J Fluoresc (2006) 16:245–250
DOI 10.1007/s10895-005-0034-z

ORIGINAL PAPER

Resonance Energy Transfer in New Fullerene–Coumarin Diads

**Susana Nascimento · Maria J. Brites · Célia Santos ·
Bárbara Gigante · Alexander Fedorov ·
Mário N. Berberan-Santos**

Received: 1 November 2005 / Accepted: 8 November 2005 / Published online: 31 March 2006

Abstract The fluorescence properties of new [60] and [70] fullerene–coumarin diads are studied. These diads were synthesized by covalently linking a coumarin dye to a fullerene (C_{60} or C_{70}) by a cyclopropanation reaction. The absorption and fluorescence spectra, quantum yields and lifetimes of the diads are reported. The fluorescence quenching of the coumarin moiety by the fullerene was observed in all diads, indicating the occurrence of resonance energy transfer between the coumarin and fullerene moieties.

Keywords C_{60} · C_{70} · Coumarin · Diads · Resonance energy transfer

Introduction

Fullerenes, and in particular C_{60}, have been incorporated in a wide variety of molecular structures, containing photoactive and/or electroactive units, to form donor-bridge-acceptor diads and triads [1–3]. In these molecular systems, the fullerene unit is usually the electron acceptor owing to its relatively low reduction potential, extended π-electron system and low reorganization energy [3–5]. Recently, C_{60} has been introduced in combination with electroluminescent organic conjugated polymers and oligomers as a component for organic solar cells [6–9]. In donor-bridge-acceptor systems, electronic energy transfer from the higher energy moiety to the lower energy one is also possible in principle, whenever a spectral overlap between the fluorescence of the donor moiety and the absorption of the acceptor moiety exists. As is well known, in the case of transfer by the dipole–dipole mechanism, this implies a distance not larger than twice the critical radius.

The diads studied in this work were obtained by covalently linking a coumarin dye (donor) to fullerene (acceptor) by the cyclopropanation reaction [3]. Two coumarin derivatives and two different spacers (rigid/flexible) were used. Here we report the fluorescence properties of the diads and discuss the fluorescence quenching process of the coumarin moiety by the fullerene moiety.

Experimental

C_{60} (99.5%, Aldrich), C_{70} (99%, Aldrich), anthracene (Fluka), and coumarin 1 (99%, Fluka) were used as received. All solvents used were of spectroscopic grade. The synthesis of the coumarin derivatives and diads will be described elsewhere.

Spectral measurements were made with standard 1 cm quartz cells at room temperature. Electronic absorption spectra were measured using a Shimadzu 3101 UV/Vis/NIR spectrophotometer. Fluorescence spectra were obtained with a SPEX Fluorolog F112A fluorimeter, equipped with a 1681 0.22 m single monochromator on the excitation side and a 1680 0.22 m double monochromator on the emission side. Fluorescence quantum yields in room temperature toluene were determined by a comparative method, using anthracene ($\phi_F = 0.27$ [10]) and coumarin 1 ($\phi_F = 0.73$ [11]) in air-saturated ethanol as the fluorescence standard for coumarin derivatives **I** and **IV**, respectively. Fluorescence quantum yields of the diads **II** and **III** in room temperature toluene were determined using anthracene ($\phi_F = 0.27$ [10])

S. Nascimento · M. J. Brites · C. Santos · B. Gigante
Departamento de Tecnologia de Indústrias Químicas, INETI,
Lisboa, Portugal

