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Photoinduced energy transfer in a fullerene–oligophenylenevinylene conjugate†

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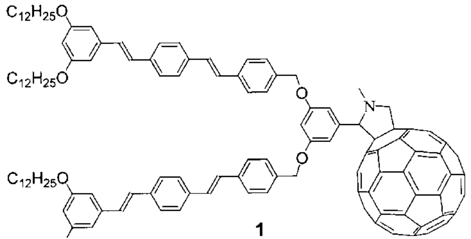
A fullerene derivative in which two oligophenylenevinylene (OPV) groups are attached to C_{60} through a pyrrolidine ring has been prepared and photophysical studies in CH_2Cl_2 solution show that photoinduced energy transfer from the OPV moieties to C_{60} occurs, and not electron transfer.

Following the observation of electron transfer from conducting oligomers and/or polymers derived from poly(phenylenevinylene) or poly(thiophene),[1] and the successful preparation of photovoltaic cells from such bulk heterojunction materials,[2] several examples of covalent fullerene derivatives bearing a conjugated oligomer substituent have been synthesized in the past few years.[3,4] As a part of this research, we have recently shown that such hybrid compounds can be incorporated in photovoltaic devices.[4] Whereas the synthesis and applications of such hybrid compounds have been investigated, their electronic properties have been probed to a much lesser degree.

In this paper, we report on the preparation and the electronic properties of fullerene derivative **1** in which two OPV groups are attached to C_{60} through a pyrrolidine ring using the related OPV derivative **2** and the fulleropyrrolidine **FP**[4] as reference compounds. Interestingly, the photophysical studies of **1** in solution show that photoinduced energy transfer from the OPV moiety to C_{60} is the main pathway and not electron transfer.



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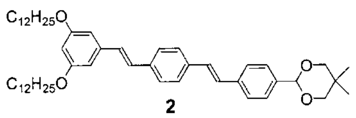

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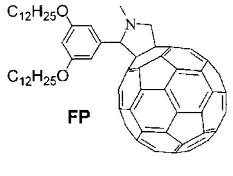

FP

The synthesis of **1** is depicted in Fig. 1 and the functionalisation of C_{60} is based on the 1,3-dipolar cycloaddition[5] of the azomethine ylide generated *in situ* from aldehyde **7**.

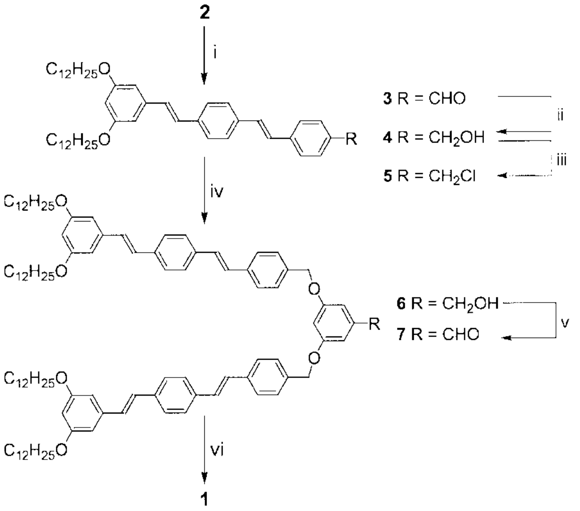

Fig. 1 *Reagents and conditions*: i, CF_3CO_2H, CH_2Cl_2, H_2O, room temp., 4 h (96%); ii, DIBAL-H, CH_2Cl_2, 0 °C, 1 h (90%); iii, TsCl, LiCl, DMAP, CH_2Cl_2, 0 °C to room temp., 12 h (80%); iv, 3,5-dihydroxybenzyl alcohol, K_2CO_3, KBr, 18-crown-6, acetone, Δ, 24 h (69%); v, MnO_2, CH_2Cl_2, room temp., 2 h (95%); vi, C_{60}, *N*-methylglycine, toluene, Δ, 16 h (40%).

