Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron Letters 45 (2004) 6927–6930

Tetrahedron
Letters

Synthesis of [60]fullerene–coumarin polyads

Maria João Brites,[a] Célia Santos,[a] Susana Nascimento,[a,b] Bárbara Gigante[a,*]
and Mário N. Berberan-Santos[b,*]

[a]*INETI—Departamento de Tecnologia de Indústrias Químicas, Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal*
[b]*Centro de Química-Física Molecular, Instituto Superior Técnico 1049-001 Lisboa, Portugal*

Received 19 May 2004; revised 13 July 2004; accepted 19 July 2004

Abstract—New polyads were obtained by covalently linking a coumarin dye to a fullerene (C_{60}) following two different strategies: 1,3-dipolar cycloaddition reaction of azomethine ylides or by cyclopropanation reaction. The new polyads are spectroscopically characterized and their fluorescence properties, including the observation of efficient singlet–singlet energy transfer, reported.

Over the past decade, a large number of C_{60}-based donor–acceptor dyads, and more complex polyads, in which C_{60} is covalently linked to photoactive groups, were obtained, aiming at exploring their excited-state donor–acceptor interactions, including photoinduced electron transfer.[1–11] Understanding of the energy and electron transfer processes involved is important towards practical applications such as photovoltaic devices for solar energy conversion.[6] For this purpose, several synthetic methodologies have been developed, which allow covalent linkages of C_{60} with other photo- and electroactive molecules.[2,3] Different donors and linkers to C_{60} have been used. In fact, the length, chemical constitution or the presence of rigid or saturated hydrocarbon bridges is known to play an important role on the electronic coupling between the donor and the acceptor chromophores.[1,6,7]

Coumarins are attractive molecules due to their extended spectral range, high emission quantum yields and photostability.[12–15] Moreover coumarin derivatives are frequently encountered as signalling units in sensors and in sophisticated photophysical systems.[16–18] However, to the best of our knowledge, no reports concerning coumarins–C_{60} systems have appeared so far.

We report here the synthesis of novel fullerene–coumarin polyads, consisting of one or two coumarin moieties covalently linked to fullerene by different approaches (Scheme 1 and 2) and then compare their photophysical properties (Table 1).

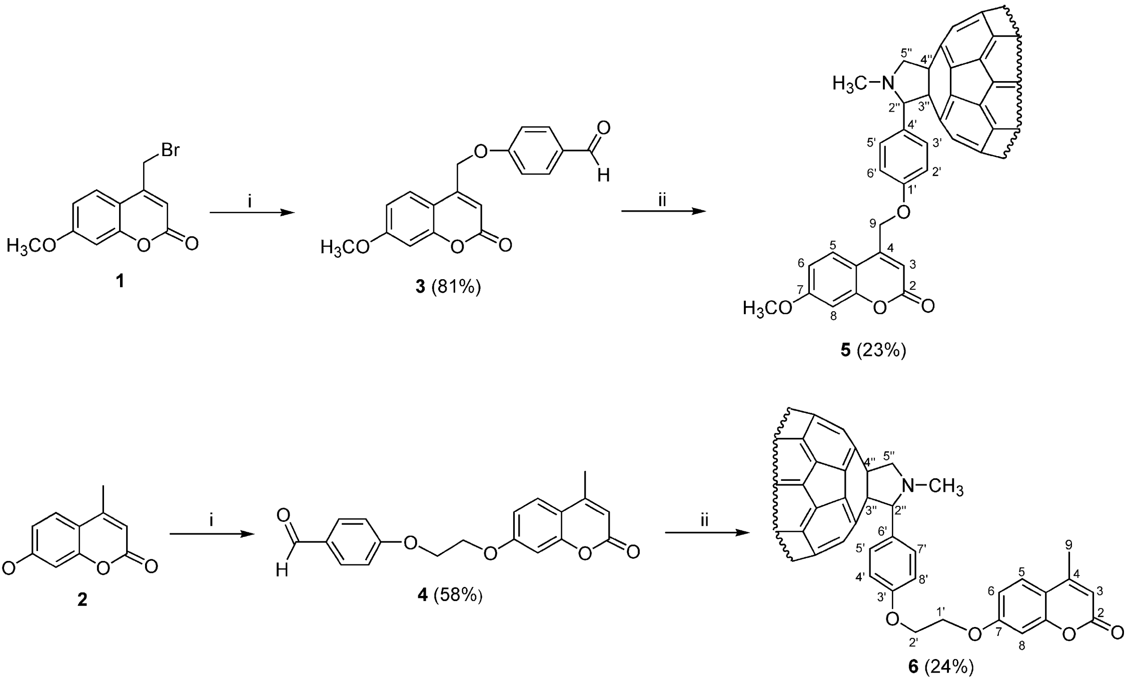
Commercially available coumarins, 4-(bromomethyl)-7-methoxycoumarin **1** and 7-hydroxy-4-methylcoumarin **2** containing active groups (bromoalkyl or hydroxyl groups) in different carbons (C-4 or C-7), were used as starting materials.

