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Synthesis and Photoinduced Electron-Transfer Process of a Novel Triphenylamine-Substituted Polyfluorene–C_{60} Triad

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Abstract: The photoinduced electron-transfer process of a newly prepared, soluble, π-conjugated poly[9,9-bis(4-diphenylaminophenyl)-2,7-fluorene] (PDPAF), covalently bridged, C_{60} triad (C_{60}-PDPAF-C_{60}) is described. The molecular orbital calculations revealed that the majority of the highest occupied molecular orbital (HOMO) is located on the polyfluorene entity, while the lowest unoccupied molecular orbitals (LUMO) are found to be entirely on the C_{60} entity. The excited-state electron-transfer processes were monitored by both steady-state and time-resolved emission as well as by transient absorption techniques in toluene and benzonitrile. By excitation of the polyfluorene moiety, fluorescence quenching of the singlet excited state of polyfluorene moiety was observed. The nanosecond transient spectra in near-IR region revealed the charge-separation process from the polyfluorene moieties to the C_{60} moiety through the excited singlet states of polyfluorene. The lifetimes of the charge separated states were evaluated to be 20–50 ns, depending on the solvent polarity.

Keywords: electron transfer · fullerenes · polyfluorene · triphenylamine

Introduction

Ultrafast photoinduced electron (charge) transfer from conjugated polymers, which are a subject of extensive academic and commercial interest for use as the active materials in solar cells, photodiodes, and light-emitting diodes, to molecular acceptors, for example, C_{60} and perylene, is a robust phenomenon that relies on the delocalized nature of the excited states.[1] Compared to planar electron acceptors, C_{60} can accelerate forward- and decelerates back-electron transfer due to its excellent electron-accepting properties, larger exciton diffusion length, and low reorganization energy.[2] This is beneficial for achieving substantially stabilized charge-separated states in C_{60}-based materials. In polymer/C_{60} composites, the conjugated polymer acts as a donor and the fullerene molecule acts as an acceptor. The photoexcitation of the conjugated polymer results in generation of negative charge on the fullerene and a positive hole of the polymer.[3] The resulting radical cation on the conjugated polymer backbone is expected to be highly delocalized and mobile. For the polymer/C_{60} blends, however, a partial incompatibility of C_{60} molecules and polymer matrices leads to difficulties in achieving homogeneous dispersions and ultimately phase separation at high loadings. Distortion of the conjugation and coplanarity of the polymer backbones and an increase of the interchain distance in these systems would hinder both intra- and interchain charge-transfer processes, leading to a lower device performance.[2] A convenient route to restrain phase separation is a linking π-conjugated soluble polymer or oligomer as donor and C_{60} as acceptor by means of a covalent bond. A variety of fully fledged diads and triads have been synthesized by 1,3-dipolar cycloaddition reaction of azomethine ylides.[4] Such materials systems have suddenly become very topical in recent months, since they represent a model for supramolecular ar-

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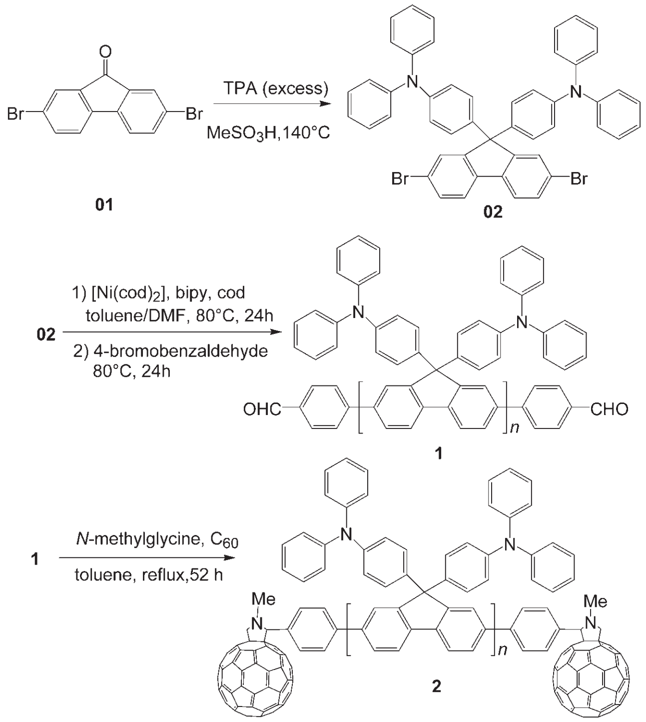
chitectures, which are potentially used in molecular nanotechnology for artificial photosynthesis and single-molecule electronics.