The electrochemical properties of **1**, **2** and **FP** were investigated by cyclic voltammetry (CV) in CH_2Cl_2–0.1 M Bu_4NPF_6 solutions (Table 1). In the cathodic region, **1** shows three reversible one-electron processes followed by a bielectronic peak ($\mathrm{IV_{red}}$), visible only at low temperature. A comparison of the $E_{1/2}$ potentials of **1** and **FP** clearly shows that the first three waves correspond to fullerene-centred reductions and the slightly negative shift observed for **1** compared to **FP** could be the result of a small interaction between the electron-accepting C_{60} unit and the electron-donating OPV groups. The fourth reduction process seen for **1** appears to be difficult to assign unambiguously as either fullerene- or OPV-based. In the anodic region, **1** presents two chemically irreversible and ill-defined peaks, corresponding to the transfer of three electrons. They can likely be attributed to the simultaneous oxidation of the two OPV groups and the bridging dialkyloxybenzene unit,[6] since these groups present in both model compounds **2** and **FP** are irreversibly oxidized in the same potential region.

The ground state electronic absorption spectrum of **1** is reported in Fig. 2 and, within the experimental error, it matches the profile obtained by summation of the spectra of the component units **FP** and **2**. Importantly, on each moiety of **1**, a fairly good excitation selectivity can be achieved. Indeed, at $\lambda >$

Table 1 $E_{1/2}$ or E_p values (V *vs.* SCE) determined by CV on a glassy carbon electrode at 298 K, unless otherwise noted,[b] of compounds **1**, **2** and **FP** in CH_2Cl_2–0.1 M Bu_4NPF_6 solutions

Compound	$\mathrm{II_{ox}}$	$\mathrm{I_{ox}}$	$\mathrm{I_{red}}$	$\mathrm{II_{red}}$	$\mathrm{III_{red}}$	$\mathrm{IV_{red}}$
1	+1.7[a,c]	+1.4[a,c]	−0.66	−1.04	−1.56	−1.98[b,d]
2	+1.82[a]	+1.28[a]	−1.88[b]	−2.11[a,b]		
FP	+1.60[a]	+1.38[a]	−0.62	−1.01	−1.54	−1.90[b]

[a] Chemically irreversible processes, peak potentials measured at 0.2 V s^{-1}. [b] T = 208 K. [c] Trielectronic process. [d] Bielectronic process.

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† Electronic supplementary information (ESI) available: CV curves for **1**, **2** and **FP**, and calculation of energy transfer rate constants. See http://www.rsc.org/suppdata/cc/b0/b000564i/

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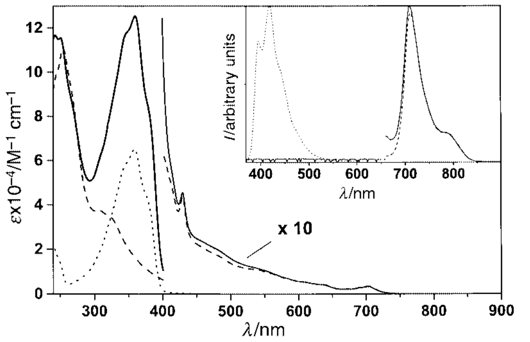

Fig. 2 Absorption spectra of **1** (full line), **FP** (dashed line) and **2** (dotted line) in CH_2Cl_2 at 298 K; above 400 nm a multiplying factor of 10 is used. Inset: fluorescence spectra of solutions of **2**, **FP** and **1** (for all samples, optical density = 0.50 at λ_{exc} = 360 nm). Above 660 nm the spectrofluorimeter sensitivity is increased by three orders of magnitude, due to the weakness of the **FP** fluorescence relative to that of **2**.

530 nm light is exclusively directed to the fullerene fragment, whereas at λ = 360 nm at least 85% of the incident light is absorbed by the OPV moieties.

