Highly Efficient Light-Harvesting Organofullerenes

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ABSTRACT



Diphenylmethanofullerene-perylenebisimide dyads and triads have been prepared as light harvesters and electron acceptors for the preparation of efficient organic solar cells. The presence of swallowtail chains on the perylene unit provides enhanced solubility and allows its complete characterization.

The possibility to use new organic semiconductor materials in place of silicon wafers in the fabrication of photovoltaic devices as substrates offers the prospect of lower manufacturing costs, particularly for large-area applications. Thus, one of the most promising tasks in fullerene research involves its potential application, mixed with π -conjugated polymers, in mimicking photosynthesis and in related solar energy conversion.¹ Although the first solar cells based on [60]fullerene showed only poor performances, optimization of devices has allowed efficiencies above 3%.² However, optimization of cells has been carried out with only a few materials, and recent findings show that new developments can be very successful if a broader scope of materials in the composite layer becomes accessible. One of the limitations of the [60]fullerene derivatives used so far is their low absorption in the red and near-infrared region of the solar spectrum, which strongly reduces the number of photons that can be converted into electricity. To overcome this problem, different [60]fullerene-based dyads³ and triads⁴ have been synthesized as photoactive materials for solar cells.⁵ Perylenebisimide dyes⁶ are of increasing interest for application in molecular electronic devices,⁷ and they have been successfully used in the fabrication of photovoltaic cells.⁸ Only

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very recently have they been used in combination with fullerene to form thermally stable dyes.⁹ Thus, in this communication we present a new approach toward the synthesis of [60]fullerene derivatives covalently linked to perylenebisimide dyes specifically designed to be used in the fabrication of photovoltaic devices.

The synthesis of the fullerene-perylene dyad **10** and triad **11** was carried out by condensation of the soluble *N*-(10-nonadecyl)-3,4,9,10-perylenetetracarboxylic acid 3,4-anhydride-9,10-imide (**9**)¹⁰ with the corresponding amino or diamino-diphenylmethano fullerenes (**3**, **8**) (Scheme 2).

The synthesis of 3 and 8 was carried out by 1,3-dipolar cycloaddition reaction of diazo compounds generated in situ by Bamford-Stevens reaction between tosylhydrazones and sodium methoxide (Scheme 1). Thus, the synthesis of the target tosylhydrazones bearing one or two amino groups was designed starting with the commercially available 4-aminobenzophenone (1) or 4,4pm'-diaminobenzophenone (4). Condensation of 1 with *p*-tosylhydrazide in ethanol affords tosylhydrazone 2, which after sequential treatment with sodium methoxide in pyridine and [60]fullerene in refluxing o-dichlorobenzene (o-DCB) affords 3 in 26% yield. Although both [6,6]-closed and [5,6]-open isomers could be expected from the cycloaddition reaction, the high temperature at which the reaction proceeds allows the obtention of the thermodynamically more stable [6,6]-closed isomer solely. Thus, only the corresponding [6,6]-closed isomer of **3** is detected by ¹³C NMR.

However, when 4,4'-diaminobenzophenone (4) was reacted with *p*-tosylhydrazide under the same reaction conditions, the expected condensation product could not be obtained. Not even under a wide range of conditions and catalysts did the condensation reaction afford the desired product. This fact can be accounted for by the presence of the second electron-donor amino group in 4, which increases the electron density of the carbonyl group. Thus, a protectingdeprotecting strategy was developed to prepare 7. Reaction of 4,4'-diaminobenzophenone with trifluoracetic anhydride affords the corresponding N-protected diamido compound (5), which readily yields the corresponding *p*-tosylhydrazone (6) under mild conditions. Hydrolysis of the trifluoroacetamido groups with sodium carbonate affords the corresponding diamino *p*-tosylhydrazone (7). Treatment of this derivative with sodium methoxide in the presence of [60]fullerene under the previously stated conditions yields the corresponding diamino-substituted [6,6]-closed diphenylmethanofullerene (8).



