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_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. 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_60 allows the preparation of many covalent C_60 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_60 appears to be a particularly interesting electron acceptor in photophysical molecular devices because of its symmetrical shape, large size and the properties of its π-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].

C_60-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_60 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_60 through a pyrrolidine ring [6].

Interestingly, the photophysical studies of this hybrid compound have shown that, in solution, photoinduced...
energy transfer from the OPV moiety to C60 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 CF3CO2H in CH2Cl2/H2O followed by LiAlH4 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 CH2Cl2 gave 5. Treatment of 5 with 3,5-dihydroxybenzyl alcohol in refluxing acetone in the presence of K2CO3, KBr and 18-Crown-6 yielded 6. Subsequent oxidation with MnO2 in CH2Cl2 afforded benzaldehyde 7. The functionalisation of C60 was based on the 1,3-dipolar cycloaddition [7] of the azomethine ylide generated in situ from 7. The reaction of C60 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 CH2Cl2, CHCl3, toluene, or THF, and complete spectroscopic characterization was easily achieved. The 1H-NMR spectrum of 1 in CDCl3 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 1. Reagents and conditions: (a) CF3CO2H, CH2Cl2, H2O, rt, 5 h (96%); (b) LiAlH4, THF, 0° C, 1 h (90%); (c) TsCl, LiCl, DMAP, CH2Cl2, 0° C to rt, 14 h (80%); (d) 3,5-dihydroxybenzyl alcohol, K2CO3, KBr, 18-Crown-6, acetone, Δ, 24 h (69%); (e) MnO2, CH2Cl2, rt, 2 h (95%); (f) C60, N-methylglycine, toluene, Δ, 16 h (40%).
Scheme 2. Reagents and conditions: (a) C₆₀, N-methylglycine, toluene, Δ, 16 h (42%).

Model fulleropyrrolidine FP was obtained in 42% yield by treatment of C₆₀ 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 ΔG‡ = 13 kcal mol⁻¹.

Electrochemistry. The electrochemical properties of 1, 2 and FP were investigated by cyclic voltammetry (CV) in CH₂Cl₂/0.1 M Bu₄NPF₆ solutions (Table 1, Figure 1).

Figure 1 shows the CV curves of 1, 2 and FP in the cathodic region at –65 °C. Compound 1 shows three reversible one-electron processes followed by a bielectronic peak (IV_red). The comparison of the E₁/₂ potentials of 1 and FP clearly shows that peaks I_red–III_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 C₆₀ 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 IV_red can be either fullerene- or OPV-centered since both 2 and FP shows a reduction process in the same potential region. Since peak IV_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-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 CH₂Cl₂ 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 λ > 530 nm light is exclusively addressed to the fullerene fragment, whereas at λ = 360 nm at least 85% of the incident light is absorbed by the OPV moieties.

In CH₂Cl₂ 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, of compounds 1, 2 and FP in CH$_2$Cl$_2$/0.1M Bu$_4$NPF$_6$ solutions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$I_{ox}$</th>
<th>$I_{red}$</th>
<th>$II_{red}$</th>
<th>$III_{red}$</th>
<th>$IV_{red}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+1.7$^{ac}$</td>
<td>-0.66</td>
<td>-1.04</td>
<td>-1.56</td>
<td>-1.98$^{ab}$</td>
</tr>
<tr>
<td>2</td>
<td>+1.82$^a$</td>
<td>-1.88$^b$</td>
<td>-2.11$^{a,b}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FP</td>
<td>+1.60$^a$</td>
<td>-0.62</td>
<td>-1.01</td>
<td>-1.54</td>
<td>-1.90$^b$</td>
</tr>
</tbody>
</table>

*a* Chemically irreversible processes, peak potentials measured at 0.2 V/s.

*b* $T = -65$ °C.

*c* Trielectronic process.

*d* Bielelectronic process.

spectra are observed [7]. This shows 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 addressed to the latter (e.g. at $\lambda = 360$ nm, see above), intercomponent processes are evidenced. Under these conditions, the intense fluorescence band of the OPV moiety ($\Phi_{em}$ = 1.0, $\tau$ = 1.0 ns) is not observed (Figure 2), whereas the typical fluorescence band of the fulleropyrrolidine fragment ($\lambda_{max}$ = 710 nm, $\tau$ = 1.3 ns) is detected; in addition, the fullerene fluorescence quantum yields of 1 and FP obtained at $\lambda_{exc}$ = 360 nm are identical ($\Phi_{em}$ = 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 $\lambda_{em}$ = 715 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.