In this contribution, we report the photoinduced electron-transfer process of a novel soluble π-conjugated poly[9,9-bis(4-diphenylaminophenyl)-2,7-fluorene] (PDPAF), covalently bridged, C_{60} triad (**2**, C_{60}-PDPAF-C_{60}, $M_n = 8.8\times10^4$, $M_w/M_n = 1.09$), which was synthesized by the reaction between sarcosine, C_{60}, and PDPAF functionalized with two aldehyde groups (**1**, OHC-PDPAF-CHO, $M_n = 8.5\times10^4$, $M_w/M_n = 1.05$) under the 1,3-dipolar cycloaddition conditions[2] (Scheme 1). Compound **02** and polymer **1** were synthesized according to the similar synthetic method reported by Ego et al.[5] The blue-light emitting polymer PDPAF, with bulky hole-transporting triphenylamine (TPA) groups as side-chains, has shown much improved hole injection over standard poly(9,9-dialkyfluorene)s.[5] The photophysical behaviors of both polymers (**1** and **2**) have been probed by using different photophysical techniques in benzonitrile (PhCN) and toluene (TN). As a result, by excitation of the polyfluorene moiety, fluorescence quenching of the singlet excited state of polyfluorene moiety was observed. The nanosecond transient spectra in the near-IR region revealed the charge-separation process from the polyfluorene moieties to the C_{60} moiety with the light excitation. The lifetimes of the charge separated states were also evaluated in solution. The absence of intermolecular electron transfer in polymers **1** and/or **2** may be suggestive of the negligible effect of the residual impurities even if these impurities existed in the sample (as a matter of fact, our resultant polymers have already been purified several times before spectroscopic studies). The photophysical measurements were done in argon-saturated solutions to eliminate the quenching pathway caused by the molecular oxygen.



Scheme 1. Synthesis of C_{60}-PDPAF-C_{60} triad.

Results and Discussion

To gain insight into the molecular and electronic structures, computational studies were performed using the Hartree–Fock method at the 3–21G level. Based on the optimized structure of polymer **1** (Figure 1), the HOMO and HOMO−1 were found to be located dominantly on PDPAF moieties, whereas the LUMO and LUMO+1 are localized on the aldehyde moieties, suggesting the formation of OHC$^{\bullet-}$-PDPAF$^{\bullet+}$-CHO and/or OHC-PDPAF$^{\bullet+}$-CHO$^{\bullet-}$ ion–pair structures. Figure 2 shows the optimized structure and HOMO/LUMOs of polymer **2**. The radii of the ion radicals DPAF (R_+) and C_{60} (R_-) were found to be 6.0 and 4.2 Å, respectively. The center-to-center distance (R_{CC}) between C_{60} and DPAF moieties was found to be 12 Å.