Upon selective excitation of **1** on the fullerene fragment, the typical fulleropyrrolidine fluorescence and triplet–triplet transient absorption spectra are observed.[6,7] This indicates that the excited state properties of the C_{60} fragment are not affected by the presence of the nearby OPV moieties. On the other hand, when excitation is directed to the latter (*e.g.* at λ = 360 nm, see above), intercomponent processes are evidenced. Under such conditions, the intense fluorescence band characteristic of the OPV moiety (Φ_{em} = 1.0, τ = 1.0 ns) is not observed (Fig. 2), whereas the typical fluorescence band of the fulleropyrrolidine fragment (λ_{max} = 710 nm, τ = 1.3 ns) is detected; in addition, the fullerene fluorescence quantum yields of **1** and **FP** obtained at λ_{exc} = 360 nm are identical (Φ_{em} = 5.5 × 10^{-4}), although in the former at least 85% of the incident light is absorbed by the OPV fragments. The excitation spectrum of **1**, taken at λ_{em} = 715 nm, matches the absorption profile throughout the UV–VIS, range including the diagnostic band of the OPV moieties around 360 nm. These findings are consistent with quantitative occurrence of singlet–singlet energy transfer from the OPV unit to the fullerene in the multicomponent array **1**.

In order to monitor the fate of the lowest triplet state centred on the fullerene moiety, following excitation of the OPV counterpart, we performed a series of transient absorption experiments by setting the excitation wavelength of an Nd:YAG laser to 355 nm. The reference compound **FP** displays a triplet–triplet transient absorption spectrum with λ_{max} = 690 nm and τ = 0.54 μs in air-equilibrated solution, which becomes 31 μs in deaerated solution due to the suppression of the well-known, very efficient quenching of fullerenes by dioxygen.[7,8] A quite similar behaviour is observed for **1**, which displays a fullerene triplet yield formation equal to that of **FP** and the same triplet lifetimes. In other words, preferential excitation of the OPV moieties (> 85%) quantitatively sensitizes the formation of the lowest fullerene singlet state, which then populates the lower lying triplet level (Fig. 3) *via* intersystem crossing.

From the electrochemical data one can place the energy of the charge separated state[9] of **1** at about 2 eV, *i.e.* well below the energy of the lowest singlet excited state of the OPV moieties (3.1 eV, as derived from the 77 K fluorescence spectrum). However, even if the population of the charge separated state following photoexcitation of the OPV units is thermodynamically allowed, this process is not evidenced in CH_2Cl_2 solution. The use of polar solvents does not change the observed pattern; for instance, quantitative evidence for OPV→C_{60} singlet–singlet energy transfer is also observed in benzonitrile solution. We have performed model calculations on the OPV→C_{60} singlet–singlet energy transfer step by following both the dipole–dipole and double-electron exchange approaches (for details, see supplementary data).† The spectral overlap between the luminescence spectrum of the donor OPV unit and the absorption spectrum of the fulleropyrrolidine acceptor unit allows calculation of the overlap integrals J^F = 1.4 × 10^{-14} cm^6 mol^{-1} and J^D = 1.4 × 10^{-4} cm for the two approaches, and results in estimated rate constants, $k_{en}{}^F$; $k_{en}{}^D \geqslant 10^{12}$ s^{-1} up to 10 Å of intercenter separation. These estimates suggest that the energy transfer step is so fast that the competing charge separation path is not effective.

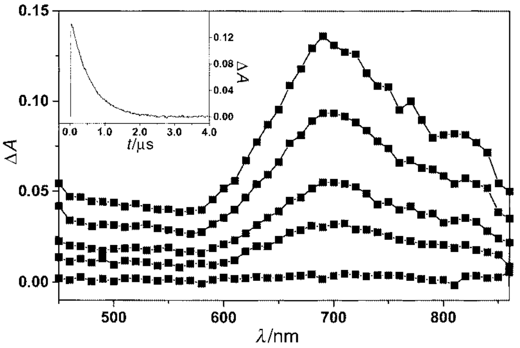

Fig. 3 Sensitized fullerene triplet–triplet transient absorption spectrum of **1** at 298 K in CH_2Cl_2 air equilibrated solution, upon laser excitation at 355 nm (energy = 5 mJ pulse^{-1}). The spectra were recorded at delays of 100, 300, 600, 900, 2000 ns following excitation (from top to bottom). The inset shows the time profile of ΔA (690 nm) from which the spectral kinetic data were obtained; the fitting is monoexponential and gives a lifetime of 540 ns.

