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Perylene-3,4:9,10-bis(dicarboximide) linked to [60]fullerene as a light-harvesting antenna

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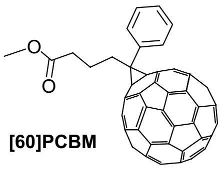
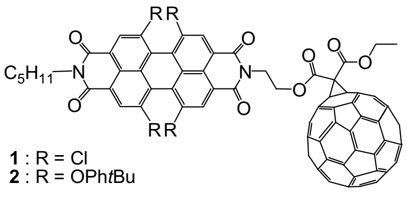
Abstract—New [60]fullerene–perylene-3,4:9,10-bis(dicarboximide) dyads **1** and **2** are described in the search of an energy transfer from the dye as a photoactive antenna to the fullerene moiety.

Thanks to the remarkable electron-accepting properties of C_{60} and the discovery of ultrafast photoinduced electron transfer (PET) from conjugated polymers to C_{60},[1] considerable effort has been devoted to the development of the organic photovoltaic devices based on the bulk heterojunction concept.[2] Until now, the photoactive layer of these solar cells consists of an interpenetrating network using a π-conjugated polymer acting as the electron donor and a functionalized [60]fullerene ([60]PCBM) as the electron acceptor. Based on this concept, plastic solar cells[3] with power conversion efficiency around 3.5% were recently reported.[4] Nevertheless, further improvement seems limited by incomplete absorption of the incident light because of a poor match between the absorption spectrum of both polymer and fullerene materials and the solar emission spectrum. Particularly [60]PCBM, which represents at least 75% of the active layer, presents a very low absorption coefficient in the visible region. The principle of improving light absorption of fullerene derivatives and its relationship with the efficiency of photovoltaic cells was recently demonstrated by either replacing [60]PCBM by [70]PCBM[5] or using a C_{60}–azothiophene dyad.[6] Another strategy consists in the search of an energy transfer using dendrimers with a C_{60} core and peripheral oligophenylenevinylene moieties.[7]

Although a large number of dyads associating C_{60} to an electron donating unit have been synthesized so far in the search of an efficient PET, dyads involving C_{60} and another electron acceptor are much less known.[8] The latter were described in order to essentially increase the solubility for blending them with molecular or polymeric materials, or to improve the electron-accepting ability of the system. But, very few dyads were designed in order to increase C_{60} absorption capability of sunlight. Consequently we were interested in the synthesis of molecular systems associating a dye to C_{60}, so that the dye could act as an antenna by absorption of sunlight with the aim of inducing an intramolecular energy transfer to the fullerene. Perylene-3,4:9,10-bis(dicarboximide) (PDI) was first chosen because of its well known property of high absorption in the visible to NIR region ($\varepsilon \approx 10^5\ \mathrm{L\ mol^{-1}\ cm^{-1}}$).[9] Here, we describe the synthesis and preliminary electrochemical and spectroscopic properties of flexible covalently linked C_{60}–PDI dyads **1** and **2**, with the dye acting as a light-harvesting antenna for their use in the fabrication of efficient photovoltaic cells. In parallel to our work, the synthesis and preliminary studies of a C_{60}–PDI dyad in which both entities are linked through a rigidified spacer was reported.[10] Another example of a C_{60}–PDI dyad was very recently described in order to form thermally stable dyes.[11]


[60]PCBM



1 : R = Cl
2 : R = OPh*t*Bu

Keywords: Fullerene; Perylenediimide; Photovoltaics.

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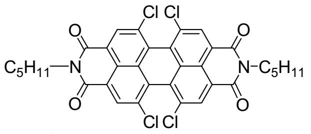
The synthesis of dyad **1**, incorporating an unsymmetrical tetrasubstituted PDI at the bay region, was performed using an efficient methodology. Instead of applying methods reported to reach 3,4:9,10-perylenetetracarboxylic monoanhydride monoimide derivatives,[12] we achieved the direct condensation of 1-pentylamine and 2-aminoethanol in a stoichiometric ratio on 1,6,7,12-tetrachloroperylene tetracarboxylic dianhydride as the starting material. After separation and purification, symmetrical compounds **3** and **5** were obtained in 31% and 34% yields, respectively, and the unsymmetrical monoalcohol **4** in 28% yield.



