

Hexaazatriphenylene Derivatives with Tunable Lowest Unoccupied Molecular Orbital Levels

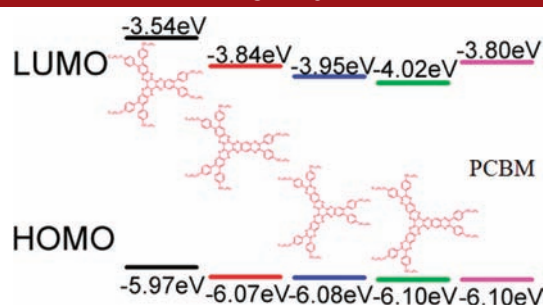
Ming Wang,^{†,‡} Ying Li,^{†,‡} Hui Tong,^{*,†} Yanxiang Cheng,[†] Lixiang Wang,^{*,†} Xiabin Jing,[†] and Fosong Wang[†]

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China, and Graduate School of Chinese Academy of Sciences, Beijing 100039, P. R. China

chemtonghui@ciac.jl.cn; lixiang@ciac.jl.cn

Received June 26, 2011

ABSTRACT



A series of n-type hexaazatriphenylene derivatives were synthesized by condensation coupling of 1,2-diamines and 1,2-diketones. The study of their photophysical and electrochemical properties showed that their lowest unoccupied molecular orbital (LUMO) energy levels could be effectively tuned from -3.54 to -4.02 eV simply by increasing the number of pyrazine units in their molecular structures.

Organic conjugated compounds are of wide current interest because of their potential applications in light-emitting diodes,^{1,2} organic photovoltaic cells,^{3,4} and thin film transistors.^{5,6} In the past two decades, the vast majority of research in the field has been devoted to p-type organic semiconductors.^{7,8} Only a few n-type organic molecules have been synthesized and studied, although n-type organic semiconductors are also very important for

developing the light-emitting diodes, organic photovoltaic cells, thin film transistors, and so on.^{9–15}

Recently, n-type organic semiconductors have been reported, include heteroaromatic compounds,¹⁶ fullerene derivatives,¹⁷ naphthalene, and perylene diimides, etc.¹⁸ Among them, heterocyclic aromatic compounds including

[†] Changchun Institute of Applied Chemistry.

[‡] Graduate School of Chinese Academy of Sciences.

(1) Kolosov, D.; Adamovich, V.; Djurovich, P.; Thompson, M. E.; Adachi, C. *J. Am. Chem. Soc.* **2002**, *124*, 9945–9954.

(2) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151–154.

(3) Leriche, P.; Piron, F.; Ripaud, E.; Frere, P.; Allain, M.; Roncali, J. *Tetrahedron Lett.* **2009**, *50*, 5673–5676.

(4) Mondal, R.; Ko, S.; Norton, J. E.; Miyaki, N.; Becerril, H. A.; Verploegen, E.; Toney, M. F.; Bredas, J. L.; McGehee, M. D.; Bao, Z. N. *J. Mater. Chem.* **2009**, *19*, 7195–7197.

(5) Babel, A.; Jenekhe, S. A. *Adv. Mater.* **2002**, *14*, 371–374.

(6) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99–117.

(7) Mitschke, U.; Bauerle, P. *J. Mater. Chem.* **2000**, *10*, 1471–1507.

(8) Facchetti, A.; Mushrush, M.; Katz, H. E.; Marks, T. J. *Adv. Mater.* **2003**, *15*, 33–38.

(9) Hanifi, D.; Cao, D.; Klivansky, L. M.; Liu, Y. *Chem. Commun.* **2011**, *47*, 3454–3456.

(10) McMenimen, K. A.; Hamilton, D. G. *J. Am. Chem. Soc.* **2001**, *123*, 6453–6454.

(11) Pieterse, K.; van Hal, P. A.; Kleppinger, R.; Vekemans, J.; Janssen, R. A. J.; Meijer, E. W. *Chem. Mater.* **2001**, *13*, 2675–2679.

(12) Kestemont, G.; de Halleux, V.; Lehmann, M.; Ivanov, D. A.; Watson, M.; Geerts, Y. H. *Chem. Commun.* **2001**, *20*, 2074–2075.

