Pergamon

Tetrahedron Letters 41 (2000) 8559–8563

TETRAHEDRON
LETTERS

# Fluorescein–fullerene dyads: a new kind of fullerene dyad—synthesis and their photophysical properties

Bingwen Jing, Deqing Zhang* and Daoben Zhu

*Organic Solids Laboratory, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China*

Received 22 June 2000; revised 30 August 2000; accepted 7 September 2000

---

## Abstract

Two novel fluorescein–$C_{60}$ dyads have been synthesized. Fluorescence quenching in the dyads indicates a photoinduced intramolecular electron transfer from the fluorescein to the $C_{60}$ moiety. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* fluorescein; fullerene; photoinduced electron transfer.

---

Over the past decade, a great variety of dyads and more complex polyads consisting of electron donors and acceptors have been designed to investigate photoinduced energy and electron transfer (ET) processes and to mimic natural photosynthesis.[1] Fullerenes as novel electron acceptors, in particular the readily available $C_{60}$, present a wide range of chemical and physical properties that make them promising chromophores in photoinduced redox processes.[2] Many investigations show that $C_{60}$ is a good electron acceptor. One of the most remarkable properties of $C_{60}$ related to electron transfer phenomena is that it can efficiently induce a rapid charge separation and a further slow charge recombination. These peculiar photophysical properties are due to the small reorganization energies of $C_{60}$ in ET.[3] Therefore, a wide variety of $C_{60}$-donor dyads in which $C_{60}$ and a donor unit are covalently attached have been recently synthesized for investigations of their photoinduced electron transfer behavior.[2] The donors in these $C_{60}$-donor dyads include porphyrins,[3–10] TTFs,[11,12] polypyridine ruthenium(II) complexes,[13] *N*,*N*-dialkylaniline,[14] ferrocene[15] and carotenoid.[16] Among these, the systems consisting of porphyrins and $C_{60}$ are the most prominent and have been extensively studied. However, to the best of our knowledge, no reports concerning fluorescein (FL)–$C_{60}$ systems have appeared so far, although FL is a very important xanthene dye, which has many technical applications[17] due to its high fluorescence quantum yield, excellent redox properties as well as relatively large