Further condensation between the fullerene derivatives bearing one (3) or two (8) functionalizable amino groups and the perylene monoanhydride derivative 9 (Scheme 2) was accomplished by refluxing them in a mixture of o-DCB and pyridine in the presence of a Lewis acid catalyst (Zn(OAc)₂). Thus, the target compounds 10 and 11 were obtained as deep red solids in 65 and 60% yields, respectively.

The presence of the swallowtail solubilizing chains on the perylene unit provides to these systems enough solubility to allow their full electrochemical and spectroscopical¹¹ characterization. Thus, the FTIR spectra of **10** and **11** show, together with the typical band corresponding to the [60]-fullerene moiety at 526 cm⁻¹, the characteristic absorption pattern of the perylene skeleton with bands at 1580 and 1593 cm⁻¹.¹² Besides, the absorption bands at 1655 and 1697 cm⁻¹ indicate the presence of the imide group. No significant bands around 1733 and 1772 cm⁻¹ are observed, proving the disappearance of the anhydride functionality. The ¹H NMR spectra in chloroform show the expected signals for the

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perylene moiety at around 8.6 ppm together with the aromatic protons corresponding to the diphenylmethane fragment and those corresponding to the alkyl chains. In the ¹³C NMR spectra, a signal at 79 ppm corresponding to the bridgehead atom and a signal at around 58 ppm corresponding to those of the sp³ carbon atoms of the [60]fullerene unit are observed, analogously to other diphenylmethanofullerenes.¹³

The solution electrochemistry of the fullerene-perylene derivatives **10** and **11** was carried out in a mixture of o-DCB/CH₃CN (4:1), due to the poor solubility of **3** (used as a reference) in other solvents. The experiments were carried out using tetrabutylammonium perchlorate as the supporting electrolyte, glassy carbon as the working electrode, a platinum wire as the counter electrode, and Ag/Ag⁺ as the reference electrode.

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The cyclic voltammograms of **10** and **11** show four reduction waves (Figure 1). By comparison (Table 1) with



Figure 1. Cyclic voltammograms of dyad 10 and triad 11 along with references 3 and 12.

the cyclic voltammograms of references **3** and the symmetrical bis(N,N'-nonadecyl)perylene bisimide (**12**, Scheme 2),¹⁰ the second reduction wave can be attributed to the second reduction potential of the perylenebisimide moiety, whereas the third and the fourth reduction waves arise from the second and third reduction processes of the fullerene moiety. Although no coulombimetric experiments have been carried out yet, the higher intensity of the first reduction wave observed for **10** and **11** in comparison with references **3** and **12** suggests that the first reduction processes of fullerene

⁽¹¹⁾ Selected data for **10**. ¹H NMR (CDCl₃, 500 MHz) δ : 8.72 (d, J = 8.02 Hz, 2H), 8.70–8.60 (m, 6H), 8.36 (d, J = 8.36 Hz, 2H), 8.18 (d, J = 8.36 Hz, 2H), 7.55–7.44 (m, 3H), 7.23–7.19 (m, 2H), 5.21 (m, 1H), 2.27 (m, 4H), 1.89 (m, 4H), 1.58–1.23 (m, 24H), 0.86 (m, 6H). ¹³C NMR (CDCl₃, 125 MHz) δ : 163.87, 148.52, 148.48, 145.73, 145.71, 145.58, 145.57, 145.49, 145.15, 145.13, 145.12, 145.11, 145.05, 145.04, 144.68, 144.67, 144.65, 144.64, 144.26, 144.25, 144.24, 144.22, 143.39, 143.38, 143.36, 143.36, 143.35, 143.33, 142.88, 142.64, 142.57, 142.56, 142.52, 141.31, 141.26, 139.85, 138.96, 138.77, 138.59, 138.59, 135.63, 135.62, 135.06, 134.56, 134.56, 134.55, 134.54, 132.99, 132.24, 132.21, 132.20, 131.62, 130.95, 130.21, 130.01, 129.92, 129.49, 129.29, 128.78, 128.11, 127.04, 126.88, 126.78, 123.76, 123.74, 123.56, 123.52, 123.50, 123.43, 115.00, 79.29, 58.11, 55.27, 55.18, 53.81, 43.23, 32.76, 32.34, 30.10, 29.91, 29.90, 29.89, 29.84, 29.82, 29.68, 27.37, 27.36, 23.06, 23.03, 23.02, 14.42, 144.05, TF-IR (KBr) ν : 526, 746, 810, 1251, 1340, 1580, 1593, 1655, 1697, 2850, 2920 cm⁻¹. MS (ESI): 1541 (M⁺ + H⁺).

