

Polycyclic Imide Derivatives: Synthesis and Effective Tuning of Lowest Unoccupied Molecular Orbital Levels through Molecular Engineering

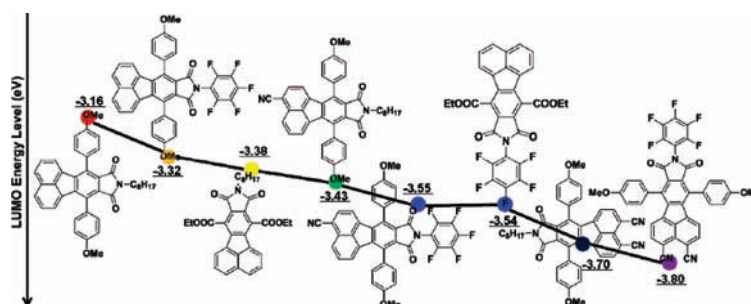
Lin Ding, Han-Ze Ying, Yan Zhou, Ting Lei, and Jian Pei*

Beijing National Laboratory for Molecular Sciences (BNLMS), the Key Laboratory of Bioorganic Chemistry and Molecular Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

jianpei@pku.edu.cn

Received October 6, 2010

ABSTRACT



A series of fluoranthene-fused imide derivatives were facilely developed through a Diels–Alder reaction followed by decarbonylation. The investigation of their photophysical and electrochemical properties demonstrated that their LUMO levels were effectively tuned from -3.2 to -3.8 eV through the introduction of a fused imide unit, which provides a platform to design new air-stable and solution-processable *n*-type materials.

For the past decades, intensive attention has been paid to organic semiconducting materials due to their potential applications in plastic displays, sensors, and RF-ID tags.¹ Among these organic semiconducting materials, air-stable *n*-type materials are important components of *p*-*n* junction diodes, bipolar transistors, and complementary circuits,² especially for application in complementary circuits due to their low power dissipation, high operating speed, and good noise margin.³ Recently, some *n*-type organic materials, such as metallophthalocyanine and fullerene derivatives,⁴ naphthalene and perylene imides,⁵ and oligothiophene derivatives

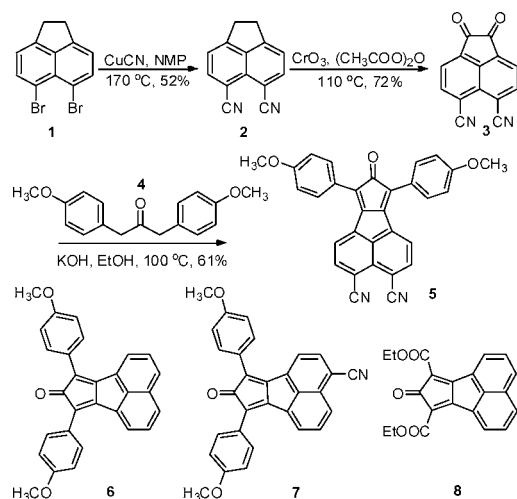
with cyano or fluoro substituents,⁶ have been intensively investigated and exhibit good *n*-type performance in opto-

(1) (a) Horowitz, G. *Adv. Mater.* **1998**, *10*, 365–377. (b) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99–117. (c) Dodabalapur, A. *Nature* **2005**, *434*, 151–152.

(2) (a) Streetman, B. G. *Solid State Electronic Devices*, 4th ed.; Prentice Hall: Englewood Cliffs, 1995. (b) Zaumseil, J.; Sirringhaus, H. *Chem. Rev.* **2007**, *107*, 1296–1323. (c) Dhar, B. M.; Kini, G. S.; Xia, G. Q.; Jung, B. J.; Markovic, N.; Katz, H. E. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 3972–3976.

(3) (a) Meijer, E. J.; Leeuw, D. M.; Setayesh, S.; Van Veenendaal, E.; Huisman, B. H.; Blom, P. W. M.; Hummelen, J. C.; Scherf, U.; Klapwijk, T. M. *Nat. Mater.* **2003**, *2*, 678–682. (b) Klauk, H.; Zschieschang, U.; Pflaum, J.; Halik, M. *Nature* **2007**, *445*, 745–748. (c) Melzer, C.; Von Seggern, H. *Adv. Polym. Sci.* **2010**, *223*, 213–257. (d) Ribierre, J. C.; Fujihara, T.; Watanabe, S.; Matsumoto, M.; Muto, T.; Nakao, A.; Aoyama, T. *Adv. Mater.* **2010**, *22*, 1722–1726.

