Synthesis and fluorescence properties of [60] and [70]fullerene–coumarin dyads: Efficient dipole–dipole resonance energy transfer from coumarin to fullerene

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New [60] and [70]fullerene–coumarin dyads were prepared by covalently linking a coumarin dye to a fullerene (C_{60} or C_{70}) *via* a 1,3-dipolar cycloaddition reaction of azomethine ylides or by a cyclopropanation reaction of fullerenes with malonate derivatives. These dyads were spectroscopically characterized and their fluorescence properties studied. Fluorescence quenching of the coumarin fluorophore in the dyads results from efficient dipole–dipole resonance energy transfer from the coumarin moiety to the fullerene moiety.

Introduction

The covalent functionalization of the fullerenes has developed rapidly in the last few years to the extent that now C_{60}, which is by far the most studied fullerene, can be considered a versatile building block in organic chemistry.[1] 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[1–9] and energy[9–22] transfer.

It is important to understand these transfer processes having in view practical applications such as photovoltaic devices for solar energy conversion.[7,23–26] For this purpose, several synthetic methodologies have been developed which allow covalent linkages of C_{60} with other photo- and electro-active molecules.[3,4] 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 in the electronic coupling between the donor and the acceptor chromophores.[2,6,7]

The idea of preparing [60]fullerene–coumarin dyads originated from the fact that coumarins are attractive molecules due to their broad absorption range, high emission quantum yields and photostability.[27–31] Moreover coumarin derivatives are frequently encountered as signalling units in sensors and in sophisticated photophysical systems.[32–34]

Recently, we reported the synthesis and fluorescence properties of new [60]fullerene–coumarin dyads **1–4** (Fig. 1), that show an efficient transfer of electronic excitation energy between the coumarin (donor) and the fullerene (acceptor) fluorophores.[35]

In order to study the influence of the substitution position in the coumarin moiety and of the type of fullerene link on the fluorescence properties of these fullerene derivatives, we proceeded with the synthesis and photophysical studies of [60]fullerene–coumarin dyads having a coumarin derivative linked through the 4- or 7-position of the coumarin moiety, by a 1,3-dipolar cycloaddition reaction of azomethine ylide to fullerene[36] and cyclopropanation reaction[37] of the C_{60} with coumarin malonate derivatives. Methanofullerene derivatives with the donor group (coumarin) covalently linked to the acceptor (fullerene) through a flexible bridging unit of different lengths were also synthesized to study the influence of the spacer length in the singlet–singlet energy transfer process. As the absorption of C_{70} in the visible is markedly stronger than that of C_{60},[38,39] we decided also to extend our studies to the synthesis of [70]fullerene–coumarin dyads.

Experimental

General techniques

Melting points were measured on a Reichert Thermovar apparatus fitted with a microscope and are uncorrected. FT-IR spectra were recorded on a Perkin-Elmer 1725 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a General Electric QE-300 spectrometer and chemical shifts are reported relative to TMS. The coupling constants (*J*) are reported in Hz. EI mass spectra were determined on a Kratos MS 25RF instrument at 70 eV and MALDITOF-MS spectra were determined on a LAZARUS III, using DCTB (3-methyl-4-(4-*tert*-butylphenyl)butadiene-1,1-dinitrile) as a matrix. HRMS (FAB) were reported on a VG Autospec M using NBA as a matrix. Elemental analyses were performed in a Fisons EA-1108 analyser. 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 Shimadzu 3101 UV/Vis/NIR and Hitachi 150–20 spectrophotometers. Fluorescence emission spectra were recorded with a Spex Fluorolog F112A fluorimeter and were not corrected for the spectral

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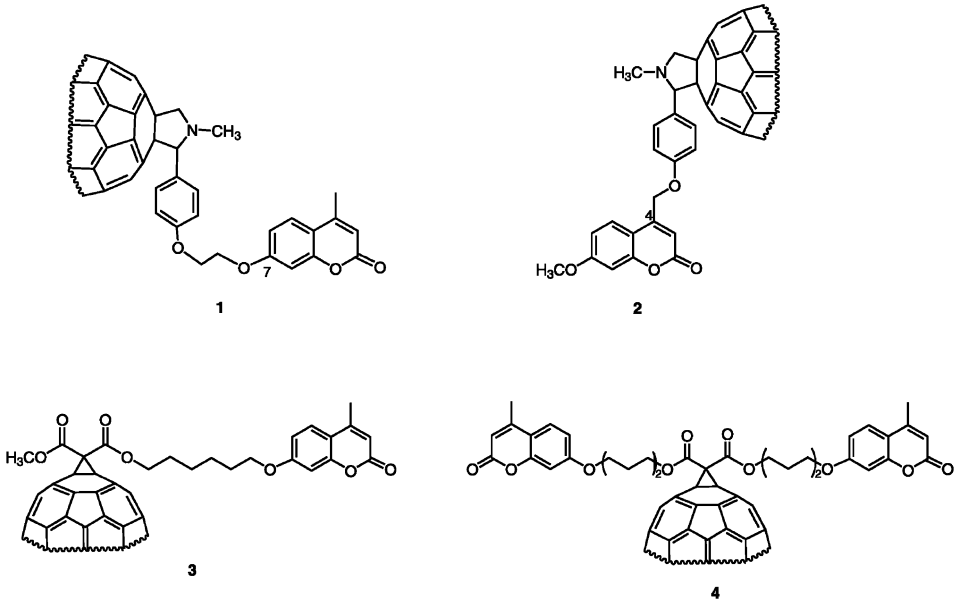


Fig. 1 [60]Fullerene–coumarin dyads.

response of the apparatus. Fluorescence quantum yields in room temperature toluene were determined by a comparative method, using anthracene (Fluka) in air-saturated ethanol ($\Phi_F = 0.27$)[40] as the fluorescence standard for coumarins and C_{60} (99.5%, Aldrich) or C_{70} (99.0%, Aldrich) in toluene (C_{60}: $\Phi_F = 2 \times 10^{-4}$, C_{70}: $\Phi_F = 5 \times 10^{-4}$)[41] as the standards for C_{60} and C_{70} fullerene derivatives, respectively. The excitation wavelength was 320 nm for coumarin compounds **6**, **8**, **12** and **13** and 300 nm for all fullerene derivatives.

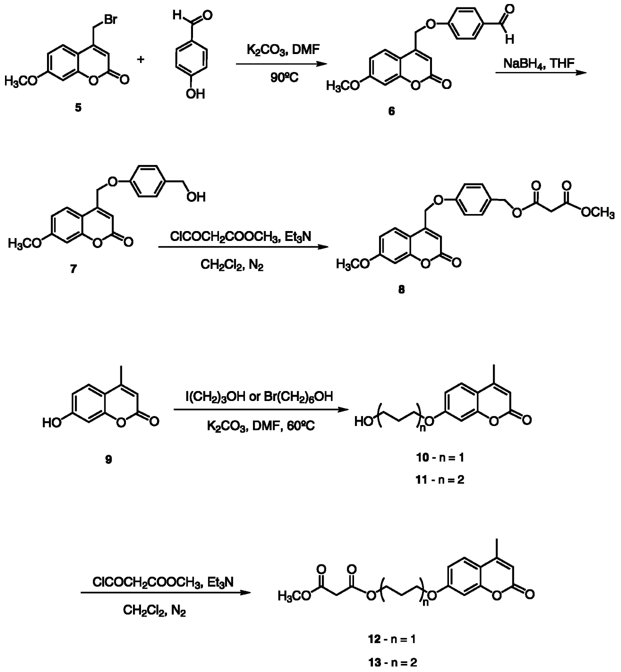
Time-resolved picosecond fluorescence measurements were performed using the single-photon timing method with laser excitation. The set-up consisted of a mode-locked Coherent Innova 400-10 argon-ion laser that synchronously pumped a cavity dumped Coherent 701-2 dye (Rhodamine 6G or DCM) laser, delivering fundamental or frequency-doubled 5 ps pulses at a frequency of 3.4 MHz, or alternatively, of a Spectra-Physics Millenia Xs Nd : YVO_4 diode pumped laser, pumping a pulse picked Spectra-Physics Tsunami titanium-sapphire laser, delivering 100 fs frequency-doubled pulses at a frequency of 4 MHz. Intensity decay measurements were made by the alternate collection of impulse and decay, with the emission polarizer set at the magic angle position. Impulse was recorded slightly away from excitation wavelength with a scattering suspension (1 cm cell). For the decays, a cut-off filter was used, effectively removing all excitation light. All solutions were excited at 320 nm. The emission signal passed through a depolarizer, a Jobin-Yvon HR320 monochromator with a grating of 100 lines nm^{-1} and was recorded on a Hamamatsu 2809U-01 microchannel plate photomultiplier as a detector. A typical time scale range of 0.86–20 ps per channel was used. The instrument response function had an effective FWHM of *ca.* 35 ps.[42]

Synthesis

The synthetic route for coumarin derivatives **6–8**, **10–13** and fullerene–coumarin dyads **14–19** are outlined in Schemes 1 and 2, respectively and the details are given below.