S. Nascimento · A. Fedorov · M. N. Berberan-Santos (✉)
Centro de Química-Física Molecular, Instituto Superior Técnico,
1049-001 Lisboa, Portugal
e-mail: berberan@ist.utl.pt

as the fluorescence standard for the coumarin moiety (340–520 nm region) and C_{60} ($\phi_F = 2 \times 10^{-4}$ [12]) and C_{70} ($\phi_F = 5 \times 10^{-4}$ [12]) in toluene for the fullerene moiety (670–800 nm region), respectively. The fluorescence quantum yield of dyad **V** in room temperature toluene was determined using coumarin 1 ($\phi_F = 0.73$ [11]) as the reference compound for the coumarin moiety (390–600 nm region) and C_{60} ($\phi_F = 2 \times 10^{-4}$ [12]) for the fullerene moiety (680–800 nm region). For this purpose, the usual procedures were followed; namely, optical densities were matched and refractive indexes corrections applied. Singlet state lifetimes were determined using the single photon timing method as described previously [13]. The excitation wavelength was 320 nm for coumarin derivative **I** and diads **II** and **III**. Compounds **IV** and **V** were excited at 375 nm.

Results and discussion

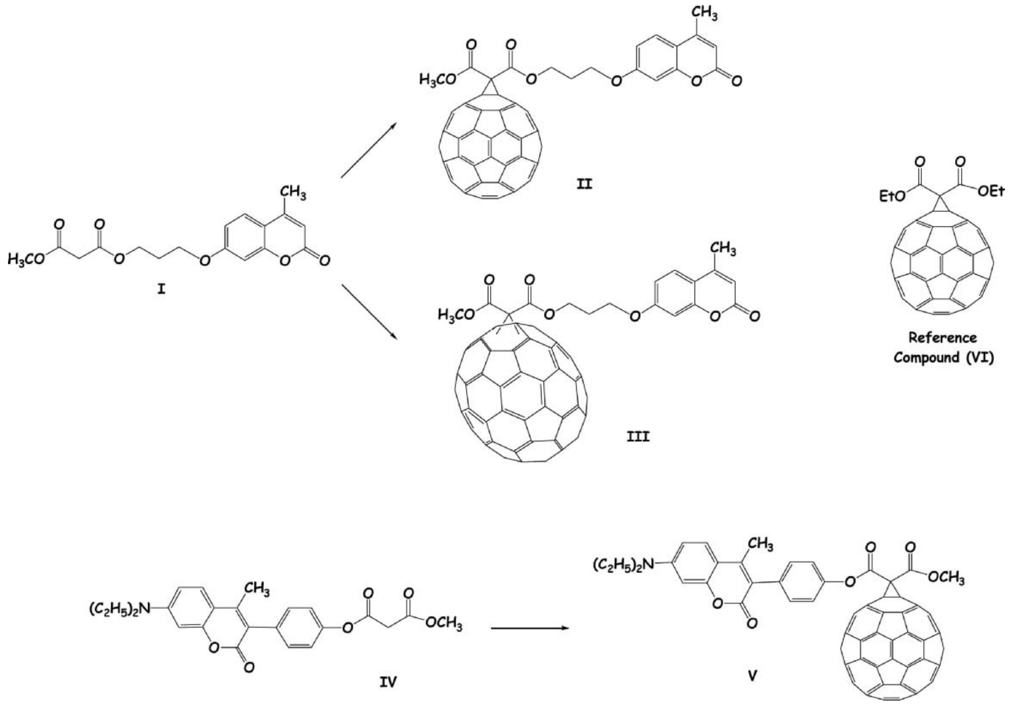
Synthesis

Among the suitable protocols for the functionalization of fullerenes, the Bingel reaction is an important methodology for the production of stable fullerene derivatives. Scheme 1 summarizes the synthetic pathways chosen. In the present case, the cyclopropanation of the fullerene (C_{60} or C_{70}) was done starting directly from malonates (**I** and **IV**). The α-halomalonate was generated *in situ*. Direct treatment of the fullerene with malonates in the presence of iodine and base (DBU) afforded the corresponding methanofullerenes in satisfactory yields. The detailed synthesis, including the synthesis of coumarin derivatives **I** and **IV**, will be described elsewhere.

