

# Synthesis and Properties of Heterocyclic Acene Diimides

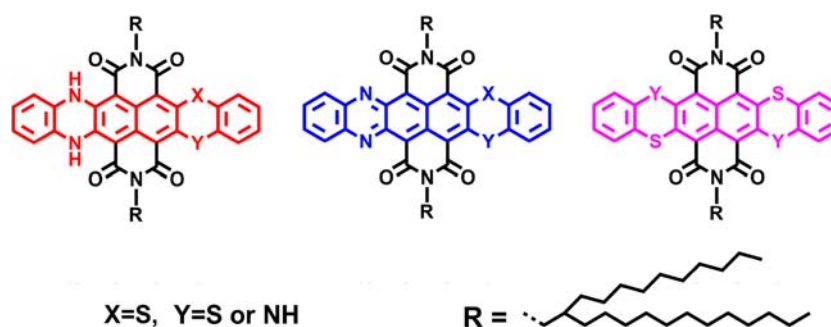
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## ABSTRACT



A series of heterocyclic acene diimides were synthesized effectively based on the condensation of *o*-phenylenediamine, 1,2-benzenedithiol, and 2-aminothiophenol with 2,3,6,7-tetrabromo-1,4,5,8-naphthalene tetracarboxylic diimide. The diimides exhibit interesting optical and electrical properties with one of them showing a hole mobility up to  $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

In recent years, naphthalene tetracarboxylic diimides (NDIs, **1**, Figure 1) and their core-expanded derivatives have attracted a great deal of attention due to their interesting electro-optical properties and potential applications as organic semiconductors in organic electronics.<sup>1</sup> The  $\pi$ -skeleton of NDIs could be expanded along two directions: the *peri* position (1, 4, 5, 8) and the *lateral* position (2, 3, 6, 7). The expansion of the  $\pi$ -system along the *peri* position has been studied for many decades because it induces impressive bathochromic shifts and

has been applied as high-performance solution-deposited ambipolar organic transistors.<sup>2</sup> In contrast, the expansion of the  $\pi$ -system along the *lateral* position of NDIs has been demonstrated only recently due to the synthetic difficulties. Recently, the synthesis of tetracene tetracarboxylic diimides based on two methods of direct double ring extension of electron-deficient NDIs involving metal-lacyclopentadienes and bismuth-triflate-mediated double-cyclization reaction of acid chlorides and isocyanates has been reported, which displays dramatic bathochromic shifts, smaller energy band gaps, and is a promising candidate for n-type semiconductors.<sup>3</sup>

Compared with lateral-extended NDIs based on a hydrocarbon aromatic core, great attention has recently been drawn to heterocyclic acene diimides, due to the benefit of unique optical and electrical properties caused by heteroatoms and contained electron-withdrawing or electron-donating groups. For example, lateral-extended NDIs fused with sulfur heterocycles and end-capped with

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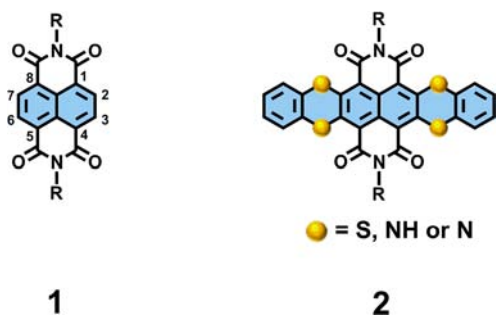
† University of Chinese Academy of Sciences.

(1) (a) Würthner, F.; Stolte, M. *Chem. Commun.* **2011**, 47, 5109. (b) Guo, X.; Kim, F. S.; Seger, M. J.; Jenekhe, S. A.; Watson, M. D. *Chem. Mater.* **2012**, 24, 1434. (c) Guo, X.; Watson, M. D. *Org. Lett.* **2008**, 10, 5333. (d) Huang, C.; Barlow, S.; Marder, S. R. *J. Org. Chem.* **2011**, 76, 2386. (e) Weil, T.; Vosch, T.; Hofkens, J.; Peneva, K.; Müllen, K. *Angew. Chem., Int. Ed.* **2010**, 49, 9068. (f) Fan, L.; Xu, Y.; Tian, H. *Tetrahedron Lett.* **2005**, 46, 4443.