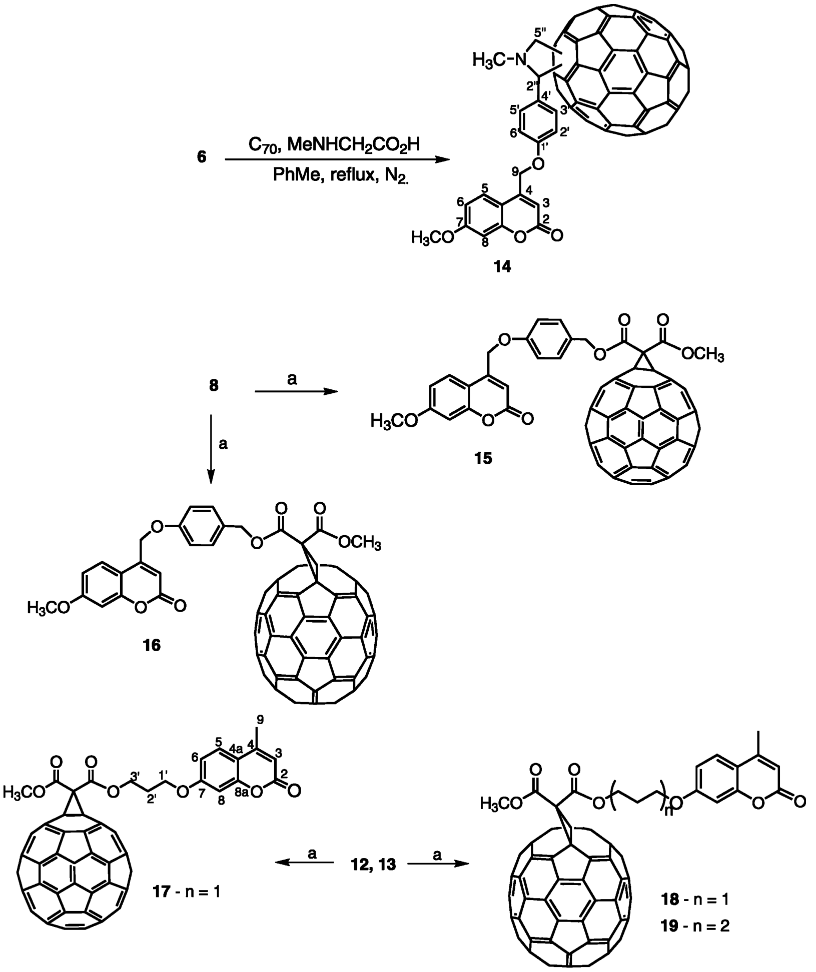
4-(7-Methoxy-2-oxo-2*H*-chromen-4-ylmethoxy)-benzaldehyde (6). To a 250 ml round bottom flask was added 4-bromomethyl-7-methoxy-chromen-2-one **5** (500 mg, 1.86 mmol), 4-hydroxy-benzaldehyde (226.9 mg, 1.86 mmol) and anhydrous potassium carbonate (513.6 mg, 3.72 mmol) in DMF (80 ml). The reaction mixture was stirred at 90 °C for 2 h under nitrogen until all starting material disappeared. Water was added and the resulting mixture was extracted with EtOAc, dried over anhydrous $MgSO_4$ and evaporated to dryness. The residue was purified by column chromatography (SiO_2, eluent CH_2Cl_2, then CH_2Cl_2/MeOH 50 : 2) to give the desired product **2** (461.1 mg, 81%) as white crystals; mp 215–217 °C (from MeOH); Found: C, 69.38; H, 4.54. $C_{18}H_{14}O_5$ requires C, 69.67; H 4.55%; ν_{max}(KBr)/cm^{-1} 1720, 1688, 1620, 1607, 1512, 1262, 864; δ_H (300 MHz; $CDCl_3$; TMS) 3.90 (3H, s, 7-OCH_3), 5.29 (2H, s, 9-H), 6.49 (1H, s, 3-H), 6.89 (1H, d, $J = 2.4$, 8-H), 6.90 (1H, dd, $J = 8.7$ and 2.4, 6-H), 7.12 (2H, d, $J = 8.7$, 2′-H and 6′-H), 7.48 (1H, d, $J = 8.7$, 5-H), 7.89 (2H, d, $J = 8.7$, 3′-H and 5′-H), 9.93 (1H, s, 4-C*H*O) ppm; δ_C (75.5 MHz; $CDCl_3$; TMS) 55.8 (7-O*C*H_3), 65.7 (C-9), 101.3 (C-8), 110.5 (C-4), 110.7 (C-3), 112.8 (C-6), 115.0 (C-2′ and C-6′), 124.3 (C-5), 130.9 (C-4′), 132.1 (C-3′ and C-5′), 149.0 (C-4a), 155.7 (C-8a), 160.8 (C-7), 162.4 (C-2), 163.0 (C-1′), 190.6 (4-*C*HO) ppm; EI-MS: *m*/*z* 310 ($M^{+\bullet}$, 98%), 281 (22), 189 (32), 161 (100).

4-(4′-Hydroxymethyl-phenoxymethyl)-7-methoxy-chromen-2-one (7). A mixture of 4-(7-methoxy-2-oxo-2*H*-chromen-4-ylmethoxy)benzaldehyde **6** (100 mg, 0.322 mmol) and $NaBH_4$ (7 mg, 0.184 mmol) in dry THF (25 mL) was stirred overnight under N_2. Diluted HCl was next added carefully until H_2 liberation ceased. The mixture was then extracted with CH_2Cl_2, dried over $MgSO_4$ and evaporated to dryness. Purification of the residue by column chromatography (SiO_2, CH_2Cl_2/MeOH 1%) yielded pure **7** (98.0 mg, 98%) as white crystals: mp 154–156 °C; ν_{max}(KBr)/cm^{-1} 3394, 3296, 3080, 2959, 2929, 2869, 1737, 1718, 1686, 1612, 1510, 1353, 1251, 1086, 859, 835; δ_H(300 MHz; $CDCl_3$; TMS) 1.88 (1H, s, 7′-O*H*), 3.90 (3H, s, OC*H*$_3$), 4.60 (2H, s, 7′-H), 5.21 (2H, s, 9-H), 6.49 (1H, s, 3-H), 6.87 (1H, d, $J = 2.4$, 8-H), 6.91 (1H, dd, $J = 8.7$ and 2.4, 6-H), 6.98 (2H, d, $J = 8.7$, 2′-H and 6′-H), 7.33 (2H, d, $J = 8.4$, 3′-H and 5′-H), 7.53 (1H, d, $J = 8.7$, 5-H) ppm; δ_C (75.5 MHz; $CDCl_3$; TMS) 55.6 (O*C*H$_3$), 63.8 (C-7′), 65.4 (C-9), 100.9 (C-8), 109.8 (C-3), 110.5 (C-4), 112.6 (C-6), 114.5 (C-2′ and C-6′), 124.5 (C-5), 128.5 (C-3′ and C-5′), 134.5 (C-4′), 150.7 (C-4a), 155.2 (C-8a), 156.9 (C-1′), 161.6 (C-7), 162.7 (C-2) ppm; EI-MS: *m*/*z* 312 ($M^{+\bullet}$, 33%), 281 (22), 190 (50), 161 (100), 145 (43), 121 (40), 77 (38); HRMS (FAB): *m*/*z* 313.1073 $(M + H)^+$. $C_{18}H_{17}O_5$ requires 313.1076.



