ORGANIC
LETTERS

2009
Vol. 11, No. 10
2069−2072

An Ambipolar Transporting Naphtho[2,3-*c*][1,2,5]thiadiazole Derivative with High Electron and Hole Mobilities

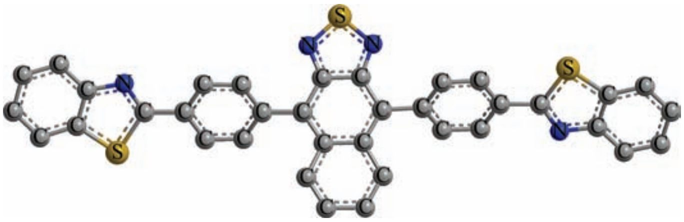
Yongduo Sun, Lian Duan, Peng Wei, Juan Qiao, Guifang Dong, Liduo Wang, and Yong Qiu*

Key Laboratory of Organic Optoelectronics and Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University,
Beijing 100084, P. R. China

qiuy@mail.tsinghua.edu.cn

Received March 3, 2009

ABSTRACT



An ambipolar transporting naphtho[2,3-*c*][1,2,5]thiadiazole derivative with both high electron and hole mobilities has been synthesized via Suzuki cross-coupling. The electron and hole mobilities are 1.7 × 10^{-3} cm^2/ (V·s) and 1.9 × 10^{-3} cm^2/ (V·s) at an electric field of 4.5 × 10^5 V/cm, respectively, as measured by using time-of-flight technique.

Organic light-emitting diodes (OLEDs) have attracted considerable interest due to their potential application in flat-panel displays and illumination.[1] The charge balance in an OLED is considered to be essential for achieving high device performance. In recent years, much attention has been paid to materials possessing an ambipolar charge transporting property, which helps to facilitate the balance of electrons and holes, simplify the device structure, and control the exciton formation zone for OLEDs.[2] A common strategy to achieve ambipolar property is to combine electron-transporting chromophores and hole transporting chromophores in a single molecule.[2] However, both electron and hole mobilities of these materials are not very high. Another strategy is to find chromophores with ambipolar transport properties. It is reported that a carbazole derivative exhibited ambipolar property and the electron and hole mobilities are up to 10^{-4} $cm^2/(V{\cdot}s)$.[3] Oligofluorenes are also reported to possess unusually high electron and hole mobilities which are close to 1 × 10^{-3} $cm^2/(V{\cdot}s)$.[3]

In our previous report, naphtho[2,3-*c*][1,2,5]thiadiazole (NTD) derivatives demonstrated good amorphous film-forming capability and ambipolar transporting property with mobility values for both charge carriers of more than 10^{-4}

---

(1) (a) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913. (b) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; MacKay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539. (c) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature (London)* **1998**, *395*, 151.

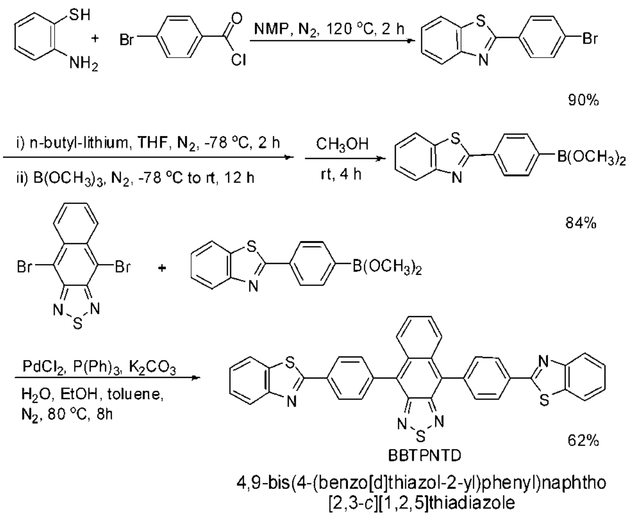
(2) (a) Li, Z.-Y.; Wong, M.-S.; Fukutani, H.; Tao, Y. *Org. Lett.* **2006**, *8*, 4271. (b) Strohriegl, P.; Grazulevicius, J. V. *Adv. Mater.* **2002**, *14*, 1439. (c) Lin, L.-B.; Jenekhe, S. A.; Borsenberger, P. M. *Appl. Phys. Lett.* **1996**, *69*, 3495. (d) Hancock, J. M.; Gifford, A. P.; Tonzola, C. J.; Jenekhe, S. A. *J. Phys. Chem. C* **2007**, *111*, 6875. (e) Zhan, X.; Liu, Y.; Zhu, D.; Jiang, X.; Jen, A. K. *Macromol. Chem. Phys.* **2001**, *202*, 2341. (f) Tokuhisa, H.; Era, M.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1995**, *66*, 3433. (g) Thomas, K. R. J.; Lin, J. T.; Tao, Y.-T.; Chuena, C. H. *J. Mater. Chem.* **2002**, *12*, 3516. (h) Qiao, J.; Tan, H.; Qiu, Y. *J. Chem. Phys.* **2006**, *124*, 024719. (i) Qiu, Y. *Digest of Technical Papers*, 2008. SID International Symposium, Philadelphia, PA; Los Angeles CA; Soc Information Display: 2008, 39, 609.

