ORGANIC
LETTERS

2011
Vol. 13, No. 11
2880–2883

Synthesis of Tetrachloro-azapentacene as an Ambipolar Organic Semiconductor with High and Balanced Carrier Mobilities

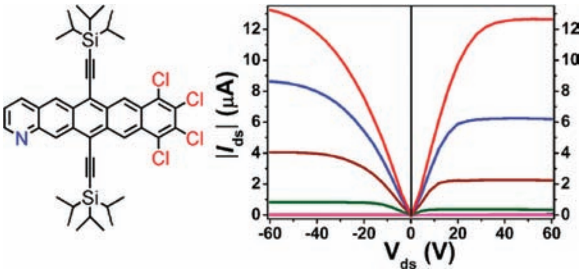
Cheng-Li Song,[†] Chong-Bo Ma,[†] Feng Yang,[†] Wei-Jing Zeng,[†] Hao-Li Zhang,*,[†] and Xiong Gong[‡]

State Key Laboratory of Applied Organic Chemistry (SKLAOC), College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, R. P. China, and Department of Polymer Engineering, College of Polymer Science and Engineering, The University of Akron, Akron, Ohio 44236, United States

haoli.zhang@lzu.edu.cn

Received April 6, 2011

ABSTRACT



Two new azapentacene derivatives 9,10-dibromo-6,13-bis(triisopropylsilylethynyl)-1-azapentacene (a) and 8,9,10,11-tetrachloro-6,13-bis-(triisopropylsilylethynyl)-1-azapentacene (b) were synthesized, and their FET properties were investigated. Compound b exhibits high and balanced ambipolar transport properties, with the hole and electron mobilities reaching up to 0.12 and 0.14 cm^2 V^{-1} s^{-1}, respectively. This work suggests that chlorination to the *N*-heteropentacene framework is an efficient way for producing high performance ambipolar organic semiconductors.

In recent years, organic ambipolar materials have attracted increasing attention for concerns from both fundamental science and device applications. They are particularly useful for making light-emitting transistors[1,2] and complementary metal oxide semiconductor (CMOS)-like logic circuits.[3,4] Since both electron and hole transports can take place within ambipolar materials,[5,6] there is no need to selectively deposit n- and p-channel materials using advanced patterning techniques; hence device fabrication can be significantly simplified. Previous efforts for making ambipolar organic field effect transistors (OFETs) centered on bilayers[7,8] or blends of small molecules and polymers,[9,10] which generally exhibited low mobilities. OFETs based on single component semiconductors have also been reported, but most of them exhibit either low or unbalanced hole and electron mobilities.[11−14]

[†] Lanzhou University.

[‡] The University of Akron.

(1) Tsuji, H.; Mitsui, C.; Sato, Y.; Nakamura, E. *Adv. Mater.* **2009**, *21*, 3776–3779.

(2) Rost, C.; Karg, S.; Riess, W. *Appl. Phys. Lett.* **2004**, *85*, 1613–1615.

(3) Zaumseil, J.; Sirringhaus, H. *Chem. Rev.* **2007**, *107*, 1296–1323.

(4) Kim, F. S.; Guo, X.; Watson, M. D.; Jenekhe, S. A. *Adv. Mater.* **2010**, *22*, 478–482.

(5) Cornil, J.; Brédas, J.-L.; Zaumseil, J.; Sirringhaus, H. *Adv. Mater.* **2007**, *19*, 1791–1799.

(6) Murphy, A. R.; Fréchet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066–1096.

(7) Wei, Q.; Tajima, K.; Hashimoto, K. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1865–1868.

(8) Ye, R. *Appl. Phys. Lett.* **2005**, *86*, 253505.

(9) Babel, A.; Wind, J. D.; Jenekhe, S. A. *Adv. Funct. Mater.* **2004**, *14*, 891–898.

(10) Shkunov, M.; Simms, R.; Heeney, M.; Tierney, S.; McCulloch, I. *Adv. Mater.* **2005**, *17*, 2608–2612.

(11) Tang, M. L.; Oh, J. H.; Reichardt, A. D.; Bao, Z. *J. Am. Chem. Soc.* **2009**, *131*, 3733–3740.

(12) Liang, Z.; Tang, Q.; Xu, J.; Miao, Q. *Adv. Mater.* **2011**, *23*, 1535–1539.

