Chinese Chemical Letters Vol. 15, No. 11, pp 1373-1376, 2004
http://www.imm.ac.cn/journal/ccl.html

Synthesis of a Novel Organic Soluble and Thermal-stable Fullerene-perylene Dyad

Jian Li HUA[1,2], Fang DING[1], Fan Shun MENG[1], He TIAN[1]*

[1]Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237
[2]Department of Chemistry, Jiangxi Normal University, Nanchang 330027

Abstract: A novel organic soluble and thermal-stable fullerene-perylene dyad, in which a perylene moietyis attached to C_{60}, has been prepared by 1, 3-dipolar cycloaddition of the azomethine ylides generated *in situ* from the aldehyde and N-methylglycine and characterized by NMR, FT-IR, TGA, absorption and fluorescent spectra *etc*.

Keywords: Fullerene, perylene, synthesis, characterization.

Since the discovery of a photoinduced electron transfer from a conjugated polymer to fullerene, these materials are considered for the cost effective fabrication of flexible large-area solar cells[1, 2]. As shown very recently, the devices made of polythiophene/ fullerene blends reached power conversion efficiency (η) up to 3.3%[3]. Because most fullerene compounds have poor solubility[4], to minimize the poor solubility and phase segregation of fullerene-polymer during blending, a number of double-cable polymers with a long conjugated donor backbone bearing a number of acceptor fullerene moieties have been reported[5]. Other promising approaches include the use of molecular dyads and triads made of a functionalized fullerene covalently linked to oligomeric, conjugated architectures[6].

In this work, we have designed and synthesized novel fullerene-perylene dyad, in which perylene 3, 4, 9, 10-tetracarboxylic monoimide aldehyde and fullerene units were linked with saturated covalent bonds. Perylene is selected because it has outstanding chemical, thermal and photochemical stability and high broad visible-light absorption, thus the perylene dyes have been proved to be potentially interesting candidates for solar cell sensitizer[7]. To our knowledge, no work has been reported concerning the pathway in which soluble fullerene is prepared by covalent linkage to a good soluble perylene monoimide. It can be expected the novel dyad exhibits good solubility, high thermal stability with high and broad visible light absorption band and would improve eletrochemical and photo-stability of the solar cell under high photocurrent density.

The general process for the synthesis of functionalized fullerene **3** is shown in