(13) Yin, J.; Qu, H. M.; Zhang, K.; Luo, J.; Zhang, X. J.; Chi, C. Y.; Wu, J. S. *Org. Lett.* **2009**, *11*, 3028–3031.

(14) Luo, M.; Shadnia, H.; Qian, G.; Du, X. B.; Yu, D. B.; Ma, D. G.; Wright, J. S.; Wang, Z. Y. *Chem.—Eur. J.* **2009**, *15*, 8902–8908.

(15) Ishi-i, T.; Murakami, K.; Imai, Y.; Mataka, S. *Org. Lett.* **2005**, *7*, 3175–3178.

(16) Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. *Science* **1995**, *267*, 1969–1972.

(17) Thompson, B. C.; Frechet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58–77.

(18) Jones, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 15259–15278.

imine nitrogen atoms (=N–) were extensively investigated because they have a less negative reduction potential compared to hydrocarbon analogues and heterocyclics containing oxygen or sulfur atoms.¹⁹ As a typical nitrogen-containing heterocyclic compound, hexaazatriphenylene has proved to be a kind of n-type organic semiconductor because it contains three strong π -deficient pyrazine units at the center and can be used to construct novel electron acceptor materials.^{20–22} For example, Tsutomu Ishi-I's group have reported a series of hexaazatriphenylene-based electron-deficient heteroaromatics with an expanded π -electron system. The first reduction potentials were evaluated at around -1.7 V with Fc/Fc⁺ as reference electrode.²² The electron affinity was enhanced by the expansion of the electron-deficient aromatic system.

Our group has reported a series of novel acene-type conjugated molecules containing n-type pyrazine units in a previous paper.²³ We studied the electrochemical and photophysical properties and found that the LUMO energy levels significantly decrease from -3.24 to -3.78 eV with increasing the number of pyrazine rings and the conjugation length of the acene-type molecules. At the same time, their absorption and emission spectra were red-shifted too. These results suggested that increasing the number of pyrazine units and the conjugation length of molecules are effective ways to obtain n-type materials.

In this contribution, we reported the synthesis and characterization of a series of hexaazatriphenylene derivatives containing a different number of pyrazine units (Figure 1). The different number of pyrazine units in their molecular structures will effectively tune their photophysical and electrochemical properties. From **1** to **4**, as the number of pyrazine units increased, our investigation demonstrated not only that both the absorption and emission spectra were red-shifted but also that their electron affinity was enhanced significantly step by step.

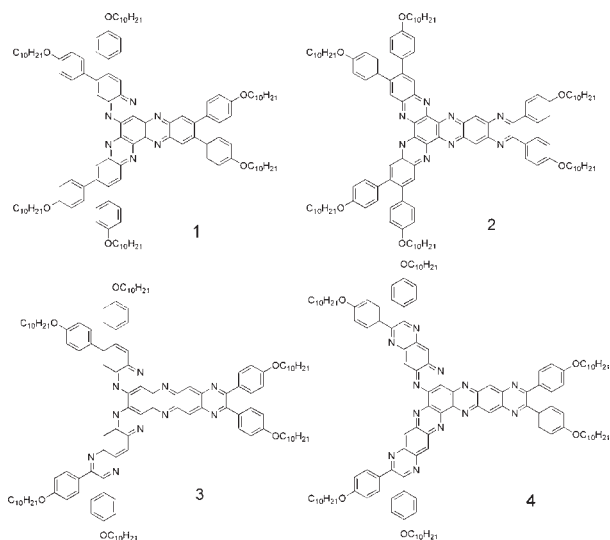
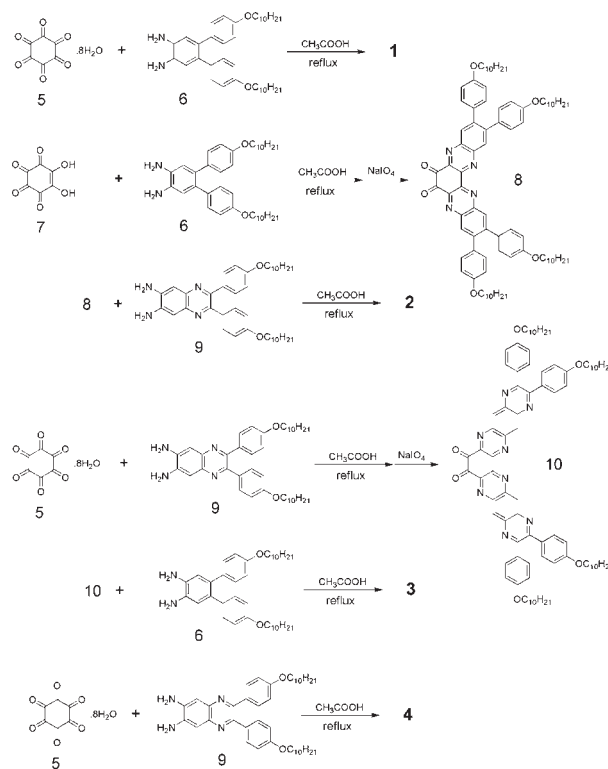