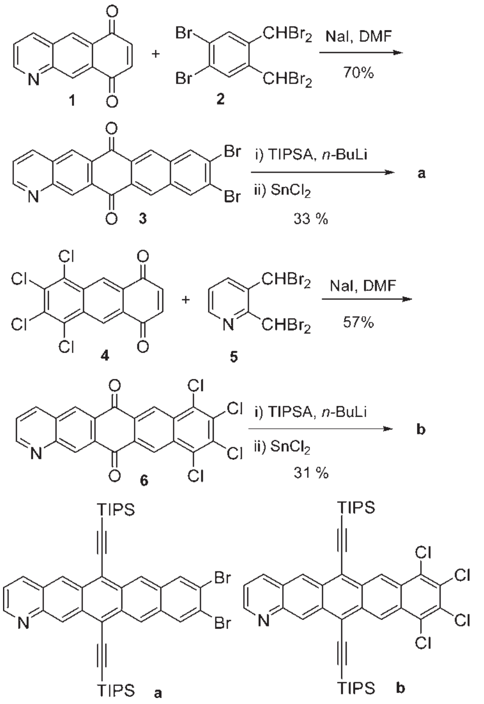
(13) Chesterfield, R. J.; Newman, C. R.; Pappenfus, T. M.; Ewbank, P. C.; Haukaas, M. H.; Mann, K. R.; Miller, L. L.; Frisbie, C. D. *Adv. Mater.* **2003**, *15*, 1278–1282.

(14) Katsuta, S.; Miyagi, D.; Yamada, H.; Okujima, T.; Mori, S.; Nakayama, K.-i.; Uno, H. *Org. Lett.* **2011**, *13*, 1454–1457.

10.1021/ol2008999

Because it is difficult to simultaneously optimize both hole and electron transport properties in the same material, the design of high performane ambipolar materials is more challenging than the design of unipolar materials. As a result, the reported carrier mobilities of ambipolar materials are generally lower than those of unipolar materials. Among the available ambipolar organic semiconductors, very few exhibit balanced carrier mobilities above 10^{-2} cm^2 V^{-1} s^{-1}.[11,14–16]

Scheme 1. Synthesis of *N*-Heteropentacenes **a** and **b**



One key issue for designing high performance ambipolar organic semiconductors is the appropriate adjustment of the molecular energy levels. In order to facilitate both hole and electron injection, both the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) need to be reasonably close to the Fermi level of the electrodes. Therefore, narrow band gap materials with appropriate LUMO and HOMO positions are needed. *N*-heteroacenes, such as azapentacnene, are promising narrow band gap materials for high performance ambipolar or n-channel organic semiconductors.[17] In our previous work, we have reported a tetrafluoro-azapentacene that showed high and balanced ambipolar FET behavior with an electron mobility up to 0.09 cm^2 V^{-1} s^{-1} and hole mobility to 0.08 cm^2 V^{-1} s^{-1}.[18] Recently, Miao has reported a silylethynylated diazapentacene, which gave a hole mobility up to 0.05 cm^2 V^{-1} s^{-1} and electron mobility to $\sim10^{-4}$ cm^2 V^{-1} s^{-1}.[12]

Halogenation as a common electronegative substitution method has been explored for its effects on tuning the optical properties of *N*-heteroacenes,[19] but the effects of different halogen substitutions on the transport properties of *N*-heteroacenes has yet been thoroughly studied. In this work, two Br and Cl modified azapentancene molecules were synthesized and characterized for the first time. High and balanced ambipolar transport properties were obtained on the OFET devices from a Cl modified azapentacene.

The new dibromi- and tetrachlorinated azapentacenes **a** (9,10-dibromo-6,13-bis(triisopropylsilylethynyl)-1-azapentacene) and **b** (8,9,10,11-tetrachloro-6,13-bis(triisopropylsilylethynyl)-1-azapentacene) were synthesized using the procedure shown in Scheme 1. The experimental details and spectroscopic data are available in the Supporting Information. Compounds **1**, **2**, **4**, and **5** were synthesized following the literature procedures.[11,20,21] The azapentacenequinons **3** and **6** were prepared by reacting 1,4-anthraquinones with α,α,α′α′-tetrabromo-*o*-xylene in NaI/DMF solution at 60 °C in an Ar atmosphere by a Diels–Alder reaction, and then the two azapentacenequinones were converted to the corresponding triisopropylsilylethynyl-substituted azapentacenes using a modified ethynylation/deoxygenation approach with SnCl$_2$ in a THF solution. The resulting deep blue compounds **a** and **b** are stable in both solution and the solid state, even when exposed to air and laboratory lighting.