(4) (a) Kastner, J.; Paloheimo, J.; Kuzmany, H. *Springer Ser. Solid-State Sci.* **1993**, 512–515. (b) Bao, Z. N.; Lovinger, A. J.; Brown, J. *J. Am. Chem. Soc.* **1998**, *120*, 207–208. (c) Locklin, J.; Shinbo, K.; Onishi, K.; Kaneko, F.; Bao, Z.; Advincula, R. C. *Chem. Mater.* **2003**, *15*, 1404–1412. (d) Singh, T. B.; Marjanovic, N.; Stadler, P.; Auinger, M.; Matt, G. J.; Günes, S.; Sariciftci, N. S.; Schwödiauer, R.; Bauer, S. *J. Appl. Phys.* **2005**, *97*, 083714–1–5. (e) Anthopoulos, T. D.; De Leeuw, D. M.; Cantatore, E.; Van't Hof, P.; Alma, J.; Hummelen, J. C. *J. Appl. Phys.* **2005**, *98*, 054503–1–6. (f) Wang, J.; Wang, H.; Yan, X.; Huang, H.; Jin, D.; Shi, J.; Tang, Y.; Yan, D. *Adv. Funct. Mater.* **2006**, *16*, 824. (g) Tang, Q. X.; Tong, Y. H.; Li, H. X.; Ji, Z. Y.; Li, L. Q.; Hu, W. P.; Liu, Y. Q.; Zhu, D. B. *Adv. Mater.* **2008**, *20*, 1511–1515. (h) Tang, Q. X.; Jiang, L.; Tong, Y. H.; Li, H. X.; Liu, Y. L.; Wang, Z. H.; Hu, W. P.; Liu, Y. Q.; Zhu, D. B. *Adv. Mater.* **2008**, *20*, 2947–2951.

Scheme 1. Synthesis of Cyclopentadienone Derivatives

electronic devices; however, the skeleton for the construction of *n*-type materials is still limited. Therefore, it is still a challenge to develop new air-stable and solution-processable *n*-type organic semiconducting materials.

In our previous contribution, we developed a series of fluoranthene derivatives in organic field-effect transistors (OFETs) with good performance.⁷ In fact, the LUMO level of a compound is crucial for the electron-transport property and the stability in air. In this contribution, we facilely developed a new series of fluoranthene-fused imide derivatives to tune their LUMO levels to make these compounds show good stability in air. Such a fluoranthene-fused imide molecular design allows probing the role of the imide unit in tuning of the photophysical and electrochemical properties. Our investigation indicates that the LUMO levels can be finely tuned from two directions by introducing electron-withdrawing groups. Although the pentafluorophenyl group is located at the node of the conjugated system, it contributes

to the LUMO-level tuning of the molecules.⁸ The LUMO level can be further lowered by introducing ethoxycarbonyl and cyano substituents. What is more, the LUMO level can be drastically reduced after modifying the molecules from two directions at the same time.

Here, we chose a Diels–Alder reaction followed by decarbonylation as the crucial step for constructing our polycyclic molecules because of its high efficiency and facile operation process. Scheme 1 illustrates the synthetic approaches to four cyclopentadienone derivatives as the precursors of the subsequent reaction. A cyaniding reaction between compound **1**⁹ and cuprous cyanide afforded 1,2-dihydroacene-5,6-dicarbonitrile **2**¹⁰ in 52% yield. Treatment of compound **2** with chromium trioxide gave **3** in 72% yield. A condensation between compounds **4**¹¹ and **3** produced cyclopentadienone **5** in 61% yield. Following a similar condensation reaction, we also obtained three other cyclopentadienones **6**, **7**, and **8**.

The synthesis of their corresponding imide compounds and the structures of the eight imide derivatives are illustrated in Scheme 2. Such molecular design gives the diversity of our synthesis of our imides. For example, with the introduction of R₁, R₂, and R₃, we realized the multifunctionalization of the fluoranthene-fused imide derivatives. The Diels–Alder reaction followed by decarbonylation of cyclopentadienones with various pyrrole-2,5-dione derivatives at 180 °C afforded imides **9–16** in 18–50% yields overall for two or three steps (see Supporting Information).

All new fluoranthene-fused imides show good solubility in common organic solvents at room temperature, which is above 10 mg/mL in CHCl₃. Their structures and purity were fully characterized and verified by ¹H and ¹³C NMR, elemental analysis, and MS (see Supporting Information). The investigation of the thermal properties of all new imides indicated that they exhibited good stability with decomposition temperature higher than 350 °C in nitrogen atmosphere.