Scheme 1 Synthetic routes to coumarin derivatives **6**, **8**, **10–13**.

General procedure for the alkylation reactions. A mixture of 7-hydroxy-4-methylcoumarin **9** (200.0 mg, 1.135 mmol), anhydrous K_2CO_3 (628.0 mg, 4.541 mmol) and 3-iodopropanol (200.0 μl, 2.092 mmol) or 6-bromohexanol (297.0 μl, 2.270 mmol) in dry DMF (20 ml) was stirred at 60 °C for 3 h under N_2. After cooling to r.t., the mixture was washed with water, extracted with CH_2Cl_2, dried over $MgSO_4$ and evaporated to dryness. The resulting compounds were purified by column chromatography (SiO_2, Et_2O).



a- C_{60} or C_{70}, I_2, DBU, PhMe, r.t.

Scheme 2 Synthesis of dyads **14–19**.

7-(3′-Hydroxy-propyloxy)-4-methyl-2-chromen-2-one (**10**). Compound **10** was obtained as white crystals (200.8 mg, 76%); mp 95–96 °C (from $\mathrm{CH_2Cl_2}$/hexane); ν_{max}(KBr)/cm^{-1} 3430, 3380, 3186, 3077, 2959, 2943, 2920, 2856, 1738, 1704, 1608, 1395, 1284, 1270, 1205, 1164, 1146, 1075, 844; δ_H(300 MHz; $\mathrm{CDCl_3}$; TMS) 1.79 (1H, s, 3′-O*H*), 2.09 (2H, qui, J = 6.0, 2′-H), 2.40 (3H, s, 9-H), 3.89 (2H, t, J = 6.0, 3′-H), 4.19 (2H, t, J = 6.0, 1′-H), 6.14 (1H, s, 3-H), 6.83 (1H, d, J = 2.4, 8-H), 6.87 (1H, dd, J = 2.4 and 8.7, 6-H), 7.49 (1H, d, J = 8.7, 5-H) ppm; δ_C (75.5 MHz; $\mathrm{CDCl_3}$; TMS) 18.4 (C-9), 31.6 (C-2′), 58.4 (C-3′), 65.4 (C-1′), 101.2 (C-8), 111.4 (C-3), 112.6 (C-6), 113.3 (C-4), 125.4 (C-5), 153.1 (C-4a), 154.9 (C-8a), 161.8 (C-7), 162.0 (C-2) ppm; EI-MS: m/z 234 (M$^{+\bullet}$, 53%), 176 (75), 148 (100, base peak); HRMS (FAB) m/z 235.0970 (M + H)$^+$. $\mathrm{C_{13}H_{15}O_4}$ requires 235.0970.

7-(6′-Hydroxy-hexyloxy)-4-methyl-2-chromen-2-one (**11**). Compound **11** was obtained as white crystals (222.4 mg, 71%), mp 81–82 °C ($\mathrm{CH_2Cl_2}$/hexane); ν_{max}(KBr)/cm^{-1} 3348, 3261, 3077, 2940, 2920, 2854, 1739, 1727, 1615, 1398, 1285, 1152, 1073, 845; δ_H (300 MHz; $\mathrm{CDCl_3}$; TMS) 1.43–1.55 (4H, m, 3′-H and 4′-H), 1.60 (2H, qui, J = 6.6, 5′-H), 1.83 (2H, qui, J = 7.2, 2′-H), 2.23 (1H, brs, 6′-O*H*), 2.39 (3H, s, 9-H), 3.67 (2H, t, J = 6.6, 6′-H), 4.00 (2H, t, J = 6.3, 1′-H), 6.12 (1H, s, 3-H), 6.75 (1H, d, J = 2.4, 8-H), 6.84 (1H, dd, J = 2.4 and 8.7, 6-H), 7.47 (1H, d, J = 8.7, 5-H) ppm; δ_C (77.0 MHz; $\mathrm{CDCl_3}$; TMS) 18.7 (C-9), 25.5 (C-3′ or C-4′), 25.8 (C-3′ or C-4′), 29.0 (C-2′), 32.6 (C-5′), 62.8 (C-6′), 68.5 (C-1′), 101.4 (C-8), 111.8 (C-3), 112.7 (C-6), 113.5 (C-4), 125.5 (C-5), 152.7 (C-4a), 155.3 (C-8a), 161.5 (C-7), 162.2 (C-2) ppm; EI-MS: m/z 276 (M$^{+\bullet}$, 22%), 176 (100, base peak), 149 (58), 148 (68), 83 (30), 57 (50), 55 (88), 43 (51), 41(79); HRMS (FAB): m/z 277.1445 (M + H)$^+$. $\mathrm{C_{16}H_{21}O_4}$ requires 277.1440.

General procedure for the synthesis of malonate derivatives. Methyl malonyl chloride was added dropwise to a solution of **7**, **10** or **11** and triethylamine in dry $\mathrm{CH_2Cl_2}$ (25 ml) at 0 °C under $\mathrm{N_2}$. The mixture was stirred at r.t. (2–4 h), then neutralized with diluted HCl, extracted, dried over $\mathrm{MgSO_4}$ and evaporated to dryness. The residue was purified by column chromatography ($\mathrm{SiO_2}$, $\mathrm{Et_2O}$).

Malonic acid 4-(7-methoxy-2-oxo-2H-chromen-4-ylmethoxy)-benzyl ester methyl ester (**8**). Compound **8** was obtained as white crystals (101.0 mg, 77%) from **7** (100 mg, 0.320 mmol), triethylamine (89.5 µl, 0.640 mmol) and methyl malonyl chloride (10.3 µl, 0.960 mmol). mp 144–145 °C; ν_{max}(KBr)/cm^{-1} 3448, 2981, 2961, 2944, 2863, 1750, 1719, 1686, 1611, 1517, 1341, 1246, 1206, 1155, 1075, 1016, 859; δ_H (300 MHz; $\mathrm{CDCl_3}$; TMS) 3.43 (2H, s, malonate C*H*$_2$), 3.74 (3H, s, $\mathrm{CO_2C}$*H*$_3$), 3.89 (3H, s, OC*H*$_3$), 5.14 (2H, s, 7′-H), 5.20 (2H, s, 9-H), 6.48 (1H, s, 3-H), 6.87 (1H, d, J = 2.4, 8-H), 6.89 (1H, dd, J = 8.7 and 2.4, 6-H), 6.99 (2H, d, J = 8.7, 2′-H and 6′-H), 7.34 (2H, d, J = 8.4, 3′-H and 5′-H), 7.50 (1H, d, J = 8.7, 5-H) ppm; δ_C (75.5 MHz; $\mathrm{CDCl_3}$; TMS) 41.2 (malonate C*H*$_2$), 52.5 ($\mathrm{CO_2}$*C*$\mathrm{H_3}$), 55.7 (O*C*$\mathrm{H_3}$), 65.6 (C-9), 66.8 (C-7′), 101.1 (C-8), 110.4 (C-3), 110.6 (C-4), 112.6 (C-6), 114.8 (C-2′ and C-6′), 124.5 (C-5), 128.7 (C-4′), 130.3 (C-3′ and C-5′), 149.8 (C-4a), 155.3 (C-8a), 157.8 (C-1′), 160.9 (C-7), 162.8 (C-2), 166.3 (*C*$\mathrm{OCH_2CO_2CH_3}$), 166.8 (*C*$\mathrm{O_2CH_3}$) ppm; EI-MS: m/z 412 (M$^{+\bullet}$, 1.5%), 295 (5), 190 (6), 151 (31), 109 (100), 80 (14), 43 (37); HRMS (FAB): m/z 413.1235 (M + H)$^+$. $\mathrm{C_{20}H_{21}O_8}$ requires 413.1236.