From **1** or **2**, following 1,3-dipolar cycloaddition reaction of azomethine ylides generated in situ, from the reaction of an aldehyde group with *N*-methylglycine to fullerene,[19] [60]fulleropyrrolidines derivatives **5** or **6** were obtained (Scheme 1). To this end, **2** was alkylated with equimolar amount of 4-(2-bromoethoxyl)-benzaldehyde or **1** by reaction with 4-hydroxybenzaldehyde both in dimethylformamide at 90 °C for 2–4 h using anhydrous potassium carbonate as base to obtain, respectively, the intermediates **4** and **3** with the aldehyde functionality at C-7 or C-4 of the coumaryl moiety. [60]Fulleropyrrolidines **5** or **6** were separated from the reaction mixtures by flash chromatography using gradients of toluene and ethyl acetate as eluent. After the unchanged C_{60}, the monoadducts **5** or **6** were separated. Minor products with higher polarity, probably bis-adducts, were discarded. After purification by precipitation from chloroform and methanol, each of the fullerene derivatives was isolated with moderated yields: **5** (23%) and **6** (24%).

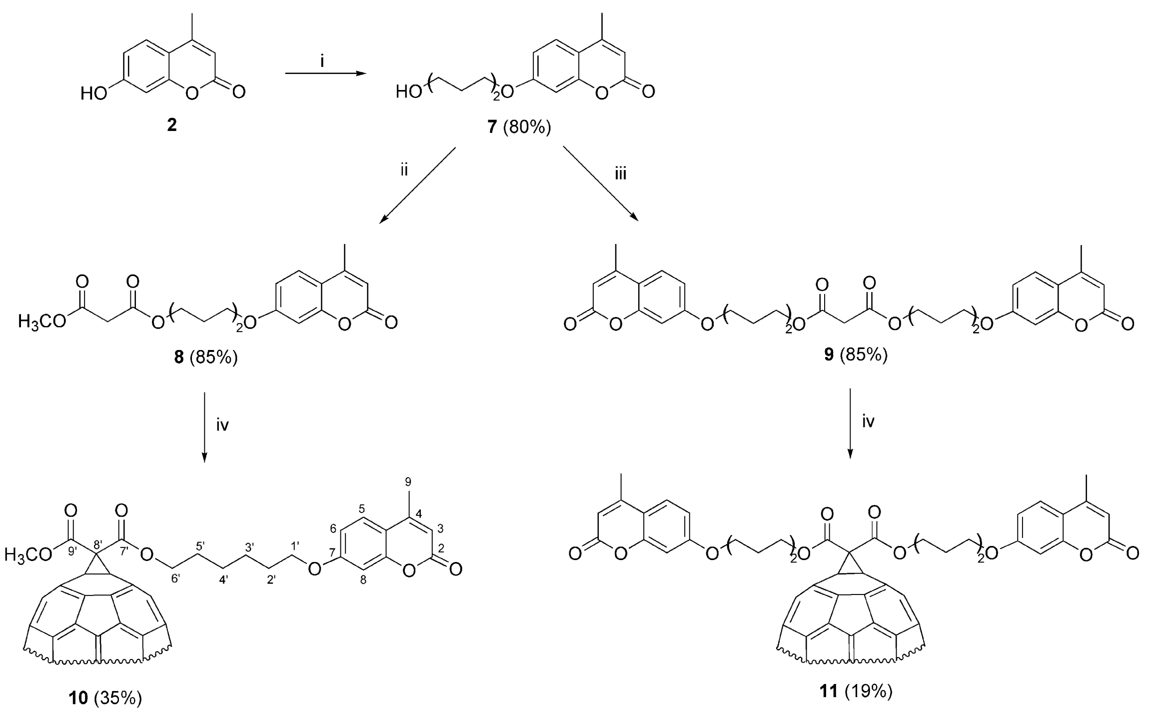
Keywords: Coumarin; C_{60}; Dyads; Polyads.