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 $\lambda_{max}$ = 690 nm and $\tau$ = 540 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 2.** Absorption spectra of 1 (full line), FP (dashed line) and 2 (dotted line) in CH$_2$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 $\lambda_{exc}$ = 360 nm) in CH$_2$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.

**Figure 3.** Sensitized fullerene triplet-triplet transient absorption spectrum of 1 at 298 K in CH$_2$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 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 CH$_2$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 $\rightarrow$ 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:

$$k_{\text{en}}^F = \frac{1}{\tau} \left( \frac{R_c}{d} \right)^{12},$$

$$R_c^{12} = \frac{9000 (\ln 10) k^2 \Phi}{128 \pi^5 N^4} F.$$

These allow to obtain estimates for (i) the energy transfer rate constant, $k_{\text{en}}^F$, and (ii) the critical transfer radius, $R_c$, i.e. the distance between the fragments for which $k_{\text{en}}^F$ equals 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, $J_F = (\int F(\nu) \epsilon(\nu) d\nu)/(\int F(\nu) d\nu)$ is the overlap integral between the luminescence spectrum on an energy scale ($\text{cm}^{-1}$) of the donor ($F(\nu)$) and the absorption spectrum of the acceptor, ($\epsilon(\nu)$ of FP). $J_F$ was $1.4 \times 10^{-14}$ cm$^6$ mol$^{-1}$; $k^2$ is a geometric factor (tentatively taken as $2/3$), $N = 6.02 \times 10^{23}$ mol$^{-1}$ and $n$ is the refractive index of the solvent. Calculations provided $R_c = 35.3$ Å, and $k_{\text{en}}^D > 10^{12}$ s$^{-1}$ for $d \leq 10$ Å.

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 photophysical 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 $J_D$, equations (3)-(5), with $J_D = 1.4 \times 10^{-3}$ cm. Estimates of $k_{\text{en}}^D$ were obtained for $H_o$ values ranging from 10 to 100 cm$^{-1}$, which correspond to moderately coupled moieties [16], and by assuming an attenuation factor $\beta = 0.1$ Å$^{-1}$ [17]. $d_o$ values ranging from 3 to 10 Å were employed, roughly corresponding to side-to-side and center-to-center geometries, respectively.

$$J_D = \frac{\int J_F(\nu) \epsilon(\nu) d\nu}{\int J_F(\nu) d\nu \int \epsilon(\nu) d\nu},$$

$$k_{\text{en}}^D = \frac{4 \pi^2 H^2}{\hbar} J_D,$$

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

We found that the Förster mechanism is mostly effective up to $d = 15$ to 20 Å 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, $k_{\text{en}} > k_d (k_{\text{en}} = k_{\text{en}}^F + k_{\text{en}}^D)$, and the sensitization step is expected to be quantitative (efficiency $> 90\%$) up to $d = 30$ Å.

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 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 $\rightarrow$ 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 OP skeleton were differently located. These results show that OPVs are quite versatile moieties for the construction of photoactive multicomponent systems containing C₆₀. In fact, upon a thorough choice and location of the substituents of the OP subunits, such moieties can act either as light harvester (the present case) or as electron relay (ref. [18]) for the C₆₀ 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 10⁻² 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 F₂₅₄ 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⁻¹) 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 CF₃CO₂H (80 mL) in CH₂Cl₂/H₂O 1:1 (150 mL) was stirred at rt for 5 h. The organic layer was then washed with water (4×), dried (MgSO₄) and evaporated to dryness. Column chromatography (SiO₂, CH₂Cl₂/hexane 1:1) gave 8 (6.98 g, 96%). H-NMR (200 MHz, CDCl₃): 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, 4H), 1.30–1.20 (m, 36H), 0.80 (t, J = 6.5 Hz, 4H), 1.30–1.20 (m, 36H), 0.80 (t, J = 6.5 Hz, 4H).

Compound 4. A 1 M LiAlH₄ 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 CH₂Cl₂. The organic layer was washed with water, dried over MgSO₄, filtered and evaporated. Column chromatography on SiO₂ (CH₂Cl₂) yielded 4 (1.13 g, 90%) as a yellow solid. H-NMR (200 MHz, CDCl₃): 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, 4H). C-NMR (50 MHz, CDCl₃): 160.48, 143.38, 138.95, 137.45, 135.80, 135.24, 131.70, 128.72, 128.50, 128.29, 128.10, 127.39, 126.87, 126.82, 126.67, 105.06, 90.11, 68.06, 65.15, 31.93, 29.61, 29.40, 29.29, 26.06, 22.70, 14.13. UV-Vis (CH₂Cl₂) 228 (16510), 359 (39940). Anal. calc. for C₇₃H₇₈O₇: 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 CH₂Cl₂ (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 Et₂O, filtered and evaporated. Column chromatography on SiO₂ (hexane/CH₂Cl₂ 7:3) yielded 5 (330 mg, 80%) as a yellow solid. H-NMR (200 MHz, CDCl₃): 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, 4H).

