

Novel soluble and thermally-stable fullerene dyad containing perylene†

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A novel fullerene dyad **C₆₀-P1** in which a perylene moiety is attached to C₆₀ through a pyrrolidine ring has been prepared by 1,3-dipolar cycloaddition of the azomethine ylides generated *in situ* from the corresponding aldehyde and sarcosine. Electrochemical and photophysical studies of the dyad in solution have revealed that there is no significant ground-state electronic interaction between the covalently bonded perylene moiety and the fullerene. The photophysical investigations have also shown that there exists an effective photoinduced energy transfer from the perylene moiety to C₆₀. A photovoltaic device made with the dyad has confirmed that photoinduced electron transfer does take place within the dyad; however, the efficiency of the electron transfer is negligible relative to the energy transfer.

Introduction

Since the discovery of a photoinduced electron transfer from a conjugated oligomer and/or polymer to a fullerene, covalently linked C₆₀ dyads have attracted great attention due to their potential application in photovoltaic devices.^{1,2} However, the disordered islands of polymer and fullerene formed in the actual bulk heterojunction devices limited further improvement of their efficiency.³ To overcome this drawback, fullerene-based double-cable polymers⁴⁻¹⁰ and donor-acceptor dyads^{1b,11-18} have been synthesized. As shown recently, the devices made of polythiophene/fullerene blends reached power conversion efficiency values (η) of up to 3.3%.¹⁹ Although such high efficiency has been achieved, there is large scope for the further improvement of the solubility for most fullerene compounds.²⁰

Another factor that limits the efficiency is the narrow absorption spectra of the polymers. Many efforts have been devoted to improving the light harvesting ability, but only a few polymers can achieve near infrared (NIR) absorption. Dyes based on 3,4,9,10-perylene tetracarboxylic diimides (PTCAs) have drawn much attention^{2c,21} for being used as sensitizers with their outstanding chemical, thermal and photochemical stability. Perylene derivatives are highly absorbing in the visible to NIR region ($\epsilon \approx 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) and emit fluorescence with a quantum yield of near unity.²² On the other hand, perylene derivatives can be also used as NIR absorber or luminescent materials, and nowadays the highly photo-luminescent and environmentally-stable NIR materials are strongly needed. Besides their conventional uses, perylenes are one kind of key chromophore for high-tech applications, spanning from electronic to biological fields, such as optical switches,²³ lasers²⁴ and DNA/RNA probes,²⁵ *etc.* Many types of PTCAs have been synthesized, but the expected low solubility of these molecules is a problem for synthesis, purification and applications in the devices. Therefore, work