Absorption and steady-state measurements

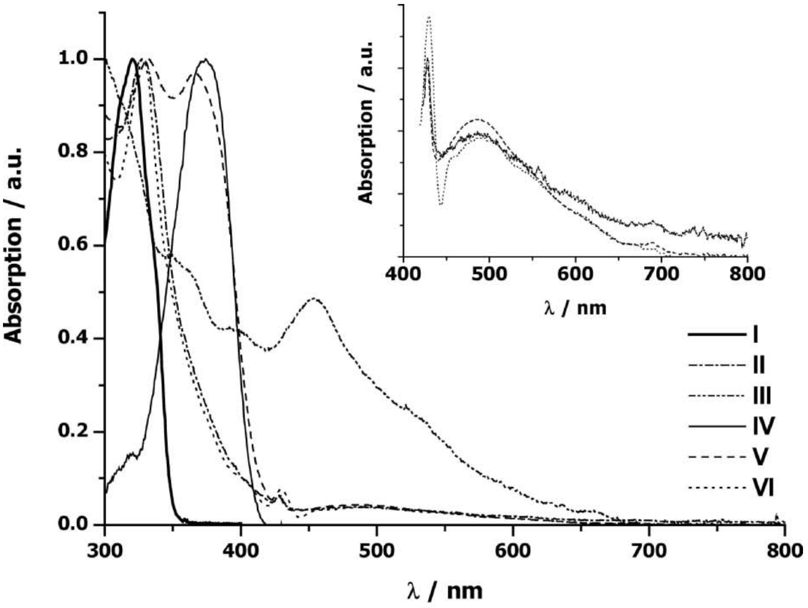
The UV-Vis spectra of diads **II**, **III,** and **V** in toluene solutions are depicted in Fig. 1, together with those of its coumarin precursors (**I** and **IV**) and reference compound methanofullerene (**VI**). The spectra of the coumarin derivatives **I** and **IV** are characterized by a sharp band, with maxima at 320 and 374 nm, respectively. The absorption spectra of diads **II** and **III** are the sum of the absorption spectra of the individual chromophores (fullerene and coumarin derivative **I**). On the other hand, the spectrum of dyad **V** differs from the sum of the spectra of the individual chromophores (i.e., C_{60} and coumarin derivative **IV**). The maximum observed at 374 nm (**IV**) does not coincide with that of **V** (365 nm) indicating the existence of ground-state electronic interaction of the individual chromophores.

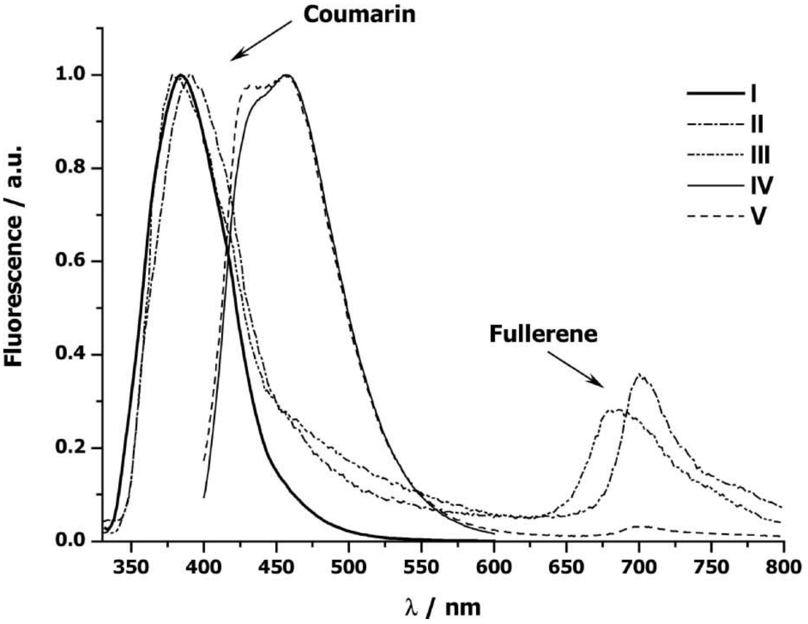
To study the interaction of the coumarin and the fullerene moieties in the excited state, fluorescence emission measurements were carried out with diads **II**, **III,** and **V** and compared to those of model compounds **I**, **IV,** and **VI** (Fig. 2). These studies will be discussed separately according