10.1021/ol900431a CCC: $40.75

cm^2/(V•s),[4,2i] and the theoretical calculation showed that the ambipolar property was mainly due to the overlap of frontier orbitals on NTD core. We think that we could further enhance the mobilities of NTD derivatives through introducing planar side substituents, since the twisted substituents would weaken the charge transport ability. In this paper, we report a new compound, 4,9-bis(4-(benzo[*d*]thiazol-2-yl)phenyl)naphtho[2,3-*c*][1,2,5]thiadiazole (BBTPNTD), which exhibits very high and close electron and hole mobilities of 1.7 × 10^{-3} cm^2/ (V•s) and 1.9 × 10^{-3} cm^2/ (V•s) at an electric field of 4.5 × 10^5 V/cm, respectively.

As shown in Scheme 1, BBTPNTD was synthesized from 4,9-dibromonaphtho[2,3-*c*][1,2,5]thiadiazole and dimethyl 4-(benzo[*d*]thiazol-2-yl)phenylboronate by a palladium-catalyzed Suzuki-coupling reaction.[5] Dimethyl 4-(benzo[*d*]thiazol-2-yl)phenylboronate was synthesized from 2-aminothiophenol and 4-bromobenzoyl chloride.[5] All the materials used in our experiments were purified by vacuum train sublimation.

Scheme 1. Synthetic Route for BBTPNTD



The thermal stability of BBTPNTD was estimated by the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). BBTPNTD displays high thermal stability with the temperature for a 5% weight loss of 448, the decomposition temperature of 512 °C, and the melting temperature of 411 °C. The electrochemical properties of BBTPNTD were studied by cyclic voltammetry (CV). As shown in Figure 1., we detected that one quasireversible oxidation potential occurred at 0.87 V and one reversible reduction potential at −1.53 V, which indicates that both the radical cations and radical anions are stable entities.[6] The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of BBTPNTD are −5.61 and −3.21 eV, respectively, which were calculated using a linear correlation with dicyclopentadienyl iron.

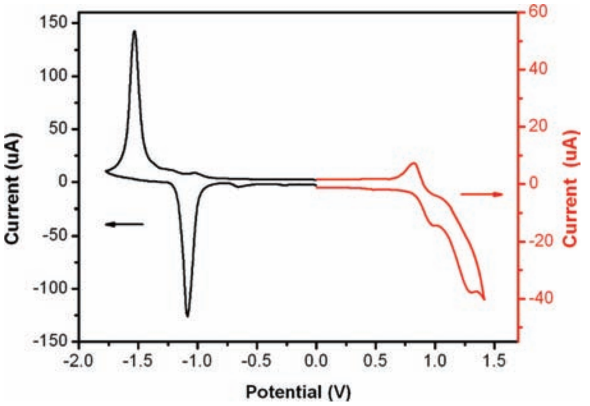


Figure 1. Cyclic voltammogram of BBTPNTD. Scan rate: 150 mV s^{-1}; working electrode: Pt disk electrode; reference electrode: Ag/AgCl. Oxidation CV was performed in dichloromethane containing with 0.1 M *n*-Bu$_4$NBF$_4$ as the supporting electrolyte. Reduction CV was performed in acetonitrile containing with 0.1 M *n*-Bu$_4$NBF$_4$ as the supporting electrolyte.