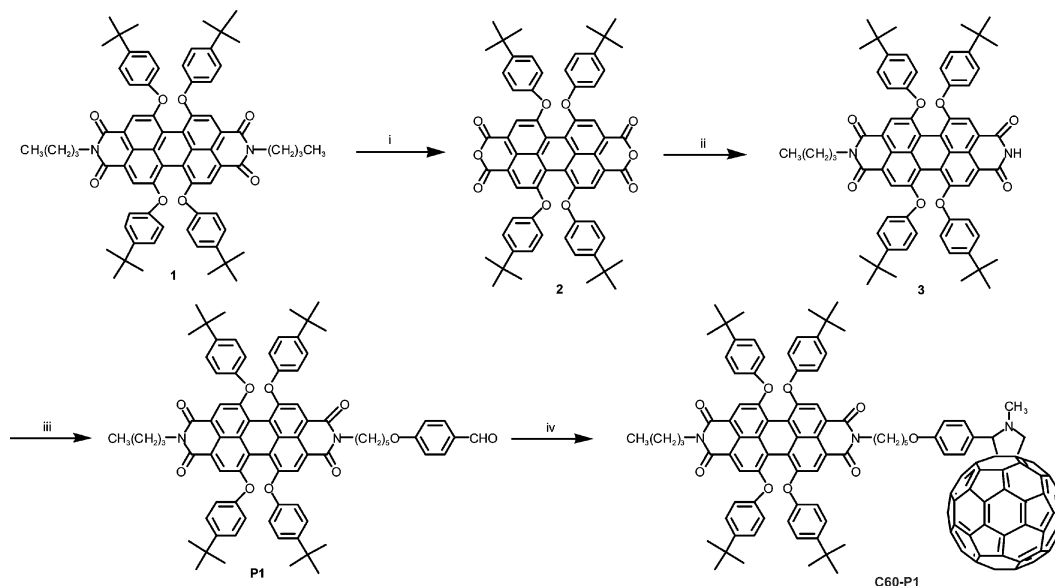
has shifted to more soluble perylenes.^{26,27} Wudl and co-workers²⁸ investigated the excited-state properties of a perylene-fulleropyrrolidine dyad with steady-state and femto-second time-resolved spectroscopy. It was shown that charge separation and energy transfer occurred in nearly equal proportions after photoexcitation and both processes took place on a sub-picosecond timescale. Here, we have designed and synthesized a novel soluble fullerene dyad containing a perylene moiety (**C₆₀-P1** in Scheme 1), in which a perylene moiety is attached to fullerene through a pyrrolidine ring, and which has been prepared by 1,3-dipolar cycloaddition of the azomethine ylides generated *in situ* from the aldehyde and sarcosine. To our knowledge, few works had been reported on good soluble fullerene compounds containing a perylene unit. The structure of the functionalized fullerene dyad was characterized using ¹H-NMR, ¹³C-NMR, MS, IR, UV-Vis absorption, luminescence spectra, CV and TGA data. It was found that the fullerene dyad containing a perylene moiety has good solubility in most common organic solvents, high thermal stability and broad visible-light absorption with high coefficients. The electrochemical and excited-state properties of the dyad in solution are discussed using the related perylene derivatives **P1** (see Scheme 1) and fulleropyrrolidine **FP** (see Scheme 2) as reference compounds. Finally, the **C₆₀-P1** dyad was incorporated into a photovoltaic cell by spin-casting the compounds onto an ITO glass substrate and depositing an aluminium film on the top.

Experimental

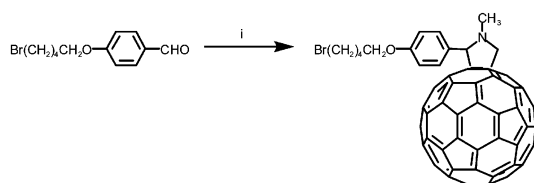
Materials

4-(5-Bromopentyl)oxy)benzaldehyde,²⁹ *N,N'*-di-(*n*-butyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-3,4,9,10-perylenetetracarboxylic diimide (**1**), 1,6,7,12-tetra(4-*tert*-butylphenoxy)-3,4,9,10-perylenetetracarboxylic dianhydride (**2**) and *N*-(*n*-butyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-3,4,9,10-perylenetetracarboxylic monoimide (**3**) were prepared following a procedure described in the literature.^{21,22,26,27,30} † 1-Methyl-2-pyrrolidinone (NMP) was refluxed with calcium hydride and distilled before use. All

† Electronic supplementary information (ESI) available: synthesis of starting materials and ¹H-NMR, ¹³C-NMR, MS spectra and emission lifetimes of the products. See <http://www.rsc.org/suppdata/jm/b3/b316996k/>



Scheme 1 Synthetic route for fullerene-perylene dyad (**C₆₀-P1**). *Reagents and conditions:* (i) KOH/isopropanol, HCl, 80%; (ii) n-butylamine, NH₃, 35%; (iii) 4-(5-bromopentyloxy)benzaldehyde, NMP/K₂CO₃, 110 °C, 24h, 70%; (iv) C₆₀, sarcosine, chlorobenzene, reflux 24 h, 25.3%.



Scheme 2 Synthetic route for **FP**. *Reagents and conditions:* (i) C₆₀, sarcosine, chlorobenzene, reflux, 24 h, 21.9%.

other reagents and solvents were of analytical or chemical grade, and were purified using standard methods.

