Novel Soluble and Thermally Stable Perylene Dye with Two [60] Fullerene Units

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A novel fullerene derivative in which perylene group is attached to two C_{60} through a pyrrolidine ring has been prepared and found to exhibit good solubility, high thermal stability and broad visible-light absorption with high coefficients, and photophysical studies shows that photo-induced energy transfer from the perylene moiety to C_{60}.

Covalently linked C_{60} dyads have attracted fair attention in view of its potential application in photovoltaic devices,[1–4] and fullerene derivatives containing two or more [60] fullerene units may exhibit interesting properties.[5] However, the synthesis and characterization of dimers and oligomers containing two or more fullerene units has been reported to a less extent due to their poor soluble, difficult synthesis and characterization.[6] Perylene derivates are well-known chromophores combining high quantum yields of photo-luminescence with excellent photochemical and thermal stability and are successfully used in optical switching, electroluminescent devices, and solar energy conversion.[7]

In this paper, we report on preparation and the electronic properties of fullerene dyad **2** in which perylene group is attached to two C_{60} through a pyrrolidine ring using the related perylene derivative **1** and the fulleropyrrolidine **FP** as reference compound (Figure 1). Interestingly, the photo-physical studies of **2** show that photoinduced energy transfer from the perylene moiety to C_{60} is the main pathway.

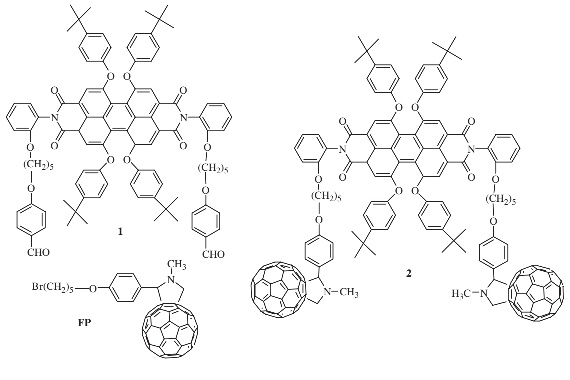

Figure 1. The chemical structures of **1**, **2** and **FP**.

4-(5-Bromopentyloxy)benzaldehyde and *N*,*N*′-bis(2-hydroxylphenyl)-1,6,7,12-tetrakis(4-butylphenoxy)-3,4,9,10-perylenetetracarboxdimide) acid monoimide (**1**′) were prepared according to the literature.[8,9] Core group **1** was synthesized by substitution reaction of compound **1**′ with 4-(5-bromopentyloxy)benzaldehyde in 52% yields. Dyad **2** was prepared in 16.7% isolated yield via the 1,3-dipolar cycloaddition of azomethine ylides to [60] fullerene by treating perylene bisaldehyde **1** with *N*-methylglycine and [60] fullerene in refluxing chlorobenzene. **FP** was obtained in 21.9% yield by treatment of C_{60} with 4-(5-bromopentyloxy)benzaldehyde and sarcosine in refluxing chlorobenzene. All spectroscopic and analytical data were consistent with the proposed molecular structure.[10]

The electrochemical properties of the compounds **1**, **2**, and **FP** were studied by cyclic voltammetry (CV) in CH_2Cl_2-0.1 M Bu_4NClO_4 solutions. Compound **2** shows three reversible reduction peaks in the cathodic region (Table 1 and Figure 2). In Table 1, the first and second reduction potentials of **2** are very close to those of perylene, indicating that both reduction peaks of fullerene in **2** is hidden. The third reversible reduction waves are C_{60}-based. The observed C_{60}-based reduction potentials ($E_{1/2}$) of **2** are shifted to more negative values when compared to model compound **FP**. This is typical of most C_{60} adducts which show small shifts due to the partial loss of conjugation upon derivation.[11,12] In the anodic region, **2** presents a reversible oxidation peak, corresponding to the **1** model compound. The electrochemical data indicates that some degree of charge transfer from the electron-donating perylene to the electron-accepting fullerene at ambient conditions in **2**, but the electronic interactions between them was very small.