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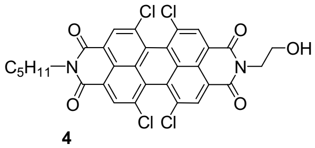

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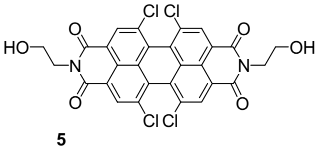

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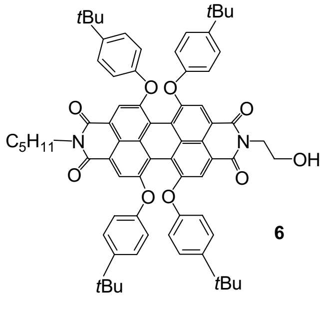
The subsequent nucleophilic substitution of chlorine atoms was carried out according to an approach firstly developed by Seybold and co-workers.[13] Using compound **4** and 4-*tert*-butylphenol in the presence of K_2CO_3, *tert*-butylphenoxyPDI **6** was synthesized in mild conditions in 87% yield. Unsymmetrical malonate derivatives **7** and **8** were obtained from monoalcohols **4** and **6** using ethyl malonyl chloride in 92% and 91% yields, respectively. Cyclopropanation of C_{60} was carried out by reaction of malonate **7** or **8** with iodine and DBU[14] affording methano[60]fullerene dyads **1** and **2** in 41% and 46% yields, respectively, after column chromatography (SiO_2, CH_2Cl_2/EtOAc 4/1 for **1** and CH_2Cl_2 for **2**). Reference compound **9** was prepared according to Bingel's methodology starting from α-bromoethyl malonate.[15] Thermogravimetric analysis (TGA) proved the thermal stability of dyads **1** and **2** with their decomposition starting at 340 °C.



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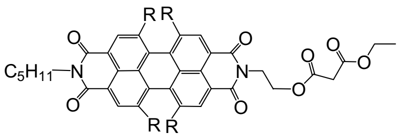
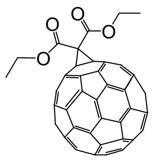


7 R = Cl
8 R = OPh*t*Bu



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The cyclic voltammogram (CV) of dyad **1** (Fig. 1A) shows three reversible reduction waves at $E_{1/2\,\text{red1}} = -0.31$ V, $E_{1/2\,\text{red2}} = -0.55$ V and $E_{1/2\,\text{red3}} = -0.93$ V (vs AgCl/Ag). By comparison with those of compounds **3** and **9** (Table 1), the first one-electron process is assigned to the formation of the anion radical of the PDI moiety (C_{60}–$PDI^{-\bullet}$). The following two-electron process corresponds to the generation of the $C_{60}^{-\bullet}$–PDI^{2-} species suggesting that the first reduction process of fullerene and the second reduction process of PDI are overlapping. The one-electron wave at more negative potential results from the formation of C_{60}^{2-}–PDI^{2-} species. We should note that a two-electron process was observed for the dyad unsubstituted at the bay region resulting from the simultaneous generation of $C_{60}^{-\bullet}$–$PDI^{-\bullet}$ species.[10] These differences are in agreement with an enhancement of the electron affinity for the PDI substituted by four chlorine atoms at the bay region, the electron-withdrawing inductive effect of the chlorine atoms stabilizing the anion radical $PDI^{-\bullet}$, this minimizing their possible electron-donating mesomeric effect. The oxidation of the C_{60} moiety is observed at +1.73 V as an irreversible process, whereas the oxidation of the PDI moiety is not observed in the experimental conditions.

The CV of dyad **2** (Fig. 1B) shows four reversible reduction waves at $E_{1/2\,\text{red1}} = -0.57$ V, $E_{1/2\,\text{red2}} = -0.71$ V, $E_{1/2\,\text{red3}} = -0.82$ V and $E_{1/2\,\text{red4}} = -0.93$ V (vs AgCl/Ag) (Table 1). The first one-electron process is assigned to the formation of the anion radical of the C_{60} moiety ($C_{60}^{-\bullet}$–PDI). This was followed by the one-electron reduction processes of the PDI moiety leading to $C_{60}^{-\bullet}$–$PDI^{-\bullet}$ then $C_{60}^{-\bullet}$–PDI^{2-} species. The last one-electron reduction wave arises from the generation of the C_{60}^{2-}–PDI^{2-} species. Reduction potentials of the PDI moiety are consequently shifted to more negative values with the substitution of chlorine atoms by *tert*-butylphenoxy groups. This can be explained by the electron-donating mesomeric effect of phenoxy groups with less consideration for their possible electron-withdrawing inductive effect. Consequently, this is the first example of a C_{60}–PDI dyad tailored so that the first reduction unambiguously occurs on the C_{60} moiety. This constitutes an important parameter since C_{60} plays the role of charge carrier in photovoltaic cells. The first reversible oxidation wave at +1.34 V is attributed to the oxidation of the PDI moiety leading to C_{60}–$PDI^{+\bullet}$ species. The second reversible oxidation of the PDI moiety is observed at +1.72 V. The oxidation of the C_{60} moiety should occur also at this same potential, as an irreversible process (Fig. 1B). Comparison of these different val-