Malonic acid methyl ester 3′-(4-methyl-2-oxo-2H-chromen-7-yloxy)-propyl ester (**12**). Compound **12** was obtained as white crystals (47.6 mg, 96%), from **10** (35.0 mg, 0.149 mmol), triethylamine (41.5 µl, 0.298 mmol) and methyl malonyl chloride (69.0 µl, 0.642 mmol): mp 101–102 °C; Found: C, 61.16; H, 5.09. $\mathrm{C_{17}H_{18}O_7}$ requires C, 61.07; H, 5.43%; ν_{max}(KBr)/cm^{-1} 3448, 2988, 2958, 2937, 2885, 1767, 1726, 1708, 1616, 1391, 1363, 1342, 1156, 1073, 1039, 856, 830; δ_H (300 MHz; $\mathrm{CDCl_3}$; TMS) 2.19 (2H, qui, J = 6.0, 2′-H), 2.40 (3H, s, 9-H), 3.42 (s, 2H, malonate C*H*$_2$), 3.74 (3H, s, $\mathrm{CO_2C}$*H*$_3$), 4.12 (2H, t, J = 6.0, 1′-H), 4.38 (2H, t, J = 6.0, 3′-H), 6.13 (1H, s, 3-H), 6.80 (1H, d, J = 2.4, 8-H), 6.86 (1H, dd, J = 2.4 and 8.7, 6-H), 7.50 (1H, d, J = 8.7, 5-H) ppm; δ_C (75.5 MHz; $\mathrm{CDCl_3}$; TMS) 18.5 (C-9), 28.1 (C-2′), 41.1 (malonate *C*$\mathrm{H_2}$), 52.4 ($\mathrm{CO_2}$*C*$\mathrm{H_3}$), 61.9 (C-3′), 64.5 (C-1′), 101.2 (C-8), 111.8 (C-3), 112.4 (C-6), 113.5 (C-4), 125.5 (C-5), 152.5 (C-4a), 155.1 (C-8a), 161.1 (C-7), 161.6 (C-2), 166.3 (*C*$\mathrm{OCH_2CO_2CH_3}$), 166.8 (*C*$\mathrm{O_2CH_3}$) ppm; EI-MS: m/z 334 (M$^{+\bullet}$, 8%), 234 (10), 176 (40), 159 (100, base peak), 148 (60), 109 (37), 101 (90), 69 (54), 41 (37).

Malonic acid methyl ester 6′-(4-methyl-2-oxo-2H-chromen-7-yloxyl)-hexyl ester (**13**). Compound **13** was obtained as a colourless oil (93.0 mg, 85%), from **11** (80.0 mg, 0.290 mmol), triethylamine (81 µl, 0.580 mmol) and methyl malonyl chloride (125 µl, 1.160 mmol). ν_{max}(KBr)/cm^{-1} 3077, 2941, 2863, 1730, 1716, 1613, 1388, 1264, 1146, 1070, 1015, 875, 847, 801; δ_H(300 MHz; $\mathrm{CDCl_3}$; TMS) 1.41–1.55 (4H, m, 3′-H and 4′-H), 1.70 (2H, qui, J = 7.0, 5′-H), 1.83 (2H, qui, J = 7.2, 2′-H), 2.40 (3H, s, 9-H), 3.39 (2H, s, malonate C*H*$_2$), 3.75 (3H, s, $\mathrm{CO_2C}$*H*$_3$), 4.02 (2H, t, J = 6.6, 1′-H), 4.17 (2H, t, J = 6.6, 6′-H), 6.12 (1H, s, 3-H), 6.80 (1H, d, J = 2.4, 8-H), 6.85 (1H, dd, J = 2.4 and 8.7, 6-H), 7.49 (1H, d, J = 8.7, 5-H) ppm; δ_C (75.5 MHz; $\mathrm{CDCl_3}$; TMS) 18.7 (C-9), 25.5 (C-3′ or C-4′), 25.6 (C-3′ or C-4′), 28.4 (C-5′), 28.9 (C-2′), 41.4 (malonate *C*$\mathrm{H_2}$), 52.5 ($\mathrm{CO_2}$*C*$\mathrm{H_3}$), 65.5 (C-6′), 68.4 (C-1′), 101.3 (C-8), 111.9 (C-3), 112.7 (C-6), 113.5 (C-4), 125.5 (C-5), 152.6 (C-4a), 155.3 (C-8a), 161.4 (C-7), 162.2 (C-2), 166.6 (*C*$\mathrm{OCH_2CO_2CH_3}$), 167.1 (*C*$\mathrm{O_2CH_3}$) ppm; EI-MS m/z 376 (M$^{+\bullet}$, 19%), 176 (100, base peak), 148 (56), 83 (41), 55 (77), 43 (51), 42(27); HRMS (FAB): m/z 377.1615. (M + H)$^+$. $\mathrm{C_{20}H_{25}O_7}$ requires 377.1600.

Pyrrolidino[70]fullerene (14). A mixture of $\mathrm{C_{70}}$ (201.1 mg, 0.24 mmol), *N*-methylglycine (76.1 mg, 0.86 mmol) and **6** (74.3 mg, 0.24 mmol) in dry toluene (230 mL) was heated at reflux under nitrogen for 12 hours. After cooling the solution to r.t., the product was purified by column chromatography (eluent toluene, then toluene/AcOEt 4 : 1). The isolated monoadduct **14** was further purified by precipitation yielding 125.3 mg (44%): ν_{max}(KBr)/cm^{-1} 1719; 1609, 1508; 1206; 834; 794, 752, 671, 640; 480; δ_H (300 MHz; $\mathrm{CDCl_3}$; TMS) 2.43, 2.52 (major isomer), 2.53 (3H, s, *N*C$\mathrm{H_3}$), 3.87, 3.88, 3.91 (3H, s, 7-OC$\mathrm{H_3}$), 3.19, 3.39, 3.49, 3.56, 4.06, 4.25 (1H, d, J = 9.0, 5″-H), 5.09, 5.12, 5.24 (1H, s, 2″-H), 5.35 (2H, s, 9-H), 6.42, 6.44, 6.48 (1H, s, 3-H), 6.80–7.20 (m, 8-H and 6-H), 7.30-7.57 (m, 2′-H and 6′-H and 5-H), 7.84 (2H, brs, 3′-H and 5′-H) ppm; δ_C (75.5

MHz; $CDCl_3$; TMS) 39.5 (*N*CH_3), 55.8 (7-OCH_3), 65.7 (C-9), 65.8, 66.0, 66.2 (C-3″), 68.2, 68.8, 70.2 (C-5″), 81.9, 83.6, 82.8 (C-2″), 79.6 (C-4″), 101.3 (C-8), 110.6 (C-4), 110.7 (C-3), 112.7 (C-6), 114.7 (C-2′ and C-6′), 124.7 (C-5), 130.1, 130.5, 131.3, 132.1, 132.4, 133.6, 133.9, 140.6, 142.8, 143.2, 144.6, 145.4, 145.8, 146.2, 146.6, 147.1, 148.1, 149.1, 149.4, 149.9, 150.8, 151.3, 155.6 (C-8a), 161.0 (C-7), 162.9 (C-2); HRMS (FAB): *m*/*z* 1178.1420 $(M + H)^+$. $C_{90}H_{20}NO_4$ requires 1178.1392.

Preparation of [60] and [70]methanofullerene derivatives 15–19. To a solution of malonate derivative, C_{60} or C_{70} (1 eq.), I_2 (1 eq.) in toluene (20 ml), under N_2 at r.t, was added DBU (2 eq.) and the mixture was stirred until the starting malonate disappeared. Then the mixture was filtered over a column of SiO_2 (PhMe/AcOEt 4 : 1) to yield unreacted fullerene and the dyad. Products with higher polarity were discharged.