The absorption and fluorescence data of **1**, **2**, and **FP** was listed in Table 2. In the UV–vis spectra, **1** and **2** showed three

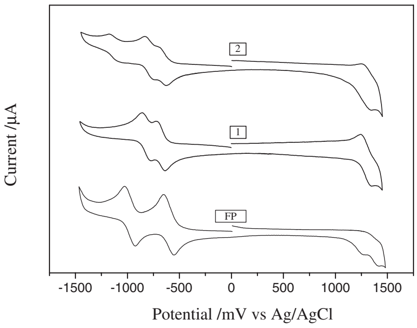

Figure 2. Cyclic voltammogram of **1**, **2**, and **FP** in CH_2Cl_2 containing tetrabutylammonium perchlorate at a scan rate of 100 mV/s.

Table 1. Electrochemical data for **1**, **2**, and **FP**

Compound	$E_{1/2}$ (oxd.)	$E_{1/2}$ (1st red)	$E_{1/2}$ (2nd red)	$E_{1/2}$ (3rd red)
1	+1.34	−0.70	−0.84	
2	+1.32	−0.69	−0.82	−1.17
FP		−0.62	−1.00	

CV measurements in dichloromethane solution using tetrabutyl ammonium perchlorate as supporting electrolyte, glassy carbon as working electrode, Pt as counter electrode and Ag/AgCl as reference electrode. The scan rate is 100 mV/s and half-wave potential ($E_{1/2}$) is expressed in volts relative to SCE.

typical perylene absorption peaks at 451, 537, and 578 nm with high coefficients. **2** matches the profile obtained by summation of the spectra of component units **FP** and **1** (Figure 3) within experimental error. **1** in CH_2Cl_2 excited by 560 nm displayed fluorescent maxima at 610 nm. And dyad **2** had emission spectra with characteristic features of the perylene unit, however, its luminescence was largely quenched (Figure 3). The fluorescence lifetimes (τ) of **1** and **2** were determined by a time-correlated single photon counting spectrometer with excitation at 370 nm. The fluorescence decay at $\lambda_{em} = 610$ nm is monoexponential for **1** ($\tau = 14.23$ ns). **2** exhibits dual-exponential decay characteristics ($\tau_1 = 6.19$ ns, 72.42% and $\tau_2 = 2.91$ ns, 27.58%), and the relative short-lived fluorescent component is attributed to the interaction between the perylene and fullerene.[13] On the other hand, solvent polarity does not lead to the shifts of the fluorescence emission band in the system although the emission intensity of **2** increased a little with increasing solvent polarity. **FP** exhibits a fluorescence band with $\lambda_{max} = 710$ nm, and its emission quantum yields of 0.0022 and excited-state lifetime of 1.2 ns. The excitation spectrum of **2** taken at $\lambda_{em} = 710$ nm matches the absorption profile throughout the UV–vis spectral region of **1**. These findings are consistent with quantitative occurrence of singlet–singlet energy transfer from perylene unit to the fullerene in the dyad **2**. The fluorescence of the perylene moiety in the dyad is strongly quenched by the intramolecular energy transfer (ca. 94%).

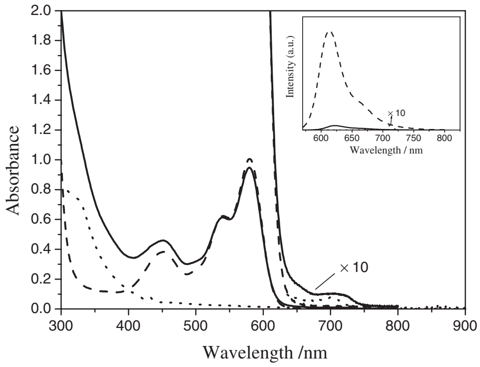

Figure 3. UV–vis absorption spectra of **1** (dashed curve), **2** (solid curve), and **FP** (dotted curve) in CH_2Cl_2 (1×10^{-5} mol L^{-1}); above 640 nm a multiplying factor of 10 is used. Inset: fluorescence spectra of solutions of **1** (dashed curve), **2** (solid curve) and **FP** (dotted curve) excited at 560 nm in CH_2Cl_2 (1×10^{-6} mol L^{-1}), and fluorescence intensity for **FP** is multiplied by a factor of 10.