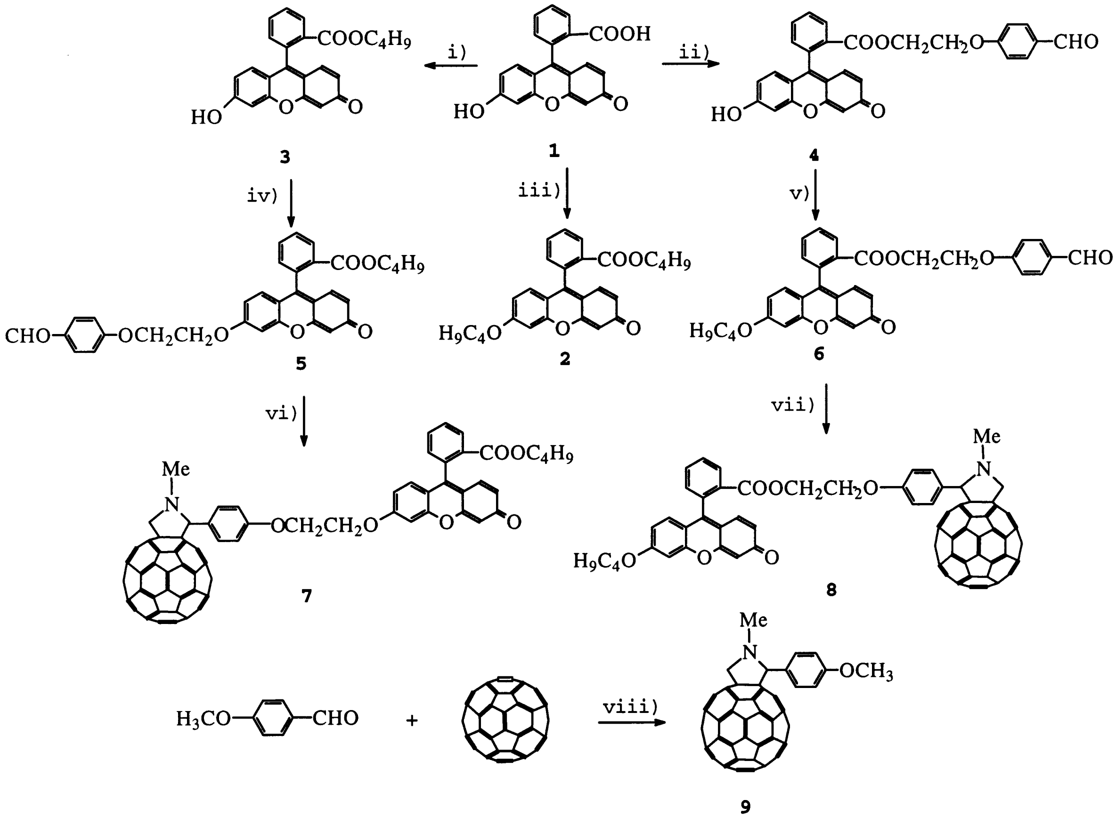
---

* Corresponding author. E-mail: dqzhang@infoc3.icas.ac.cn

PII: S0040-4039(00)01523-9

extinction coefficients at visible wavelengths. Also, FL contains two active groups—the hydroxyl and the carboxyl groups, which can be used to link FL to different electron donors or acceptors. Thus, FL was frequently used as electron donor/acceptor and sensitizer in artificial photosynthetic models.[18] Based on these considerations, the FL–$C_{60}$ system may be a good model for the study of artificial photosynthesis. In order to investigate this possibility, we have synthesized two dyads **7** and **8**, consisting of a FL covalently linked to a fullerene, as well as model compounds **2** and **9**.

The synthesis was carried out as outlined in Scheme 1. The synthetic approach to compounds **7**–**9** relies upon the 1,3 dipolar cycloaddition of azomethine ylides to $C_{60}$. This methodology has proven to be one of the most powerful procedures for the functionalization of $C_{60}$ due to its versatility and the ready availability of the starting materials. Therefore, reaction of aldehydes **5**, **6** and *p*-anisaldehyde (0.1 mmol) with *N*-methylglycine (32 mg, 0.36 mmol) and $C_{60}$ (72 mg, 0.01 mmol) in toluene (100 ml) under Ar at reflux for 8–12 hours, gave the corresponding fulleropyrolidines **7**–**9** after column chromatographic purification (silica gel, toluene/methanol, 50:1). The aldehydes **5**, **6** and dibutyl fluorescein **2** were prepared by alkylation of FL using the corresponding alkylbromide in DMF at 90°C for 2–3 hours with anhydrous potassium carbonate as base. The structures of all these compounds were verified by spectroscopic analyses.[19]



Scheme 1. (i) 1-Bromobutane, anhydrous $K_2CO_3$, DMF, 90°C for 2–3 hrs, 76%; (ii) 4-(2-bromoethoxyl)-benzaldehyde, *ibid.*, 75%; (iii) 1-bromobutane, *ibid.*, 85%; (iv) 4-(2-bromoethoxyl)-benzaldehyde, *ibid.*, 71%; (v) 1-bromotane, *ibid.*, 77%; (vi) *N*-methylglycine, Ar, toluene, reflux for 8–12 hrs, 30%; (vii) *ibid.*, 34%; (viii) *ibid.*, 28%

The UV–vis spectra of the dyads **7** and **8** (Fig. 1) consist simply of a superposition of the absorption spectra of the $C_{60}$ and FL subunits, indicating that there is no appreciable interaction between the FL and $C_{60}$ in the ground state. However, the steady-state fluorescence spectra of **7** and **8** (Fig. 2), taken in chloroform with the same concentration and excited at 460 nm where