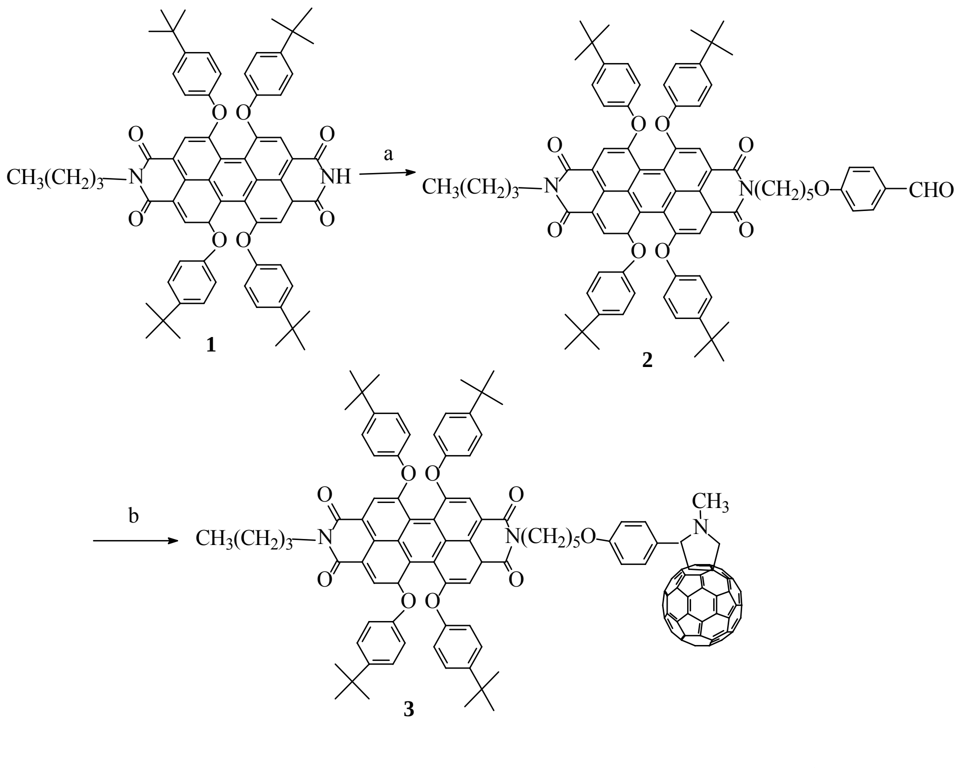
---

* E-mail: tianhe@ecust.edu.cn

Scheme 1. 4-(5-Bromopentyloxy)benzaldehyde and N-(*n*-butyl)-1, 6, 7, 12-tetra (4-tertbutylphenoxy)- 3, 4, 9, 10- perylene tetracarboxylic acid monoimide **1** were prepared according to the literature[8,9]. Core group **2** was synthesized by substitution reaction of compound **1** with 4-(5-bromopentyloxy)benzaldehyde in 70 % yields. Dyad **3** was prepared in 20.7 % isolated yield *via* the 1, 3-dipolar cycloaddition of azomethine ylides to [60] fullerene by treating perylene aldehyde **2** with N-methylglycine and [60] fullerene in refluxing chlorobenzene. All spectroscopic and analytical data were consistent with the proposed molecular structure[10].

The absorption and fluorescence data of **2** and **3** was listed in **Table 1**. In the UV-Vis spectra, **2** and **3** showed three typical perylene absorption peaks at 451, 537, and 578 nm with high coefficients, but dyad **3** exhibited distinctive strong absorption at 300~400 nm (**Figure 1**), indicating electronic interaction between fullerene and perylene. Perylene **2** in CH_2Cl_2 excited by 560 nm displayed fluorescent maxima at 611 nm. And dyad **3** had emission spectra with characteristic features of the perylene unit, however, its luminescence was largely quenched (**Figure 1**), showing that the intramolecular chargetransfer and/or energy transfer to be expected to occur[11].

Scheme 1 Synthesis of fullerene-perylene dyad



Reagents and conditions: (a) 4-(5-bromopentyloxy)benzaldehyde, NMP/K_2CO_3, 110℃, 24h; (b) C_{60}, CH_3NHCH_2COOH, chlorobenzene, reflux 24h

Table 1 Absorption and fluorescence data of **2, 3** in CH_2Cl_2

Compounds	λ^{ab}_{max}/nm (log ε)			λ^{fl}_{max}/nm
2	578 (4.73)	537 (4.52)	451 (4.32)	611
3	579 (4.76)	541 (4.56)	451 (4.41)	613

Figure 1 The absorption and fluorescence spectra (λ_{ex}: 560 nm) of **2, 3** in CH_2Cl_2

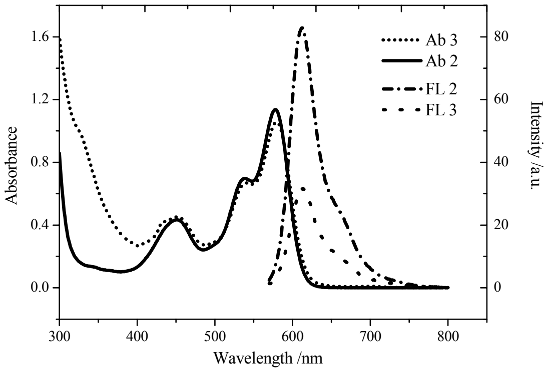
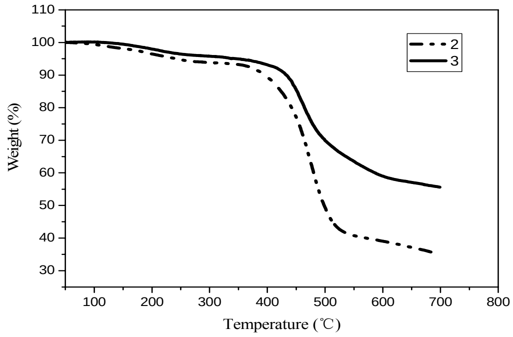