* Corresponding authors. Tel.: +351 210924600; fax: +351 217168100 (B.G.); tel.: +351 218419254; fax: +351 218464455 (M.N.B.-S.); e-mail addresses: barbara.gigante@ineti.pt; berberan@ist.utl.pt

0040-4039/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2004.07.079



Scheme 1. Reagents and conditions: (i) 4-(2-bromoethoxyl)-benzaldehyde for **4** and 4-hydroxybenzaldehyde, for **3**, K_2CO_3, DMF, 90 °C; (ii) C_{60}, $MeNHCH_2CO_2H$, N_2, toluene, reflux.



Scheme 2. Reagents and conditions: (i) 6-bromo-hexanol, K_2CO_3, DMF, 60 °C; (ii) methyl-3-chloro-3-oxopropionate, Et_3N, CH_2Cl_2, N_2, 0 °C–rt; (iii) malonyl dichloride, Et_3N, CH_2Cl_2, N_2, 0 °C–rt; (iv) C_{60}, DBU, I_2, toluene, rt.

From **2**, methano[60]fullerene dyad **10** and triad **11** were also obtained by cyclopropanation[20] of C_{60} with the appropriate malonate derivative **8** or **9** (Scheme 2).

The malonate derivatives **8** and **9** containing one and two coumarin moieties were obtained, respectively, by alkylation of the 7-hydroxyl group of coumarin **2** with 6-bromo-1-hexanol, followed by the reaction of the resulting alcohol **7** with the appropriate malonyl chloride (methyl malonyl chloride or malonyl dichloride) in high yield (85%). Cyclopropanation reaction of C_{60} with malonates **8** or **9** afforded **10** or **11**, respectively. Separation from the reaction mixture by column chromatography (toluene–ethyl acetate 4:1) gave the mono-

Table 1. Absorption and fluorescence peak wavelengths, and fluorescence quantum yields of C_{60}, coumarin intermediates **3**, **4**, **8** and **9**, and of fullerene derivatives **5**, **6**, **10** and **11**.

Compound	λ_{abs} (nm)	λ_{em} (nm)	$\Phi_F/10^{-3}$	
C_{60}	328, 408 (sh), 404, 689	712	—	0.2
3	322	398, 468 (sh), 498 (sh)	18	—
4	320, 337(sh)	382	18	—
8	322, 337 (sh)	384	16	—
9	321	383	—	—
5	322, 434, 706	382, 710	—	1.7[a]
6	320, 434, 704	378, 712	—	1.8[a]
10	327, 429, 496, 688	380, 700	1.7	1.0[a]
11	326, 429, 490, 687	384, 700	1.3	0.77[a]

[a] Direct excitation of the fullerene moiety (excitation wavelength: 400 nm).

adducts **10** (35%) and **11** (19%). Either the intermediates as final products were characterized by UV–vis, FT-IR, ^{1}H and ^{13}C NMR and mass spectroscopy including MALDITOF-MS for fullerene derivatives.

The fluorescence quantum yields of the coumarin compounds (**3**, **4** and **8**), at room temperature in toluene, are of the order of 0.02. The absorption spectra of **10** and **11** are the sum of the absorption spectra of the C_{60} and coumarin subunits, respectively, **8** and **9**. On the other hand, the absorption spectra of **5** and **6**, when compared to those of **3**, **4** and of [60]fulleropyrrolidines without coumarin moiety, reveal the existence of ground state interactions.

The fluorescence of the fullerene derivatives **5**, **6**, **10** and **11**, obtained at room temperature in toluene and with 300 nm excitation, differs significantly from that of **3**, **4** and **8**, as shown in Table 1. Apart from the coumarin emission that occurs in the 340–520 nm range, a second emission band, characteristic of the fullerene moiety, is observed in the 670–800 nm region. Furthermore, in the polyads (**5**, **6**, **10** and **11**), there is a dramatic decrease of the coumarin moiety quantum yield when compared with that of the coumarin intermediates (**3**, **4** and **8**). This implies a strong intramolecular quenching of the coumarin fluorescence by the fullerene moiety. Simultaneously, an increase in the emission quantum yield of the C_{60} moiety (680–705 nm) compared to that of directly excited fullerene mono-adduct, is observed, indicating the existence of fast and efficient singlet–singlet energy transfer from the coumarin moiety to the fullerene. This process is consistent with a dipole–dipole mechanism, as will be discussed elsewhere.

