

# A fulleropyrrolidine with two oligophenylenevinylene substituents: synthesis, electrochemistry and photophysical properties

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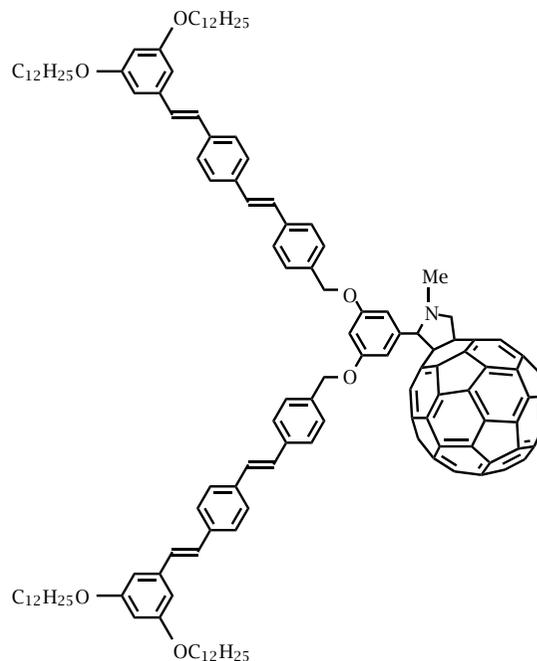
**ABSTRACT.** A fullerene derivative in which two oligophenylenevinylene (OPV) groups are attached to C<sub>60</sub> through a pyrrolidine ring has been prepared and photophysical studies in CH<sub>2</sub>Cl<sub>2</sub> solution show that photoinduced energy transfer from the OPV moieties to C<sub>60</sub> occurs, and not electron transfer. On passing to a more polar solvent such as benzonitrile, again no evidence of electron transfer is found.

## 1. INTRODUCTION

The recent progress in the chemistry of C<sub>60</sub> allows the preparation of many covalent C<sub>60</sub> derivatives bearing electro- and/or photoactive substituents [1]. Some of these systems provided entry into intramolecular processes such as electron or energy transfer, and C<sub>60</sub> appears to be a particularly interesting electron acceptor in photochemical molecular devices because of its symmetrical shape, large size and the properties of its  $\pi$ -electron system. Following the observation of electron transfer from conducting oligomers and/or polymers derived from polyphenylenevinylene or polythiophene [2], and the successful preparation of photovoltaic cells from such bulk heterojunction materials [3], a few examples of covalent fullerene derivatives bearing a conjugated oligomer substituent have been reported in the past years [4–6]. As part of this research, we have recently shown that such hybrid compounds can be used for the preparation of plastic solar cells [5]. The

C<sub>60</sub>-oligophenylenevinylene (OPV) hybrid compound has been incorporated in a photovoltaic cell constructed by spin-casting the compound on a glass substrate covered with indium-tin oxide (ITO) and depositing an aluminum film on top. In such a device configuration, the compound is not only able to generate electrons and holes under light irradiation, but it also provides pathways for their subsequent collection at opposite electrodes, and a photocurrent is obtained. This

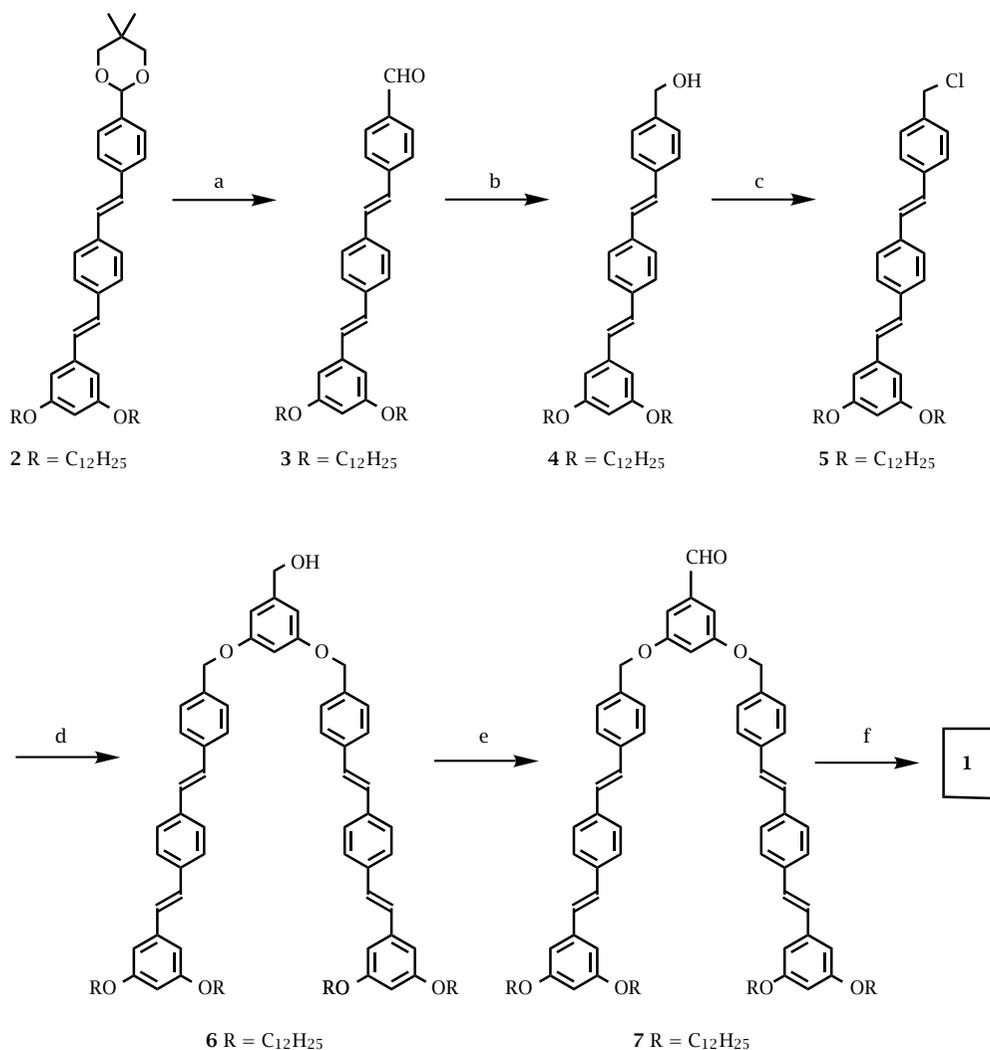
molecular approach to photovoltaic cells appears to be promising since the bicontinuous network obtained by chemically linking the hole-conducting OPV moiety to the electron-conducting fullerene subunit prevents any problems arising from bad contacts at the junction as observed for OPV/C<sub>60</sub> blends. In this paper, we now report in detail the preparation and the electronic properties of fullerene derivative **1** in which two OPV groups are attached to C<sub>60</sub> through a pyrrolidine ring [6]. Interestingly, the photophysical studies of this hybrid compound have shown that, in solution, photoinduced



