/vis absorption and emission spectra of **9** (red) and **10** (black) in $CHCl_3$ (10^{-5} M) at room temperature.

9 and **10** exhibit broad and bathochromic-shifted absorption. Compound **9** shows three major absorption bands in the 350−600 nm range with maxima at 378, 441, and 516 nm, whereas compound **10** has two absorption bands in the 400−650 nm range with maxima at 494 and 586 nm. Both of these compounds have weak fluorescence with maxima at 600 nm for **9** and 622 nm for **10**, corresponding to Stokes shifts of 84 and 36 nm, respectively.

The electrochemical properties of NDI, **9**, and **10** were also investigated by cyclic voltammetry against the potential of the ferrocene/ferrocenium redox couple in CH_2Cl_2 (Figure S2), and the reduction potentials and energy levels are shown in Table 1. Compounds **9** and **10** exhibit two reversible reduction waves, whereas within the accessible scanning range no oxidation waves could be detected. The first half-wave reduction waves for **9** and **10** are observed at −0.94 V, and −0.85 V vs Fc/Fc^+, respectively, both of which have stronger electron-accepting ability than NDI. Meanwhile, compounds **9** and **10** have lower LUMO levels indicating their potential applications as n-type organic semiconductors.

Table 1. Summary of Electrochemical Properties of Laterally Extended Naphthalene Diimides

	E_{1r}[a] (V)	E_{2r}[a] (V)	LUMO[b] (eV)	E_g[c] (eV)
NDI[d]	−1.04	−1.60	−3.98	3.02
9	−0.94	−1.44	−4.04	2.12
10	−0.85	−1.27	−4.14	1.96

[a] Half-wave reduction potentials (vs Fc/Fc^+) measured in CH_2Cl_2 at a scan rate of 0.1 V/s. The plot includes the signal of the ferrocene standard with its oxidation potential at 0.47 V. [b] Estimated from the onset potential of the first reduction wave with the onset potential of the ferrocene standard at 0.38 V. [c] Obtained from the edge of the absorption spectra. [d] NDI: *N,N′*-di(2,6-diisopropylphenyl)-naphthalene-1,4,5,8-tetracarboxylic acid diimide.

In summary, we report novel laterally extended naphthalene diimides composed of a fully conjugated naphthobisbenzothiophene or naphthobenzothiophene skeleton and two imide groups. Single-crystal X-ray analysis reveals that the molecules have a herringbone-like or dimeric stack arrangement despite the steric encumbrance effect of the imide groups. In light of the interesting packing arrangements and optoelectrical properties, these laterally extended NDIs are promising for use as n-type organic semiconductors. Further studies of the laterally extended NDIs bearing different substituents and applications in electronic devices are currently underway.

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Supporting Information Available. Experimental details and characterization of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.