1. Experimental

All spectral measurements were made in quartz cells of 1 cm path length, at room temperature and all solvents used were of spectroscopic grade. Electronic absorption spectra were measured using a Shimadzu 3101 UV/vis/NIR and a Hitachi 150-20 spectrophotometers. Fluorescence quantum yields at room temperature in toluene were determined by a comparative method, using anthracene (Fluka) in air-saturated ethanol ($\phi_F = 0.27$)[21] as the fluorescence standard for coumarins and C_{60} (99.5%, Aldrich) in toluene ($\phi_F = 2 \times 10^{-4}$)[22] as the standard for fullerene derivatives. The excitation wavelength was 320 nm for coumarin compounds **3**, **4**, **8**, **9** and 300 nm for all fullerene derivatives. FT-IR spectra were recorded on a Perkin–Elmer 1725 spectrometer. NMR spectra were run on a General Electric QE-300 spectrometer with resonance frequency of 300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C, with appropriate solvent. The chemical shifts (δ) are reported in parts per million, and coupling constants (J) in hertz. MALDITOF-MS spectra were determined on a LAZARUS II, using DCTB (3-methyl-4-(4-*tert*-butylphenyl)butadiene-1,1-dinitrile) as a matrix.

1.1. [60]Fulleropyrrolidine 5

UV–vis (toluene) λ_{max} 322, 434, 706 nm; Fluorescence (toluene) λ_{max} 382, 710 nm; FT-IR (KBr) ν_{max} 2778, 1720, 1611, 1509, 1207, 834, 802, 527, 481 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS): δ 2.80 (s, 3H, 1″-H), 3.87 (s, 3H, 7-OCH_3), 4.26 (d, $J = 9.0$, 1H, 5″-H), 4.91 (s, 1H, 2″-H), 4.97 (d, $J = 9.0$, 1H, 5″-H), 5.18 (s, 2H, 9-H), 6.48 (s, 1H, 3-H), 6.84 (d, $J = 2.4$, 1H, 8-H), 6.85 (dd, 1H, $J = 9.0$ and 2.4, 6-H), 7.03 (d, $J = 8.7$, 2H, 2′-H and 6′-H), 7.46 (d, $J = 9.0$, 1H, 5-H), 7.74 (br s, 2H, 3′-H and 5′-H) ppm; ^{13}C NMR ($CDCl_3$, TMS): δ 40.3 (C-1″), 55.9 (7-O*C*H$_3$), 65.9 (C-9), 66.0 (C-3″), 69.2 (C-5″), 83.2 (C-2″), 77.1 (C-4″), 101.4 (C-8), 109.9 (C-4), 111.0 (C-3), 112.9 (C-6), 114.9 (C-2′ and (C-6′), 124.7 (C-5), 130.7 (C-3′ and C-5′); 131.0.0 (C-4′), 130-148 (C(sp^2)–C_{60}), 149.8 (C-4a), 156.0 (C-8a), 160.7 (C-7), 163.0 (C-2), MALDITOF-MS (DCTB) *m*/*z* 1057 (M$^-$).