Compound 1

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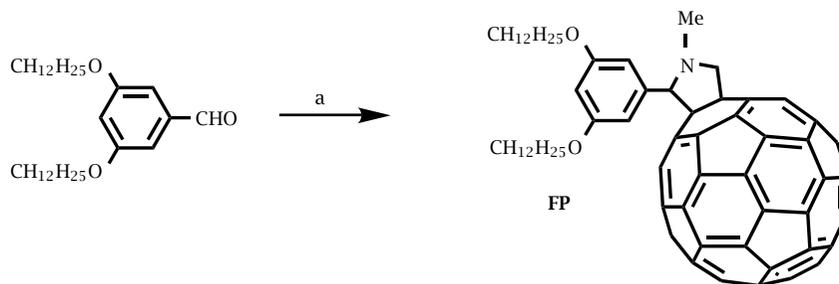
Scheme 1. *Reagents and conditions:* (a) CF<sub>3</sub>CO<sub>2</sub>H, CH<sub>2</sub>Cl<sub>2</sub>, H<sub>2</sub>O, rt, 5 h (96%); (b) LiAlH<sub>4</sub>, THF, 0° C, 1 h (90%); (c) TsCl, LiCl, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, 0° C to rt, 14 h (80%); (d) 3,5-dihydroxybenzyl alcohol, K<sub>2</sub>CO<sub>3</sub>, KBr, 18-Crown-6, acetone, Δ, 24 h (69%); (e) MnO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt, 2 h (95%); (f) C<sub>60</sub>, *N*-methylglycine, toluene, Δ, 16 h (40%).

energy transfer from the OPV moiety to C<sub>60</sub> is the main deactivation pathway and not electron transfer.

## 2. RESULTS AND DISCUSSIONS

**Synthesis.** The preparation of Compound 1 is depicted in Scheme 1. The protected OPV trimer 2 was prepared in seven steps as previously reported [5]. Deprotection of compound 2 with CF<sub>3</sub>CO<sub>2</sub>H in CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O followed by LiAlH<sub>4</sub> reduction of aldehyde 3 in dry THF yielded alcohol 4. Subsequent reaction with *p*-toluenesulfonyl chloride (TsCl) in the presence of 4-dimethylaminopyridine (DMAP) and LiCl in CH<sub>2</sub>Cl<sub>2</sub> gave 5. Treatment of 5 with 3,5-dihydroxybenzyl alcohol in refluxing acetone in the presence of K<sub>2</sub>CO<sub>3</sub> and 18-Crown-6 yielded 6. Subsequent oxidation with MnO<sub>2</sub>

in CH<sub>2</sub>Cl<sub>2</sub> afforded benzaldehyde 7. The functionalisation of C<sub>60</sub> was based on the 1,3-dipolar cycloaddition [7] of the azomethine ylide generated *in situ* from 7. The reaction of C<sub>60</sub> with 7 in the presence of an excess of *N*-methylglycine in refluxing toluene afforded fulleropyrrolidine 1 in 40% yield. All of the spectroscopic studies and elemental analysis results were consistent with the proposed molecular structures. Thanks to the presence of the dodecyloxy substituents, Compound 1 is highly soluble in common organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, toluene, or THF, and complete spectroscopic characterization was easily achieved. The <sup>1</sup>H-NMR spectrum of 1 in CDCl<sub>3</sub> solution shows all the expected signals. Interestingly, the signals corresponding to some of the protons of the pyrrolidine ring and those of the phenyl group directly attached to it



Scheme 2. Reagents and conditions: (a)  $C_{60}$ , *N*-methylglycine, toluene,  $\Delta$ , 16 h (42%).

are broad at room temperature. A variable-temperature NMR study showed a clear coalescence at *ca.* 10 °C and the reversible narrowing of all these peaks shows that a dynamic effect occurs [5, 8]. This indicates restricted rotation of the phenyl substituent on the pyrrolidine ring and the activation free energy of the rotation was estimated as  $\Delta G^\ddagger = 13 \text{ kcal mol}^{-1}$  by following the coalescence of the aromatic C – H. This result is in good accordance with the data previously reported by F. Langa and coworkers [8].