*Methano[60]fullerene (***15***).* Dyad **15** was obtained as a dark-brown solid (10.5 mg, 12%) from **8** (31.2 mg, 0.076 mmol), C_{60} (54.4 mg, 0.076 mmol), I_2 (19.3 mg, 0.076 mmol) and DBU (22.8 μl, 0.152 mmol). ν_{max}(KBr)/cm^{-1} 2952, 2925, 2848, 1751, 1736, 1721, 1708, 1701, 1655, 1619, 1610, 1561, 1510, 1500, 1458, 1266, 1255, 1235, 1085, 853, 705, 580, 527; δ_H (300 MHz; $CDCl_3$; TMS) 3.89 (3H, s, OCH_3), 4.03 (3H, s, CO_2CH_3), 5.19 (2H, s, 9-H), 5.48 (2H, s, 7′-H), 6.49 (1H, s, 3-H), 6.87 (1H, d, J = 2.4, 8-H), 6.89 (1H, dd, J = 7.2 and 2.4, 6-H), 7.00 (2H, d, J = 8.7, 2′-H and 6′-H), 7.48 (3H, m, 5-H, 3′-H and 5′-H) ppm; δ_C (75.5 MHz; $CDCl_3$; TMS) 52.6 (methano bridge), 53.9 (CO_2CH_3), 55.7 (OCH_3), 65.9 (C-9), 68.5 (C-7′), 71.4 (C(sp^3)-C_{60}), 101.2 (C-8), 110.0 (C-4), 110.8 (C-3), 112.7 (C-6), 115.0 (C-2′ and C-6′), 124.5 (C-5), 128.3 (C-4′), 131.2 (C-3′ and C-5′), 138.6, 139.4, 140.9, 141.8, 141.9, 142.2, 143.0, 143.9, 144.3, 144.5, 144.6, 144.9, 145.0, 145.1, 149.7 (C-4a), 155.7 (C-8a), 158.3 (C-1′), 160.7 (C-7), 162.9 (C-2), 163.3 ($COCCO_2CH_3$), 163.8 (CO_2CH_3) ppm; HRMS (FAB): *m*/*z* 1131.1052 $(M + H)^+$. $C_{82}H_{19}O_8$ requires 1131.1080.

*Methano[70]fullerene (***16***).* Dyad **16** was obtained as a dark-brown solid (10.0 mg, 17%) from **8** (20.0 mg, 0.048 mmol), C_{70} (40.3 mg, 0.048 mmol), I_2 (12.2 mg, 0.048 mmol) and DBU (14.6 μl, 0.097 mmol). ν_{max}(KBr)/cm^{-1} 2927, 2848, 1752, 1741, 1736, 1720, 1701, 1655, 1618, 1611, 1561, 1509, 1459, 1266, 1251, 1233, 1089, 1069, 794, 672, 579, 532, 517; δ_H (300 MHz; $CDCl_3$; TMS) 3.83 (3H, s, OCH_3), 3.99 (3H, s, CO_2CH_3), 5.15 (2H, s, 9-H), 5.44 (2H, s, 7′-H), 6.46 (1H, s, 3-H), 6.85 (1H, d, J = 2.4, 8-H), 6.85 (1H, dd, J = 9.6 and 2.4, 6-H), 6.99 (2H, d, J = 8.7, 2′-H and 6′-H), 7.44 (1H, d, J = 9.6, 5-H), 7.48 (2H, d, J = 8.7, 3′-H and 5′-H) ppm; δ_C (75.0 MHz; $CDCl_3$; TMS) 29.7 (methano bridge), 54.0 (CO_2CH_3), 55.8 (OCH_3), 66.0 (C-9), 66.1 and 66.8 (C(sp^3)–C_{60}), 68.6 (C-7′), 101.3 (C-8), 110.7 (C-3 and C-4), 112.7 (C-6), 115.1 (C-2′ and C-6′), 124.5 (C-5), 128.2 (C-4′), 129.0, 130.8, 131.3 (C-3′ and C-5′), 132.8, 133.5, 136.6, 136.8, 140.3, 141.6, 141.8, 142.4, 142.8, 143.5, 143.8, 144.9, 145.8, 147.0, 147.3, 147.5, 148.3, 148.5, 149.2, 149.7 (C-4a), 150.5, 151.1, 151.3, 154.9, 155.0, 155.6 (C-8a), 158.4 (C-1′), 160.8 (C-7), 162.8 (C-2), 163.2 ($COCCO_2CH_3$), 163.8 (CO_2CH_3) ppm; HRMS (FAB): *m*/*z* 1251.1088 $(M + H)^+$. $C_{92}H_{19}O_8$ requires 1251.1080.

*Methano[60]fullerene (***17***).* Dyad **17** was obtained as a dark-brown solid (13.5 mg, 9%) from **12** (50.0 mg, 0.149 mmol), C_{60} (107.7 mg, 0.149 mmol), I_2 (37.9 mg, 0.149 mmol) and DBU (44.6 μl, 0.298 mmol). ν_{max}(KBr)/cm^{-1} 2923, 2848, 1752, 1743, 1736, 1722, 1655, 1618, 1561, 1459, 1266, 1236, 1070, 669, 580, 527; δ_H (300 MHz; $CDCl_3$; TMS) 2.38 (3H, s, 9-H), 2.39 (2H, qui, J = 6.0, 2′-H), 4.08 (3H, s, CO_2CH_3), 4.18 (2H, t, J = 6.0, 1′-H), 4.74 (2H, t, J = 6.0, 3′-H), 6.13 (1H, s, 3-H), 6.77 (1H, d, J = 2.7, 8-H), 6.88 (1H, dd, J = 2.7 and 8.7, 6-H), 7.46 (1H, d, J = 8.7, 5-H) ppm; δ_C (75.5 MHz; $CDCl_3$; TMS) 18.7 (C-9), 28.1 (C-2′), 52.0 (methano brigde), 54.1 (CO_2CH_3), 63.5 (C-3′), 64.2 (C-1′), 71.4 (C(sp^3)–C_{60}), 101.3 (C-8), 112.2 (C-3), 112.7 (C-6), 113.9 (C-4), 125.7 (C-5), 138.4, 139.4, 140.9, 141.6, 141.9, 142.2, 142.9, 143.0, 143.7, 143.9, 144.4, 144.7, 144.8, 144.9, 145.2, 152.4 (C-4a), 155.3 (C-8a), 161.1 (C-7), 161.7 (C-2), 163.5 ($COCCO_2CH_3$), 164.0 (CO_2CH_3) ppm; HRMS (FAB): *m*/*z* 1053.0961 $(M + H)^+$. $C_{77}H_{17}O_7$ requires 1053.0974.

*Methano[70]fullerene (***18***).* Dyad **18** was obtained as a dark-brown solid (10.3 mg, 8.5%) from **12** (35.0 mg, 0.105 mmol), C_{70} (88.3 mg, 0.105 mmol), I_2 (26.8 mg, 0.105 mmol) and DBU (31.45 μl, 0.210 mmol). ν_{max}(KBr)/cm^{-1} 2926, 2848, 1752, 1742, 1736, 1719, 1655, 1618, 1561, 1460, 1428, 1268, 1236, 1137, 1089, 669, 579, 532, 517; δ_H (300 MHz; $CDCl_3$; TMS) 2.35 (3H, s, 9-H), 2.37 (2H, qui, J = 6.3, 2′-H), 4.04 (3H, s, CO_2CH_3), 4.20 (2H, t, J = 6.3, 1′-H), 4.69 (2H, t, J = 6.3, 3′-H), 6.13 (1H, s, 3-H), 6.75 (1H, d, J = 2.7, 8-H), 6.84 (1H, dd, J = 2.7 and 8.7, 6-H), 7.40 (1H, d, J = 8.7, 5-H) ppm; δ_C (75.5 MHz; $CDCl_3$; TMS) 18.7 (C-9), 28.0 (C-2′), 29.7 (methano brigde), 54.1 (CO_2CH_3), 63.4 (C-3′), 64.1 (C-1′), 66.2 and 66.7 (C(sp^3)–C_{60}), 101.4 (C-8), 112.2 (C-3), 112.8 (C-6), 113.9 (C-4), 125.7 (C-5), 130.6, 130.8, 130.9, 132.6, 132.8, 133.4, 133.5, 136.4, 137.0, 140.2, 141.1, 141.3, 141.6, 141.7, 142.3, 142.5, 142.8, 143.0, 143.5, 143.6, 143.9, 144.4, 144.9, 145.5, 145.7, 145.9, 146.4, 146.9, 147.2, 147.5 148.4, 148.9, 149.2, 150.5, 150.7, 151.1, 151.3, 152.4 (C-4a), 155.3 (C-8a), 161.0 (C-7), 161.7 (C-2), 163.3 ($COCCO_2CH_3$), 163.9 (CO_2CH_3) ppm; HRMS (FAB): *m*/*z* 1173.0973 $(M + H)^+$. $C_{87}H_{17}O_7$ requires 1173.0974.