1.2. [60]Fulleropyrrolidine 6

UV–vis (toluene) λ_{max} 320, 434, 704 nm; Fluorescence (toluene) λ_{max} 378, 712 nm; FT-IR (KBr) ν_{max} 2778, 1718, 1611, 1509, 1248, 848, 804 528, 466 cm^{-1}; ^{1}H NMR ($CDCl_3/CS_2$, TMS): δ 2.40 (s, 3H, 9-H), 2.80 (s, 3H, 1″-H), 4.25 (d, $J = 9.3$, 1H, 5″-H), 4.38 (m, 4H, 1′-H and 2′-H), 4.90 (s, 1H, 2″-H), 4.98 (d, $J = 9.3$, 1H, 5″-H), 6.15 (s, 1H, 3-H), 6.87 (d, $J = 2.4$, 1H, 8-H), 6.90 (dd, $J = 8.7$ and 2.4, 1H, 6-H), 7.02 (d, $J = 8.7$, 2H, 4′-H and 8′-H), 7.50 (d, $J = 8.7$, 1H, 5-H), 7.75 (br s, 2H, 5′-H and 7′-H) ppm; ^{13}C NMR ($CDCl_3/CS_2$, TMS): δ 18.7 (C-9), 40.0 (C-1″), 66.1 (C-1′ or C-2′), 67.1 (C-1′ or C-2′), 69.0 (C-3″), 70.0 (C-5″), 77.3 (C-4″), 83.2 (C-2″), 101.6 (C-8), 112.2 (C-3), 112.7 (C-6), 113.9 (C-4), 114.9 (C-4′ and C-8′), 125.6 (C-5), 129.7 (C-6′), 130.6 (C-5′ and C-7′), 130-148 (C(sp^2)C$_{60}$), 152.4 (C-4a), 154.1 (C-3′), 155.2 (C-8a), 161.2 (C-7), 161.6 (C-2) ppm; MALDITOF–MS (DCTB) *m*/*z* 1071 (M$^-$).

1.3. [60]Methanofullerene 10

UV–vis (toluene) $\lambda_{\max}$ 327, 429, 496, 688 nm Fluorescence (toluene) $\lambda_{\max}$ 380, 700 nm; FT-IR (KBr) $\nu_{\max}$ 2928, 2848, 1742, 1734, 1719, 1610, 1387, 1266, 1235, 1144, 1069, 849, 527 cm^{-1}; ^{1}H NMR (CDCl$_3$, TMS): δ 1.56–1.61 (m, 4H, 3′-H and 4′-H), 1.82-1.92 (m, 4H, 2′-H and 5′-H), 2.39 (s, 3H, 9-H), 4.03 (t, *J* = 6.3, 2H, 1′-H), 4.09 (s, 3H, 9′-OCH$_3$), 4.53 (t, *J* = 6.3, 2H, 6′-H), 6.12 (s, 1H, 3-H), 6.79 (d, *J* = 2.4, 1H, 8-H), 6.84 (dd, *J* = 2.4 and 8.7, 1H, 6-H), 7.47 (d, *J* = 8.7, 1H, 5-H) ppm; ^{13}C NMR (CDCl$_3$, TMS): δ 18.7 (C-9), 25.7 (C-3′ or C-4′), 25.8 (C-3′ or C-4′), 28.5 (C-5′), 28.97 (C-2′), 52.2 (methano bridge, C-8′), 54.0 (C–O*C*H$_3$), 67.3 (C-6′), 68.3 (C-1′), 71.5 (C(sp^3)–C$_{60}$), 101.4 (C-8), 111.9 (C-3), 112.7 (C-6), 113.6 (C-4), 125.6 (C-5), 138.0-146.0 (C(sp^2)–C$_{60}$), 152.5 (C-4a), 155.3 (C-8a), 161.3 (C-7), 162.1 (C-2), 163.6 (C–CO), 164.1 (C–CO) ppm; MALDITOF-MS (DCTB) *m*/*z* 1094 (M$^{+\cdot}$).

1.4. [60]Methanofullerene 11

UV–vis (toluene) $\lambda_{\max}$ 326, 429, 490, 687 nm; Fluorescence (toluene) $\lambda_{\max}$ 384, 700 nm; FT-IR (KBr) $\nu_{\max}$ 2966, 2931, 2870, 1730, 1718, 1618, 1459, 1388, 1094, 802, 787, 527 cm^{-1}: ^{1}H NMR (CDCl$_3$, TMS) δ 1.45–1.70 (m, 8H, 3′-H and 4′-H), 1.83–1.91 (m, 8H, 2′-H and 5′-H), 2.39 (*s*, 6H, 9-H), 4.02 (t, *J* = 6.3, 4H, 1′-H), 4.54 (t, *J* = 6.3, 4H, 6′-H), 6.12 (s, 2H, 3-H), 6.77 (d, *J* = 2.4, 2H, 8-H), 6.84 (dd, *J* = 2.6 and 9.3, 2H, 6-H), 7.47 (d, *J* = 8.7, 2H, 5-H) ppm; ^{13}C NMR (CDCl$_3$, TMS): δ 18.7 (C-9), 25.7 (C-3′ or C-4′), 25.9 (C-3′ or C-4′), 28.6 (C-5′), 28.9 (C-2′), 52.4 (methano bridge, C-8′), 67.3 (C-6′), 68.3 (C-1′), 71.6 (C(sp^3)–C$_{60}$), 101.4 (C-8), 111.9 (C-3), 112.6 (C-6), 113.5 (C-4a), 125.6 (C-5), 138.0-146.0 (C(sp^2)–C$_{60}$), 152.6 (C-4a), 155.3 (C-8a), 161.3 (C-7), 162.1 (C-2), 163.7 (C-7′ and C-9′) ppm; MALDITOF-MS (DCTB) *m*/*z* 1339 (MH$^{+\cdot}$).