The photophysical properties of these imides were investigated in dilute CH₂Cl₂ solutions and in thin films. Their

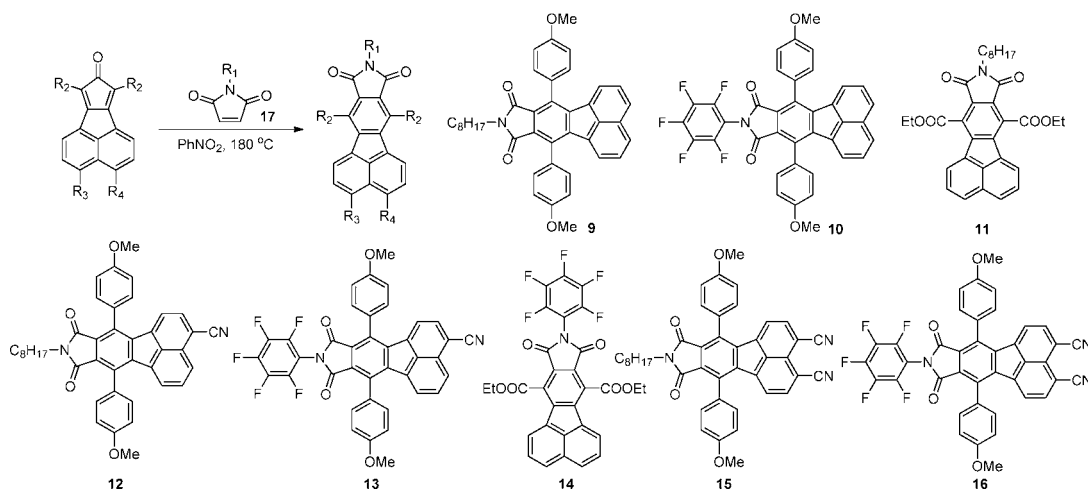
Scheme 2. Synthesis and Structures of the Corresponding Imides **9–16**

Table 1. Photophysical and Electrochemical Properties of Compounds **9–16** in Solutions and in Thin Films

compd	$\lambda_{\text{onset}}, \lambda_{\text{max abs.}}^a$ [nm] ($\log \epsilon$)	$\lambda_{\text{max emis.}}^b$ [nm]	$\lambda_{\text{max abs.}}^c$ [nm]	$\lambda_{\text{max emis.}}^c$ [nm]	E_{red}^d [V]	E_{HOMO} [eV]	E_{LUMO} [eV]	$E_{\text{g(opt)}}$ [eV]
9	450, 403 (4.57)	469	408	488	-1.27	-6.00	-3.16	2.84
10	460, 413 (4.62)	484	421	508	-1.11	-6.11	-3.32	2.79
11	429, 393 (4.69)	457	398	476	-1.05	-6.38	-3.38	3.00
12	466, 404 (4.53)	510	410	520	-1.00	-6.06	-3.43	2.73
13	475, 408 (4.53)	517	416	525	-0.88	-6.22	-3.55	2.67
14	433, 403 (4.53)	438	405	495	-0.89	-6.48	-3.54	2.94
15	488, 413 (4.48)	545	413	523	-0.73	-6.29	-3.70	2.59
16	500, 410 (4.52)	553	412	571	-0.63	-6.36	-3.80	2.56

^a λ_{onset} (left) and λ_{max} (right) in dichloromethane solution (5×10^{-5} M). ^b In dichloromethane solution (5×10^{-5} M). ^c In thin films. ^d Reference electrode: Ag/AgCl. Onsets in dichloromethane solution (1×10^{-3} M).

photophysical data in solutions and in thin films are summarized in Table 1. Figure S1 (Supporting Information) illustrates the absorption features of these eight imides in CH_2Cl_2 solutions and in thin films. As shown in Figure S1,

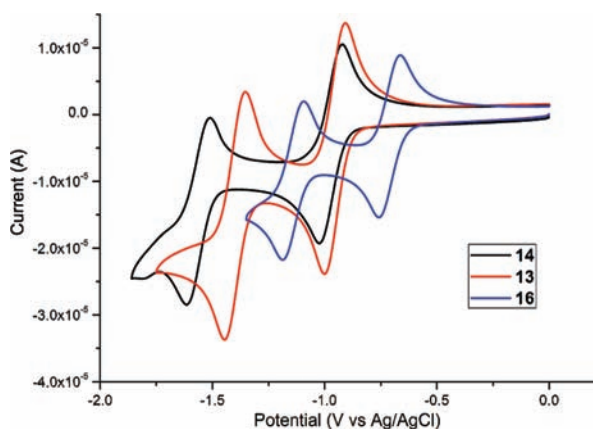


Figure 1. CV curves of the double-site modified fluoranthene derivatives in CH_2Cl_2 .

the absorption of **9** revealed a strong absorption band at 304 nm, a weaker one at 338 nm and a broad one at 403 nm.