Model fulleropyrrolidine **FP** was obtained in 42% yield by treatment of  $C_{60}$  with 3,5-didodecyloxybenzaldehyde and sarcosine in refluxing toluene (Scheme 2). Restricted rotation of the phenyl substituent on the pyrrolidine ring was also observed for compound **FP**. As in the case of **1**, a variable temperature NMR study showed a clear coalescence at *ca.* 10 °C and the activation free energy of the rotation of the phenyl group was estimated as  $\Delta G^\ddagger = 13 \text{ kcal mol}^{-1}$ .

**Electrochemistry.** The electrochemical properties of **1**, **2** and **FP** were investigated by cyclic voltammetry (CV) in  $\text{CH}_2\text{Cl}_2/0.1 \text{ M Bu}_4\text{NPF}_6$  solutions (Table 1, Figure 1).

Figure 1 shows the CV curves of **1**, **2** and **FP** in the cathodic region at  $-65^\circ\text{C}$ . Compound **1** shows three reversible one-electron processes followed by a bielectronic peak ( $\text{IV}_{\text{red}}$ ). The comparison of the  $E_{1/2}$  potentials of **1** and **FP** clearly shows that peaks  $\text{I}_{\text{red}}-\text{III}_{\text{red}}$  correspond to fullerene-centred reductions and the slightly negative shift observed for **1** compared to **FP** is likely due to a small electronic interaction between the electron accepting  $C_{60}$  unit and the electron donating OPV groups. However, solvation effects caused by the presence of the surrounding OPV groups could also be the source of the observed shift in potential. Peak  $\text{IV}_{\text{red}}$  can be either fullerene- or OPV-centered since both **2** and **FP** shows a reduction process in the same potential region. Since peak  $\text{IV}_{\text{red}}$  observed for **1** is bielectronic, it can likely be interpreted as the superposition of a one-electron fullerene reduction and a one-electron OPV reduction.

In the anodic region, **1** presents two chemically ir-

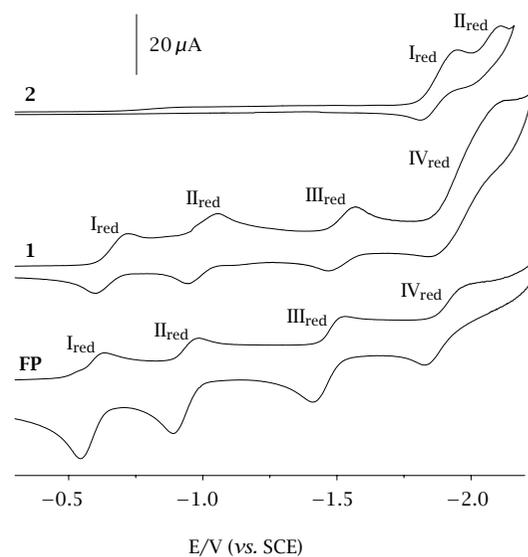


Figure 1. CV curves for a  $\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{NPF}_6$  solution of **1**, **2** and **FP** (0.8 mM) at  $T = -65^\circ\text{C}$  and  $v = 0.2 \text{ V/s}$ . Working electrode: glassy carbon disk.

reversible 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 [9] since these groups, present in both model compounds **2** and **FP**, are irreversibly oxidized in the same potential region.

**Photophysical properties.** The UV-VIS electronic absorption spectrum of **1** in  $\text{CH}_2\text{Cl}_2$  is reported in Figure 2 and it is superimposable to the profile obtained by summing the spectra of the reference component units **FP** and **2**. Importantly, on each moiety of **1**, a fairly good excitation selectivity can be achieved. At  $\lambda > 530 \text{ nm}$  light is exclusively addressed to the fullerene fragment, whereas at  $\lambda = 360 \text{ nm}$  at least 85% of the incident light is absorbed by the OPV moieties.

In  $\text{CH}_2\text{Cl}_2$  solution, upon selective excitation of the fullerene fragment of **1**, the typical fulleropyrrolidine fluorescence and triplet-triplet transient absorption

Table 1.  $E_{1/2}$  or  $E_p$  values (V vs. SCE) determined by CV on a glassy carbon electrode at room temperature, unless otherwise noted,<sup>b</sup> of compounds **1**, **2** and **FP** in  $\text{CH}_2\text{Cl}_2/0.1\text{ M Bu}_4\text{NPF}_6$  solutions.

Compound	$\Pi_{\text{ox}}$	$I_{\text{ox}}$	$I_{\text{red}}$	$\Pi_{\text{red}}$	$\text{III}_{\text{red}}$	$\text{IV}_{\text{red}}$
<b>1</b>	+1.7 <sup>a,c</sup>	+1.4 <sup>a,c</sup>	-0.66	-1.04	-1.56	-1.98 <sup>b,d</sup>
<b>2</b>	+1.82 <sup>a</sup>	+1.28 <sup>a</sup>	-1.88 <sup>b</sup>	-2.11 <sup>a,b</sup>	-	-
<b>FP</b>	+1.60 <sup>a</sup>	+1.38 <sup>a</sup>	-0.62	-1.01	-1.54	-1.90 <sup>b</sup>

<sup>a</sup> Chemically irreversible processes, peak potentials measured at 0.2 V/s.

<sup>b</sup>  $T = -65^\circ\text{C}$ .

<sup>c</sup> Trielectronic process.