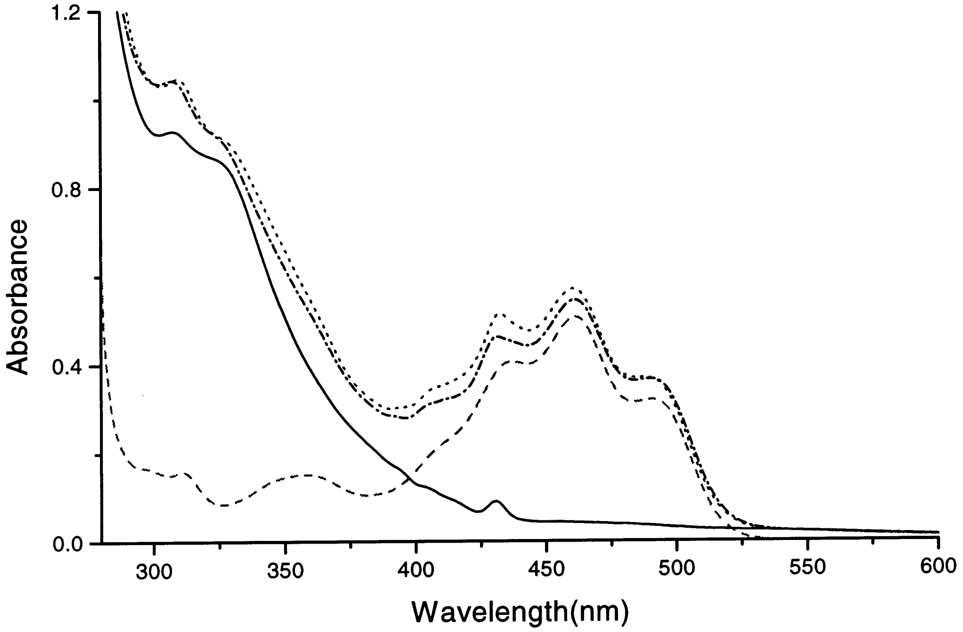


Figure 1. Electronic absorption spectra of **2** (dash), **7** (dot), **8** (dash dot) and **9** (solid) in $CHCl_3$ ($2\times10^{-5}$ M)

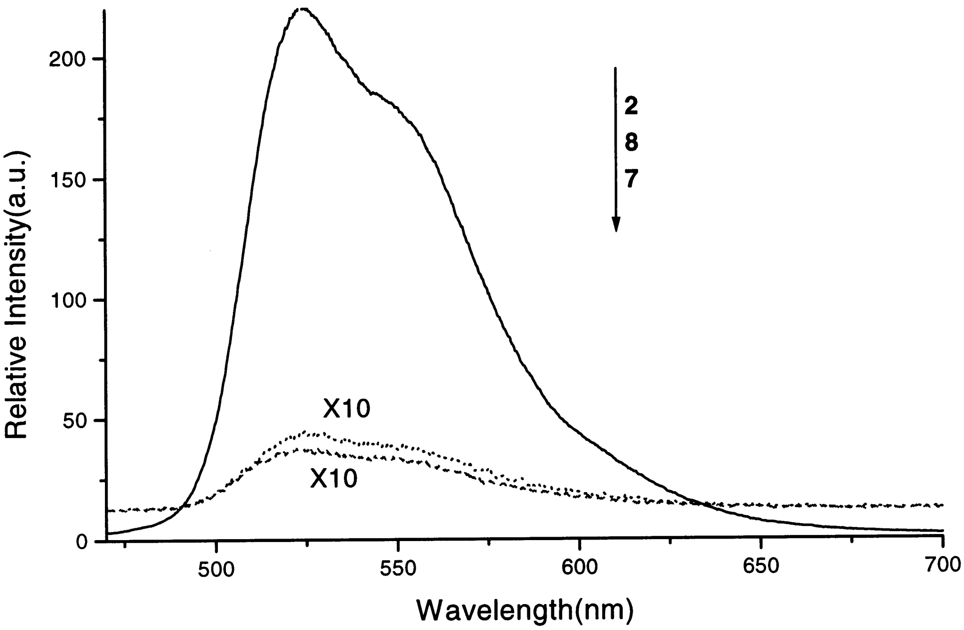


Figure 2. Fluorescence spectra of **2**, **7** and **8** in $CHCl_3$ ($2\times10^{-5}$ M) excited at 460 nm

the FL part mainly absorbs, show a significant difference compared with those of **2**, **5** and **6**. Whereas with **2**, **5** and **6** a strong emission could be observed, the emissions of **7** and **8** are very weak, showing rapid quenching of the excited singlet state of FL by $C_{60}$. Besides, the emissions of **7** and **8** (480–650 nm) were observed only from the FL, without detectable emission from the $C_{60}$ (680–750 nm), while the emission from $C_{60}$ in model **9** was observed (680–750 nm). This shows there is no evidence for the existence of singlet-singlet energy transfer from $^1$FL* to the $C_{60}$. These results imply that intramolecular photoinduced electron transfer from the FL to $C_{60}$ is a main pathway for the emission quenching in chloroform. The detailed photophysical properties of the two dyads, such as their fluorescence lifetimes and the rates of formation and lifetime of charge separation state are under investigation.