Characterization

¹H-NMR and ¹³C-NMR spectra were obtained with a Bruker AM-500 spectrometer. The mass spectra were determined on a 4700 Proteomics analyzer spectrometer. FT-IR spectra were recorded on a Nicolet Magna-IR550 spectrophotometer in the region of 4000–400 cm⁻¹ using KBr pellets. UV-Visible spectra were determined with a Varian Cary 500 spectrometer. Fluorescent spectra were recorded on Varian Cary Eclipse spectrometer. Thermogravimetric analysis (TGA) was conducted using a Mettler Toledo Thermal Analyzer SDTA 851 at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere.

Synthesis of compound P1

A mixture of *N*-(n-butyl)-1,6,7,12-tetra-(4-*tert*-butylphenoxy)-3,4,9,10-perylenetetracarboxylic monoimide (0.74 g, 0.61 mmol), 4-(5-bromopentyloxy)benzaldehyde (0.33 g, 1.23 mmol), potassium carbonate (1.4 g, 10 mmol), and NMP (20 mL) was stirred at 110 °C under argon for 24 h. The reaction mixture was cooled, then poured into water (350 mL), extracted with ethyl acetate, washed with water, dried over anhydrous magnesium sulfate, and chromatographed on silica gel with a mixture of CH₂Cl₂/CCl₄ (2:1) to give the product (0.6 g, 70%) as a red powder. ¹H-NMR (500 MHz, CDCl₃): δ 9.85 (s, 1 H), 8.23 (s, 4 H), 7.79 (d, *J* = 8.67 Hz, 2 H), 7.24 (d, *J* = 8.23 Hz, 8 H), 6.94 (d, *J* = 8.77 Hz, 2 H), 6.84 (d, *J* = 8.39 Hz, 8 H), 4.14 (m, 4 H), 4.01 (t, 2 H), 1.85 (m, 2 H), 1.80 (m, 2 H), 1.67 (m, 2 H), 1.56 (m, 2 H), 1.39 (m, 2 H), 1.29 (s, 36 H), 0.93 (t, 3 H). Anal. calc. for C₈₀H₈₀N₂O₁₀ (*M* = 1229.51): C, 78.15; H, 6.56; N, 2.28. Found: C, 78.21; H, 6.48; N, 2.23%.

Synthesis of C₆₀-P1

A mixture of C₆₀ (0.26 g, 0.36 mmol), compound **P1** (0.54 g, 0.38 mmol), and sarcosine (0.13 g, 1.44 mmol) in dry chlorobenzene was refluxed for 24 h under an argon atmosphere. The resulting mixture was concentrated and separated on a silica gel column using toluene/dichloromethane (8:1) to give the product (0.18 g, 25.3 %). IR (KBr pellets, cm⁻¹): 3059, 2961, 2780, 1697, 1660, 1586, 1503, 1261, 1017, 573, 525; ¹H-NMR (500 MHz, CDCl₃): δ 8.21 (s, 4 H), 7.65 (br, 2 H), 7.22 (d, *J* = 12.25 Hz, 8 H), 6.89 (d, *J* = 8.14 Hz, 2 H), 6.83 (d, *J* = 11.75 Hz, 8 H), 4.95 (d, *J* = 9.36 Hz, 1 H), 4.84 (s, 1 H), 4.21 (d, *J* = 10.46 Hz, 1 H), 4.10 (m, 4 H), 3.95 (t, 2 H), 2.77 (s, 3 H), 1.92 (m, 2 H), 1.82 (m, 2 H), 1.66 (m, 2 H), 1.58 (m, 2 H), 1.41 (m, 2 H), 1.29 (s, 36 H), 0.94 (t, 3 H); ¹³C-NMR (125 MHz, CDCl₃): δ 164.09, 156.69, 156.61, 153.57, 147.92, 147.42, 147.11, 146.97, 146.66, 146.47, 146.34, 146.10, 145.87, 145.26, 145.14, 144.95, 143.65, 143.53, 143.22, 143.11, 143.06, 142.98, 142.22, 142.83, 142.69, 142.63, 142.55, 142.49, 142.36, 142.24, 142.08, 140.72, 140.49, 140.14, 137.34, 137.19, 136.36, 129.71, 127.33, 123.23, 123.08, 121.31, 121.15, 120.63, 120.58, 120.18, 120.05, 120.01, 83.85, 70.66, 69.59, 68.25, 53.49, 42.66, 41.08, 40.63, 35.04, 32.15, 31.04, 30.89, 30.38, 30.04, 29.49, 28.47, 27.71, 25.32, 24.18, 23.37, 23.22, 21.05, 14.80, 14.48; MALDI-TOF *m/z*: 1976.71 [*M* + 1]⁺. Anal. calc. for C₁₄₂H₈₅N₃O₉ (*M* = 1975.71): C, 86.25; H, 4.34; N, 2.13. Found: C, 86.31; H, 4.37; N, 2.15%.