<sup>d</sup> Bielectronic process.

spectra are observed [7]. This shows that the excited state properties of the  $\text{C}_{60}$  fragment are not affected by the presence of the nearby OPV moieties. On the other hand, when excitation is addressed to the latter (e.g. at  $\lambda = 360\text{ nm}$ , see above), intercomponent processes are evidenced. Under these conditions, the intense fluorescence band of the OPV moiety ( $\Phi_{\text{em}} = 1.0$ ,  $\tau = 1.0\text{ ns}$ ) is not observed (Figure 2), whereas the typical fluorescence band of the fulleropyrrolidine fragment ( $\lambda_{\text{max}} = 710\text{ nm}$ ,  $\tau = 1.3\text{ ns}$ ) is detected; in addition, the fullerene fluorescence quantum yields of **1** and **FP** obtained at  $\lambda_{\text{exc}} = 360\text{ nm}$  are identical ( $\Phi_{\text{em}} = 5.5 \times 10^{-4}$ ), although in the former at least 85% of the incident light is absorbed by the OPV fragments. The excitation spectrum of **1**, taken at  $\lambda_{\text{em}} = 715\text{ nm}$ , matches the absorption profile throughout the UV-VIS, 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**.

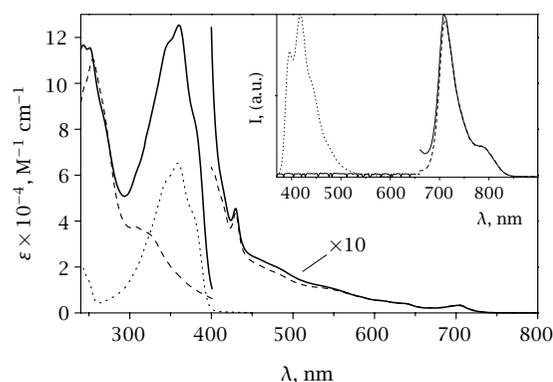


Figure 2. Absorption spectra of **1** (full line), **FP** (dashed line) and **2** (dotted line) in  $\text{CH}_2\text{Cl}_2$  at 298 K; above 400 nm a multiplying factor of 10 is applied. Inset: fluorescence spectra of **2**, **FP**, and **1** (for all samples, O.D. = 0.50 at  $\lambda_{\text{exc}} = 360\text{ nm}$ ) in  $\text{CH}_2\text{Cl}_2$ ; above 660 nm the instrumental sensitivity is increased by three orders of magnitude, due to the weakness of the **FP** fluorescence relative to that of **2**.

In order to monitor the fate of the lowest triplet state centred on the fullerene moiety, following excitation of the OPV unit, we performed a series of transient absorption experiments by exciting at 355 nm (Nd:YAG laser). The reference compound **FP** displays a triplet-triplet transient absorption spectrum with  $\lambda_{\text{max}} = 690\text{ nm}$  and  $\tau = 540\text{ ns}$  in air-equilibrated solution, which becomes 31000 ns in deaerated solution due to the suppression of the well known dioxygen quenching process [10, 11]. A quite similar behaviour is observed for **1**, which gives 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 sensitises the formation of the lowest fullerene singlet state, which then populates the lower lying triplet level (Figure 3) via intersystem crossing [7].

From the electrochemical data one can place the energy of the charge separated state [12] of **1** at about 2 eV, e.g. well below the energy of the lowest singlet

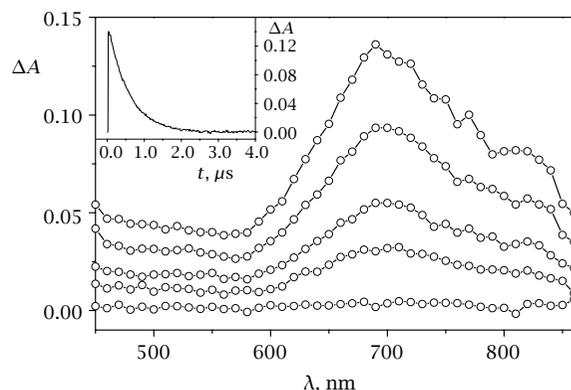


Figure 3. Sensitized fullerene triplet-triplet transient absorption spectrum of **1** at 298 K in  $\text{CH}_2\text{Cl}_2$  air equilibrated solution, upon laser excitation at 355 nm (energy = 5 mJ/pulse). Spectra were recorded at delays of 100, 300, 600, 900, 2000 ns after excitation. Inset: time profile of  $\Delta A$  (690 nm) from which the spectral kinetic data were obtained ( $\tau = 540\text{ ns}$ , monoexponential).

excited state of the OPV moieties (3.1 eV, as derived by 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  $\text{CH}_2\text{Cl}_2$  solution. This prompted us to set up a series of experiments in more polar benzonitrile, but the results did not change. For example, fluorescence spectra of optically matched solutions of **1** and **FP** in benzonitrile ( $\lambda_{\text{exc}} = 363$  nm) again suggest that in the fullerene-OPV hybrid **1** quantitative OPV  $\rightarrow$   $\text{C}_{60}$  singlet-singlet energy transfer occurs (Figure 4), since quantitative sensitization of the fullerene emission is observed.