## Acknowledgements

The authors thank the CAS for the financial support (KJ-951-A1-50103).

## References

1. Fox, M. A.; Chanon, M. *Photoinduced Electron Transfer*; Elsevier: Amsterdam, 1988.
2. Martín, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527–2547.
3. Hiroshi, I.; Yoshiteru, S. *Eur. J. Org. Chem.* **1999**, 2445–2457.
4. Kuciauskas, D.; Liddell, P. A.; Lin, S.; Johnson, T. E.; Weghorn, S. J.; Lindsey, J. S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1999**, *121*, 8604–8614.
5. Wedel, M.; Montforts, F.-P. *Tetrahedron Lett.* **1999**, *40*, 7071–7074.
6. Koji, Y.; Hiroshi, I.; Yoshinobu, N.; Iwao, Y.; Yoshiteru, S. *Chem. Lett.* **1999**, 895–896.
7. Manoru, F.; Osamu, I.; Hiroshi, I.; Koji, Y.; Hiroko, Y.; Yoshiteru, S. *Chem. Lett.* **1999**, 721–722.
8. Cheng, P.; Wilson, S. R.; Schuster, D. I. *Chem. Commun.* **1999**, 89–90.
9. Koichi, T.; Hiroshi, I.; Yoshinobu, N.; Iwao, Y.; Yoshiteru, S. *Chem. Commun.* **1999**, 625–626.
10. Tkachenka, N. V.; Rantala, L.; Tauber, A. Y.; Helaja, J.; Hynninen, P. H.; Lemmetyinen, H. *J. Am. Chem. Soc.* **1999**, *121*, 9378–9387.
11. Martín, N.; Sánchez, L.; Seoane, C.; Andreu, R.; Garín, I.; Orduna, J. *Tetrahedron Lett.* **1996**, *37*, 5979.
12. Simonsen, K. B.; Konovalov, V. V.; Konovalova, T. A.; Kawai, T.; Cava, M. P.; Kispert, L. D.; Metzger, R. M.; Becher, J. *J. Chem. Soc., Perkin Trans. 2* **1999**, 657–665.
13. Maggini, M.; Dono, A.; Scorrano, G.; Prato, M. *J. Chem. Soc., Chem. Commun.* **1995**, 845.
14. Williams, R. M.; Zwier, J. M.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 4093.
15. Guldi, D. M.; Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1997**, *119*, 974–980.
16. Liddell, P. A.; Kuciauskas, D.; Sumida, J. P.; Nash, B.; Nguyen, D.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1997**, *119*, 1400–1405.
17. Neckers, C. D.; Oscar, M. V.-A. *Adv. Photochem.* **1995**, *18*, 315.
18. Zhang, H.; Zhang, M.; Shen, T. *Sci. China* (*Ser. B*) **1997**, *40* (5), 449–456.
19. Spectroscopic data for **7**: $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.28 (1H, d), 7.76–7.68 (4H, m), 7.25 (1H, d), 7.20–6.92 (5H, m), 6.90–6.65 (3H, m), 5.04–5.01 (2H, d, unresolved, 1H of $CH_AH_{B+}$ 1H of CH in pyrrolidine), 4.47–4.25 (5H, m, 1H of $CH_AH_B$ in pyrrolidine+$OCH_2CH_2O$), 3.98 (2H, m, $-COOCH_2-$), 2.84 (3H, s, $-NCH_3$), 1.38–1.28 (2H, m, $-CH_2CH_2CH_2CH_3$), 1.13–1.03 (2H, m, $-CH_2CH_2CH_2CH_3$), 0.81–0.76 (3H, t, $-(CH_2)_3CH_3$). $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ 165.2, 163.7, 158.8, 158.2, 154.6, 147.1, 146.1, 146.0, 145.9, 145.7, 145.3, 145.2, 145.1, 145.0, 144.9, 144.5, 144.2, 144.1, 142.9, 142.5, 142.4, 142.0, 141.8, 141.7, 141.5, 141.3, 139.9, 139.7, 139.6, 139.3, 136.7, 136.4, 135.7, 135.5, 133.7, 133.6, 132.5, 131.3, 131.2, 131.0, 130.9, 130.8, 130.4, 130.1, 129.7, 129.3, 129.2, 128.9, 128.8, 128.7, 128.6, 128.4, 128.0, 127.5, 117.5, 115.2, 114.6, 105.3, 100.6, 82.8, 77.5, 76.4, 69.5, 68.6, 67.4, 65.4, 39.8, 30.0, 18.9, 13.4; FT-IR $\nu$/cm$^{-1}$, 2953, 1720, 1642, 1597, 1510, 1448, 1377, 1285, 1247, 1206, 1105, 853, 758,