Synthesis of FP

A mixture of 4-(5-bromopentyloxy)benzaldehyde (0.162 g, 0.6 mmol), C₆₀ (0.288 g, 0.4 mmol), and sarcosine (0.143 g, 1.6 mmol) in dry chlorobenzene (120 mL) was refluxed under argon for 24 h. After cooling, the resulting solution was evaporated to dryness and column chromatography (SiO₂, petroleum ether/toluene 2:3) gave **FP** (0.09 g, 21.9%) as a brown solid. ¹H-NMR (500 MHz, CDCl₃): δ 7.72 (br, 2 H), 6.94 (d, *J* = 8.62 Hz, 2 H), 4.97 (d, *J* = 9.94 Hz, 1 H), 4.88 (s, 1 H), 4.24 (d, *J* = 9.53 Hz, 1 H), 3.96 (t, *J* = 6.43 Hz, 2 H), 3.43 (t, *J* = 6.74 Hz, 2 H), 2.79 (s, 3 H), 1.93 (m, 2 H), 1.81 (m, 2 H), 1.62 (m, 2 H). Anal. calc. for C₇₄H₂₀BrNO (*M* = 1018.88): C, 87.23; H, 1.98; N, 1.37. Found: C, 87.32; H, 2.04; N, 1.39%.

Results and discussion

The synthetic route of functionalized fullerene **C₆₀-P1** is shown in Scheme 1. The synthetic approach to prepare those compounds relies upon the 1,3-dipolar cycloaddition of azomethine ylides to **C₆₀**.³¹ This method has been proven to be very efficient for the functionalization of **C₆₀** due to its versatility and the ready availability of the starting materials.³¹ The 1,3-dipolar cycloaddition of the azomethine ylides generated *in situ* from **P1** and sarcosine in refluxing chlorobenzene with **C₆₀** leads to the fulleropyrrolidine **C₆₀-P1** in 25.3% yield. Owing to the presence of the branched *tert*-butyl phenyl substitute on the bay of the perylene moiety, compound **C₆₀-P1** is highly soluble in common solvents such as toluene, CH₂Cl₂, CHCl₃, THF, or NMP, and its complete spectroscopic characterization was easily achieved. The IR spectrum of **C₆₀-P1** shows a characteristic absorption band of **C₆₀** at around 525 cm⁻¹, and the ¹H-NMR spectrum of **C₆₀-P1** in CDCl₃ solution also shows all the expected signals, such as those corresponding to the pyrrolidine ring at δ = 4.95, 4.84, and 4.21 ppm. Interestingly, the signals (δ = 7.65 ppm) corresponding to some of the protons of the phenyl group directly attached to the pyrrolidine ring are broad (for details, see ESI†), which indicates restricted rotation of the phenyl substitute on the pyrrolidine ring.³² This result is in good accordance with the data previously reported by Eckert *et al.*⁹ The structure of **C₆₀-P1** is also characterized by MALDI-TOF mass spectroscopy with a molecular isotopic peak at *m/z* = 1976.71 ([*M* + 1]⁺, calculated for C₁₄₂H₈₅N₃O₉: 1975.71). The fragment showing the peak at 1256.71, corresponding to [*M* - C₆₀]⁺ (calculated for C₈₂H₈₅N₃O₉: 1255.71), is also consistent with the structure of **C₆₀-P1**. Thermal properties of compounds **P1** and **C₆₀-P1** are investigated by means of thermogravimetric analysis (TGA) at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere, which shows that **C₆₀-P1** has better thermal stability than **P1** with its decomposition temperature up to 432 °C as shown in Fig. 1.