By using the luminescence data of the fragment which act as energy donor (**1**) and the absorption spectrum of the acceptor (**FP**), it is possible to draw some conclusions regarding the type of energy transfer mechanism that is operative in **1**. Two mechanisms, the dipole-dipole (Förster, F) [13] or the double electron exchange (Dexter, D) [14], may be involved. The possible contribution by the dipole-dipole energy transfer, which is pertinent to singlet-singlet interaction schemes, can be evaluated on the basis of the following equations:

$$k_{\text{en}}^{\text{F}} = \frac{1}{\tau} \left( \frac{R_c}{d} \right)^6, \quad (1)$$

$$R_c^6 = \frac{9000(\ln 10)K^2\Phi}{128\pi^5 N n^4} J_{\text{F}}. \quad (2)$$

These allow to obtain estimates for (i) the energy transfer rate constant,  $k_{\text{en}}^{\text{F}}$ , and (ii) the critical transfer radius,  $R_c$ , i.e. the distance between the fragments for which  $k_{\text{en}}^{\text{F}}$  equalizes the intrinsic deactivation of the donor,  $k_d = \tau^{-1}$ . In equations (1) and (2),  $\Phi$  and  $\tau$  are the luminescence quantum yield and lifetime of the donor fragment **1**,  $J_{\text{F}} = (\int F(\bar{\nu})\epsilon(\bar{\nu})/\bar{\nu}^4 d\bar{\nu})/(\int F(\bar{\nu})d\bar{\nu})$

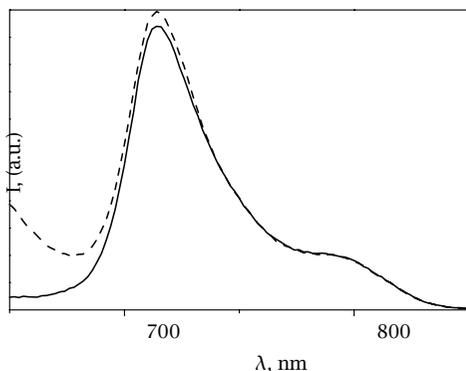


Figure 4. Fullerene fluorescence spectra of **1** (dashed line) and **FP** (full line) at  $\lambda_{\text{exc}} = 363$  nm, O.D. = 0.32 in benzonitrile. In the bichromophoric system **1** the excitation light partition is: OPV, 80%; fullerene, 20%.

is the overlap integral between the luminescence spectrum on an energy scale ( $\text{cm}^{-1}$ ) of the donor ( $F(\nu)$  of **1**) and the absorption spectrum of the acceptor, ( $\epsilon(\bar{\nu})$  of **FP**);  $J^{\text{F}}$  was  $1.4 \times 10^{-14} \text{ cm}^6 \text{ mol}^{-1}$ ;  $K^2$  is a geometric factor (tentatively taken as 2/3),  $N = 6.02 \times 10^{23} \text{ mol}^{-1}$  and  $n$  is the refractive index of the solvent. Calculations provided  $R_c = 35.3 \text{ \AA}$ , and  $k_{\text{en}}^{\text{F}} > 10^{12} \text{ s}^{-1}$  for  $d \leq 10 \text{ \AA}$ .

It should be pointed out that these findings are appropriate for a two-center system whose donating and accepting components retain their electronic identity [15], as it happens in our case (see absorption spectra and electrochemical properties). However, one can consider also the double-electron exchange Dexter-type transfer [14]. This latter mechanism requires a certain amount of through-bond electronic communication (represented by the electronic coupling term  $H$ , see below), and is usually found to be important for triplet-triplet transfers. According to this approach we evaluated the pertinent spectral overlap  $J_{\text{D}}$ , equations (equations (3)–(5)), with  $J_{\text{D}} = 1.4 \times 10^{-4} \text{ cm}$ . Estimates of  $k_{\text{en}}^{\text{D}}$  were obtained for  $H_o$  values ranging from 10 to  $100 \text{ cm}^{-1}$ , which correspond to moderately coupled moieties [16], and by assuming an attenuation factor  $\beta = 0.1 \text{ \AA}^{-1}$  [17].  $d_o$  values ranging from 3 to  $10 \text{ \AA}$  were employed, roughly corresponding to side-to-side and center-to-center geometries, respectively.

$$J_{\text{D}} = \frac{\int F(\bar{\nu})\epsilon(\bar{\nu})d\bar{\nu}}{\int F(\bar{\nu})d\bar{\nu} \int \epsilon(\bar{\nu})d\bar{\nu}}, \quad (3)$$

$$k_{\text{en}}^{\text{D}} = \frac{4\pi^2 H^2}{h} J_{\text{D}}, \quad (4)$$

$$H = H_o \exp[-0.5\beta(d - d_o)]. \quad (5)$$

We found that the Förster mechanism is mostly effective up to  $d = 15$  to  $20 \text{ \AA}$  and that an interplay of the two energy transfer mechanisms can only be operative for longer distances or for larger  $H$  values; at any rate, energy transfer is always found to predominate over intrinsic deactivation,  $k_{\text{en}} \gg k_d$  ( $k_{\text{en}} = k_{\text{en}}^{\text{F}} + k_{\text{en}}^{\text{D}}$ ), and the sensitization step is expected to be quantitative (efficiency > 90%) up to  $d = 30 \text{ \AA}$ .

These estimates suggest also that the energy transfer step is so fast that the competing charge separation path is not effective.