Acknowledgements

To Dr. H. Luftmann, Institute of Organic Chemistry, University of Muenster, Germany, for MALDITOF-MS spectra. This work was carried out within projects POCTI 34400/QUI/2000 and POCTI 34836/FIS/2000 from Fundação para a Ciência e a Tecnologia (Portugal).

References and notes

1. Prato, M. *J. Mater. Chem.* **1997**, *7*, 1097–1109.
2. Martin, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527–2547.
3. Diekers, M.; Hirsch, A.; Pyo, S.; Riviera, J.; Echegoyen, L. *Eur. J. Org. Chem.* **1998**, 1111–1121.
4. Kadish, K. M.; Ruoff, R. S. *Fullerenes: Chemistry, Physics and Technology*; Wiley-Interscience: New York, 2000.
5. Cattarin, S.; Ceroni, P.; Guildi, M. D.; Maggini, M.; Menna, E.; Paolucci, F.; Roffia, S.; Scorrano, G. *J. Mater. Chem.* **1999**, *9*, 2743–2750.
6. Gust, D.; Moore, T. A.; Moore, A. L. *J. Photochem. Photobiol. B: Biol.* **2000**, *58*, 63–71.
7. Imahori, H.; Sakata, Y. *Eur. J. Org. Chem.* **1999**, 2445–2457.
8. Zhu, D.; Li, Y.; Wang, S.; Shi, Z.; Du, C.; Xiao, S.; Fang, H.; Zhou, Y. *Synth. Met.* **2003**, *133-134*, 679–683.
9. Ammar, H.; Fery-Forgues, S.; Gharbi, R. E. *Dyes Pigments* **2003**, *57*, 259–265.
10. Jing, B.; Zhu, D. *Tetrahedron Lett.* **2004**, *45*, 221–224.
11. de la Torre, M. D. L. A.; Rodrigues, G. P.; Tomé, A. C.; Silva, A. M. S.; Cavaleiro, J. A. S. *Tetrahedron* **2004**, *60*, 3581–3592.
12. Christie, R. M.; Lui, C. *Dyes Pigments* **1999**, *42*, 85–93.
13. Christie, R. M.; Lui, C. *Dyes Pigments* **2000**, *47*, 79–89.
14. Kovac, B.; Novak, I. *Spectrochim. Acta A* **2002**, *58*, 1483–1488.
15. Zhou, X.; Blochwitz-Nimoth, J.; Pfeiffer, M.; Maenning, B.; Drechsel, J.; Werner, A.; Leo, K. *Synth. Met.* **2003**, *138*, 193–196.
16. Hara, K.; Sayama, K.; Ohga, Y.; Shinpo, A.; Suga, S.; Arakawa, H. *Chem. Commun.* **2001**, 569–570.
17. Hara, K.; Tachibana, Y.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Sugihara, H.; Arakawa, H. *Sol. Energy Mater. Sol. Cells* **2003**, *77*, 89–103.
18. Jiao, C.; Niu, C.; Chen, L.; Shen, G.; Yu, R. *Sens. Actuators B* **2003**, *94*, 176–183.
19. Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798–9799.
20. Bingel, C. *Chem. Ber.* **1993**, *126*, 1957–1959; Imahori, H.; Sakata, Y. *Eur. J. Org. Chem.*, **1999**, 2445–2457.
21. Eaton, D. F. *J. Photochem. Photobiol. B* **1988**, *2*, 523–530.
22. Sun, Y. P. Molecular and Supramolecular Photochemistry. In *Organic Chemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel Dekker: New York, 1997; Vol. 1, Chapter 9.