(2) (a) Quante, H.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1323. (b) Holtrup, F. O.; Müller, G. R. J.; Quante, H.; Feyter, S. D.; Schryver, F. C. D.; Müllen, K. *Chem.—Eur. J.* **1997**, *3*, 219. (c) Geerts, Y.; Quante, H.; Platz, H.; Mahrt, R.; Hopmeier, M.; Böhm, A.; Müllen, K. *J. Mater. Chem.* **1998**, *8*, 2357. (d) Avlasevich, Y.; Li, C.; Müllen, K. *J. Mater. Chem.* **2010**, *20*, 3814. (e) Liu, C.; Liu, Z.; Lemke, H. T.; Tsao, H. N.; Naber, R. C. G.; Li, Y.; Banger, K.; Müllen, K.; Nielsen, M. M.; Sirringhaus, H. *Chem. Mater.* **2010**, *22*, 2120.

(3) (a) Yue, W.; Gao, J.; Li, Y.; Jiang, W.; Di Motta, S.; Negri, F.; Wang, Z. *J. Am. Chem. Soc.* **2011**, *133*, 18054. (b) Katsuta, S.; Tanaka, K.; Maruya, Y.; Mori, S.; Masuo, S.; Okujima, T.; Uno, H.; Nakayama, K.; Yamada, H. *Chem. Commun.* **2011**, *47*, 10112. (c) Mohebbi, A. R.; Munoz, C.; Wudl, F. *Org. Lett.* **2011**, *13*, 2560.

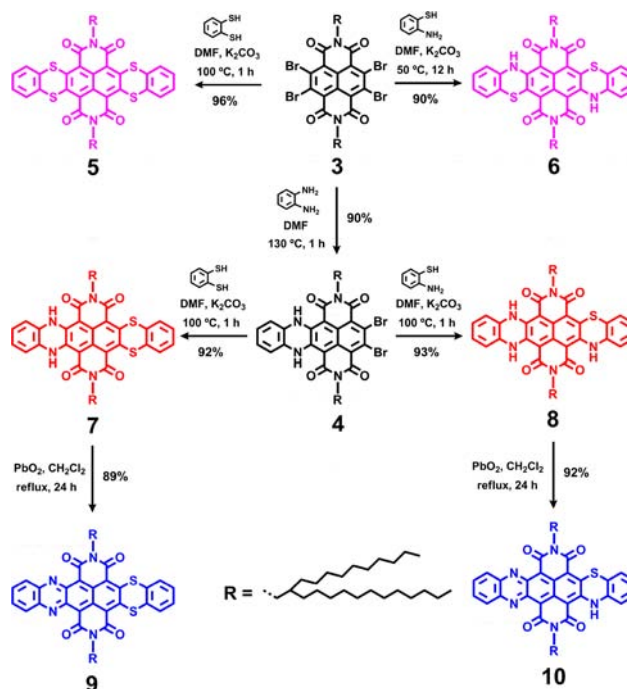
electron-withdrawing groups usually exhibit excellent ambient stability and high electron mobilities,<sup>4</sup> whereas the lateral expansion on both sides of the NDI core by fusion with highly electron-rich carbazole rings leads to ambipolar semiconductors.<sup>5</sup> When NDIs were laterally extended with imidazole rings, they provide colored and highly fluorescent materials, and the pyrrole-like annulated NDI compound derived from NDI and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is a novel pH-controlled fluorescence switch.<sup>6</sup> Until now, naphthalene diimides fused with five-membered heterocycles have gained great progress in the synthesis and application as organic semiconductors; however, NDIs coupled with six-membered heterocycles are less explored. Recently, the self-assembly of six-membered one-sided heterocyclic acene diimides prepared by reacting the tetrabromo-NDI with *ortho*-amines was reported.<sup>7</sup> The tautomerism of dihydro- and tetrahydrotetraazaacene diimides containing six or seven laterally fused six-membered rings was also explored.<sup>8</sup> However, the electro-optical properties and potential applications as organic semiconductors of six-membered heterocyclic acene diimides linked or annulated by the mixture of sulfur, nitrogen, and hydronitrogen bridges are rarely reported.