The model fulleropyrrolidine **FP** was obtained in 21.9% yield by treatment of **C₆₀** with 4-(5-bromopentyloxy)benzaldehyde and sarcosine in refluxing chlorobenzene (Scheme 2). The ¹H-NMR spectra of **FP** shows all the expected signals, and restricted rotation of the phenyl substitute on the pyrrolidine ring is also observed for compound **FP**.†

The electrochemistry of the compounds **C₆₀-P1**, and **FP** were studied by cyclic voltammetry (CV). All the experiments were performed in dichloromethane solution using tetrabutylammonium perchlorate as the supporting electrolyte, glassy carbon as the working electrode, Pt as the counter electrode and Ag/AgCl as the reference electrode. The scan rate was 100 mV s⁻¹. The voltammetric results are presented in Fig. 2 and the data are collected in Table 1.

C₆₀-P1 shows three reversible reduction peaks characterized

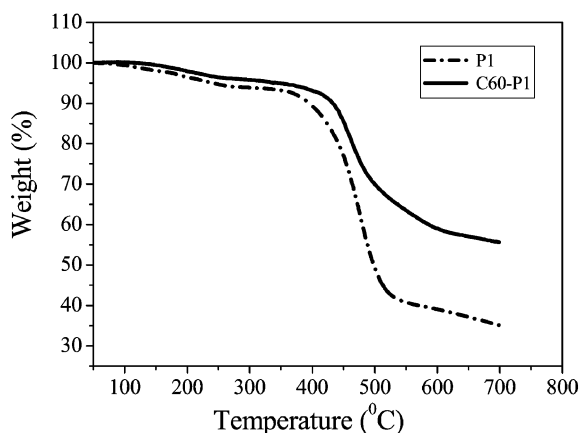


Fig. 1 TGA spectrum of **C₆₀-P1** and **P1**.

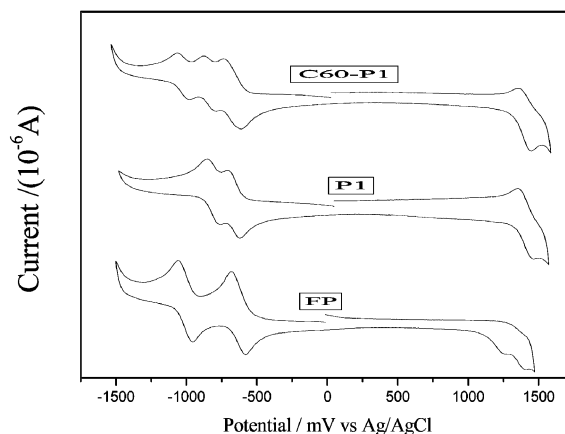


Fig. 2 Cyclic voltammogram of **C₆₀-P1**, **P1**, and **FP** in CH₂Cl₂ containing tetrabutylammonium perchlorate at the scan of 100 mV s⁻¹.

with one-electron in the cathodic region (Table 1 and Fig. 2). The first and second reduction potentials of **C₆₀-P1** are very close to those of **P1**, which indicates that both reduction peaks of fullerene in **C₆₀-P1** are hidden. The third reversible reduction wave is **C₆₀**-based. The observed **C₆₀**-based reduction potential (*E*_{1/2}) of **C₆₀-P1** is shifted to a more negative value compared with the model compound **FP**. This is typical for most **C₆₀** adducts which show small shifts due to the partial loss of conjugation upon derivation.³³ In the anodic region, **C₆₀-P1** presents one, reversible oxidation peak characterized with one-electron corresponding to the **P1** model compound. The electrochemical data indicate that there is no distinct ground-state electronic interaction between the electron-donating perylene and the electron-accepting fullerene.