*Methano[70]fullerene (***19***).* Dyad **19** was obtained as a dark-brown solid (13.5 mg, 12%) from **13** (36.0 mg, 0.096 mmol), C_{70} (80.0 mg, 0.096 mmol), I_2 (24.8 mg, 0.096 mmol) and DBU (28.7 μl, 0.192 mmol). ν_{max}(KBr)/cm^{-1} 2966, 2929, 2863, 1732, 1719, 1655, 1461, 1266, 1072, 1056, 672, 578, 542, 462; δ_H (300 MHz; $CDCl_3$; TMS) 1.55–1.75 (4H, m, 3′-H and 4′-H), 1.75–1.95 (4H, m, 2′-H and 5′-H), 2.39 (3H, s, 9-H), 4.03 (2H, t, J = 6.3, 1′-H), 4.05 (3H, s, CO_2CH_3), 4.49 (2H, t, J = 6.3, 6′-H), 6.13 (1H, s, 3-H), 6.79 (1H, d, J = 2.4, 8-H), 6.84 (1H, dd, J = 2.4 and 8.7, 6-H), 7.48 (1H, d, J = 8.7, 5-H) ppm; δ_C (75.5 MHz; $CDCl_3$; TMS) 18.7 (C-9), 25.7 (C-3′ or C-4′), 25.9 (C-3′ or C-4′), 28.5 (C-5′), 29.0 (C-2′), 38.7 (methano brigde), 54.1 (CO_2CH_3), 66.2 and 66.8 (C(sp^3)–C_{70}), 67.4 (C-6′), 68.3 (C-1′), 101.4 (C-8), 111.9 (C-3), 112.7 (C-6), 113.6 (C-4), 125.6 (C-5), 128.8, 130.8, 130.9, 132.4, 132.8, 133.5, 136.8, 140.7, 141.7, 142.8, 143.5, 143.9, 144.7, 144.9, 145.9, 145.93, 146.4, 146.9, 147.3, 147.5, 147.6, 148.4, 148.5, 148.6, 148.7, 149.1, 149.2, 149.3, 149.33, 150.5, 150.7, 151.1, 151.3, 152.6

(C-4a), 155.3 (C-8a), 161.7 (C-7), 162.1 (C-2), 163.5 (*C*OC-CO_2CH_3), 164.0 (CO_2CH_3) ppm; HRMS (FAB): *m*/*z* 1215.1429 $(M + H)^+$. $C_{90}H_{23}O_7$ requires 1215.1444.

Results and discussion

Synthesis and structural characterization

The new fullerene–coumarin dyads were synthesized following two different strategies to covalently link a coumarin dye to the fullerene: cyclopropanation reaction of fullerene[37] which led to methanofullerene derivatives and 1,3-dipolar cycloaddition reaction of azomethine ylide to fullerene[36] which led to pyrrolidinofullerene derivatives.

As starting materials we chose commercial coumarins **5** and **9** substituted at the 4- or 7-position by active groups, respectively bromoalkyl and hydroxyl groups that allow the easy introduction of the appropriate functionality necessary for the selected fullerene linking strategies.

Coumarin intermediates **6** and **8** for covalent linkage to fullerene through the 4-position of the coumarin moiety were prepared as indicated in Scheme 1. Reaction of **5** with 4-hydroxybenzaldehyde in dimethylformamide at 90 °C for 2–3 hours using anhydrous potassium carbonate, as a base, gave the desired compound **6** in good yield, reduction of which with sodium borohydride afforded alcohol **7** (98%). The reaction of this compound with methyl malonyl chloride in the presence of triethylamine gives the malonate derivative **8**.

Coumarin intermediates **10–13** were prepared as indicated in Scheme 1. From **9**, different length saturated hydrocarbon bridged malonate derivatives were synthesized. In this way, alkylation of **9** with 3-iodopropan-1-ol or 6-bromohexan-1-ol followed by the reaction of the resulting alcohols **10** and **11** with methyl malonyl chloride, in the presence of triethylamine, gave the corresponding malonate derivatives **12** and **13**.

The synthesis of pyrrolidino[70]fullerene **14** (Scheme 2) relies upon the 1,3-dipolar cycloaddition of azomethine ylides generated *in situ* (reaction of the aldehyde group with *N*-methylglycine) to [70]fullerene. This cycloaddition reaction was carried out in refluxing toluene, under a nitrogen atmosphere. The reaction mixture was separated by flash chromatography using gradients of toluene/ethyl acetate as eluent. The first fraction was the unchanged C_{70} and the next one was the monoadducts. Products with higher polarity were discarded. After purification by precipitation from chloroform and methanol, the [70]fullerene derivative **14** was isolated in moderated yield (44%).

Table 1 Quantum yields (Φ_F) and average fluorescene lifetimes (τ_F) in room temperature toluene

		Coumarin[a]		Fullerene[b]	
Class	Compound	$\Phi_F/10^{-3}$	τ/ps	$\Phi_F/10^{-4}$	τ/ns
4-Coumarin	**6** (model)	18	150	—	—
	14 (C_{70} dyad)	0.57	90	6.6	0.96
	8 (model)	13	280	—	—
	15 (C_{60} dyad)	6.9	560	3.2	—
	16 (C_{70} dyad)	2.0	120	8.2	0.85
7-Coumarin	**12** (model)	12	100	—	—
	17 (C_{60} dyad)	0.99	540	4.0	1.47
	18 (C_{70} dyad)	1.9	340	7.9	0.85
	13 (model)	16	90	—	—
	19 (C_{70} dyad)	1.0	190	8.9	0.85

[a] $\lambda_{exc} = 320$ nm (model coumarins) or $\lambda_{exc} = 300$ nm (dyads). [b] $\lambda_{exc} = 400$ nm (direct excitation of the fullerene moiety).

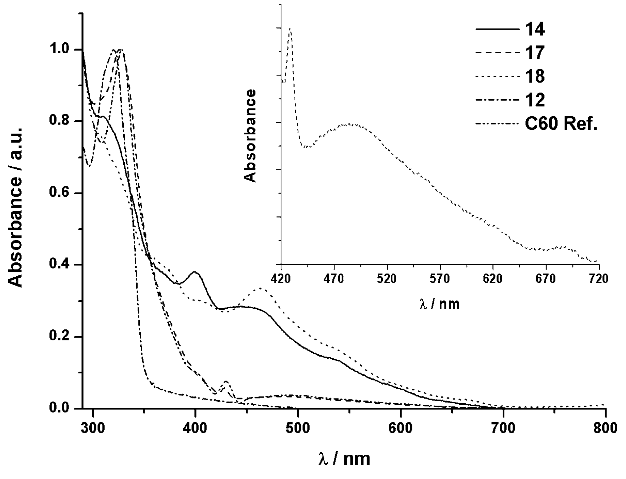


Fig. 2 Absorption spectra of **14** (solid line), **17** (dashed line, very similar to **15**, not shown), **18** (dotted line, very similar to **16** and **19**, not shown), **12** (dashed-dotted line, very similar to **6**, **8** and **13**, not shown) and methano[60]fullerene reference compound (dashed-dotted-dotted line) in toluene. Inset: absorption spectrum of **17**, magnified in the 420–720 nm region.