**Figure 1.** Naphthalene diimides (**1**) and heterocyclic acene diimides (**2**).

We are particularly interested in the design and synthesis of heterocyclic rylene dyes which have unique optoelectronic properties and supramolecular self-assembly behavior. In previous work, we reported the facile synthesis of a novel perylene diimide that is S-heterocyclic annulated in two bay regions, which easily converts an extremely

**Scheme 1.** Synthesis of Heterocyclic Acene Diimides



twisted precursor molecule to a planar product.<sup>9</sup> Meanwhile, we also reported the synthesis of S- and N-heterocyclic annulated di(erylene diimide) by Stille-type and Buchwald–Hartwig reactions, respectively, both of which have extraordinary doubly bowl-shaped structures.<sup>10</sup> Recently, we successfully introduced S-, Se-, and N-atoms to the bay region of perylenes and found that the integration of S- and Se-heteroatom induced an extraordinary solid-state packing arrangement with high hole mobilities,<sup>11</sup> whereas the introduction of the N-heteroatom provided active sites in the *peri* position of perylenes to build higher homologues.<sup>12</sup>

Inspired by the previous work, herein, we designed and synthesized a series of six-membered heterocyclic acene diimides linked or annulated by the mixture of S-, N-, and NH-atoms (**2**, Figure 1) through the condensation of *o*-phenylenediamine, 1,2-benzenedithiol, and 2-aminothiophenol with tetrabromo-NDI. The introduction of heteroatoms to the lateral position of NDIs made the optical

(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. (c) 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.

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

(6) (a) Langhals, H.; Kinzel, S. *J. Org. Chem.* **2010**, *75*, 7781. (b) Zhou, C.; Li, Y.; Zhao, Y.; Zhang, J.; Yang, W.; Li, Y. *Org. Lett.* **2011**, *13*, 292.

(7) (a) Bhosale, S. V.; Jani, C.; Lalander, C. H.; Langford, S. J. *Chem. Commun.* **2010**, *46*, 973. (b) Bhosale, S. V.; Jani, C. H.; Lalander, C. H.; Langford, S. J.; Nerush, I.; Shapter, J. G.; Villamaina, D.; Vauthey, E. *Chem. Commun.* **2011**, *47*, 8226.

(8) Cai, K.; Yan, Q.; Zhao, D. *Chem. Sci.* **2012**, *3*, 3175.

(9) Qian, H.; Liu, C.; Wang, Z.; Zhu, D. *Chem. Commun.* **2006**, *42*, 4587.

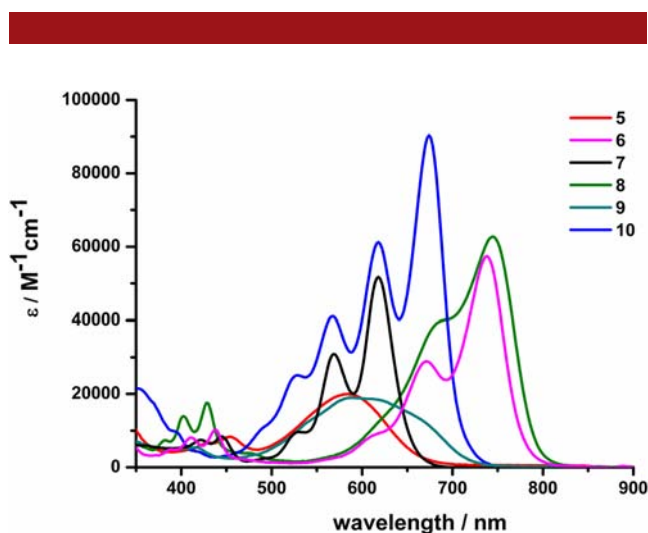
(10) Qian, H.; Yue, W.; Zhen, Y.; Di Motta, S.; Di Donato, E.; Negri, F.; Qu, J.; Xu, W.; Zhu, D.; Wang, Z. *J. Org. Chem.* **2009**, *74*, 6275.

(11) (a) Jiang, W.; Qian, H.; Li, Y.; Wang, Z. *J. Org. Chem.* **2008**, *73*, 7369. (b) Sun, Y.; Tan, L.; Jiang, S.; Qian, H.; Wang, Z.; Yan, D.; Di, C.; Wang, Y.; Wu, W.; Yu, G.; Yan, S.; Wang, C.; Hu, W.; Liu, Y.; Zhu, D. *J. Am. Chem. Soc.* **2007**, *129*, 1882. (c) Tan, L.; Jiang, W.; Jiang, L.; Jiang, S.; Wang, Z.; Yan, S.; Hu, W. *Appl. Phys. Lett.* **2009**, *94*, 153306. (d) Jiang, S.; Qian, H.; Liu, W.; Wang, C.; Wang, Z.; Yan, S.; Zhu, D. *Macromolecules* **2009**, *42*, 9321. (e) Jiang, W.; Zhou, Y.; Geng, H.; Jiang, S.; Yan, S.; Hu, W.; Wang, Z.; Shuai, Z.; Pei, J. *J. Am. Chem. Soc.* **2011**, *133*, 1.