### 3. CONCLUSION

We have synthesized a multicomponent array containing a  $\text{C}_{60}$  fulleropyrrolidine and two oligophenylenevinylene (OPV) subunits (**1**). The study of its electrochemical and photophysical properties, corroborated by model calculations, demonstrates that singlet-singlet (OPV  $\rightarrow$   $\text{C}_{60}$ ) photoinduced energy transfer is so fast that electron transfer is unable to compete even in a polar solvent like benzonitrile. It has been recently shown by Janssen et. al. [18] that in similar systems electron transfer can occur, but in that case the –OR

residues on the OPV skeleton were differently located. These results show that OPVs are quite versatile moieties for the construction of photoactive multicomponent systems containing C<sub>60</sub>. In fact, upon a thorough choice and location of the substituents of the OPV subunits, such moieties can act either as light harvester (the present case) or as electron relay (ref. [18]) for the C<sub>60</sub> carbon sphere.

#### 4. EXPERIMENTAL SECTION

**General methods.** Reagents and solvents were purchased as reagent grade and used without further purification. Compound **2** [5] and 3,5-didodecyloxybenzaldehyde [19] were prepared as previously reported. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done at water aspirator pressure and drying *in vacuo* at 10<sup>-2</sup> Torr. Column chromatography: silica gel 60 (230–400 mesh, 0.040–0.063 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on glass sheets coated with silica gel 60 F<sub>254</sub> purchased from E. Merck, visualization by UV light. Melting points were measured on an *Electrothermal Digital Melting Point* apparatus and are uncorrected. IR spectra (cm<sup>-1</sup>) were measured on an *ATI Mattson Genesis Series FTIR* instrument. NMR spectra were recorded on a *Bruker AC 200* (200 MHz) or a *Bruker AM 400* (400 MHz) with solvent peaks as reference. Elemental analysis were performed by the analytical service at the Institut Charles Sadron (Strasbourg, France).

**Compound 3.** A mixture of **2** (8.0 g, 10.4 mmol) and CF<sub>3</sub>CO<sub>2</sub>H (80 mL) in CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O 1:1 (150 mL) was stirred at rt for 5 h. The organic layer was then washed with water (4×), dried (MgSO<sub>4</sub>) and evaporated to dryness. Column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/hexane 1:1) gave **8** (6.98 g, 96%). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): 9.60 (s, 1H), 7.88 (d, *J* = 9.5 Hz, 2H), 7.67 (d, *J* = 9.5 Hz, 2H), 7.55 (m, 4H), 7.22 (q, *J* = 16.5 Hz, 2H), 7.08 (s, 2H), 6.66 (d, *J* = 2 Hz, 2H), 6.39 (t, *J* = 2 Hz, 1H) 3.98 (t, *J* = 6.5 Hz, 4H), 1.79–1.76 (m, 4H), 1.43–1.27 (m, 36H), 0.90 (t, *J* = 6.5 Hz, 6H). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>): 191.59, 160.48, 143.38, 138.95, 137.45, 135.80, 135.24, 131.70, 130.20, 129.28, 128.26, 127.23, 127.05, 126.94, 126.83, 105.12, 101.01, 68.06, 31.90, 29.62, 29.35, 29.28, 26.06, 22.67, 14.12. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>): 232 (24700), 375 (58140). Anal. calc. for C<sub>47</sub>H<sub>66</sub>O<sub>3</sub> (679.0): C 83.13, H 9.80; found C 83.08, H 9.83.

**Compound 4.** A 1 M LiAlH<sub>4</sub> solution in THF (500 μL) was added to a stirred solution of **3** (1.26 g, 1.85 mmol) in dry THF (18 mL) at 0 °C under argon. After 1 h, the reaction was quenched with methanol and water. The resulting mixture was filtered over celite and evaporated. The crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water, dried over MgSO<sub>4</sub>,

filtered and evaporated. Column chromatography on SiO<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>) yielded **4** (1.13 g, 90%) as a yellow solid. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): 7.53 (AB, *J* = 8 Hz, 2H), 7.51 (s, 4H), 7.37 (AB, *J* = 8 Hz, 2H), 7.12 (s, 2H), 7.06 (s, 2H), 6.66 (d, *J* = 2 Hz, 2H), 6.40 (t, *J* = 2 Hz, 1H), 4.72 (s, 2H), 3.98 (t, *J* = 6.5 Hz, 4H), 1.80–1.70 (m, 4H), 1.50–1.20 (m, 36H), 0.90 (t, *J* = 6.5 Hz, 6H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): 160.48, 140.25, 139.13, 136.78, 136.62, 128.72, 128.50, 128.29, 128.10, 127.39, 126.87, 126.82, 126.67, 105.06, 100.91, 68.06, 65.15, 31.93, 29.61, 29.40, 29.29, 26.06, 22.70, 14.13. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>) 228 (16510), 359 (39940). Anal. calc. for C<sub>47</sub>H<sub>68</sub>O<sub>3</sub> (681.06): C 82.89, H 10.06 ; found C 83.02, H 10.19.

**Compound 5.** A mixture of **4** (400 mg, 0.58 mmol), LiCl (147 mg, 3.48 mmol), DMAP (85 mg, 0.7 mmol), and TsCl (133 mg, 0.7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was stirred for 2 h at 0 °C, then 12 h at rt. The resulting mixture was evaporated and the product taken up in Et<sub>2</sub>O, filtrated and evaporated. Column chromatography on SiO<sub>2</sub> (hexane/CH<sub>2</sub>Cl<sub>2</sub> 7:3) yielded **5** (330 mg, 80%) as a yellow solid. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): 7.53 (AB, *J* = 8 Hz, 2H), 7.51 (s, 4H), 7.37 (AB, *J* = 8 Hz, 2H), 7.12 (s, 2H), 7.06 (s, 2H), 6.66 (d, *J* = 2 Hz, 2H), 6.40 (t, *J* = 2 Hz, 1H), 4.61 (s, 2H), 3.98 (t, *J* = 6.5 Hz, 4H), 1.80–1.70 (m, 4H), 1.50–1.20 (m, 36H), 0.90 (t, *J* = 6.5 Hz, 6H).