The BBTPNTD film was prepared by vacuum sublimation on glass and was characterized by X-ray diffraction. There was no diffraction peaks except for the peaks from glass, indicating that the film was amorphous. The absorption spectra and photoluminescence (PL) spectra of BBTPNTD in CHCl$_3$ (2 × 10^{-5} M) and as thermally evaporated film are show in Figure 2. BBTPNTD displays absorption peaks at 485 and 509 nm in solution and as thin film, respectively. And its PL emission peaks are at 587 and 621 nm in solution and as thin film, respectively.

The carrier mobilities of BBTPNTD in amorphous thin film were characterized by the time-of-flight (TOF) transient photocurrent technique.[7,3b,c] The configuration of the device is ITO/Ag (60 nm)/BBTPNTD (2.0 μm)/ Ag (200 nm). The carrier mobility was calculated according to the following formula: $\mu = D/(T_tE) = D^2/(VT_t)$, where V is the applied bias, T_t is the charge transit time, and D is the thickness of the organic layer.

---

(3) (a) Shen, J.-Y.; Yang, X.-Y.; Huang, T.-H.; Lin, J. T.; Ke, T.-H.; Chen, L.-Y.; Wu, C.-C.; Yeh, M.-C. P. *Adv. Funct. Mater.* **2007**, *17*, 983. (b) Liao, Y.-L.; Lin, C.-Y.; Liu, Y.-H.; Wong, K.-T.; Hung, W.-Y.; Chen, W.-J. *Chem. Commun.* **2007**, 1831. (c) Wu, C.-C.; Liu, T.-L.; Hung, W.-Y.; Lin, Y.-T.; Wong, K.-T.; Chien, Y.-Y. *J. Am. Chem. Soc.* **2003**, *125*, 3710. (d) Tse, S. C.; So, S. K.; Yeung, M. Y.; Lo, C. F.; Wen, S. W.; Chen, C. H. *Jpn. J. Appl. Phys.* **2006**, *45*, 555. (e) Lai, M.-Y.; Chen, C.-H.; Huang, W.-S.; Lin, J.-T.; Ke, T.-H.; Chen, L.i-Y.; Tsai, M.-H.; Wu, C.-C. *Angew. Chem.* 2008, *120*, 591;*Angew. Chem., Int. Ed.* **2008**, *47*, 581. (f) Tsai, T.-C.; Hung, W.-Y.; Chi, L.-C.; Wong, K.-T.; Hsieh, C.-C.; Chou, P.-T. *Org. Electron.* **2009**, *10*, 158.

(4) (a) Qiu, Y.; Wei, P.; Zhang, D.; Qiao, J.; Duan, L.; Li, Y.; Gao, Y.; Wang, L. *Adv. Mater.* **2006**, *18*, 1607. (b) Wei, P.; Duan, L.; Zhang, D.; Qiao, J.; Qiu, Y. *J. Mater. Chem.* **2008**, *18*, 806.

(5) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Neeff, R.; Bayer, O. *Chem. Ber.* **1957**, *90*, 1137. (c) Wu, F.-I.; Shih, P.-I.; Tseng, Y.-H.; Chen, G.-Y.; Chien, C.-H.; Tung, Y.-L. *J. Mater. Chem.* **2005**, *15*, 4753. (d) Laskar, I. R.; Chen, T.-M. *Chem. Mater.* **2004**, *16*, 111. (e) Moghaddam, F.-M.; Bardajee, G.-R.; Ismaili, H.; Taimoory, S.-M. *Synth. Commun.* **2006**, *36*, 2543. (f) Kato, S.-I.; Matsumoto, T.; Ishi-i, T.; Thiemann, T.; Shigeiwa, M.; Gorohmaru, H.; Maeda, S.; Yamashita, Y.; Mataka, S. *Chem. Commun.* **2004**, 2342.

(6) (a) Doi, H.; Kinoshita, M.; Okumoto, K.; Shirota, Y. *Chem. Mater.* **2003**, *15*, 1080. (b) Shirota, Y.; Kinoshita, N.; Noda, T.; Okumoto, K.; Ohara, T. *J. Am. Chem. Soc.* **2000**, *122*, 1102.