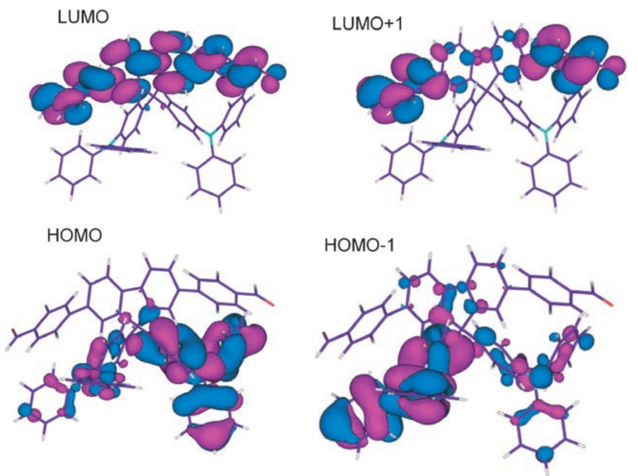


Figure 1. Optimized structures and HOMO, HOMO−1, LUMO, and LUMO+1 of OHC-PDPAF-CHO calculated with an HF(3–21G) basis set.

The redox behavior of polymers **1** and **2** was measured by differential pulse voltammetry in benzonitrile solution (Figure 3). For OHC-PDPAF-CHO, the oxidation potentials of the donor moiety (E_{ox}) were located at 474 and 700 mV versus Ag/Ag$^+$, while the reduction potential of aldehyde moieties (E_{red}) was measured as −1285 mV versus Ag/Ag$^+$. For C_{60}-PDPAF-C_{60}, the E_{ox} values were located at 438 and 668 mV, respectively, while the E_{red} values of C_{60} were located at −701 and −1132 mV. The driving forces for charge recombination ($-\Delta G_{CR}$) and charge separation ($-\Delta G_{CS}$) can be calculated based on the electrochemical data by the Rehm–Weller equations [Eqs. (1) and (2)]:[6]

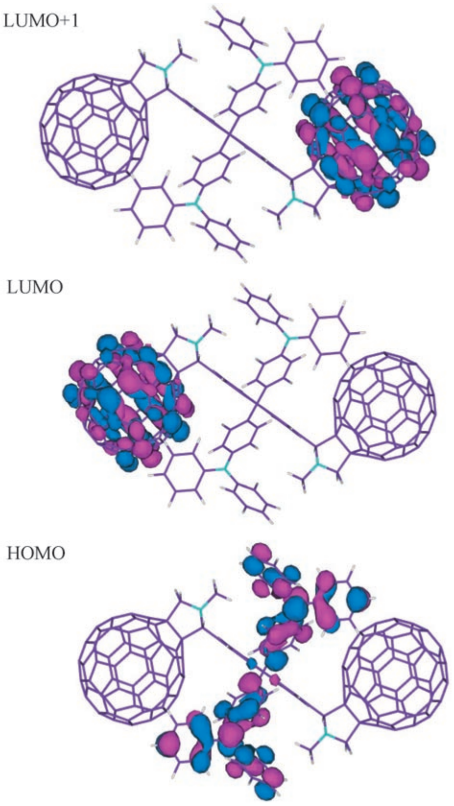


Figure 2. Optimized structures and HOMO and LUMO of C_{60}-PDPAF-C_{60} calculated with an HF(3–21G) basis set.

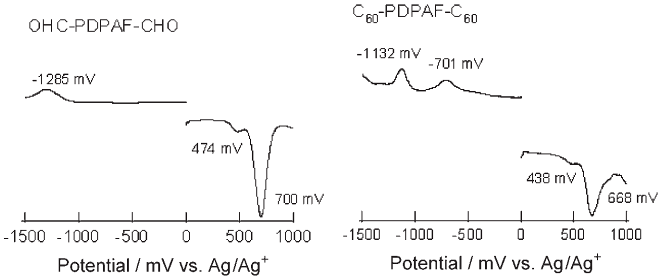


Figure 3. The redox potentials of a) OHC-PDPAF-CHO and b) C_{60}-PDPAF-C_{60} in benzonitrile by applying differential pulse voltammetry technique.