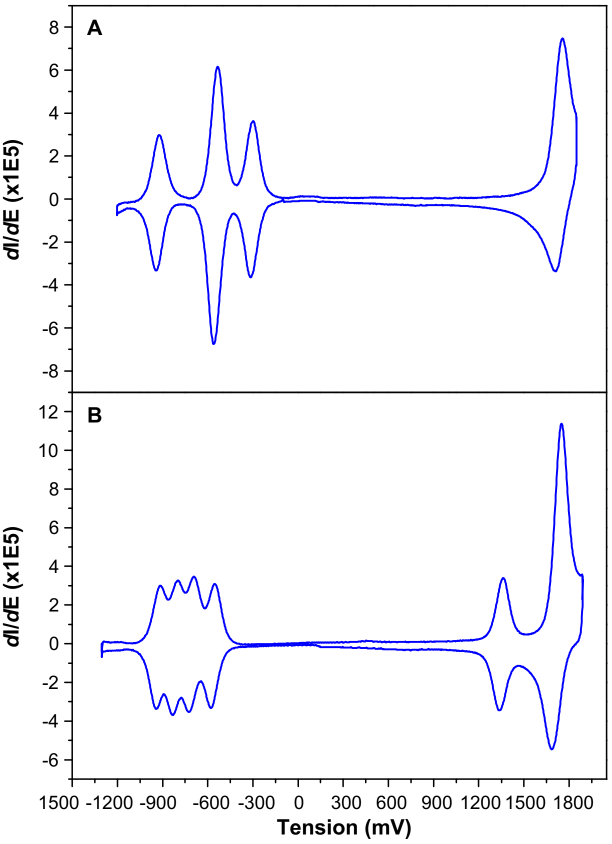

Figure 1. Deconvoluted cyclic voltammograms of dyads **1** (A) and **2** (B), respectively. Experimental conditions are detailed in Table 1.

Table 1. Redox potentials (V) of dyads **1** and **2** and reference compounds **3**, **8** and **9**

Compound	$E_{1/2\,\mathrm{red}4}$	$E_{1/2\,\mathrm{red}3}$	$E_{1/2\,\mathrm{red}2}$	$E_{1/2\,\mathrm{red}1}$	$E_{1/2\,\mathrm{ox}1}$	$E_{1/2\,\mathrm{ox}2}$
1	—	−0.93	−0.55[a]	−0.31	+1.73[b]	—
2	−0.93	−0.82	−0.71	−0.57	+1.34	+1.72[c]
3	—	—	−0.54	−0.34	—[d]	—
8	—	—	−0.83	−0.69	+1.32	+1.66
9	—	—	−0.94	−0.55	+1.71[b]	—

Values recorded in a CH_2Cl_2 solution using Bu_4NPF_6 0.1 M as the supporting electrolyte, AgCl/Ag as the reference, platinum wires as counter and working electrodes. Scan rate: 100 mV/s.

[a] Two-electron process.

[b] Irreversible process.

[c] Irreversible plus one-electron reversible process.

[d] Not measurable in experimental conditions.

ues for dyads **1** and **2** with reference compounds **3**, **8** and **9** suggest that no significant interaction takes place between both electroactive moieties in the ground state.

The absorption and steady-state fluorescence spectra of dyads **1** and **2** in toluene are shown in Figure 2 and selected data are collected in Table 2. The UV–vis absorption spectra of **1** and **2** match the profile obtained by superimposition of the spectra of corresponding reference compounds (compounds **3** and **9** for **1**, compounds **6** and **9** for **2**), indicating the absence of significant