(12) (a) Li, Y.; Wang, Z. *Org. Lett.* **2009**, *11*, 1385. (b) Li, Y.; Gao, J.; Di Motta, S.; Negri, F.; Wang, Z. *J. Am. Chem. Soc.* **2010**, *132*, 4208. (c) Li, Y.; Hao, L.; Fu, H.; Pisula, W.; Feng, X.; Wang, Z. *Chem. Commun.* **2011**, *47*, 10088.

and electrical properties change greatly and turned NDIs from potential n-type materials to promising p-type semiconductors.

The synthesis of heterocyclic acene diimides is shown in Scheme 1. The starting material 2,3,6,7-tetrabromo-1,4,5,8-naphthalene tetracarboxylic diimide **3** (4Br-NDI) was prepared according to a known procedure.<sup>13</sup> When 1,2-benzenedithiol was added to *N,N*-dimethylformamide (DMF) solution containing 4Br-NDI in the presence of K<sub>2</sub>CO<sub>3</sub> and reacted at 100 °C for 1 h, compound **5** was obtained in high yield. Analogously, compound **6** was prepared by reacting 2-aminothiophenol with 4Br-NDI. It should be noted that regioisomerically pure compound **6** could be obtained in high yield at 50 °C as evidenced by <sup>1</sup>H NMR, the chemical structure of which could be confirmed by reported references.<sup>14</sup> However, when *o*-phenylenediamine was reacted with 4Br-NDI in DMF, one-sided concentrated product **4** instead of the two-side one was obtained in 90% yield and even prolonged the reaction time from 1 h to 2 days with more *o*-phenylenediamine. The two remaining bromine atoms of compound **4** are very important to the construction of unsymmetrical heterocyclic acene diimides. When compound **4** was reacted with 1,2-benzenedithiol and 2-aminothiophenol, respectively, compounds **7** and **8** were obtained in high yield. To study the difference between heteroatoms linked and annulated NDIs, compounds **6**, **7**, and **8** were further oxidized with PbO<sub>2</sub>. It was found that compound **6** was very hard to oxidize even in CHCl<sub>3</sub> and reflux for 1 day, whereas oxidation of compound **7** was accomplished smoothly at room temperature in CH<sub>2</sub>Cl<sub>2</sub>, and product **9** had a very good stability even when exposed to silica gel during column chromatography. What is interesting is that the two NH-atoms in the same lateral position of compound **8** were fully oxidized while the other NH-atom remained, and compound **10** still had good stability in air.



**Figure 2.** UV/vis absorption spectra of heterocyclic acene diimides **5** (red), **6** (magenta), **7** (black), **8** (olive), **9** (dark cyan), and **10** (blue) in CH<sub>2</sub>Cl<sub>2</sub> (1 × 10<sup>−5</sup> M) at room temperature.

**Table 1.** Summary of Electrochemical Properties of Heterocyclic Acene Diimides

	$E_{1r}^a$	$E_{1o}$	LUMO <sup>b</sup>	HOMO <sup>c</sup>	$E_g^d$
NDI <sup>e</sup>	−0.63		−3.90	−7.02 <sup>f</sup>	3.12 <sup>g</sup>
<b>5</b>	−0.54		−3.95	−5.72 <sup>f</sup>	1.77 <sup>g</sup>
<b>6</b>	−0.93	0.63	−3.56	−4.98	1.42
<b>7</b>	−1.00	0.88	−3.52	−5.23	1.71
<b>8</b>	−1.12	0.40	−3.39	−4.74	1.35
<b>9</b>	−0.12		−4.38	−6.04 <sup>f</sup>	1.66 <sup>g</sup>

<sup>a</sup> Half-wave reductive potentials (in V vs Ag/AgCl) measured in CH<sub>2</sub>Cl<sub>2</sub> at a scan rate of 0.1 V/s with ferrocene as an external potential marker. <sup>b</sup> Estimated from the onset potential of the first reduction wave (eV). <sup>c</sup> Estimated from the onset potential of the first oxidation wave (eV). <sup>d</sup> Estimated from LUMO and HOMO levels (eV). <sup>e</sup> NDI: *N,N*-di-*n*-octylnaphthalene-1,4,5,8-tetracarboxylic acid diimide. <sup>f</sup> Estimated from LUMO levels and  $E_g$  (eV). <sup>g</sup> Obtained from the edge of the absorption spectra (eV).