The ground-state electronic absorption spectra of the compounds **C₆₀-P1**, **P1**, and **FP** in CH₂Cl₂ are shown in Fig. 3. **C₆₀-P1** matches the profile obtained by summation of the spectra of component units **FP** and **P1** (Fig. 3) within experimental error. This result is in agreement with previous studies on donor-acceptor dyads in solution³⁴ and suggests that there is no significant ground-state interaction between the perylene moiety and the fullerene. Interestingly, the absorption spectrum of **FP** in CH₂Cl₂ displays two very intense bands in the UV and much weaker features in the visible spectral region (Table 2). In particular, two band maxima attributed to the lowest (λ_{max}: 702 nm) and lowest allowed (λ_{max}: 430 nm) singlet transitions are observed. The absorption spectrum of **FP** is very similar to that of the simple *N*-methylfulleropyrrolidine reported by Prato and Maggini,³¹ thus showing modest perturbations induced by the phenylene fragment bound to the pyrrolidine ring.

The absorption and fluorescence data of **C₆₀-P1**, **P1**, and **FP** are listed in Table 2. In the UV-Vis spectra, **C₆₀-P1** and **P1** show three typical perylene absorption peaks at 451, 537, and 578 nm with high coefficients. **P1** in CH₂Cl₂ excited at 560 nm displays a fluorescence maximum at 610 nm. Also, dyad **C₆₀-P1** has emission spectra with characteristic features of the

Table 1 Electrochemical data^a for **C₆₀-P1**, **P1**, and **FP**

Compound	<i>E</i> _{1/2} (ox.)	<i>E</i> _{1/2} (1st red.)	<i>E</i> _{1/2} (2nd red.)	<i>E</i> _{1/2} (3rd red.)
C₆₀-P1	+1.32	-0.67	-0.83	-1.01
P1	+1.34	-0.70	-0.84	
FP		-0.62	-1.00	

^a CV measurements in dichloromethane solution using tetrabutylammonium 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⁻¹ and half-wave potentials (*E*_{1/2}) are expressed in volts relative to SCE.