Figure 2 The TGA spectrum of **2** and **3**



The electrochemistry of the dyad **2** was studied using cyclic voltametry (CV). The measurements were recorded on a CHI voltametric analyzer in dry dichloromethane using 0.1 mol / L tetrabutyl-ammonium perchlorate ($TBAClO_4$) as supporting electrolyte, glassy carbon as working electrode, Pt as counter electrode, Ag/AgCl as reference electrode and each measurement was calibrated as usual with the standard ferrocene/ferrocenium redox system[12]. We obtained LUMO energy of 4.03 eV *vs*. vacuum (-1V *vs* Ag/AgCl). Since the LUMO of C_{60} (4.4 eV *vs*. vacuum) [13] is lower than the respective LUMO energy of perylene, we infer that C_{60} should behave as acceptor for the perylene.

Thermal property of compounds **2** and **3** was investigated by means of thermogravimetric analysis (TGA) at a heating rate of 10 °C/min under nitrogen atmosphere, **3** revealing better thermal stability up to 432 °C as shown in **Figure 2**. It has been found that **3** has good solubility in common organic solvents such as toluene, $CHCl_3$, THF, NMP and branched *tert*-butyl phenyl group on the bay of perylene moiety has proven to be effective in enhancing their solubility.

In summary, we have synthesized a novel soluble and highly thermal stable perylene dyad containing fullerene as electronic acceptor. It shows the broad visible-light absorption with high coefficients and might provide a path toward the realization of high efficiency solar cells. The measurement of its photovoltaic properties is in progress.

Acknowledgments

J. L. Hua thanks the grant support from Postdoctoral Science Foundation of China and Science Committee of Shanghai (No.03dz12034). H. Tian acknowledges the support from NNSFC (No.20273020) and Education Committee of Shanghai.