Scheme 1

Fig. 1 Normalized absorption spectra of diads **II** (*dashed-dotted line*), **III** (*dashed-dotted-dotted line*) and **V** (*dashed line*) along with its precursors **I** (*solid line*) and **IV** (*thin solid line*) and methanofullerene **VI** (*dotted line*), in room temperature toluene. (*Inset*) Absorption spectra of **II**, **V** and **VI**, magnified in the 422–800 nm region





to the coumarin moiety and linker of the diads. The fluorescence of diads **II** and **III** obtained in room temperature toluene and with 320 nm excitation, differ significantly from that of **I**. Apart from the coumarin emission that occurs up to 600 nm, a second emission band, characteristic of the fullerene moiety, is observed in the 650–800 nm region. As a result of its stronger emission, the band of the C_{70} moiety in dyad **III** is broader and blue-shifted, as compared to that of C_{60} in dyad **II**. Furthermore, in the diads there is a dramatic decrease of the coumarin moiety quantum yield when compared with that of the coumarin precursor (**I**). This implies a strong intramolecular quenching of the coumarin fluorescence by the fullerene moiety (C_{60} or C_{70}). Simultaneously, an increase in the emission quantum yield of the C_{60} or C_{70} moiety compared to that of directly excited fullerene monoadducts is observed, indicating the existence of efficient singlet-singlet energy transfer from the coumarin moiety to the C_{60} (or C_{70}). From the fluorescence quantum yields (Φ_F) and lifetimes (τ_F) of photoexcited **I** (X), **II,** and **III**, the average rate constant (k_{ET}) for intramolecular energy transfer in the diads (Y), can be calculated according to Eq. (1):

$$k_{ET}(Y) = [\Phi(X)/\Phi(Y) - 1]/\tau(X) \qquad (1)$$

The computed rate constants are 1.1×10^{11} s^{-1} and 5.4×10^{10} s^{-1} for diads **II** and **III**, respectively. Förster radii (R_0), energy transfer efficiencies (Φ_{ET}) and average

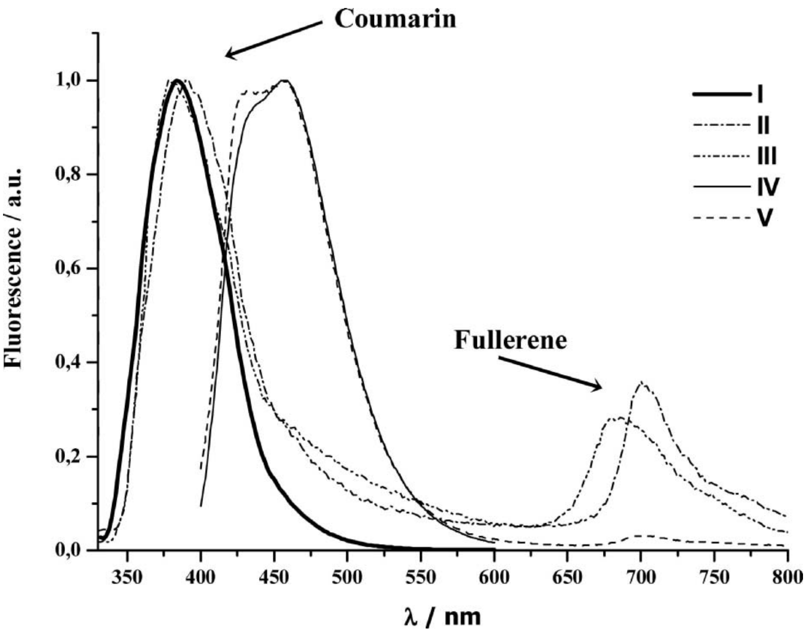


Fig. 2 Normalized fluorescence spectra of diads **II** (*dashed-dotted line*), **III** (*dashed-dotted-dotted line*) and **V** (*dashed line*) along with its precursors **I** (*solid line*) and **IV** (*thin solid line*), in room temperature toluene

donor-acceptor distances (r) were also determined, and are summarized in Table 1.