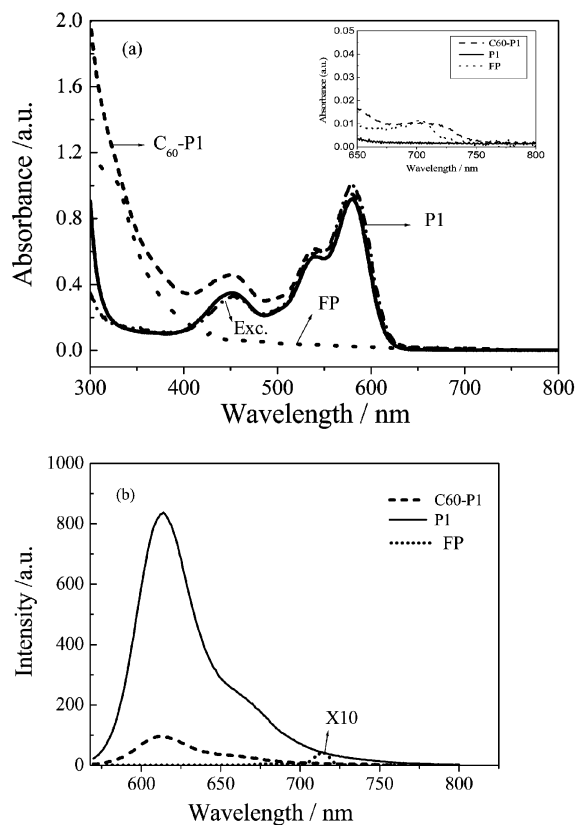


Fig. 3 (a) UV-Vis absorption spectra of **C₆₀-P1** (dashed curve), **P1** (solid curve), and **FP** (dotted curve) in CH_2Cl_2 ($1 \times 10^{-5} \text{ mol L}^{-1}$). In the inset, their absorption spectrum is multiplied by a factor of 40 above 650 nm. The corrected excitation spectrum of **C₆₀-P1** (dash dot curve) is taken at $\lambda_{\text{em}} = 710 \text{ nm}$ (maximum of the fullerene moiety fluorescence). (b) Fluorescence spectra of **C₆₀-P1** (dashed curve) and **P1** (solid curve) excited at 560 nm in CH_2Cl_2 ($1 \times 10^{-6} \text{ mol L}^{-1}$). Fluorescence intensity for **FP** (dotted curve) is multiplied by a factor of 10.

perylene unit; however, its luminescence was largely quenched (Fig. 3). The fluorescence lifetimes (τ) of **P1** and **C₆₀-P1** were determined by a time-correlated single photon counting spectrometer with excitation at 370 nm. The fluorescence decay at $\lambda_{\text{em}} = 610 \text{ nm}$ is mono-exponential for **P1** ($\tau = 15.4 \text{ ns}$). **C₆₀-P1** exhibits dual-exponential decay characteristics ($\tau_1 = 6.69 \text{ ns}$, 94% and $\tau_2 = 2.6 \text{ ns}$, 6%),[†] and the relative short-lived fluorescent component is attributed to the interaction between the perylene and the fullerene.³⁶ It seems to be common sense that the solvent effect of the fluorescence quenching can be observed if intramolecular charge transfer occurs in a system.³⁷ In this system, solvent polarity neither led to the shifts of the fluorescence emission band nor influenced the excited-state lifetime, although the emission intensity of **C₆₀-P1** increased a little with increasing solvent polarity. This evidence disallows the possibility of the intramolecular charge transfer process in **C₆₀-P1** at room temperature. **FP** exhibits a fluorescence band with $\lambda_{\text{max}} = 710 \text{ nm}$, and a emission quantum yield of 0.0022 and an excited-state lifetime of 1.2 ns. The excitation spectrum of **C₆₀-P1** taken at $\lambda_{\text{em}} = 710 \text{ nm}$

Table 2 Absorption and fluorescence data for **C₆₀-P1**, **P1**, and **FP** in CH_2Cl_2 ^a

Compound	$\lambda_{\text{max}}^{\text{abs.}}/\text{nm}$ (log ϵ)				$\lambda_{\text{max}}^{\text{fl.}}/\text{nm}$	$\Phi_{\text{em}}^{\text{b}}$
C₆₀-P1	702 (0.3)	579 (4.76)	541 (4.56)	451 (4.41)	610	0.115
P1		578 (4.73)	537 (4.52)	451 (4.32)	610	1
FP	702 (0.3)	430 (0.72)	302 (4.62)		710	0.0022

^a For **C₆₀-P1** and **P1** the fluorescence spectra and quantum yields were obtained upon excitation at their absorption maxima (λ_{ex} : 560 nm); for **FP** the fluorescence spectra and quantum yield values are independent of the excitation wavelength. ^b Fluorescence quantum yields Φ_{em} were measured with the method using perylene as a standard.³⁵

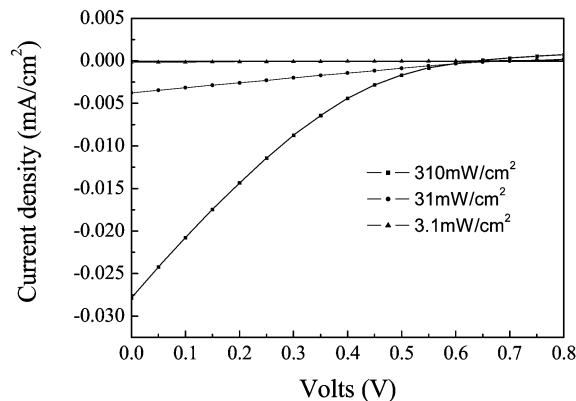


Fig. 4 Current-voltage characteristics of the ITO/**C₆₀-P1**/Al device under different white light intensities.