**Compound 6.** A mixture of **5** (570 mg, 0.81 mmol), 3,5-dihydroxybenzyl alcohol (56 mg, 0.40 mmol), 18-Crown-6 (21 mg, 0.08 mmol), KBr (cat.), and K<sub>2</sub>CO<sub>3</sub> (139 mg, 1.00 mmol) in acetone (20 mL) was refluxed for 24 h. The solvent was evaporated under reduce pressure and the product was taken up with CH<sub>2</sub>Cl<sub>2</sub>. The organic solution was washed with water, dried over MgSO<sub>4</sub>, filtered and evaporated. Column chromatography on SiO<sub>2</sub> (hexane/CH<sub>2</sub>Cl<sub>2</sub> 7:3) yielded **6** (400 mg, 69%) as a yellow solid. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): 7.53 (AB, *J* = 8 Hz, 4H), 7.51 (s, 8H), 7.37 (AB, *J* = 8 Hz, 4H), 7.13 (s, 4H), 7.06 (s, 4H), 6.66 (m, 6 H), 6.57 (t, *J* = 2 Hz, 1 H), 6.40 (t, *J* = 2 Hz, 2 H), 5.06 (s, 4 H), 4.65 (s, 2 H), 3.98 (t, *J* = 6.5 Hz, 8 H), 1.80–1.70 (m, 8 H), 1.50–1.20 (m, 72 H), 0.90 (t, *J* = 6.5 Hz, 12 H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): 160.48, 160.04, 143.48, 139.08, 137.03, 136.59, 136.52, 136.11, 128.70, 128.44, 127.97, 127.84, 126.83, 126.63, 105.65, 105.04, 101.23, 100.90, 69.74, 68.02, 65.18, 31.90, 29.62, 29.40, 29.34, 29.28, 26.05, 22.67, 14.12. Anal. calc. for C<sub>101</sub>H<sub>140</sub>O<sub>7</sub> (1466.23) : C 82.74, H 9.62; found C 82.26, H 9.63.

**Compound 7.** A mixture of **6** (390 mg, 0.26 mmol) and MnO<sub>2</sub> (2 g) in CH<sub>2</sub>Cl<sub>2</sub> was stirred at rt for 2 h. The resulting mixture was filtered on celite and evaporated. Column chromatography on SiO<sub>2</sub> (hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:1) yielded **7** (370 mg, 95%) as a yellow solid. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): 9.69 (s, 1H), 7.53 (AB, *J* = 8.2 Hz, 4 H), 7.51 (s, 8 H), 7.37 (AB, *J* = 8.2 Hz, 4 H), 7.08 (s, 10 H), 6.90 (t, *J* = 2 Hz, 1 H), 6.66 (d, *J* = 2 Hz, 4 H), 6.40 (t, *J* = 2 Hz, 2 H), 5.11 (s, 4 H), 3.98 (t, *J* = 6.5 Hz, 8 H), 1.80–1.70 (m, 8 H), 1.50–1.20 (m, 72 H), 0.90 (t, *J* = 6.5 Hz, 12 H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): 191.77,

160.46, 160.30, 139.07, 138.38, 137.32, 136.68, 136.49, 135.47, 128.77, 128.67, 128.44, 127.93, 127.23, 126.85, 126.72, 108.63, 108.30, 105.05, 100.92, 70.11, 68.03, 31.90, 29.61, 29.40, 29.34, 29.28, 26.06, 22.67, 14.12. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>) 360 (109900).

**Compound 1.** A mixture of **7** (370 mg, 0.25 mmol), C<sub>60</sub> (202 mg, 0.28 mmol), and sarcosine (181 mg, 2.00 mmol) in toluene (200 mL) was refluxed for 16 h. The solvent was evaporated and column chromatography on SiO<sub>2</sub> (hexane/toluene 1:1) yielded **1** (246 mg, 40%) as a brown solid (mp 122 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.59 (m, 16 H), 7.08 (AB, *J* = 17 Hz, 8 H), 6.68 (d, *J* = 2 Hz, 4 H), 6.64 (t, *J* = 2 Hz, 1 H), 6.41 (t, *J* = 2 Hz, 2 H), 5.12 (s, 4 H), 4.97 (d, *J* = 9.5 Hz, 1 H), 4.82 (s, 1 H), 4.16 (d, *J* = 9.5 Hz, 1 H), 4.00 (t, *J* = 6.5 Hz, 8 H), 2.84 (s, 3 H), 1.80–1.70 (m, 8 H), 1.50–1.20 (m, 72 H), 0.90 (t, *J* = 6.5 Hz, 12 H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): 160.45, 159.76, 155.97, 153.93, 153.20, 147.20, 146.66, 146.34, 146.22, 146.16, 145.99, 145.37, 145.23, 145.16, 145.08, 144.98, 144.56, 144.50, 144.30, 142.97, 142.87, 142.58, 142.52, 142.45, 142.13, 142.07, 141.92, 141.83, 141.56, 140.04, 139.78, 139.40, 139.11, 137.00, 136.57, 136.30, 136.11, 135.63, 128.73, 128.48, 128.06, 127.63, 126.84, 126.73, 107.13, 105.05, 102.87, 100.93, 83.39, 76.79, 69.78, 68.92, 68.03, 40.05, 31.90, 29.61, 29.40, 29.34, 29.29, 26.06, 22.67, 14.12. Anal. calc. for C<sub>163</sub>H<sub>143</sub>O<sub>6</sub>N<sub>1</sub> (2211.94): C 88.51, H 6.52; N 0.63, found C 88.10, H 6.61, N 0.62.