The synthesis of new [60] and [70]methanofullerenes were carried out by cyclopropanation[37] of C_{60} and C_{70} with the appropriate malonate derivatives **8**, **12** and **13** to give the final dyads **15–19** in moderate yield (Scheme 2), which were isolated as described earlier for **3**.[35]

All the new compounds were characterized by ^1H and ^{13}C NMR, MS and elemental analysis or high-resolution MS. The

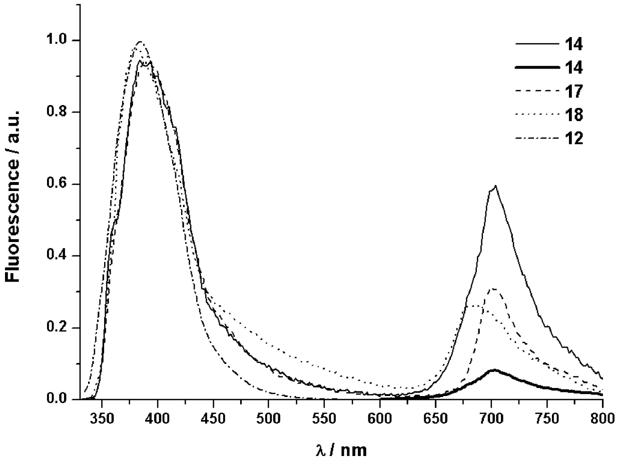


Fig. 3 Uncorrected fluorescence spectra of pyrrolidino[70]fullerene **14** (solid lines, both total emission and estimated direct excitation contribution), methano[60]fullerene **17** (dashed line, very similar to **15**, not shown), methano[70]fullerene **18** (dotted line, very similar to **16** and **19**, not shown) and coumarin derivative **12** (dashed-dotted line, very similar to **6**, **8** and **13**, not shown) in toluene. Excitation wavelength: 320 nm, the spectra were normalized at the maximum fluorescence wavelength. The fullerene emission is in fact stronger than shown and extends further into the near infrared.

Table 2 Average rate constants for energy transfer (k_{ET}), energy transfer quantum yields (Φ_{ET}), Förster radii (R_0) and average donor–acceptor distances (r) computed from eqn (3) for dyads **3**, **4** and **14–19**

Dyad		k_{ET}/ns^{-1}	Φ_{ET}	R_0/Å^a	r/Å
C_{60} acceptor moiety	**15**	3	0.48	16	16
	3	88	0.89	17	12
	17	110	0.92	17	11
	4	120	0.92	17	11
C_{70} acceptor moiety	**16**	20	0.84	21	16
	18	54	0.84	21	16
	19	150	0.93	22	14
	14	200	0.97	23	13

[a] Computed[50] from the emission and absorption data for the donor and acceptor moieties, respectively.

structures of **14–19** as monoadducts are supported by MALDITOF mass spectra, which display the expected molecular ion peaks in each case.

The pyrrolidino[70]fullereno **14** was obtained as a mixture of isomeric monoadducts due to the known reactivity of C_{70}.[43] The presence of three distinct *N*-methyl resonances (δ 2.43, 2.52 and 2.53 ppm) in the ^{1}H NMR spectrum of **14** indicated a mixture of three isomers in a 38 : 36 : 26 ratio. Three monoadducts resulted from addition to 6,6-ring fusions of C_{70} at the 1,9-, 7,8- and 22,23-bonds, as previously reported for the cycloaddition of *N*-methylazomethine ylide to [70]fullerene.[43] The proton and carbon resonances of the coumarin moiety of dyad **14** are similar to those of the starting compound **6**, with the exception of the signal corresponding to the *ortho* protons of the phenyl group directly attached to the pyrrolidine ring that is broadened. This broad signal is the result of a dynamic phenomenon arising from restricted rotation around the phenyl–pyrrolidine bond.[44] The ^{1}H and ^{13}C NMR signals of **14** are consistent with the pyrrolidinofullerene structure. In the ^{13}C NMR spectra of methano[60]fullerene dyads **15** and **17** the signals corresponding to the methano bridge appear at *ca.* 52.2 ppm, while the signals corresponding to C_{60}-sp^3 carbons appear at *ca.* 71.5 ppm. The ^{1}H NMR spectrum of the methano[70]fullerene dyads **16**, **18** and **19** displays only one signal for CO_2CH_3 at 3.99, 4.04 and 4.05 ppm, respectively, which indicates the presence of a single isomer. As reported by Diederich and co-workers,[45] the cyclopropanation reaction of C_{70} under Bingel conditions affords only one regioisomer as a result of the addition of malonate derivatives to the 1,9-bond of C_{70}. In the ^{13}C NMR spectra of methano[70]fullerene dyads **16** and **18** the signals corresponding to the methano bridge appear at *ca.* 29.7 ppm while for **19** the corresponding carbon appears at *ca.* 38.7 ppm. The C_{70}-sp^3 carbons of **16**, **18** and **19** appear as two signals between 66.0 and 67.0 ppm. Comparison of the recorded electronic absorption spectrum with absorption spectra of the regioisomers of C_{70} monoadducts with five-[43] and six-membered[46] protruding rings confirms that the obtained isomer is the 1,9 (or α) isomer.

Photophysical properties

The UV-Vis absorption spectra of some of the dyads, along with the spectra of model compounds for the coumarin and fullerene moieties are shown in Fig. 2. The coumarin moieties absorb only below 500 nm, while the fullerene moieties absorb both in the long and in the short wavelength regions. The features observed in the visible (beyond 400 nm) are also characteristic of the type of fullerene moiety, C_{60} or C_{70} derived, with the C_{70} cage displaying a stronger absorption, as already observed in the parent fullerenes.

The absorption spectra of the [60]fullerene dyads (**15** and **17**) are the sum of the spectra of the C_{60} reference compound (malonic acid diethyl ester derivative $C_{60}[C(COOEt)_2]$) and coumarin moiety and display a weak band at 687 nm and a sharp peak at 429 nm, characteristic of the methano monoadducts of C_{60}. The spectra of the methano[70]fullerene dyads

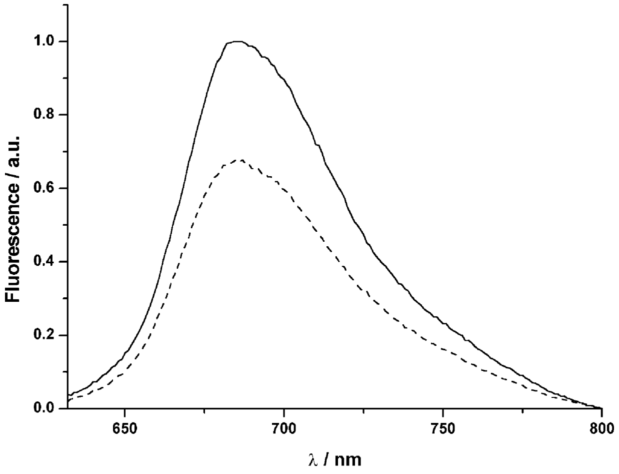


Fig. 4 Uncorrected fluorescence spectra in toluene of an equimolar (5×10^{-6} M) mixture of coumarin model compound **12** and a methano[70]fullerene model compound (dashed line) and of dyad **18** (solid line) with the same concentration. Spectra recorded under identical instrumentation conditions. Excitation wavelength: 320 nm. The absorbances of the two solutions at the excitation wavelength were identical within experimental error.

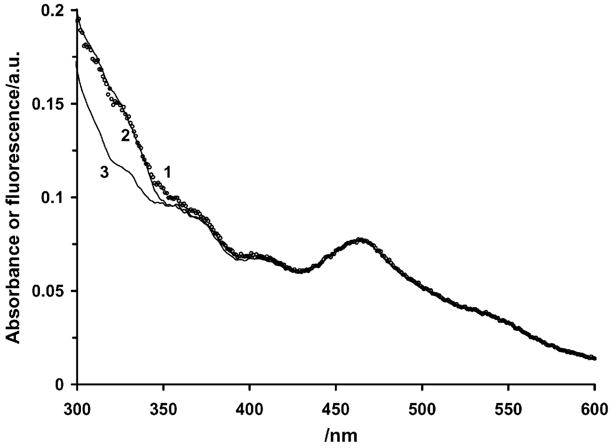


Fig. 5 Corrected fluorescence excitation spectrum of a dilute (2×10^{-6} M) solution of dyad **18** (1, hollow circles) in toluene. The emission wavelength was 700 nm. The absorption spectra of **18** (2) and of the C_{70} methanoderivative model compound (3) are also shown.

(**16**, **18** and **19**) also do not show evidence of any ground-state interaction of the two chromophores.