All of the heterocyclic acene diimides have good solubility in common organic solvents such as dichloromethane, chloroform, and toluene. Room temperature absorption spectra of compounds **5**–**10** in CH<sub>2</sub>Cl<sub>2</sub> are shown in Figure 2. The absorption spectra of heterocyclic acene diimides **5**–**10**, especially compounds **6** and **8**, display significant bathochromic shifts compared to that of parent NDI (*N,N*-di-*n*-octylnaphthalene-1,4,5,8-tetracarboxylic acid diimide), suggesting the possible application as NIR dyes.<sup>15</sup> Compounds **5** and **9** exhibit broad absorption with low absorptivity ( $\epsilon_{\max}$  is about 20 000 M<sup>−1</sup> cm<sup>−1</sup>) over much of the visible region, whereas others having one or more NH bridges show relatively well-defined vibronic structures of the absorption bands with high absorptivity. Compound **7** shows three major bands in the 500–700 nm range with low-energy maxima at 618 nm. Compound **10** shows four major bands in the 500–700 nm range with low-energy maxima at 674 nm, which has the highest absorptivity ( $\epsilon_{\max}$  is about 90 000 M<sup>−1</sup> cm<sup>−1</sup>). Compounds **6** and **8** have the largest bathochromic shifts of about 360 nm relative to that of NDI with low-energy maxima at about 740 nm. Fluorescence spectra of compounds **5**–**10** are also exhibited in Figure S1 (Supporting Information). Compounds **5** and **7** show high fluorescence in dichloromethane solution with maxima at 698 nm for **5** and 680 nm for **7**. However, compound **9** produced by oxidative dehydrogenation of **7** has no fluorescence, maybe caused by

(13) 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.

(14) (a) Heda, L.; Pareek, C.; Pareek, D.; Mosalpuri, S. *Cent. Eur. J. Chem.* **2010**, *8*, 51. (b) Kistenmacher, A.; Adam, M.; Baumgarten, M.; Pawlik, J.; Räder, H.; Müllen, K. *Chem. Ber.* **1992**, *125*, 1495. (c) Nishi, H.; Hatada, Y.; Kitahara, K. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1482. (d) Nishi, H.; Minami, S.; Kitahara, K. *J. Heterocycl. Chem.* **1989**, *26*, 875. (e) Andreani, F.; Bizzarri, P. C.; Casa, C. D.; Fiorini, M.; Salattelli, E. *J. Heterocycl. Chem.* **1991**, *28*, 295. (f) Boros, E. E.; Harfenist, M. *J. Org. Chem.* **1998**, *63*, 10045. (g) Dalton, L. R.; Sapochak, L. S.; Yu, L. *J. Phys. Chem.* **1993**, *97*, 2871.

(15) (a) Pschirer, N. G.; Kohl, C.; Nolde, F.; Qu, J.; Müllen, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 1401. (b) Avlasevich, Y.; Müllen, K. *J. Org. Chem.* **2007**, *72*, 10243. (c) Lin, M.; Fimmel, B.; Radacki, K.; Würthner, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 10847.