Figure 1. The structures of the hexaazatriphenylene derivatives.

Scheme 1. Synthetic Routes of the Four Hexaazatriphenylene Compounds



The synthetic routes are outlined in Scheme 1. As most of the literature methods for the preparation of the hexaazatriphenylene derivatives,^{20,24} all the target molecules were obtained by a typical high yield condensation-coupling reaction between 1,2-diketones and corresponding 1,2-diamines in refluxing acetic acid. The four starting materials (**5**, **6**, **7**, **9**) are either commercial available or have been prepared previously in our lab.^{20,23} The synthesis of the key intermediate **8** and **10** is also rather simple and straightforward. Although their synthetic procedures are similar, it should be noted that the starting material of **8** and **10** must be **7** and **5**, otherwise the yield will be very low or even no product can be obtained. The easy preparation of these hexaazatriphenylene derivatives promises our further investigation.

Compound **1** is obtained as a yellow solid, while **2**, **3**, and **4** are deep-red solids. They are all soluble in common organic solvents, such as dichloromethane, chloroform, and tetrahydrofuran (THF). Their structures and purity were characterized by ¹H NMR, ¹³C NMR, MALDI-TOF,

(19) Tonzola, C. J.; Alam, M. M.; Kaminsky, W.; Jenekhe, S. A. *J. Am. Chem. Soc.* **2003**, *125*, 13548–12558.

(20) Gao, B. X.; Liu, Y. L.; Geng, Y. H.; Cheng, Y. X.; Wang, L. X.; Jing, X. B.; Wang, F. S. *Tetrahedron Lett.* **2009**, *50*, 1649–1652.

(21) Secondo, P.; Fages, F. *Org. Lett.* **2006**, *8*, 1311–1314.

(22) Ishi-i, T.; Yaguma, K.; Kuwahara, R.; Taguri, Y.; Mataka, S. *Org. Lett.* **2006**, *8*, 585–588.

(23) Gao, B. X.; Wang, M.; Cheng, Y. X.; Wang, L. X.; Jing, X. B.; Wang, F. S. *J. Am. Chem. Soc.* **2008**, *130*, 8297–8306.

(24) Lee, D. C.; Jang, K.; McGrath, K. K.; Uy, R.; Robins, K. A.; Hatched, D. W. *Chem. Mater.* **2008**, *20*, 3688–3695.

and elemental analysis (see Supporting Information). The thermal properties of these four molecules were evaluated by thermogravimetric analysis (TGA), which revealed their good thermal stability with decomposition temperature higher than 400 °C.

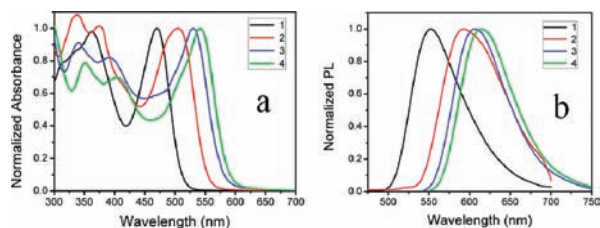


Figure 2. (a) Normalized absorption and (b) normalized PL spectra of **1**, **2**, **3**, and **4** in chloroform (10^{-5} M).