In the case of dyad **V**, a decrease of the coumarin moiety quantum yield relatively to that of the coumarin derivative **IV** is also observed. As in diads **II** and **III**, the coumarin fluorescence is strongly (two orders of magnitude) quenched by C_{60}.

Despite almost exclusive excitation of the coumarin moiety at 375 nm, the fullerene fluorescence spectrum appears with its characteristic emission band at 701 nm. For example, the absorption ratio at 375 nm of the fullerene and coumarin moieties in dyad **V** is 2.5/7.5 based on the absorbance values of the components at 375 nm. This indicates the existence of energy transfer from the singlet excited state of coumarin moiety to C_{60}, with a rate constant of 1.2×10^{11} s^{-1}. However, in this case the quenching mechanism may be in part different, owing to the ground-state electronic interaction between the individual chromophores, as indicated by the absorption spectra, and by the weaker fullerene emission.

As summarized in Table 2, fluorescence quantum yields of the coumarin derivatives **I** and **IV** are significantly different, with values of 0.012 and 0.38, respectively. This large difference is due to the substitution pattern, namely in three positions which are known to affect the photophysical properties of coumarin derivatives [14–16]. The fluorescence quantum yields of the diads range from 0.99×10^{-3} to 2.7×10^{-3} for the coumarin moiety, and from 4.0×10^{-4} to 7.9×10^{-4}

Table 1 Average rate constants for energy transfer (k_T), energy transfer quantum yields (Φ_{ET}), Förster radii (R_0), and average donor-acceptor distances (r) for diads II, III, and V.

Compound	$k_{ET}/10^{11}$ (s^{-1})	Φ_{ET}	R_0 (Å)	r (Å)
II	1.1	0.92	17	11
III	0.54	0.84	21	16
V	1.2	0.99	26	12

Table 2 Quantum yields (Φ_F), average lifetimes (τ_F), and radiative (k_F) and nonradiative (k_{nr}) rate constants, in room temperature toluene.

Compound	Φ_F	τ_F (ps)	k_F (s^{-1})	k_{nr} (s^{-1})
I	0.012^c	100^h	1.2×10^8	1.0×10^{10}
II				
C^a	9.9×10^{-4d}	540^h	–	–
F^b	4.0×10^{-4e}	1470^h	–	–
III				
C^a	1.9×10^{-3d}	340^h	–	–
F^b	7.9×10^{-4e}	850^h	–	–
IV	0.38^f	1020^h { 920(0.89) 1770(0.11)	3.8×10^8	6.1×10^8
V				
C^a	2.7×10^{-3f}	1250^h { 910(0.50) 1600(0.50)	–	–
F^b	4.0×10^{-4g}	1520	–	–

[a] Coumarin moiety.

[b] Fullerene moiety.

[c] $\lambda_{exc.} = 320$ nm.

[d] $\lambda_{exc.} = 300$ nm.

[e] $\lambda_{exc.} = 400$ nm.

[f] $\lambda_{exc.} = 375$ nm.

[g] $\lambda_{exc.} = 500$ nm.

[h] Average lifetime, calculated from $\sum \alpha_i \tau_i^2 / \sum \alpha_i \tau_i$.

for fullerene moiety (direct excitation). The latter values are comparable to those of other monoadducts, including reference compound **VI** [17, 18].

In practice, there is no wavelength at which the donor (coumarin moiety) can be excited with negligible absorption of the acceptor (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. In Table 2, the displayed fluorescence quantum yields of the coumarin moiety in the diads are the corrected values.