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 Table 1.
 Redox Potentials^a (V) of Fullerene Derivatives 10 and 11 and Reference Compounds 3 and 12

compd	E^{1}_{red}	$E^2_{ m red}$	$E^3_{ m red}$	$E^4_{ m red}$	E_{ox}
10	-0.61	-0.85	-0.99	-1.56	+1.75
11	-0.62	-0.84	-0.98	-1.54	+1.79
3	-0.61	-1.00	-1.53		
12	-0.63	-0.89			+1.78

^{*a*} Values recorded in a 4:1 *o*-DCB/CH₃CN solution using Bu₄NClO₄ (0.3 mg L^{-1}) as the supporting electrolyte and Ag/Ag⁺, platinun wire, and glassy carbon as reference, counter, and working electrodes, respectively. Cathodic peak values. Scan rate: 200 mV/s.

and perylenebisimide are overlapping, and only a broader single wave can be observed. These redox potentials are similar to those reported for other diphenylmethanofullerene derivatives¹⁴ showing very high values of open circuit voltages in photovoltaic devices. On the other hand, these values suggest that no significant interaction takes place between both electroactive moieties in the ground state.

The UV-vis spectra of **10**, **11**, and **12** (Figure 2) show the three typical perylene absorptions at 459, 490, and 527



Figure 2. UV-vis absorption spectra of 3 and 10-12 in dichloromethane solution ($c = 3.55 \ 10^{-5} \ M$).

nm, respectively, with high extinction coefficients. The UV-vis spectra of 10 and 11 match the profile obtained by superimposition of the spectra of their component units 3 and 12 within experimental error. This is in agreement with the lack of interaction observed in the electrochemical measurements between the electroactive moieties in the ground state. As expected, the relative absorption of triad

11, bearing two perylenebisimide moieties, was higher than that of dyad **10** in the visible region (Figure 2).

Unlike the UV—vis spectra that are noninteractive, emission spectra show interactions in the dyad and triad. Although **11** also shows an emission spectra with characteristic features of the perylenebisimide unit, its luminescence is largely quenched (95%). Luminescence quenching above 99% was observed for **10** indicating a more efficient quenching of the perylenebisimide fluorescence in the system containing one fullerene unit per perylenebisimide moiety.

Together with the quenching of the fluorescence of the perylene moiety, the characteristic methanofullerene fluorescence with a maximum at 709 nm³ can be observed despite the selective excitation of the perylenebisimide moiety.

The excitation spectra of **10** and **11** taken at 710 nm resemble the absorption spectrum of perylene, indicating that the energy deposited into the perylene excited state migrates to the fullerene excited-state orbitals. The perfect match between the excitation and the absorption spectrum strongly suggests a quantitative energy transfer. This behavior is in agreement with the energy position of the lowest singlet excited state of the perylenebisimide and fullerene units, which can be estimated at 2.33 and 1.75 eV, respectively.¹⁵ Competition with electron-transfer process can be ruled out considering that the fullerene singlet excited state (1.75 eV) is stabilized in comparison with the charge separated state (2.00 eV) as determined by the ΔG values (see Supporting Information).¹⁶

In conclusion, we have developed a synthetic route toward the preparation of novel [60]fullerene derivatives bearing one or two perylenebisimide moieties. These new materials show analogous electrochemical behavior to that observed in other diphenylmethanofullerene derivatives exhibiting high opencircuit voltages when combined with conjugated polymers in photovoltaic devices. This fact, together with the high light absorption exhibited by these materials throughout the whole visible spectrum, make them suitable candidates for the fabrication of photovoltaic devices. Work is in progress in order to investigate their potential use in organic solar cells.

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Supporting Information Available: Experimental details and photoluminescence. This material is available free of charge via the Internet at http://pubs.acs.org.

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