Coumarin compounds **6**, **8**, **12** and **13** display similar photophysical behaviour. Their fluorescence quantum yields, in room temperature toluene, range from 0.012 to 0.018, as shown in Table 1. The fluorescence decays are fast and complex (bi or triexponential) and only the average lifetimes are reported in Table 1.

The fluorescence of the dyads, obtained at room temperature in toluene and with 300 nm excitation, exhibits a low energy band not present in the spectra of the coumarin model compounds **6**, **8**, **12** and **13**, Fig. 3. Apart from the coumarin emission, which occurs in the 340–520 nm range, the characteristic fullerene emission is now observed in the 670–800 nm region. The increase of the spacer carbon chain length in methanofullerenes **3**/**17** and **18**/**19**, from three to six carbon atoms, has no major effect on the fluorescence intensity. The emission of the C_{70} moiety in **14**, **16**, **18** and **19** is broader and slightly blue-shifted, as compared to that of C_{60} in **2**, **3**, **4**, **15** and **17**. There is no wavelength at which the coumarin moiety can be selectively excited, with negligible absorption of the fullerene (C_{60} or C_{70} moiety). Thus, a procedure to correct the fluorescence quantum yields was necessary, which takes into account the fractional absorption of excitation light by the coumarin and fullerene chromophores. The fluorescence quantum yields of the coumarin moiety in the dyads given in Table 1 are always corrected values. The contribution of direct excitation for the global fullerene emission is shown in Fig. 3 for dyad **14**.

In all coumarin–fullerene (C-F) dyads synthesized, **14–19**, there is a significant decrease of the coumarin fluorescence quantum yield as compared to that of the model compounds, see Table 1. This implies a strong quenching of the excited coumarin by the fullerene moiety. Simultaneously, an increase in the apparent or technical[47,48] fluorescence quantum yield of the C_{60} or C_{70} moiety (680–705 nm), compared to that of the directly excited fullerene monoadducts is observed, indicating the existence of fast and efficient singlet–singlet energy transfer from the coumarin moiety to the fullerene moiety,

$$\mathrm{C{-}F} \xrightarrow[300\mathrm{nm}]{h\nu} \mathrm{C^{*}{-}F} \xrightarrow{k_{\mathrm{ET}}} \mathrm{C{-}F^{*}} \qquad (1)$$

From the donor (coumarin) fluorescence quantum yields (Φ_D) and average lifetimes (τ_D) in the coumarin reference compounds (°) and coumarin moieties in the dyads, the average rate constants (k_{ET}) for intramolecular energy transfer in the dyads were calculated according to eqn (2):

$$k_{\mathrm{ET}} = (\Phi_{\mathrm{D}}{}^{\circ}/\Phi_{\mathrm{D}} - 1)/\tau_{\mathrm{D}}{}^{\circ} \qquad (2)$$

see Table 2.

To confirm that energy transfer was operative, two additional methods were used.[49,50] In the first, the fluorescence intensity of a dilute solution of dyad **18** (5×10^{-6} M) was compared with that of an equimolar mixture (5×10^{-6} M) of the coumarin model compound **12** and of a methano[70]fullerene (malonic acid dimethyl ester derivative $C_{70}[C(COOMe)_2]$) model compound, see Fig. 4.

The fullerene emission in the dyad is higher by a factor of 1.5, confirming the existence of intramolecular energy transfer. Assuming that the molar absorption coefficients at the excitation wavelength of both moieties are identical in the model compounds and in the dyad, it can be shown that the ratio of intensities of the acceptor (fullerene) emission is given by[49,50]

$$I_{\mathrm{A}}/I_{\mathrm{A}}{}^{\circ} = 1 + (\varepsilon_{\mathrm{D}}/\varepsilon_{\mathrm{A}})\ \Phi_{\mathrm{ET}} \qquad (3)$$

Using the measured absorption coefficients of the model compounds and the energy transfer efficiency computed with eqn (2), a value of 1.3 was obtained for the fullerene emission in the dyad relative to the emission of the model fullerene. The agreement with the experimental value of 1.5 is satisfactory, considering the approximation made with respect to the absorption coefficients.[49]

According to the second additional method,[49,50] the excitation spectrum of the fullerene moiety in the dyad **18** was recorded and compared with the absorption spectrum of the dyad and with the absorption spectrum of the fullerene model compound, see Fig. 5.

The appropriate equation (see *e.g.* ref. 47) is

$$I_{\mathrm{A}}(\lambda) = C\,[A_{\mathrm{A}}(\lambda) + \Phi_{\mathrm{ET}}A_{\mathrm{D}}(\lambda)] \qquad (4)$$

where C is a constant, I_A is the fluorescence intensity for the excitation wavelength λ, measured at the acceptor band and A_A and A_D are the acceptor and donor absorbances at excitation wavelength λ.

For 100% transfer efficiency, excitation and absorption spectra of the dyad must have the same shape. For a lower efficiency, there is a decrease in the region of the excitation spectrum corresponding to the donor. However, this decrease cannot be seen when the acceptor has a broad absorption spectrum that overlaps and dominates that of the donor, see eqn (4). This is precisely what happens with dyad **18**, with the exception of a narrow spectral range (300–350 nm) where curves 2 and 3 differ. It can be concluded from Fig. 5 that the transfer efficiency is high, in agreement with the computed value of 0.84 (see Table 2), as the excitation spectrum nearly coincides with the absorption spectrum of the dyad.

A Förster mechanism was invoked in some studies of energy transfer in dyads and polyads involving a fullerene moiety as the acceptor.[13–15,17,20] In the present dyads, the quenching process is also consistent with a dipole–dipole energy transfer mechanism. Indeed, the average distances computed according to this mechanism, eqn (5),

$$k_{\mathrm{ET}} = \frac{1}{\tau}\left(\frac{R_0}{r}\right)^6 \qquad (5)$$

where R_0 is the Förster radius, see Table 2, agree with the expected average distances obtained from molecular models within 2 Å. Owing to some conformational flexibility, maximum and minimum distances between donor and acceptor moieties typically differ by 3 to 4 Å (dyads **15** and **17**, respectively), as estimated from molecular models. The near coincidence of computed and estimated average distances is quite reasonable taking into account all approximations involved. Note for instance the identical average distance recovered for dyads **15** and **16**, as is expected from the similar structures, in spite of the very different energy transfer efficiencies. Note also that the energy transfer process should lead in all dyads to very short components in the decay of the donor moiety (from 5 to 50 ps on average, see Table 2) *i.e.*, a situation of quasi-static quenching, not readily accounted for by a single or double exponential analysis of weakly emitting samples and owing to limited experimental time resolution (a few picoseconds). Moreover, the decays of the coumarin model compounds are already complex (bi or triexponential), precluding a detailed analysis of the decay of the dyads. For these reasons, the existence of efficient quenching and resonance transfer, as implied by the computed critical radii and demonstrated by the steady-state data, is not apparent from the reported average lifetime values of the coumarin moieties, that correspond mainly to conformers and/or relative donor–acceptor orientations unfavourable for energy transfer, all other cases being strongly quenched by energy transfer and thus not contributing to the experimental decay recorded within a limited time window.

Conclusions

A series of [60] and [70]fullerene–coumarin dyads with coumarin derivatives linked through the 4- or 7- position to the fullerene by flexible saturated hydrocarbon spacer units with different lengths was synthesized. The absorption and fluorescence spectra, quantum yields and lifetimes of the coumarin derivatives and dyads were measured in toluene at room temperature. The emission of the coumarin moiety is strongly quenched by the fullerene moiety in all dyads investigated. This quenching is in agreement with an intramolecular energy transfer process from the coumarin moiety to the fullerene moiety, owing to the concomitant increase of the fluorescence of the fullerene moiety, which cannot be explained either by radiative (trivial) transfer or solely by direct excitation. The computed Förster radii are in all cases significant, pointing to a dipole–dipole resonance energy transfer quenching mechanism. From the computed average rate constants for energy transfer and with the assumption of a dipolar mechanism, average distances were obtained. These distances are reasonable, given all the approximations involved and the expected average distances between moieties in the dyads studied. It is therefore concluded that in these dyads the coumarin fluorescence is strongly quenched by efficient dipole–dipole resonance energy transfer, the fullerene moiety acting as the acceptor.

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