References and Notes

1. a) H. Imahori, Y. Sakata, *Adv. Mater.*, **1997,** *9,* 537. b) A. Gouloumis, S. Liu, A. Saatre, P. Vazuquen, L. Echegoyen, T. Torres, *Chem. Eur. J.,* **2000**, *19*, 3600. c) C. J. Brabed, N. S. Sariciftci, *Monatsch. Chem.*, **2001,** *132*, 421.
2. a) G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science*, **1995,** *270*, 1789. b) J. J. M. Halls, C. A. Walsh, N. C. Greenham *et al.*, *Nature*, **1995,** *376*, 498. c) L. Schmidt-Mende, A. Fechtenkötter, K. Müllen *et al.*, *Science*, **2001,** *293*, 1119.
3. F. Padinger, R. S. Rittberger, N. S. Saariciftci, *Adv. Funct. Mater.*, **2003,** *13*, 85.
4. R. C. Haddon, A. S. Perel, R.C.Morris, T. *et al., Appl. Phys. Lett.*, **1995,** *67*, 121.
5. a) A. M. Ramos, M. T. Rispens, J. K. J. van Duren *et al.*, *J. Am. Chem, Soc.*, **2001,** *123*, 6741. b) F. Zhang, M. Svensson, M. R. Andersson *et al.*, *Adv. Mater.*, **2001,** *13*, 171.
6. M. Maggini, G. Possamai, E. Menna *et al.*, *Chem. Commun*, **2002**, 2028.
7. a) W. H. Zhu, H. Tian, E. Q. Gao *et al., Chem. Lett.,* **2000**, 778. b) H. Tian, P. H. Liu, W. H. Zhu *et al.*, *J. Mater. Chem.,* **2000,** *10*, 2708.
8. P. K. Sudeep, B. I. Ipe, K. G. Thomas, *Nano Lett.*, **2002,** *2,* 29.
9. J. S. Park, C. W. Lee, M. S. Gong, *Synthetic Metals*, **2003,** *132*, 177.
10. The FT-IR (KBr) and NMR analysis data for compound **2** and **3** are as follows: **2:** yield 70 %; IR (KBr) : 3039, 2958, 2866, 1697, 1659, 1588, 1504, 1286, 1014 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$, δ_{ppm}): 9.85 (s, 1H), 8.23 (s, 4H), 7.79 (d, 2H, J=8.67Hz), 7.24 (d, 8H, J=8.23Hz), 6.94 (d, 2H, J=8.77Hz), 6.84 (d, 8H, J=8.39Hz), 4.14 (m, 4H), 4.01 (t, 2H, J=7.08Hz), 1.85 (m, 2H), 1.80 (m, 2H), 1.67(m, 2H), 1.56 (m, 2H), 1.39 (m, 2H), 1.29 (s, 36H), 0.93 (t, 3H, J=7.26Hz). **3:** yield 20.7 %; IR (KBr): 3059, 2961, 2780, 1697, 1660, 1586, 1503, 1261, 1017, 573, 525 cm^{-1}; ^{1}H- NMR (500 MHz, $CDCl_3$, δ_{ppm}): 8.21 (s, 4H), 7.65 (d, 2H, J=9.24Hz), 7.22 (d, 8H, J=12.25Hz), 6.89 (d, 2H, J=8.14Hz), 6.83 (d, 8H, J=11.75Hz), 4.95 (d, 1H, J=9.36Hz), 4.84 (s, 1H), 4.21 (d, 1H, J=10.46Hz), 4.10 (m, 4H), 3.95 (t, 2H, J=7.08Hz), 2.77 (s, 3H), 1.92 (m, 2H), 1.82 (m, 2H), 1.66 (m, 2H), 1.58 (m, 2H), 1.41 (m, 2H), 1.29 (s, 36H), 0.94 (t, 3H, J=7.26Hz); ^{13}C-NMR (125 MHz, $CDCl_3$, δ_{ppm}): 164.09 [$(CO)_2NR$], 156.69, 156.61, 153.57, 147.92, 147.42, 147.11, 146.97, 146.66, 146.47, 146.34, 146.10, 145.87, 145.26, 145.14, 144.95, 143.65, 143.53, 143.22, 143.11, 143.06, 142.98, 142.22, 142.83, 142.69, 142.63, 142.55, 142.49, 142.36, 142.24, 142.08, 140.72, 140.49, 140.14, 137.34, 137.19, 136.36, 129.71, 127.33, 123.23, 123.08, 121.31, 121.15, 120.63, 120.58, 120.18, 120.05, 120.01, 83.85, 70.66, 69.59, 68.25, 53.49, 42.66, 41.08, 40.63, 35.04, 32.15, 31.04, 30.89, 30.38, 30.04, 29.49, 28.47, 27.71, 25.32, 24.18, 23.37, 23.22, 21.05, 14.80, 14.48 ; MALDI-TOF *m/z* : 1976.7 [M+1].
11. a) J. L. Yang, H. Z Lin, S. Wang *et al.*, *J. Polymer & Sci. Part A: Chem.,* **2001**, *39*, 3981. b) I. B. Martini, B. Ma, T. D. Ros *et al.*, *Chem. Phys. Lett.*, **2000**, *327*, 253.
12. C. Hohle, U. Hofmann, S. Schloter *et al.*, *J. Mater. Chem.,* **1999**, *9*, 2205.
13. C. Rogere, J. I. Pascual, J. Gómez-Herrero *et al.*, *J. Chem. Phys.*, **2002**, *116*, 83.

Received 17 September, 2003