Normalized absorption and PL emission spectra of compounds **1–4** in chloroform solutions (10^{-5} M) are shown in Figure 2. All spectra are well-resolved with clear vibronic structures, which was consistent with the rigid structural feature of the compounds. The colors of these compounds in chloroform solution are changed from yellow in **1** to deep-red in **4**. The absorption peaks were red-shifted from 471 nm in **1** to 543 nm in **4** with the increase of pyrazine number in their molecular structures. The optical band gaps of the compounds **1–4**, calculated from these absorption onsets, were 2.43, 2.23, 2.13, and 2.08 eV, respectively, indicating that the longer effective conjugation length and the lowered energy gap can be achieved by the introduction of more pyrazine units. The emission maximum was also red-shifted from 552 nm in **1** (yellow emission) to 615 nm in **4** (red emission). Meanwhile, the PL quantum yield decreased from 76% for **1** to 21% for **4**, perhaps due to the increasing aggregation tendency from **1** to **4** with the increasing of the number of pyrazine rings.^{23,25}

Absorption and PL emission spectra of compounds **1–4** in thin films were also examined (Figure S1 in Supporting Information). Their absorption spectra were similar to those in chloroform solutions. The main absorption band was also progressively red-shifted from 481 to 543 nm. However, the PL spectra of hexaazatriphenylene derivatives in thin films were different from those in solutions. Only the emission of **1** at 563 nm can be observed. The emission spectra of **2–4** were too weak to be detected, possibly also due to their enhanced aggregation tendency in the film state. The aggregation tendency of **1–4** was also studied by means of ^1H NMR. According to their concentration-dependent ^1H NMR spectra in chloroform-*d* (Figure S2 in Supporting Information), the chemical shifts of their aromatic protons are shifted upfield as the concentration is increased from 3×10^{-4} to 6×10^{-3} mol/L, while for their temperature-dependent ^1H NMR spectra in 1,2-dichlorobenzene-*d*₄ (Figure S3 in Supporting

Information), the chemical shifts of their aromatic protons are shifted lowfield as the temperature increase from 25 to 120 °C. For both concentration- and temperature-dependent ^1H NMR spectra, it is clear that the tendency in molecular aggregation is raised with increasing the number of pyrazine rings,²³ which is consistent with their PL behaviors (Table 1).

Table 1. Physical Properties of Four Hexaazatriphenylene Molecules

compd	λ_{max} absorption ^a	λ_{max} emission ^a	Φ^b (%)	T^c (°C)
1	471	552	76	405
2	508	593	32	410
3	530	605	26	414
4	543	615	21	438

^a In chloroform solution (1×10^{-5} M). ^b Fluorescence quantum yield of **1** relative to Coumarin 6 in acetonitrile (63%). Fluorescence quantum yields of **2**, **3**, **4** relative to Rhodamine B in water (31%). ^c Onset decomposition temperature measured by TGA under nitrogen.

The electrochemical properties of these four molecules in dichloromethane were studied in a three-electrode electrochemical cell with Bu_4NClO_4 (0.1 M) as electrolyte and Ag/AgCl as reference electrode (Figure 3). The data of cyclic voltammograms are shown in Table S1 (Supporting Information). **1** and **2** exhibited two reversible redox processes in the negative potential region. Compounds **3** and **4** exhibited three reversible redox processes in the negative potential region. The LUMO energy level was determined according to the empirical formula $E_{\text{LUMO}} = -[4.8 - E_{\text{FOC}} + E_{\text{onset}}^{\text{red}}]$ eV.²⁶ The E_{FOC} is the half-wave potential of ferrocene as the standard. The LUMO energy levels of four molecules were estimated from the reduction onset. The LUMO level (−3.84 eV) of **2** was 0.3 eV lower than that of **1** (−3.54 eV), and the LUMO levels of **3** and **4** were further decreased to −3.95 eV of **3** and −4.02 eV of **4**, respectively. These facts indicated the enhanced electron affinity clearly correlated with the introduction of more