$$-\Delta G_{\mathrm{CR}} = E_{\mathrm{ox}} - E_{\mathrm{red}} - \Delta G_{\mathrm{S}} \tag{1}$$

$$-\Delta G_{\mathrm{CS}} = \Delta E_{0-0} - (-\Delta G_{\mathrm{CR}}) \tag{2}$$

Here, $\Delta E_{0\text{-}0}$ is the energy of the 0–0 transition between the lowest excited state and the ground state of the donor moiety, which evaluated as 2.50 eV from the fluorescence peak at 495 nm. ΔGs refers to the static energy calculated as $\Delta G_{\mathrm{S}} = -e^2/(4\pi\varepsilon_0\varepsilon_{\mathrm{R}}R_{\mathrm{CC}})$, in which the terms e, ε_0 and ε_{R} are defined as elementary charge, vacuum permittivity, and static dielectric constant of the solvent used for rate measurements and redox potential measurements, respectively. The driving force for the charge separation process (ΔG_{CS}) of **1** and **2** in benzonitrile were calculated, based on the first oxidation and reduction potentials, as −0.80 and −1.42 eV, respectively. The negative ΔG_{CS} value suggests that the charge-separation process via ^{1}PDPAF* is exothermic and favorable in benzonitrile. However, the calculated energy value of the charge-separated state in toluene may not be completely reliable, since the Weller model [Eq. (3)], in which static dielectric constant of the solvent used for rate measurements (ε_{S} in toluene) is different from ε_{R} in benzonitrile, is likely to be oversimplified.

$$\begin{aligned}\Delta G_{\mathrm{S}} =& e^2/(4\pi\Delta\varepsilon_0)[(1/2R_+ + 1/2R_- - 1/R_{\mathrm{CC}})1/\varepsilon_{\mathrm{R}} - \\ & (1/2R_+ + 1/2R_-)1/\varepsilon_{\mathrm{S}}]\end{aligned} \tag{3}$$

The driving force for the charge separation process of the resulting polymer **2** was estimated as −0.60 eV.

The UV/Vis absorption spectra of polymers **1** and **2** in benzonitrile are similar due to the low C_{60} content in polymer **2**. The weak absorption in the visible region can be typically assigned to the fullerene moiety. The fluorescence measurements of these two polymers were carried out in benzonitrile and toluene by applying 400 nm as excitation wavelength (Figure 4). The intensity of the emission band of **1** at 495 nm was quenched as compared to PDPAF suggesting intramolecular quenching from PDPAF to aldehyde groups. However, the intensity of the emission band of **2** was significantly quenched as compared to **1** owing to the presence of C_{60}. Such intramolecular quenching process may involve energy and/or electron transfer between the excited singlet states of the PDPAF moiety and the C_{60} moiety. It may also be mentioned here that changing the solvent from toluene to a more polar benzonitrile increased the overall quenching efficiency. In benzonitrile, the fluorescence time profile of **1** exhibited a bi-exponential decay with lifetimes of 136 ps (33 %) and 2400 ps (67 %). The lifetime of the short-lived component suggests the occurrence of intramolecular charge separation from the singlet-excited PDPAF to the acceptor entity, yielding OHC$^{\bullet-}$-PDPAF$^{\bullet+}$-CHO ion-pair

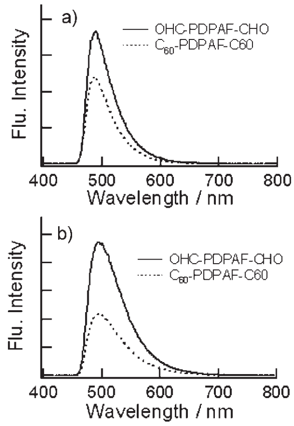


Figure 4. Steady-state fluorescence spectra of OHC-PDPAF-CHO and C_{60}-PDPAF-C_{60} in a) toluene and b) benzonitrile.

radicals. In case of **2**, the fluorescence decay of PDPAF moiety shows almost the same decay lifetime indicating that both the aldehyde and C_{60} moieties act as electron acceptor. In nonpolar solvent toluene (Figure 5), the fluorescence lifetime was observed as 113 ps (26 %) and 2400 ps (74 %). The rate constants (k_{CS}) and quantum yields (Φ_{CS}) for the charge separation process were calculated from Equations (4) and (5).