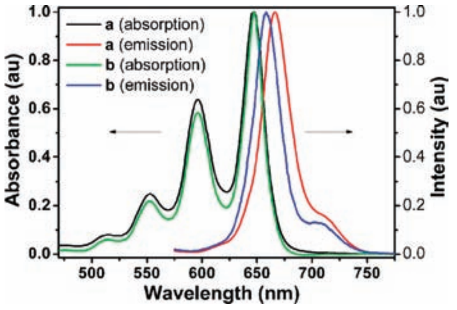


Figure 1. The UV–vis absorption and emission spectra of compound **a** and **b** in dilute toluene solution.

Molecular energy levels were estimated from the cyclic voltammetric measurements in CH$_2$Cl$_2$ at room temperature. UV–vis and fluorescence spectra were recorded in solution and of the thin films. The DFT calculations at the B3LYP/6-31G(d) level were used to study the molecular

---

(15) Tang, M. L.; Reichardt, A. D.; Miyaki, N.; Stoltenberg, R. M.; Bao, Z. *J. Am. Chem. Soc.* **2008**, *130*, 6064–6065.

(16) Tang, M. L.; Reichardt, A. D.; Wei, P.; Bao, Z. *J. Am. Chem. Soc.* **2009**, *131*, 5264–5273.

(17) Winkler, M.; Houk, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 1805–1815.

(18) Liu, Y.-Y.; Song, C.-L.; Zeng, W.-J.; Zhou, K.-G.; Shi, Z.-F.; Ma, C.-B.; Yang, F.; Zhang, H.-L.; Gong, X. *J. Am. Chem. Soc.* **2010**, *132*, 16349–16351.

(19) Appleton, A. L., Brombosz, S. M., Barlow, S., Sears, J. S., Bredas, J.-L., Marder, S. R., Bunz, U. H. F. *Nat. Commun.* **2010**, *1*, Article 91.

(20) Shepherd, M. K. *J. Chem. Soc., Perkin Trans. 1* **1986**, *8*, 1495–1498.

(21) Okamoto, T.; Senatore, M. L.; Ling, M.-M.; Mallik, A. B.; Tang, M. L.; Bao, Z. *Adv. Mater.* **2007**, *19*, 3381–3384.

Table 1. Summary of Optical, Electrochemical, and DFT-MO Theoretical Calculated Energy Levels (eV) of Compounds **a** and **b**

	UV–vis (soln[a])			UV–vis (film[a])			FL (soln)	CVs[b]			DFT[c]		
mol.	λ_{max} (nm)	λ_{onset} (nm)	E_g (eV)	λ_{max} (nm)	λ_{onset} (nm)	E_g (eV)	peak (nm)	E_{LUMO} (eV)	E_{HOMO} (eV)	E_g (eV)	E_{LUMO} (eV)	E_{HOMO} (eV)	E_g (eV)
a	647	693	1.79	702	760	1.63	666	−3.42	−5.42	2.00	−3.35	−5.17	1.82
b	647	689	1.80	677	752	1.65	658	−3.53	−5.50	1.97	−3.43	−5.25	1.82

[a] Optical HOMO–LUMO gaps determined from long wavelength absorption edge. [b] 0.1 M Bu_4NBF_4 in CH_2Cl_2 at a scan rate of 100 mV/s. [c] The LUMO, HOMO levels and energy gaps were obtained by DFT-MO calculation with B3LYP/6-31G(d).