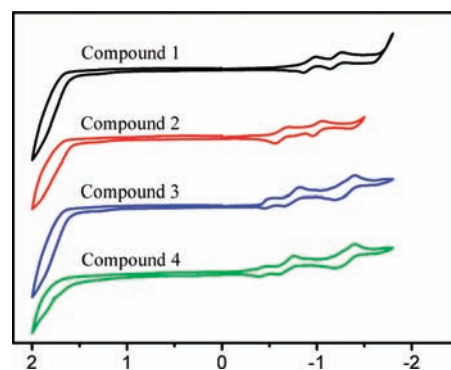


Figure 3. Cyclic voltammograms of **1**, **2**, **3**, and **4** in dichloromethane at a scan rate of 100 mV/s.

(25) Wasserfallen, D.; Kastler, M.; Pisula, W.; Hofer, W. A.; Fogel, Y.; Wang, Z.; Müllen, K. *J. Am. Chem. Soc.* **2006**, *128*, 1334–1339.

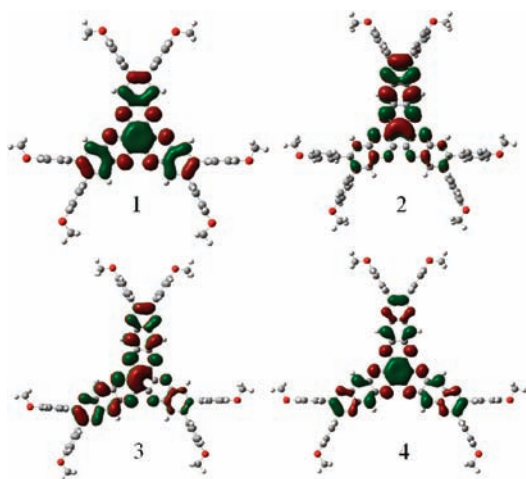


Figure 4. LUMO molecular orbitals of compounds **1–4** calculated by density functional theory calculations at the B3LYP/6-31G* level.

pyrazine units. Their HOMO energy levels were calculated from the corresponding LUMO energy levels and the optical band gap. The HOMO energy levels of **2**, **3**, and **4** were very close, suggesting that the influence of the pyrazine units on the HOMO levels are trivial.

Furthermore, the LUMO molecular orbitals were calculated by density functional theory calculations at the B3LYP/6-31G* level (Figure 4). The LUMO was located mainly on the pyrazine units. As for the electrochemical and

(26) Jiang, Z. Q.; Zhang, W. J.; Yao, H. Q.; Yang, C. L.; Cao, Y.; Qin, J. G.; Yu, G.; Liu, Y. Q. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 3651–3661.

optical results, the calculated LUMO energy levels and band gaps were decreased effectively with increasing the pyrazine unit number from **1** to **4**, while the changes of the calculated HOMO energy levels were rather small. It was also clear that their conjugation length were increased as well.

In summary, we have synthesized a series of hexaazatriphenylene derivatives by a typical condensation-coupling reaction between 1,2-diketones and corresponding 1,2-diamines. These materials were investigated by photophysical and electrochemical methods. The absorption and emission spectra were red-shifted with the increase of the pyrazine unit number. Especially, the LUMO energy levels were drastically decreased from -3.54 eV (**1**) to -4.02 eV (**4**), even lower than a well-known n-type material PCBM (-3.8 eV),²⁷ indicating that the electron affinity of these compounds could be significantly enhanced. The low LUMO energy levels and ease of structural modification clearly demonstrated that these hexaazatriphenylene derivatives with different number of pyrazine units are excellent n-type materials.

Acknowledgment. This work was supported by the Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (CX07QZJC-24), the National Natural Science Foundation of China (nos. 21074130, 50633040, 20904055), the Science Fund for Creative Research Groups (no. 20921061), and the 973 Project (2009CB623601).

Supporting Information Available. ¹H NMR, ¹³C NMR, MALDI-TOF, UV–vis spectra, fluorescence spectra, and experimental procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(27) Zhao, H. Y.; Guo, X. Y.; Tian, H. K.; Li, C. Y.; Xie, Z. Y.; Geng, Y. H.; Wang, F. S. *J. Mater. Chem.* **2010**, *20*, 3092–3097.