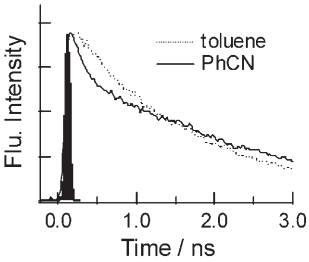


Figure 5. Fluorescence decay profiles monitored at 400–600 nm region of C_{60}-PDPAF-C_{60} in toluene and benzonitrile.

$$k_{CS} = (1/\tau_{sample})-(1/\tau_{reference}) \quad (4)$$

$$\Phi_{CS} = (1/\tau_{sample})-(1/\tau_{reference})/(1/\tau_{sample}) \quad (5)$$

From the initial quick decay, the k_{CS} of **2** are evaluated as $8.5\times10^{9}\,s^{-1}$ (in benzonitrile) and $7.2\times10^{8}\,s^{-1}$ (in toluene). The Φ_{CS} values are evaluated as 0.96 (in benzonitrile) and 0.65 (in toluene).

The nanosecond transient absorption technique was performed to monitor the charge recombination process by applying 355 nm with 6 ns laser pulses. As shown in Figure 6a, the transient spectra of **1** in argon-saturated benzonitrile show the absorption band at 630 nm due to the excited triplet state ^{3}PDPAF*. The observed broad absorption band in the near-IR region (900–1600 nm), which might be assigned to the radical cation PDPAF$^{\bullet+}$,[7] suggests: 1) the photo-ejection of the polymer in polar solvent generating the radical cation of the donor moiety and/or 2) the charge separation from the donor PDPAF moiety to the aldehyde groups yielding the charge-separated state OHC$^{\bullet-}$-PDPAF$^{\bullet+}$-CHO, which is in agreement with molecular orbital structures as shown earlier. From the decay of the transient band at 1380 nm, the rate of the charge-recombination (k_{CR}) was evaluated as $3.0\times10^{7}\,s^{-1}$.

In nonpolar toluene (Figure 6b), the nanosecond transient absorption spectra of **1** are quite similar to that in benzonitrile, showing a weak broad absorption peak in the near-IR region with fast decaying peak of the radical cation of the donor moiety around 1380 nm ($k_{CR}=7.1\times10^{7}\,s^{-1}$) in addition to the slow decaying 620 nm band of the triplet ^{3}PDPAF*. Since the photo-ejection process in toluene is unlikely to occur, the charge-separation process is expected to be dominant in benzonitrile and toluene. The assignment of the broad transient absorption in the near-IR region (900–1600 nm) as the radical cation of the donor moiety was supported by recording the nanosecond transient spectra of mixture of C_{60} and OHC-PDPAF-CHO in argon-saturated benzonitrile (Figure 7). The spectra revealed the same broad band of the radical cation in the IR region, besides the characteristic peak of $C_{60}^{\bullet-}$ at 1090 nm.

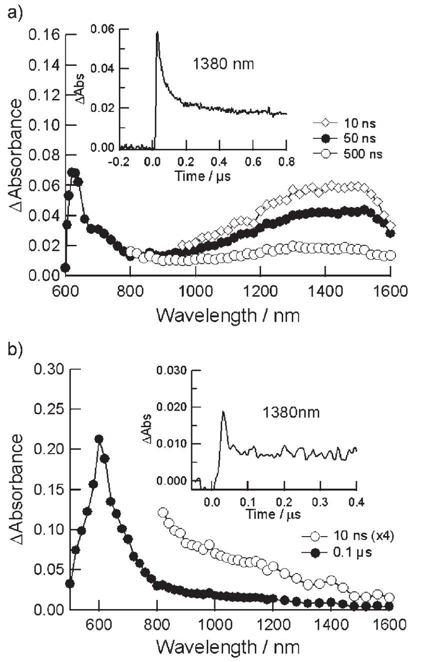


Figure 6. Transient absorption spectra obtained by 355 nm laser light of OHC-PDPAF-CHO in a) argon-saturated benzonitrile and b) toluene. Inset: time profiles.