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 K₂CO₃ (139 mg, 1.00 mmol) in acetone (20 ml) was refluxed for 24 h. The solvent was evaporated under reduced pressure and the product was taken up with CH₂Cl₂. The organic solution was washed with water, dried over MgSO₄, filtered and evaporated. Column chromatography on SiO₂ (hexane/CH₂Cl₂ 7:3) yielded 6 (400 mg, 69%) as a yellow solid. H-NMR (200 MHz, CDCl₃): 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, 6H), 6.57 (t, J = 2 Hz, 1H), 6.40 (t, J = 2 Hz, 2H), 5.06 (s, 4H), 4.65 (s, 2H), 3.98 (t, J = 6.5 Hz, 8H), 1.80–1.70 (m, 8H), 1.50–1.20 (m, 72H), 0.90 (t, J = 6.5 Hz, 12H). C-NMR (50 MHz, CDCl₃): 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, 105.05, 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 C₁₀₁H₁₄₀O₇ (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 MnO₂ (2 g) in CH₂Cl₂ was stirred at rt for 2 h. The resulting mixture was filtered on celite and evaporated. Column chromatography on SiO₂ (hexane/CH₂Cl₂ 1:1) yielded 7 (370 mg, 95%) as a yellow solid. H-NMR (200 MHz, CDCl₃): 9.69 (s, 1H), 7.53 (AB, J = 8 Hz, 4H), 7.51 (s, 8H), 7.37 (AB, J = 8 Hz, 4H), 7.08 (s, 10H), 6.90 (t, J = 2 Hz, 1H), 6.66 (d, J = 2 Hz, 4H), 6.40 (t, J = 2 Hz, 2H), 5.11 (s, 4H), 3.98 (t, J = 6.5 Hz, 8H), 1.80–1.70 (m, 8H), 1.50–1.20 (m, 72H), 0.90 (t, J = 6.5 Hz, 12H). C-NMR (50 MHz, CDCl₃): 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 (CH2Cl2) 360 (109900).

**Compound 1.** A mixture of 7 (370 mg, 0.25 mmol), C60 (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 SiO2 (hexane/toluene 1:1) yielded 1 (246 mg, 40%) as a brown solid (mp 122 °C). 1H NMR (400 MHz, CDCl3): 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), 1.50–1.29 (m, 36 H), 0.91 (t, J = 6.5 Hz, 1 H). 13C NMR (50 MHz, CDCl3): 160.45, 159.76, 155.97, 153.93, 153.20, 147.20, 146.66, 146.34, 146.22, 146.16, 145.39, 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, 141.81, 141.61, 140.04, 139.78, 139.40, 139.11, 137.00, 136.53, 136.30, 136.11, 135.63, 128.73, 128.48, 128.06, 127.63, 126.84, 127.13, 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 C60H143O6N12 (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), C60 (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 SiO2 (hexane/toluene 1:1) yielded FP (254 mg, 42%) as a brown solid. 1H NMR (400 MHz, CDCl3): 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). 13C NMR (50 MHz, CDCl3): 160.29, 156.08, 154.04, 153.69, 153.42, 147.00, 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, 141.63, 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 C39H50O2N (1221.50): C 91.41, 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 CH2Cl2 (Romil Hi-Dry fumed) solutions at room temperature or −65 °C (by employing a liquid N2/ETOH low-temperature bath) with an EcoChemie Autolab 30 multipurpose instrument interfaced to a personal computer. In the cyclic voltammetry (CV) the working electrode was a glassy carbon electrode (0.08 cm2, 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 × 10−4 M; 0.1 M tetrabutylammonium hexafluorophosphate (Bu4NPF6) was added as supporting electrolyte. Cyclic voltammograms were obtained with scan rates in the range 0.05–10 V s−1. 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 CH2Cl2 (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 spectrophluorimeter 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-halon 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 H2SO4 (Φ = 0.546) [22] and [Os(phen)3]2+ in acetonitrile (Φem = 0.005) [23]. Corrected excitation spectra were recorded with a Perkin-Elmer LS-50B spectrophluorimeter (pulsed Xe lamp). Emission lifetimes were determined with an IBH single photon counting spectrometer equipped with a thyatron gated nitrogen lamp working at 40 KHz (λexc = 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.

**REFERENCES**


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