In conclusion, **1** appears to be a multicomponent array containing a fullerene unit as a terminal receptor of excitation energy.[10] These results suggest the possibility of building up more complex arrays where a larger number of OPV fragments allow an even more pronounced excitation selectivity with an antenna effect, and the attachment of a suitable electron donor to the C_{60} unit would result in multicomponent artificial photosynthetic systems where light energy harvesting is followed by charge separation.[11]

Notes and references

1 L. Pasimeni, A. L. Maniero, M. Ruzzi, M. Prato, T. Da Ros, G. Barbarella and M. Zambianchi, *Chem. Commun.*, 1999, 429; R. A. J. Janssen, M. P. T. Christiaans, K. Pakbaz, D. Moses, J. C. Hummelen and N. S. Sariciftci, *J. Chem. Phys.*, 1995, **102**, 2628; R. A. J. Janssen, J. C. Hummelen, K. Lee, K. Pakbaz, N. S. Sariciftci, A. J. Heeger and F. Wudl, *J. Chem. Phys.*, 1995, **103**, 788; N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl, *Science*, 1992, **258**, 1474.

2 L. Ouali, V. V. Krasnikov, U. Stalmach and G. Hadziioannou, *Adv. Mater.*, 1999, **11**, 1515; L. S. Roman, M. R. Andersson, T. Yohannes and O. Inganäs, *Adv. Mater.*, 1997, **9**, 1164; G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, **270**, 1789.

3 S.-G. Liu, L. Shu, J. Rivera, H. Liu, J.-M. Raimundo, J. Roncali, A. Gorgues and L. Echegoyen, *J. Org. Chem.*, 1999, **64**, 4884; J. L. Segura and N. Martin, *Tetrahedron Lett.*, 1999, **40**, 3239; T. Yamashiro, Y. Aso, T. Otsubo, H. Tang, Y. Harima and K. Yamashita, *Chem. Lett.*, 1999, 443; F. Effenberger and G. Grube, *Synthesis*, 1998, 1372.

4 J.-F. Nierengarten, J.-F. Eckert, J.-F. Nicoud, L. Ouali, V. Krasnikov and G. Hadziioannou, *Chem. Commun.*, 1999, 617; J.-F. Nierengarten, J.-F. Eckert, D. Felder, J.-F. Nicoud, N. Armaroli, G. Marconi, V. Vicinelli, C. Boudon, J.-P. Gisselbrecht, M. Gross, G. Hadziioannou, V. Krasnikov, L. Ouali, L. Echegoyen and S.-G. Liu, *Carbon*, 2000, in press.

5 M. Prato and M. Maggini, *Acc. Chem. Res.*, 1998, **31**, 519.

6 M. Goez and G. Eckert, *J. Phys. Chem.*, 1991, **95**, 1179.

7 C. Luo, M. Fujitsuka, A. Watanabe, O. Ito, L. Gan, Y. Huang and C.-H. Huang, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 527.

8 F. Prat, R. Stackow, R. Bernstein, W. Qian, Y. Rubin and C. S. Foote, *J. Phys. Chem. A*, 1999, **103**, 7230.

9 V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, UK, 1991, p. 44.

10 D. M. Guldi, G. Torres-Garcia and J. Mattay, *J. Phys. Chem. A*, 1998, **102**, 9679.

11 H. Imahori and Y. Sakata, *Eur. J. Org. Chem.*, 1999, 2445; D. Kuciauskas, P. A. Liddel, S. Lin, T. E. Johnson, S. J. Weghorn, J. S. Lindsey, A. L. Moore, T. A. Moore and D. Gust, *J. Am. Chem. Soc.*, 1999, **121**, 8604.

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