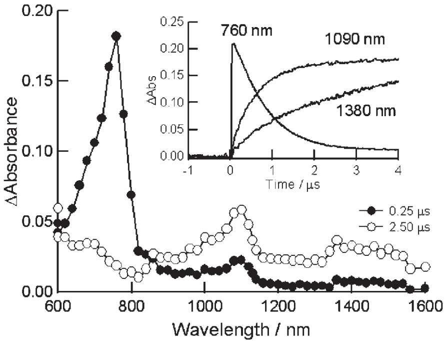


Figure 7. Transient absorption spectra obtained by 355 nm laser light of mixture systems of C_{60} and OHC-PDPAF-CHO in argon-saturated benzonitrile. Inset: time profiles.

The nanosecond transient absorption spectra of polymer **2** were observed in argon-saturated benzonitrile (Figure 8a), and exhibited the characteristic triplet–triplet absorption bands of PDPAF and C_{60} at 630 and 720 nm, respectively. The peak of radical cation of PDPAF (PDPAF$^{\bullet+}$) moiety was clearly observed in the range of 900–1600 nm, while the peak of radical anion of C_{60} ($C_{60}^{\bullet-}$) at 1020 nm[8] was in over-

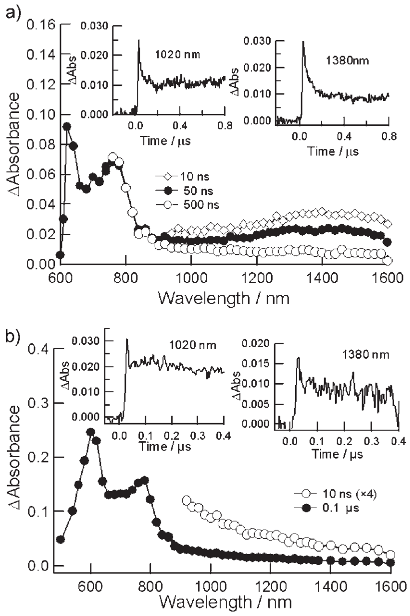


Figure 8. Transient absorption spectra obtained by 355 nm laser light of C_{60}-PDPAF-C_{60} in a) argon-saturated benzonitrile and b) toluene. Inset: time profiles.

lap with that of PDPAF$^{\bullet+}$. The slow decay part of the time profiles of **2** in the 900–1600 nm region began to decay very fast by addition of oxygen into solution, suggesting that the slow decay might be attributed to the tail of the triplet states. The absorption peak of the PDPAF$^{\bullet+}$ moiety at 1380 nm was employed to determine the charge-recombination rate constant (k_{CR}) of the charge-separated state. From the k_{CR} value ($1.9\times10^{7}\,s^{-1}$), the lifetime of the radical ion-pair (τ_{RIP}) in benzonitrile was evaluated as 53 ns. In toluene (Figure 8b), the lifetime of ion-pair was evaluated as <20 ns.

In conclusion, we have synthesized the covalently bridged conjugated-polymer/C_{60} triad. The steady-state and time-resolved emission, and transient absorption experiments revealed the occurrence of electron transfer mainly from the PDPAF to the fullerene entity in both benzonitrile and toluene. Further studies on the photovoltaic and nonlinear optical properties of C_{60}-PDPAF-C_{60} are currently in progress.