Table 2. The optical properties of **1**, **2**, and **FP** in dichloromethane

Compound	$\lambda_{max}{}^{ab}$ (nm) (log ε)	$\lambda_{max}{}^{fl}$ (nm)	Φ^a
1	451(4.32), 537(4.52), 578(4.73)	610	1
2	451(4.41), 541(4.56), 579(4.76)	610	0.06
FP	302(4.62), 430(0.72), 702(0.3)	710	0.0022

[a] Fluorescence quantum yields Φ were relative to perylene (defined as 1).

Thermal property of compounds **1** and **2** was investigated by means of thermogravimetric analysis (TGA) at the heating rate of 10 °C/min under nitrogen atmosphere, **2** revealing better thermal stability up to 409 °C as shown in Figure 4. It has been found that **2** has good solubility in common organic solvents such as toluene, $CHCl_3$, THF, NMP, and branched tert-butyl phenyl group on the bay of perylene moiety has proven to be effective in enhancing their solubility.

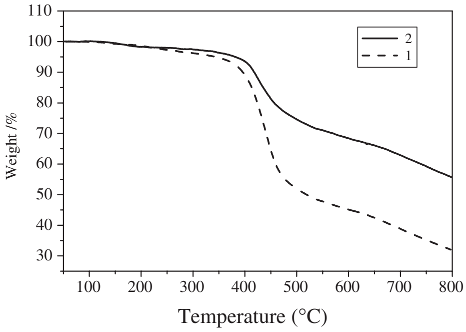

Figure 4. The TGA spectra of compounds **1** and **2**.

In summary, we have synthesized a novel soluble and highly thermally stable perylene dyad with two [60] fullerene units as electronic acceptor. The electrochemical and photophysical studies have shown that singlet–singlet energy transfer from the perylene unit to the fullerene in dyad **2** takes place whereas electron transfer is a minor process. The IPCE (incident photo-to-current conversion efficiency) at 580 nm of the ITO/dyad **2**/AI device is about 0.01%. The optimal measurement of its photovoltaic properties is in progress.

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10 The FT–IR (KBr) and H NMR (500 MHz, $CDCl_3$) analysis data for **1**: yield 52%; IR (KBr) : 3048, 2952, 2861, 1709, 1679, 1582, 1509, 1281, 1014 cm^{-1}; ^{1}H NMR (δ_{ppm}): 9.27 (s, 2H), 8.23 (s, 4H), 7.56 (d, 4H, $J = 8.65$ Hz), 7.40 (m, 2H), 7.30 (m, 2H), 7.21 (d, 8H, $J = 8.54$ Hz), 7.08 (t, 2H, $J = 7.24$ Hz), 7.03 (d, 2H, $J = 8.05$ Hz), 6.83 (d, 8H, $J = 8.54$ Hz), 6.76 (d, 4H, $J = 8.71$ Hz), 4.02 (t, 4H, $J = 5.96$ Hz), 3.79 (t, 4H, $J = 6.21$ Hz), 1.64–1.72 (m, 8H) 1.39–1.45 (m, 4H), 1.24 (s, 36H); **2**: yield 16.7%; IR (KBr): 3057, 2959, 2782, 1710, 1675, 1594, 1523, 1271, 1024, 525 cm^{-1}; ^{1}H NMR (δ_{ppm}): 8.23 (br, 4H), 7.56 (m, 4H), 7.38 (m, 4H), 7.16 (m, 8H), 7.03 (m, 4H), 6.57 (d, 12H, $J = 9.05$ Hz), 4.69 (s, 2H), 4.23 (d, 2H, $J = 9.15$ Hz), 3.98 (d, 2H, $J = 9.07$ Hz), 2.78–2.83 (m, 8H), 2.45 (s, 6H), 1.43–1.65 (m, 12H), 1.24 (s, 36H); MALDI–TOF Mass: 3044.3 (9%, $[M + 1]^+$, calcd for $C_{224}H_{104}O_{12}N_4$ 3043.3), 2324.3 (100%, $[M - C_{60}]^+$, calcd for $C_{164}H_{104}O_{12}N_4$ 2323.3), 1604.3 (52%, $[M - 2C_{60}]^+$, calcd for $C_{104}H_{104}O_{12}N_4$ 1603.3).
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