**Compound FP.** A mixture of 3,5-didodecyloxybenz-aldehyde (238 mg, 0.50 mmol), C<sub>60</sub> (400 mg, 0.55 mmol), and sarcosine (444 mg, 5.00 mmol) in toluene (200 mL) was refluxed for 16 h. The solvent was evaporated and column chromatography on SiO<sub>2</sub> (hexane/toluene 1:1) yielded **FP** (254 mg, 42%) as a brown solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.04 (broad, 2 H), 6.48 (t, *J* = 1.5 Hz, 1 H), 5.02 (d, *J* = 9.5 Hz, 1 H), 4.90 (s, 1 H), 4.31 (d, *J* = 9.5 Hz, 1 H), 4.02 (t, *J* = 5 Hz, 4 H), 2.90 (s, 3 H), 1.81 (m, 4 H), 1.50–1.29 (m, 36 H), 0.91 (t, *J* = 5.5 Hz, 6 H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): 160.29, 156.08, 154.04, 153.69, 153.42, 147.25, 147.02, 146.42, 146.24, 146.16, 146.07, 145.90, 145.74, 145.48, 145.21, 145.11, 144.65, 144.60, 144.34, 143.10, 142.93, 142.62, 142.52, 142.17, 141.98, 141.88, 141.76, 141.63, 141.55, 140.13, 140.07, 139.74, 139.56, 138.99, 136.58, 136.37, 135.75, 101.89, 83.68, 69.91, 68.99, 68.17, 40.10, 31.90, 29.64, 29.41, 29.35, 29.14, 26.02, 22.69, 14.15. Anal. calc. for C<sub>93</sub>H<sub>59</sub>O<sub>2</sub>N (1221.50): C 91.37, H 4.86, N 1.15; found C 91.41 H 4.88, N 1.14.

**Electrochemical experiments.** The electrochemical experiments were carried out in argon-purged CH<sub>2</sub>Cl<sub>2</sub> (Romil Hi-Dry™) solutions at room temperature or –65 °C (by employing a liquid N<sub>2</sub>/EtOH low-temperature bath) with an EcoChemie Autolab 30 multi-purpose instrument interfaced to a personal computer. In the cyclic voltammetry (CV) the working electrode was a glassy carbon electrode (0.08 cm<sup>2</sup>, Amel); its surface was routinely polished with a 0.05 μm alumina-

water slurry on a felt surface, immediately prior to use. In all cases, the counter electrode was a Pt spiral, separated from the bulk solution with a fine glass frit, and a silver wire was employed as a quasi-reference electrode (AgQRE). The potentials reported are referred to SCE by measuring the AgQRE potential with respect to ferrocene. The concentration of the compounds examined was of the order of 8 × 10<sup>–4</sup> M; 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) was added as supporting electrolyte. Cyclic voltammograms were obtained with scan rates in the range 0.05–10 V s<sup>–1</sup>. The number of electrons exchanged in each process was estimated by comparing the current intensity of the corresponding CV wave with that observed for the mono-electronic oxidation of ferrocene, after correction for differences in the diffusion coefficients [20]. The experimental error on the potential values was estimated to be ±10 mV.

**Spectroscopic and photophysical measurements.** The solvent used for the photophysical investigations are spectrofluorimetric grade CH<sub>2</sub>Cl<sub>2</sub> (Carlo Erba) and benzonitrile (Aldrich). Absorption spectra were recorded with a Perkin-Elmer Lambda 5 spectrophotometer. Uncorrected emission spectra were obtained with a Spex Fluorolog II spectrofluorimeter equipped with a continuous 150 W Xe lamp as excitation source and a Hamamatsu R-928 photomultiplier tube as detector. The corrected spectra were obtained via a calibration curve determined by means of a 45 W quartz-halogen tungsten filament lamp (Optronic Laboratories) calibrated in the range 400–1800 nm. Fluorescence quantum yields were measured with the method described by Demas and Crosby [21] using as standards quinine sulphate in 1 N H<sub>2</sub>SO<sub>4</sub> (Φ = 0.546) [22] and [Os(phen)<sub>3</sub>]<sup>2+</sup> in acetonitrile (Φ<sub>em</sub> = 0.005) [23]. Corrected excitation spectra were recorded with a Perkin-Elmer LS-50B spectrofluorimeter (pulsed Xe lamp). Emission lifetimes were determined with an IBH single photon counting spectrometer equipped with a thyratron gated nitrogen lamp working at 40 KHz (λ<sub>exc</sub> = 337 nm, 0.5 ns time resolution after deconvolution of the flash profile); the detector was a red-sensitive (185–850 nm) Hamamatsu R-3237-01 photomultiplier tube. The nanosecond transient absorption spectra and lifetimes were recorded by using the third harmonic (355 nm) of a Nd:YAG laser (JK Lasers) with 20 ns pulse and 2–5 mJ of energy per pulse. The details on the flash-photolysis system are reported elsewhere [24]. Experimental uncertainties are estimated to be ±7% for lifetime determination, ±15% for quantum yields, and ±3 nm for emission and absorption peaks.

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