Time-resolved measurements

Fluorescence decays of coumarin derivatives and diads in room-temperature toluene were measured using the single photon timing method. Preliminary results are reported here. The fluorescence decays of coumarin derivatives **I** and **IV** were fitted to sums of three- and two-exponentials, respectively. The average lifetimes obtained were 100 ps and 1.0 ns for coumarin derivatives **I** and **IV**, respectively. For the diads, the fluorescence decay was measured at two different wavelengths corresponding to the maxima of emission of the coumarin and fullerene moieties. The excited state C_{60} moiety lifetimes in diads **II** and **V** were 1.47 ns and 1.52 ns, respectively. For the C_{70} moiety in dyad **III,** a double exponential fit gave 0.18 ns and 0.87 ns components. The average lifetimes are summarized in Table 2. The fluorescence decays of the coumarin moiety in diads **II** and **III** were measured at 384 nm and 416 nm, respectively and were more complex. The intensity was very weak with a strong Raman scattering component. The fluorescence decay of the coumarin moiety in dyad **V** was fitted with a sum of two exponentials with 0.91 ns and 1.60 ns lifetimes. Note that the energy transfer process should lead in all diads to very short components (i.e., quasi-static quenching), not readily accounted for by a single or double exponential analysis. Furthermore, the decays of the coumarin precursors are already complex. For these reasons, the existence of efficient quenching and transfer, as shown by steady-state data, is not easy to infer from the reported average values. Studies are in progress to further elucidate the fluorescence decays in these systems.

The radiative, k_f, and nonradiative, k_{nr}, rate constants of coumarin precursors **I** and **IV** were computed from the fluorescence decay times and fluorescence quantum yields, and are given in Table 2.

Conclusions

The synthesis of the methanofullerenes covalently linked to coumarins has been carried out from suitably functionalized coumarins by cyclopropanation of C_{60} or C_{70}. The absorption and fluorescence spectra, quantum yields and lifetimes of the coumarin derivatives and diads have been measured in toluene at room temperature. The emission of the coumarin moiety is quenched by the fullerene moiety in all diads investigated. This quenching is in agreement with an intramolecular energy transfer 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 direct excitation or by radiative (trivial) transfer. From the computed critical radii, it is concluded that resonance energy transfer is a likely mechanism of quenching. The average distances computed from an average rate constant for quenching are reasonable, given all approximations involved and the expected distances between moieties in the diads studied. A more refined analysis of the energy transfer process, with due allowance for a distribution of donor-acceptor distances and orientations, and possibly for diffusion, will be presented elsewhere. Additionally, the absorption spectrum of dyad **V** revealed the existence of a ground-state interaction of the two moieties, which can also be responsible in part for the quenching of the coumarin emission in this compound.

Acknowledgements This work was supported by Fundação para a Ciência e a Tecnologia (FCT, Portugal). S. Nascimento was supported by a doctoral grant from FCT (SFRH/BD/18622/2004).