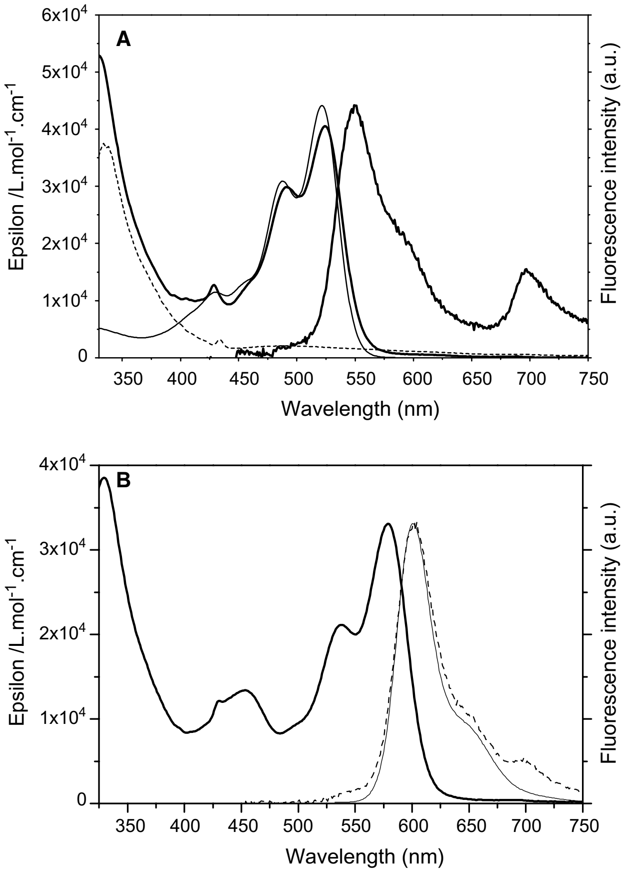

Figure 2. (A) Absorption and fluorescence emission ($\lambda_{\mathrm{exc}} = 521$ nm) spectra of **1** (bold line), absorption spectra of **9** (dotted line) and **3** (full line) in toluene at 298 K ($c < 10^{-6}$ M). (B) Absorption spectra of **2** (bold line) and fluorescence emission spectrum of **2** (dashed line, $\lambda_{\mathrm{exc}} = 400$ nm) and **6** (full line, $\lambda_{\mathrm{exc}} = 400$ nm), in toluene at 298 K ($c < 10^{-6}$ M).

Table 2. Selected photophysical data in toluene

Compound	$\lambda_{\max}$[a] (nm)	ε (L mol^{-1} cm^{-1})	$\lambda_{\max}$[b] (nm)	Φ_f[d]
1	524	29,800	549, 696	3.3×10^{-3}
2	579	36,800	602, 698	3.4×10^{-3}
3	522	33,900	548	1
6	575	42,000	601	1
9	689 (492, 428)[c]	612 (2070, 2280)[c]	697	5×10^{-4}

[a] Absorption maxima.

[b] Fluorescence emission maxima.

[c] Other absorption bands and their corresponding epsilon values.

[d] Determined using cresyl violet as a standard ($\Phi_f = 0.54$ at 20 °C in methanol).

interaction in the ground state between PDI and C_{60} moieties, in agreement with electrochemical results. The absorption spectrum of **9** is very similar to that of other C_{60} malonate derivatives[16] and shows the characteristic band of [6–6] substituted C_{60} at 428 nm. The lowest singlet transition is observed at 689 nm. Compound **3** exhibits the three typical PDI absorption peaks at 431, 488 and 522 nm. A bathochromic effect is noticed for compound **6** (absorption peaks at 448, 533 and 574 nm) as a result of the electron-donating effect of phenoxy groups.

Apart from a fluorescence emission centred on the PDI moiety that occurs in the 500–650 nm range, a second emission band, characteristic of the methanofullerene moiety, is observed in the 670–750 nm region for both dyads. Furthermore, there is a dramatic decrease (ca. 99% and 98%, respectively) of the PDI moiety quantum yield in dyads **1** and **2** compared to the one of compounds **3** and **6**, respectively. This implies a strong quenching of the PDI fluorescence by the fullerene moiety. This process must be intramolecular as the quantum yield of neither **3** nor **6** is affected in a mixture of PDI reference compound (**3** or **6**) and **9** in the same concentration as in the dyads.