Experimental Section

General: All chemicals were purchased from Aldrich and used without further purification. Organic solvents were purified, dried and distilled under dry nitrogen. The operations for synthesis prior to the termination reaction were carried out under purified argon. The UV/Vis spectral measurements were carried out with a Jasco model V570 DS spectrophotometer. Steady-state fluorescence spectra were measured on a Shimadzu RF-5300 PC spectrofluorophotometer equipped with a photomultiplier tube in the 700–800 nm region. The sample for the fluorescence measurement was dissolved in the dry toluene or benzonitrile, filtered, transferred to a long quartz cell, and then capped and bubbled with highly pure argon(without O_2 and moisture) for at least 15 min before measurement. The ^{1}H NMR spectra were performed with a LAMBDA 400 MHz spectrometer in $CDCl_3$ solvent. Gel permeation chromatography (GPC) trace of the resultant polymer was recorded on a LC-908 Recycling Preparative HPLC (Japan Analytical Industry C., Ltd). THF was used as the eluent, and linear polystyrene was used as the standard.

The redox values were measured by using the differential pulse voltammetry (DPV) technique by applying BAS CV-50W Voltammetric Analyzer (Japan). A platinum disk electrode was used as working electrode, while a platinum wire served as a counter electrode. An Ag/AgCl electrode was used as a reference electrode. All measurements were carried out in different solvents containing 0.1 M tetrabutylammonium percholarate [$(n\text{-}C_4H_9)_4NClO_4$] as a supporting electrolyte. The scan rate used was $0.1\,V\,s^{-1}$.

The lifetime measurements were measured by a single-photon counting method by using a second harmonic generation (SHG, 400 nm) of Ti:sapphire laser (Spectra-Physica, Tsunami 3950-L2S, 1.5 ps fwhm) and a streakscope (Hamamatsu Photonics) equipped with a polychromator (Action Research, SpectraPro 150) as an excitation source and a detector, respectively. Lifetimes were evaluated with software attached to the equipments. The nanosecond transient absorption measurements in the near-IR region were measured by means of laser-flash photolysis; 355 nm light from a Nd:YAG laser (Spectra-Physics and Quanta-Ray GCR-130, 6 ns fwhm) was used as an excitation source. For transient absorption spectra in the near-IR region (600–1600 nm), monitoring light from a pulsed Xe-lamp was detected with Ge-avalanche photodiode module (Hamamatsu Photonics). All the samples in a quartz cell (1×1 cm) were deaerated by argon bubbling through the solution for 20 min.

Synthesis of polymer 2 [C_{60}-PDPAF-C_{60}]: Polymer **1** (300 mg), C_{60} (30 mg) and *N*-methylglycine (20 mg) were dissolved in anhydrous toluene (70 mL), and the mixture was then refluxed under argon for 52 h. After the termination of reaction, methanol (400 mL) was poured into the stirred reaction mixture at room temperature to give the crude product. This product was extracted with THF (40 mL) for 24 h in a Soxhlet apparatus. Methanol (100 mL) was then added into the extractant to afford the polymer-bridged C_{60} triad. $M_n=8.8\times10^4$, $M_w/M_n=1.09$; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta=2.26$ (s, NCH_3), 4.23–4.40 (m, NCH_2), 4.53 (s, NCH), 6.85–7.22 (m, aryl H), 7.45–7.70 ppm (m, fluorenyl H); IR (KBr): $\tilde{\nu}=2964$ (s), 2908 (m), 2361 (m), 2342 (m), 1734 (m), 1592 (m), 1494 (m)s, 1426 (w),1416 (m), 1325 (m), 1262 (s), 1095vs, 1028vs, 865 (s), 800 (s), 753 (m), 696 (ms), 634 (w), 617 (w), 577 (w), 527 (m), 502 cm^{-1} (w); for pure C_{60}: $\tilde{\nu}=526$ (s), 575 (ms), 1181 (m), 1427 cm^{-1} (m).

Acknowledgements

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