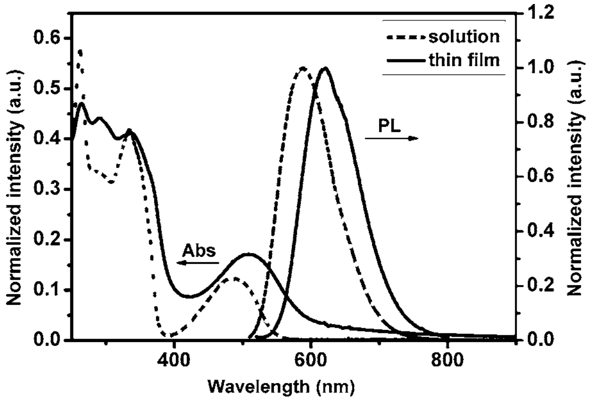


Figure 2. Absorption and PL emission spectra of $CHCl_3$ solution and thermally evaporated film of BBTPNTD.

The TOF transients of electrons and holes for BBTPNTD in air at room temperature are shown in Figure 3. The electron and hole mobilities of BBTPNTD are very close and extremely high, reaching 1.7×10^{-3} $cm^2/(V\cdot s)$ and 1.9×10^{-3} $cm^2/(V\cdot s)$ at an electric field of 4.5×10^5 V/cm, respectively. No plateau is observed in Figure 3, indicating dispersive transport for electrons and holes in BBTPNTD. The field-dependence of the electron and hole mobilities of BBTPNTD are shown in Figure 4. The field-dependence of both the electron and hole are well-agreed with the Poole-Frenkel (PF) relationship, $\mu = \exp(\beta E^{1/2})$, where β is the Poole−Frenkel factor.

To acquire a better understanding of the ambipolar property, theoretical calculations on the electronic states of BBTPNTD were carried out at the B3LYP/6-13G(d) level in the Gaussian 98 program.[8] The electron-density distributions of HOMO and LUMO as well as the schematic representation of the packing of the adjacent BBTPNTD molecules are shown in Figure 5. It is noted that both HOMO and LUMO are mainly located on the NTD chromophore in BBTPNTD; thus, electrons and holes can perform intermolecular hopping in similar spatial extent between the adjacent NTD chromophores through the $\pi-\pi$ stacking interaction. That is, BBTPNTD molecules exhibit similar charge-transfer integrals for electrons and holes. The electron and hole reorganization energies were also calculated to be very close (0.32 eV for electrons and 0.25 eV for holes), indicating that the abilities of the molecules to accept and donate electrons are similar. According to the Marcus theory, similar charge-transfer integrals and reorganization energies for electrons and holes will lead to the ambipolar transport property.[8] Moreover, as the result of theoretical calculations, the dihedral angle between the phenyl and benzothiaol is only

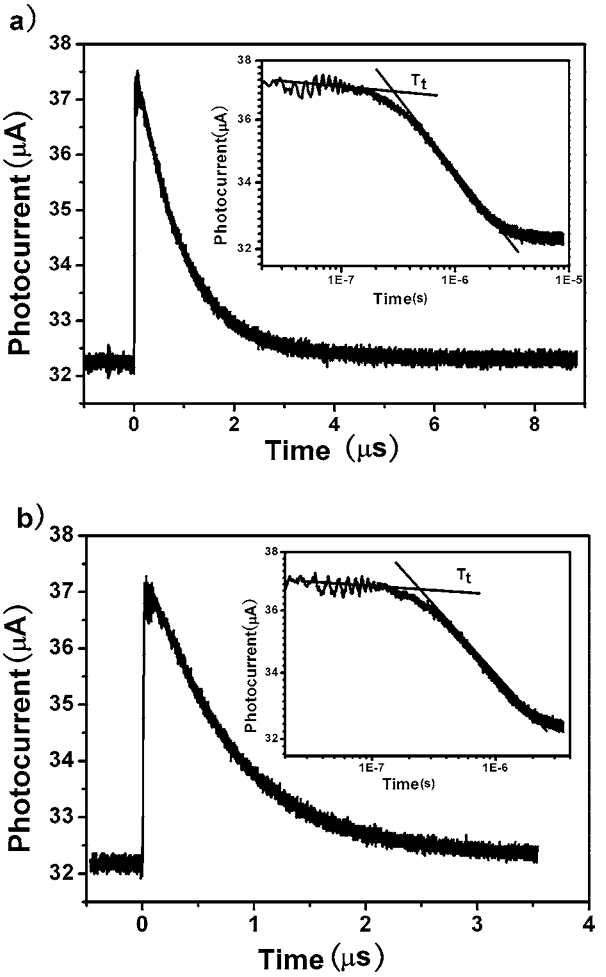


Figure 3. TOF transients for BBTPNTD at the electric field of 4.5×10^5 V/cm: (a) electrons; (b) holes. The insets display the corresponding double-logarithmic plots.