In the case of dyad **1**, the relative weight of each band (centred at 544 and 697 nm) in the steady state luminescence spectrum depends on the excitation wavelength. By selectively exciting the PDI moiety in dyad **1**, at wavelength above 520 nm, an emission from $^1C_{60}$*–PDI was still recorded, giving evidence of a singlet–singlet energy transfer from the PDI moiety to C_{60} moiety. This is in agreement with the energy levels of both units (2.32 eV for **3** and 1.79 eV for **9**) and was also confirmed by the excitation spectrum recorded at 700 nm. Indeed, this latter matches the absorption profile of **3** throughout the UV–vis spectral region. These results are consistent with a quantitative energy transfer according to the different quantum yield values calculated. Competition with electron transfer process can be ruled out as the corresponding charge separated state (energy level was estimated to be 2.04 eV according to a ΔG value of -0.28 eV, calculated using the Rehm–Weller equation)[17] lies above the fullerene singlet excited state. Further experiments are currently underway in order to estimate the rate of energy transfer in the system.

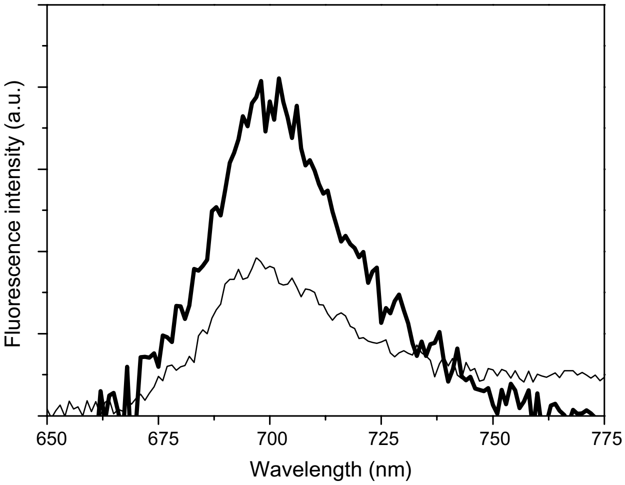

Figure 3. C_{60} emission contribution in **2** (bold line, $\lambda_{exc} = 521$ nm) and fluorescence emission spectrum of **9** (full line, $\lambda_{exc} = 493$ nm) in toluene at 298 K ($c < 10^{-6}$ M).

In the case of dyad **2**, evidencing the energy transfer from PDI to C_{60} is more complex. Indeed, emission from PDI moiety is red-shifted compared to dyad **1** (602 and 544 nm, respectively). Therefore, emission bands characteristic of the PDI and fullerene moieties are overlapping. Whatever, by subtracting the contribution of PDI from emission spectrum of **2**, the fullerene emission is still observed, even when PDI moiety is selectively excited at wavelength above 520 nm (Fig. 3). These results, in addition to energy levels of both units (2.11 eV for **6** and 1.79 eV for **9**), give evidence of a singlet–singlet energy transfer from PDI to C_{60}. Competition with oxidative electron transfer process can be ruled out for the same reasons underlined for **1** (energy level of charge separated state for **2** was estimated to be 1.91 eV according to a ΔG value of -0.20 eV, calculated using the Rehm–Weller equation).[18]

In conclusion, the synthesis and spectroscopic studies of new C_{60}–perylene-3,4:9,10-bis(dicarboximide) dyads are described. It was clearly demonstrated that the position of the first reduction potential and consequently the behaviour towards C_{60} can be fine tuned by molecular engineering around the perylenediimide core. In order to demonstrate the role of a light-harvesting antenna grafted onto C_{60} in the efficiency of solar cells, blends of polymer with C_{60}–PDI dyads are currently underway. Such C_{60}-antenna dyads that absorb strongly in the visible range could be good candidates for the development of efficient photovoltaic devices.

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Supplementary data

Spectroscopic data of dyads **1** and **2**. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.tetlet.2005.04.132.

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17. Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271. For dyad **1**: $\Delta G = E_{(\mathrm{ox})} - E_{(\mathrm{red})} - E^{0-0}(\mathbf{3}) - \mathrm{e}^2/4\pi\varepsilon r$ with $E_{(\mathrm{ox})} = +1.73$ eV, $E_{(\mathrm{red})} = -0.31$ eV, E^{0-0} (**3**) = 2.32 eV and $\varepsilon = 9$, $r = 4$ Å (the distance between the two ions has been estimated by geometrical optimization using PM3 semi-empirical method).
18. For dyad **2**: $\Delta G = E_{(\mathrm{ox})} - E_{(\mathrm{red})} - E^{0-0}$ (**6**) $- \mathrm{e}^2/4\pi\varepsilon r$ with $E_{(\mathrm{ox})} = +1.34$ eV, $E_{(\mathrm{red})} = -0.57$ eV, E^{0-0} (**6**) = 2.11 eV and $\varepsilon = 9$, $r = 4$ Å.