(5) (a) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Siegrist, T.; Li, W.; Lin, Y.-Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478–481. (b) Yan, H.; Chen, Z. H.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dötter, F.; Kastler, M.; Facchetti, A. *Nature* **2009**, *457*, 679–687. (c) Jones, B. A.; Ahrens, M. J.; Yoon, M. H.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6363–6366. (d) Jones, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 15259–15278. (e) Wen, Y. G.; Liu, Y. L.; Di, C. A.; Wang, Y.; Sun, X. N.; Guo, Y. L.; Zheng, J.; Wu, W. P.; Ye, S. H.; Yu, G. *Adv. Mater.* **2009**, *21*, 1631–1635.

(6) (a) Facchetti, A.; Deng, Y.; Wang, A.; Koide, Y.; Siringhaus, H.; Marks, T. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 4547–4551. (b) Handa, S.; Miyazaki, E.; Takimiya, K.; Kunugi, Y. *J. Am. Chem. Soc.* **2007**, *129*, 11684–11685. (c) Gao, X. K.; Di, C. A.; Hu, Y. B.; Yang, X. D.; Fan, H. Y.; Zhang, F.; Liu, Y. Q.; Li, H. X.; Zhu, D. B. *J. Am. Chem. Soc.* **2010**, *132*, 3697–3699.

(7) Yan, Q. F.; Zhou, Y.; Ni, B. B.; Ma, Y. G.; Wang, J.; Pei, J.; Cao, Y. *J. Org. Chem.* **2008**, *73*, 5328–5339.

(8) Schmidt, R.; Oh, J. H.; Sun, Y.-S.; Deppisch, M.; Krause, A.-M.; Radacki, K.; Braunschweig, H.; Könemann, M.; Erk, P.; Bao, Z. N.; Würthner, F. *J. Am. Chem. Soc.* **2009**, *131*, 6215–6228.

(9) Tesmer, M.; Vahrenkamp, H. *Eur. J. Inorg. Chem.* **2001**, 1183–1188.

For **9**, **11**, **12**, and **15** with an octyl group in their structures, relative to **9**, the onset of the absorption for **11** blue-shifted from 450 to 429 nm, and absorption maximum λ_{max} also blue-shifted almost 10 nm, which was due to the introduction of the ethoxycarbonyl group; while for **12** and **15**, their absorption maximum λ_{max} exhibited the successive red-shift, which was in agreement with the increase of the conjugation length. Compared to **9**, the onset and absorption maximum λ_{max} of the pentafluorophenyl-substituted derivative **10** showed 10 nm red-shift because the pentafluorophenyl group is located at the node of the molecule which has little contribution to the photophysical properties of the compounds. For the pentafluorophenyl-substituted derivatives, they have the same wavelength-shift tendency with the octyl-substituted derivatives as shown in Table 1.¹² Compared to the solution state, the absorption wavelengths of all the compounds have a little red-shift in the thin film as shown in Table 1 and Figure S1 (Supporting Information), because of the aggregation of the compounds in the solid state.

The fluorescence spectra of these compounds were also investigated as shown in Figure S2 (Supporting Information). Compared to **9**, the emission maximum λ_{max} exhibited blue-shift from 469 to 457 nm for **11**; however for **12** and **15**, they exhibited the successive red-shift from 469 to 510 nm and 545 nm; while for **10**, it changed a little, the emission maximum λ_{max} red-shifted from 469 to 484 nm. The results are consistent with the wavelength-shift tendency of their absorption spectra and can be explained with the same reasons mentioned above.

All these eight imides were investigated by cyclic voltammetry in CH_2Cl_2 . Two reduction bands were observed for these compounds. The first reduction band can be attributed to the monoanion and the second band can be attributed to dianion formation of the conjugated fluoranthene-fused imide chromophore.¹³ From the CV curve, the reduction band shifted gradually by introducing

(10) Rieke, L. I.; Milligan, S. N.; Rieke, R. D. *J. Org. Chem.* **1983**, *48*, 2949–2953.