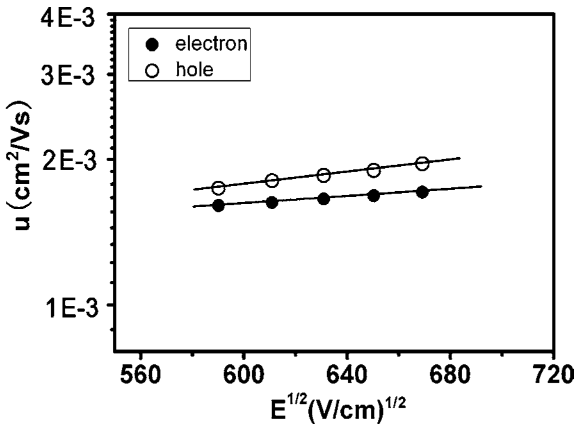


Figure 4. Electron and hole mobilities vs $E^{1/2}$ for BBTPNTD.

---

(7) (a) Kepler, R. G. *Phys. Rev.* **1960**, *119*, 1226. (b) Fong, H. H.; Lun, K. C.; So, S. K. *Chem. Phys. Lett.* **2002**, *353*, 407.

(8) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B. G.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; AlLaham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, ; Pople, C. J. A. Gaussian 98, Revision A.9, Gaussian: Pittsburgh, PA 1998.

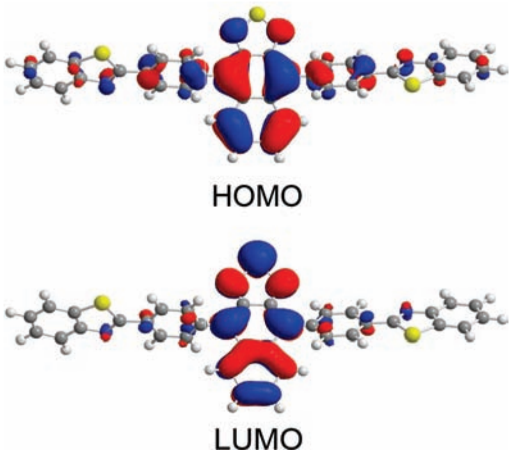


Figure 5. Molecular orbital surfaces of HOMO and LUMO of BBTPNTD obtained at the B3LYP/6-31G* level. All the MO surfaces correspond to an isocontour value of $\Psi = \pm 0.0025$.

0.5°, which means that all the atoms in the (benzothiaol-2-yl)phenyl are nearly on the same plane. The good planarity of the side groups facilitates reducing the distance between the adjacent molecules and enhancing the $\pi-\pi$ staking interaction between the adjacent molecules, finally improving the carrier transporting property. On the other hand, the whole molecule is twisted with the dihedral angle of 54° between the NTD group and the (benzol[*d*]thiazol-2-yl)phenyl group, which is similar to those of other NTD derivatives.[4]

In summary, we have synthesized and characterized a new naphtho[2,3-*c*][1,2,5]thiadiazole derivative which possesses ambipolar carrier transporting property. Both the electron and hole mobilities reached as high as 10^{-3} cm^2/(V•s) at room temperature. The unusual ambipolar carrier transporting property in the amorphous state is explained according to the molecular reorganization energy, the distribution of electrons on frontier orbitals as well as the configuration of the molecule.

Acknowledgment. We thank the National Natural Science Foundation of China (No. 60877026) and the National Key Basic Research and Development Program of China under Grant No. 2006CB806203 for support.

Supporting Information Available: Spectroscopic characterization of BBTPNTD. This material is available free of charge via the Internet at http://pubs.acs.org.

OL900431A