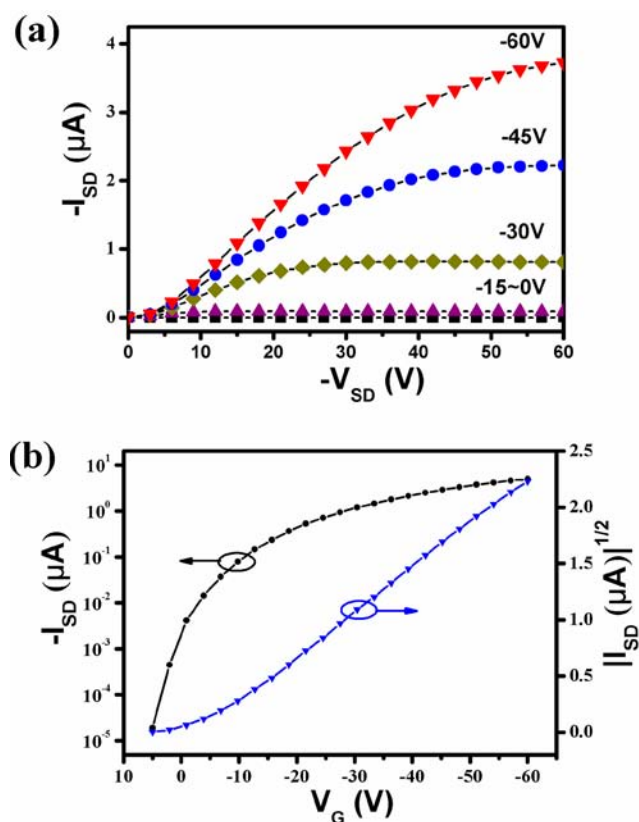


the intramolecular electron-donating and electron-withdrawing groups. Compounds **6**, **8**, and **10** have relatively weak fluorescence with maxima at 780 nm for **6**, 792 nm for **8**, and 708 nm for **10**.

The electrochemical properties of these heterocyclic acene diimides are also investigated by cyclic voltammetry in dichloromethane (vs Ag/AgCl) and summarized in Table 1. The heterocyclic annulated compounds **5** and **9** exhibit two reversible reduction waves, whereas within the accessible scanning range no oxidation waves could be detected. The first and second reduction waves for **5** and **9** are observed at  $-0.54$ ,  $-0.87$  V, and  $-0.12$ ,  $-0.49$  V vs Ag/AgCl, respectively, which implies a stronger electron-accepting ability. On the contrary, compounds **6**, **7**, and **8** show not only two reversible reduction waves ( $-0.93$ ,  $-1.15$  V for **6**,  $-1.00$ ,  $-1.32$  V for **7**, and  $-1.12$ ,  $-1.38$  V for **8**) but also reversible oxidation waves ( $0.63$ ,  $0.77$ ,  $1.23$  V for **6**,  $0.88$ ,  $1.17$  V for **7**, and  $0.40$ ,  $0.62$ ,  $1.02$  V for **8**), indicating that the introduction of NH bridges into the *lateral* position of NDIs makes them potential electron-donor materials. The CVs of compound **10** did not provide well-defined reversible or quasi-reversible reduction and oxidation peaks. From the energy levels, we can also see that the heterocyclic acene diimides have a much smaller band gap ( $E_g$ ) than that of NDI, and the HOMO levels go up to  $-4.7$  to  $-6.0$  eV, implying that it is easier for the hole to be injected and transported.

To explore the viability of our concept, the semiconducting properties of the heterocyclic acene diimides in thin-film transistors (TFTs) are further investigated. Thin films of compound **6** with a thickness of 40–60 nm were spin-coated from chloroform/*n*-hexane (2:1) solution onto octadecyltrichlorosilane-treated SiO<sub>2</sub>/Si substrates. Gold electrodes with width/length of 1 mm/0.05 mm were applied on the organic thin films through a shadow mask as the source/drain electrodes. Then a bottom-gate top-contact device configuration was afforded, and all devices were tested under ambient conditions. The unannealed thin-film devices showed a low hole mobility of  $0.004 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The highest hole mobility ( $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) was achieved after annealing at  $140^\circ\text{C}$  with a threshold voltage of  $-3$  V and an on/off ratio of  $10^5$  (Figure 3). The morphology of the thin film under different temperatures was also investigated by AFM, which is a useful tool to determine the degree of crystallinity of thin-film surfaces. From Figure S3, we can see that the morphology shows larger crystallites after annealing at  $140^\circ\text{C}$  than at  $25$  and  $80^\circ\text{C}$ . However, it has very poor connectivity, and the crystallites are not large enough, which indicates that there is a lot of room for film morphology improvement.

In summary, we report the facile and 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. The introduction of different heteroatoms to the



**Figure 3.** Output (a) and transfer (b) characteristics of thin-film OFETs of compound **6** after annealing at  $140^\circ\text{C}$ .

lateral position of NDIs has great influence on the optical and electrical properties, which makes heterocyclic acene diimides exhibit drastic bathochromic-shifted absorption and remarkable energy increase of the occupied orbitals, and turns NDIs from potential n-type materials to promising p-type semiconductors. Further studies of the heterocyclic acene diimides bearing different substituents applied in electronic devices and NIR dyes are the focus of our upcoming research work.

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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.