orbital levels. The results are summarized in Table 1. Compounds **a** and **b** showed similar absorption properties with identical λ_{max} at 647 nm and absorption onset around at 690 nm in solution (Figure 1). The HOMO–LUMO gaps estimated from the onset of UV–vis absorption is 1.79 eV for **a** and 1.80 eV for **b**, which are very similar with the calculated value (1.82 eV). Compound **a** exhibits a slightly larger Stokes shift in its fluorescence spectrum than compound **b**, possibly suggesting a bigger change in geometry upon photoexcitation.[22] Compared with their absorptions in solution, both of the two new compounds demonstrated a significant red shift in thin films (Supporting Information), indicating a strong electronic interaction between molecules in the films.[23] The cyclic voltammograms (Supporting Information) confirm that the band gaps of **a** and **b** are quite similar. The LUMO energies of both **a** and **b** are much lower than that of pentacene, suggesting that they have higher electron affinities and are candidates for n-channel semiconductors.[24,25] Meanwhile, not only are the LUMO positions gradually lowered, but also the HOMO positions as well, so that the energy gaps of the molecules remain nearly unchanged. The LUMO of compound **b** (−3.53 eV) is lower than that of compound **a** (−3.42 eV), which is consistent with the higher electronegativity of Cl vs Br. In addition, both the higher electronegativity of the Cl and the higher degree of halogenation may contribute to the lower LUMO of compound **b**.

The single crystal structure of molecule **a** was obtained by slow evaporation of its toluene solutions. In the solid state, the azapentacene backbone displays near-perfect flat stacking and exhibits significant $\pi-\pi$ intermolecular overlaps. As shown in Figure 2, the distance between the π-stacks of adjacent molecules is 3.43 Å, which is very close to the van der Waals radii between neighboring stacks. Furthermore, the interaction is reinforced by close intermolecular Br...H contacts, for the Br...H distance is only 2.99 Å. Zhu has suggested that such a double-channel fashion of molecular packing may facilitate carrier transport and result in high device performance.[26] Unfortunately, we were not able to obtain the single-crystal structure of **b**.

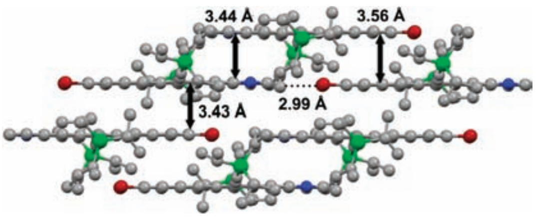


Figure 2. Solid-state arrangements of compound **a**, with view along the axis that is formed by two ethynyl substituents. It shows significant overlaps between the stacks and close intermolecular Br...H contact.

Thermal stabilities of the compounds were investigated at a heating rate of 10 °C/min under N_2 by thermogravimetric analysis (TGA) (Supporting Information). Compounds **a** and **b** show decomposition temperatures at 307 and 354 °C, respectively. The relatively low decomposition temperature of compound **a** prevented us from obtaining high purity thin films by thermal deposition.

Tapping mode AFM images of **a** and **b** (Supporting Information) were recorded on the 20 nm thin films deposited on the octadecyltrimethoxysilane (OTS) functionalized SiO_2/Si surfaces by vacuum deposition under a substrate temperature (T_{sub}) of 80 °C. The thin films of compound **a** exhibit a granular structure with a small grain size. In contrast, large grains on the order of 0.2 μm with well-resolved terraces are observed on the thin film of compound **b**, which is expected to improve the FET properties.

Top-contact/bottom gate transistors were made by evaporating molecules **a** and **b** on OTS-treated SiO_2[27] at T_{sub} = 80 °C. For compound **a**, we can only observe hole transport properties, and the mobility is very low, around 5×10^{-3} cm^2 V^{-1} s^{-1}. The relatively low mobility is mainly attributed to the impurity induced by thermal decomposition during evaporation. Electron transport behavior was

---

(22) Sancho-García, J. C.; Brédas, J.-L.; Beljonne, D.; Cornil, J.; Martínez-Álvarez, R.; Hanack, M.; Poulsen, L.; Gierschner, J.; Mack, H.-G.; Egelhaaf, H.-J.; Oelkrug, D. *J. Phys. Chem. B* **2005**, *109*, 4872–4880.

(23) Gao, J.; Li, R.; Li, L.; Meng, Q.; Jiang, H.; Li, H.; Hu, W. *Adv. Mater.* **2007**, *19*, 3008–3011.

(24) Usta, H.; Risko, C.; Wang, Z.; Huang, H.; Deliomeroglu, M. K.; Zhukhovitskiy, A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 5586–5608.

(25) Swartz, C. R.; Parkin, S. R.; Bullock, J. E.; Anthony, J. E.; Mayer, A. C.; Malliaras, G. G. *Org. Lett.* **2005**, *7*, 3163–3166.

(26) 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*, 1882–1883.