References

1. M. D. L. de la Torre, A. G. P. Rodrigues, A. C. Tome, A. M. S. Silva, and J. A. S. Cavaleiro (2004). [60]Fullerene-flavonoid diads. *Tetrahedron* **60**(16), 3581–3592.
2. L. Garlaschelli, I. Messina, D. Pasini, and P. P. Righetti (2002). Fullerene ylidene malonate supramolecular triads. *Eur. J. Org. Chem.* **20**, 3385–3392.
3. D. Zhu, Y. Li, S. Wang, Z. Shi, C. Du, S. Xiao, H. Fang, and Y. Zhou (2003). Design, synthesis and properties of functional materials based on fullerene. *Synth. Metals* **133–134**, 679–683.
4. M. Diekers, A. Hirsch, S. Pyo, J. Rivera, and L. Echegoyen (1998). Synthesis and electrochemical properties of new C_{60}-acceptor and donor diads. *Eur. J. Org. Chem.* **6**, 1111–1121.
5. M. Prato and M. Maggini (1998). Fulleropyrrolidines: A family of full-fledged fullerene derivatives. *Acc. Chem. Res.* **31**(9), 519–526.
6. J. L. Segura, R. Gómez, N. Martín, C. Luo, and D. Guldi (2000). Competition between photosensitization and charge transfer in soluble oligo(naphthylenevinylene)-fullerene diads. *Chem. Comm.* **8**, 701–702.
7. F. Langa, M. J. Gomez-Escalonilla, J. M. Rueff, T. M. F. Duarte, J. F. Nierengarten, V. Palermo, P. Samorì, Y. Rio, G. Accorsi, and N. Armaroli (2005). Pyrazolino[60]fullerene-oligophenylene dumbbell-shaped arrays: Synthesis, electrochemistry, photophysics, and self-assembly on surfaces. *Chem. Eur. J.* **11**(15), 4405–4415.
8. J. L. Segura, N. Martín, and D. M. Guldi (2005). Materials for organic solar cells: The C_{60}/π-conjugated oligomer approach. *Chem. Soc. Rev.* **34**(1), 31–47.

9. J. F. Nierengarten, T. Gu, G. Hadziioannou, D. Tsamouras, and V. Krasnikov (2004). A new iterative approach for the synthesis of oligo(phenyleneethynediyl) derivatives and its application for the preparation of fullerene-oligo(phenyleneethynediyl) conjugates as active photovoltaic materials. *Helv. Chim. Acta* **87**(11), 2948–2966.
10. D. F. Eaton (1988). Reference materials for fluorescence measurement. *J. Photochem. Photobiol. B* **2**(4), 523–531.
11. G. Jones II, W. R. Jackson, C. Choi, and W. R. Bergmark (1985). Solvent effects on emission yield and lifetime for coumarin laser dyes. Requirements for a rotatory decay mechanism. *J. Phys. Chem.* **89**(2), 294–300.
12. Y. P. Sun (1997). in V. Ramamurthy and K. S. Schanze (Eds.), *Molecular and Supramolecular Photochemistry*, Marcel Dekker, New York, pp. 325–390.
13. A. Fedorov, M. N. Berberan-Santos, J. P. Lefèvre, and B. Valeur (1997). Picosecond time-resolved and steady-state studies of the polarization of the fluorescence of C_{60} and C_{70}. *Chem. Phys. Lett.* **267**, 467–471.
14. H. Ammar, S. Fery-Forgues, and R. El Gharbi (2003). UV/vis absorption and fluorescence spectroscopic study of novel symmetrical biscoumarin dyes. *Dyes Pigments* **57**(3), 259–265.
15. J. S. S. de Melo, R. S. Becker, and A. L. Maçanita (1994). Photophysical behavior of coumarins as a function of substitution and solvent: Experimental evidence for the existence of a lowest lying^1(n,π^*) state. *J. Phys. Chem.* **98**, 6054–6058.
16. R. Giri, S. S. Rathi, M. K. Machwe, and V. V. S. Murti (1988). Effect of substituents on the fluorescence and absorption spectra of coumarins. *Spectrochim. Acta A* **44**(8), 805–807.
17. N. Armaroli, G. Marconi, L. Echegoyen, J. P. Bourgeois, and F. Diederich (2000). Charge-transfer interactions in face-to-face porphyrin-fullerene systems: Solvent-dependent luminescence in the infrared spectral region. *Chem. Eur. J.* **6**(9), 1629–1645.
18. D. M. Guldi, C. Luo, A. Swartz, R. Gómez, J. L. Segura, N. Martín, C. Brabec, and N. S. Sariciftci (2002). Molecular engineering of C_{60}-based conjugated oligomer ensembles: Modulating the competition between photoinduced energy and electron transfer processes. *J. Org. Chem.* **67**(4), 1141–1152.