527; MALDI-TOF *m*/*z* 1283 ($M^+$). Spectroscopic data for **8**: $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 8.32 (1H, d), 7.91–7.60 (4H, m), 7.25 (1H, d), 6.91–6.80 (2H, m), 6.72–6.64 (3H, m), 6.58–6.01 (3H, m), 5.03–4.94 (2H, m, 1H of $CH_AH_{B+}$ 1H of CH in pyrrolidine), 4.30–4.20 (3H, m, 1H of $CH_AH_B$ in pyrrolidine and $COOC\mathbf{H}_2CH_2O–C_6H_4–$), 4.05–3.70 (2H, m, $–OC\mathbf{H}_2C_3H_7$), 3.75–3.52 (2H, m, $–COOCH_2C\mathbf{H}_2O–C_6H_4–$), 2.83 (3H, s, $NCH_3$), 1.90–1.70 (2H, m, $–OCH_2C\mathbf{H}_2C_2H_5$), 1.60–1.40 (2H, m, $–OCH_2CH_2C\mathbf{H}_2CH_3$) 1.05–0.96 (3H, m, $OC_3H_6CH_3$); $^{13}C$ NMR (300 MHz, $CDCl_3$): $\delta$ 165.2, 158.8, 158.7, 158.1, 156.3, 154.6, 154.5, 154.0, 153.9, 153.7, 153.5, 147.3, 146.5, 146.3, 146.2, 146.1, 145.9, 145.5, 145.4, 145.3, 145.2, 145.1, 144.7, 144.4, 143.2, 143.0, 142.7, 142.6, 142.2, 142.1, 142.0, 141.6, 140.2, 139.6, 136.4, 135.9, 135.8, 134.2, 132.9, 131.8, 130.4, 129.8, 129.5, 129.3, 129.0, 117.4, 114.8, 114.5, 105.5, 100.7, 100.6, 83.0, 77.3, 77.2, 69.9, 68.9, 65.2, 63.8, 40.0, 30.9, 19.2, 13.9; FT-IR $\nu/cm^{-1}$ 2953, 1725, 1642, 1596, 1510, 1376, 1282, 1250, 1207, 1179, 1106, 853, 758, 527; MALDI-TOF *m*/*z* 1283 ($M^+$). Spectroscopic data for **9**: $^1H$ NMR (300 MHz, $CS_2$): $\delta$ 7.87 (2H, d, H *m* to methyl in phenyl), 7.10 (2H, d, H *o* to methyl in phenyl), 5.15 (1H, d, 1H of $CH_AH_B$ in pyrrolidine), 5.09 (1H, s, CH in pyrrolidine), 4.48 (1H, d, 1H of $CH_AH_B$ in pyrrolidine), 4.02 (3H, s, $–OCH_3$), 3.03 (3H, s, $–NCH_3$); $^{13}C$ NMR (300 MHz, $CS_2$): 153.9, 147.5, 147.2, 146.9, 146.7, 146.5, 146.4, 146.2, 146.0, 145.9, 145.7, 145.6, 145.5, 145.4, 145.3, 145.2, 145.1, 144.9, 144.7, 144.3, 143.4, 143.3, 142.9, 142, 7, 142.5, 142.4, 142.4, 142.0, 141.9, 141.8, 141.6, 141.2, 140.5, 139.9, 137.0, 136.1, 135.0, 130.8, 128.6, 114.2 (2), 83.1, 77.7, 70.0, 69.8, 64.3, 40.0; FT-IR $\nu/cm^{-1}$ 2778, 1611, 1511, 1643, 1332, 1302, 1249, 1179, 1107, 1035, 841, 832, 765, 527; MALDI-TOF *m*/*z* 883 ($M^+$).