(27) Ito, Y.; Virkar, A. A.; Mannsfeld, S.; Oh, J. H.; Toney, M.; Locklin, J.; Bao, Z. *J. Am. Chem. Soc.* **2009**, *131*, 9396–9404.

Table 2. Summary of Mobilities (μ), On/Off Ratio, and Threshold Voltage (V_{th}) of **a** and **b** on OTS-Modified SiO_2 at 80 °C

mol.	electrode	carrier	μ ($cm^2\,V^{-1}\,s^{-1}$)	$I_{on/off}$	V_{th} (V)
a	Au	h	5×10^{-3}	3×10^2	−60
		e	no signal	–	–
b	Au	h	0.12	3×10^4	−22
		e	0.14	5×10^4	+28
	Ag	h	0.11	2×10^3	−36
		e	0.10	7×10^3	+45

not observed in the devices. In contrast, excellent ambipolar OFET devices were obtained from compound **b**, whose performances are summarized in Table 2. It is noted that the hole transporting properties could be observed in both the air and glovebox, but the electron transporting property can only be observed in the glovebox.[24]The reported mobility data are the average values of around 20 devices, and device statistics are available in the Supporting Information. Figure 3 shows the typical output curves of compound **b** in the glovebox. When using Au as the electrodes, the electron and hole mobilities are both very high, at 0.14 and 0.12 $cm^2\,V^{-1}\,s^{-1}$, respectively. The FET performance of compound **b** is even higher than that of tetrafluoro-substituted azapentacene, indicating that chlorination is a more efficient means than fluorination to produce a high performance ambipolar organic semiconductor.[11] The good performance of compound **b** can be understood on the basis that the unoccupied 3d orbital in Cl can delocalize electrons from the conjugated core and thus Cl atoms act as an additional electron pathway.[11,28] Furthermore, the high and balanced ambipolar OFET performance was also obtained by using Ag as source–drain electrodes, in which the average electron and hole mobilities reached 0.10 and 0.11 $cm^2\,V^{-1}\,s^{-1}$, respectively.

To conclude, our results suggest that chlorination to the *N*-heteropentacene framework is an efficient means to tune the molecular levels and bring about the balanced hole and electron mobilities. When using Au electrodes, the hole and electron mobililties reach 0.12 and 0.14 $cm^2\,V^{-1}\,s^{-1}$, respectively, demonstrating the high performance of the ambipolar organic semiconductors based on the azapentacene framework. Futhermore, OFET devices using Ag as electrodes also exhibit high and balanced charge carrier mobilities, which is highly desirable for reducing device cost without sacrificing performance. The excellent ambipolar transport properties of compound **b** make it very promising for future device applications. Further device fabrication and optimization based on these compounds are currently underway.

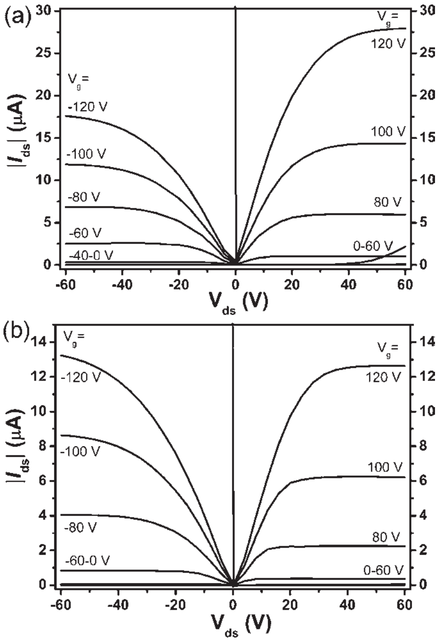


Figure 3. Typical output characteristics of compound **b** deposited on OTS-modified SiO_2 substrates at T_{sub} = 80 °C with Au (a) and Ag (b) electrodes.

Acknowledgment. This work is supported by National Natural Science Foundation of China (NSFC. 21073079, 50828301, J0730425), the Fundamental Research Funds for the Central Universities, Chunhui Project and 111 Project.

Supporting Information Available. Details of experimental procedures, UV–vis spectra of thin films, TGA graphs, AFM images, DFT caculation, XRD pattern, out and transfer curves. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(28) Gsänger, M.; HakOh, J.; Könemann, M.; Höffken, H. W.; Krause, A.-M.; Bao, Z.; Würthner, a. F. *Angew. Chem., Int. Ed.* **2009**, *122*, 752–755.