(11) Bhandari, S.; Ray, S. *Synth. Commun.* **1998**, *28*, 765–771.

(12) Wilson, J. N.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2005**, *127*, 4124–4125.

(13) You, C. C.; Dobrawa, R.; Saha-Möller, C. R.; Würthner, F. *Top. Curr. Chem.* **2005**, *258*, 39–82.

electron-withdrawing substituents (Figures 1 and S3, Supporting Information). The onset of the first reduction band is directly relevant to the LUMO level as shown in Table 1. The CV investigation indicated that the LUMO level is -3.16 eV for **9**, and -3.32 eV for **10**, which indicated that the introduction of the pentafluorophenyl group locating at the node of the molecule lowered the LUMO level of the molecule.⁸ The introduction of the electron-withdrawing group reduced the LUMO level of **11** to -3.38 eV. The LUMO levels were further lowered to -3.43 eV for **12** and -3.70 eV for **15** due to the introduction of the cyano substituents. Our investigation demonstrated that the most efficient way to lower the LUMO level of the compounds was the modification at the R_3 position, especially for introducing two cyano substituents. Such results were due to two effects: one is the strong electron-withdrawing ability of cyano groups and the other is the location of the R_3 group in the para-position of the largest π -conjugated core of the molecules, in contrast to the R_2 group in the ortho-position and the R_1 group in the node position. The LUMO levels can be continuously lowered by double-site modification. When the ethoxycarbonyl group and perfluorophenyl group were employed together, the LUMO level could be -3.54 eV for **14**. While cyano and perfluorophenyl groups were combined, the LUMO level could be -3.55 eV for **13** and -3.80 eV for **16**. The molecules with such electronic energy level are potential good candidates for air-stable n -type semiconductors.

Furthermore, the LUMO and HOMO distributions were demonstrated by calculations applying the method of B3LYP/6-311+g(d,p)//B3LYP/6-31G(d). The HOMO is located mainly on the bis(methoxyphenyl) benzene-conjugated core and a little on the fluoranthene imide conjugated core. For the ethoxycarbonyl substituted derivative, HOMO is located only on the fluoranthene imide π -system because of the absence of the electron-donating methoxyphenyl group. For the cyano substituted derivatives, HOMO is located only on the dimethoxyphenyl benzene motif because of the strong electron-withdrawing ability of cyano groups. The LUMO is mainly located on the fluoranthene imide group for all the compounds (Figure 2). The above calculation is consistent with the results obtained by absorption and PL spectra.

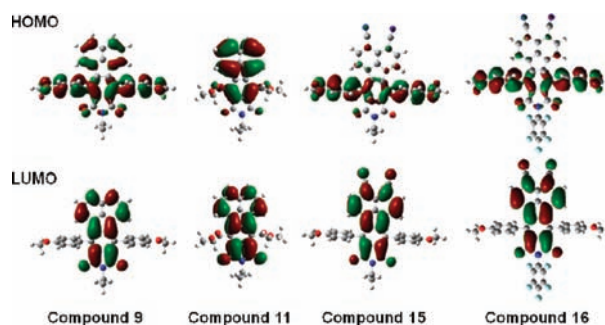


Figure 2. LUMO and HOMO distribution obtained by calculation method (B3LYP/6-311+g(d,p)//B3LYP/6-31G(d)).

In conclusion, we have successfully synthesized a series of polycyclic fluoranthene-fused imide derivatives through the Diels–Alder reaction as the crucial step in the synthetic strategy. Such molecular design gives a diversity approach to develop new polycyclic imide derivatives for n -type materials through two-directional functionalization. Our investigation in detail indicates that the photophysical and electrochemical properties of these eight imides are effectively tuned by introduction of some functional substituents. For example, the LUMO energy levels of the fluoranthene core are modulated through introducing electron-withdrawing substituents. The LUMO levels are drastically reduced from -3.2 to -3.8 eV after modifying the molecules from three different positions using high electron-withdrawing groups, so they are in agreement with the LUMO level of the typical n -type materials.

Acknowledgment. This work was supported by the Major State Basic Research Development Program (No. 2009CB623601) from the Ministry of Science and Technology and National Natural Science Foundation of China.

Supporting Information Available: Experimental procedures, ^1H and ^{13}C NMR, MS data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL1024103