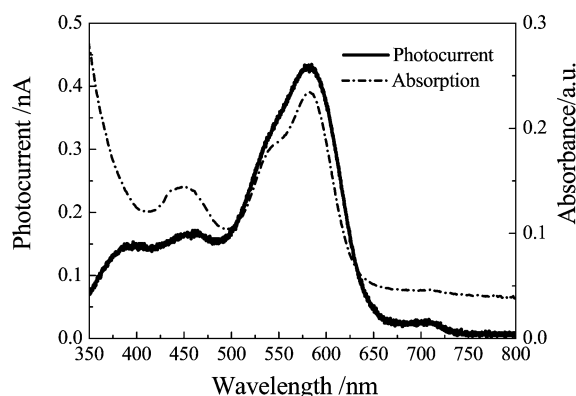


Fig. 5 Photocurrent spectra of the ITO/**C₆₀-P1**/Al device.

matches the absorption profile throughout the UV-Vis spectral region of **P1** [Fig. 3(a)]. These findings are consistent with quantitative occurrence of singlet-singlet energy transfer from the **P1** unit to the fullerene in the dyad **C₆₀-P1**. The fluorescence of the perylene moiety in the dyad is strongly quenched by the intramolecular energy transfer (*ca.* 88.4%).

The photovoltaic device consists of a metal (Al) contact on the surface of an organic film of the **C₆₀-P1** on a partially coated ITO glass. The organic layer was prepared by spin coating from chlorobenzene solution. The current-voltage characteristics of the ITO/**C₆₀-P1**/Al device under different white light intensities are depicted in Fig. 4. Under an intensity of 31 mW cm^{-2} , the short-circuit current density and the open-circuit voltage of the device are about $3.76 \mu\text{A cm}^{-2}$ and 0.67 V, respectively. The IPCE (incident photo-to-current conversion efficiency) of the ITO/**C₆₀-P1**/Al device is equal to 0.01%. The performance of the ITO/**C₆₀-P1**/Al device is not as good as that observed for some fullerene-azothiophene-based solar cells.¹³ It is well known that the photocurrent is the result of photoinduced electron transfer from the donor to the acceptor. As shown in Fig. 5, the photocurrent spectrum of the ITO/**C₆₀-P1**/Al device matches the absorption spectrum of the dyad. This indicates that the characteristic electron transportation of the perylene moiety in the dyad dominates the performance of

the device. We believe that the low efficiency of the device could result from the fact that hole transportation in the device is poor since the perylene moiety and the fullerene unit are both electron transporting domain species. Secondly, it is possible that the introduction of the pentyl group between the fullerene and the perylene may reduce charge transfer. On the other hand, the lower IPCE value is due to the fact that the device has not been optimized for layer thickness and device architectures.

Summary

In summary, a novel soluble and high thermally-stable fullerene dyad containing perylene as electronic donor has been synthesized. The electrochemical and photophysical studies in solution have revealed that there is no significant ground-state electronic interaction between the covalently bonded perylene and the fullerene sphere in **C₆₀-P1**. The photophysical study in dichloromethane solution has also shown that singlet-singlet energy transfer from the perylene unit to the fullerene in the dyad **C₆₀-P1** takes place whereas electron transfer is a minor process. A photocurrent observed for ITO/**C₆₀-P1**/Al photovoltaic devices has shown that photoinduced electron transfer from the perylene moiety to **C₆₀** does occur, but the efficiencies of the photovoltaic devices are low, namely 0.01%. We believe that the main part of the light energy absorbed by the perylene fragment is promptly conveyed to the fullerene lowest singlet excited-state, and only a small part of absorbed light is able to contribute effectively to the photocurrent. The use of new donor-linked fullerenes that absorb in the visible range will be important for a broad absorption of the sunlight and as models for the study of charge mobility and transportation.

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