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Synthesis and characterization of new C_{60}–PPV dyads containing carbazole moiety

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Abstract

New C_{60} covalently linked PPV derivatives containing carbazole moiety poly{(2,5-di-pentoxyl-phenylene)-1,4-diylvinylene-3,6-[9-(1-azafulleroid-propyl)carbazolenevinylene]} (PPV-AFCAR) were synthesized and characterized. The polymers containing different percentage of C_{60} were obtained through the percentage of azido unit being controlled by the initial feed ratio. Cyclic voltametric analysis showed that the electronic characteristic remained while it covalently attached to polymer by the cycloaddition reaction. The fluorescences of PPV moieties were strongly quenched due to the presence of fullerene. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polyphenylenevinylene; Fullerene; Synthesis

1. Introduction

With its unusual electrochemical and electronic properties, the fullerene C_{60} has been an attractive building block for supramolecular assemblies and new advanced materials [1–4]. In recent years, photovoltaic cells using conducting conjugated polymers such as polyphenylenevinylene (PPV) and polythiophene blended with fullerene and modified fullerene have gained much attention [5–7]. The higher conversion efficiencies, around 1%, have been reported [8], being one of the most outstanding applications of fullerenes. Composite films made by simple mixing of conducting polymers and C_{60} in different molar ratios have been employed during these investigations. However, the drawback is that the C_{60} tends to form crystalline, which makes the donor and acceptor molecules incompatible and tend to phase separation. This results in poor homogeneity and low optical quality of the films. These questions will be overcome with the use of chemically connected donor–acceptor molecules. Some covalent C_{60} derivatives bearing electron donors have been synthesized in order to obtain efficient intramolecular energy or electron transfer and to generate long-lived charge separated states [9,10]. The intramolecular charge transfer interaction has been claimed in some cases. To the best of our knowledge, the conductive conjugated polymer containing C_{60} moiety has not been reported, although many covalent C_{60} derivatives have been synthesized. In addition, the polymers containing carbazole have good electro-photoactive properties, which make them as suitable materials for light-emitting diodes and other optoelectronic devices [11,12]. We and other group have found that poly(*N*-vinylcarbazole) (PVK) doped with C_{60} or C_{60} derivatives can improve its charge-generation efficiency [13,14]. The most likely site in PVK is the carbazole moiety. Here we report the synthesis and characterization of novel C_{60}–PPV dyads in which the carbazole-containing PPV is as donor part and C_{60} is as acceptor moiety.

2. Experimental part

2.1. Materials and measurements

1,4-Bis(pentoxy)-benzene **1** [15] and *N*-(3-bromopropyl)-carbazole **4** [16] were prepared according to literature procedure. All solvents were redistilled before use. NMR spectra were collected on either Varian WM-300 (300 MHz) or Varian XL-200 (200 MHz) spectrometers. Mass spectra were obtained on Bruker BIFLEXIII spectrometer. FT-IR spectra were measured on a Bruker EQUINOX55 spectrometer. The UV–vis and fluorescence spectra were obtained on a Hitachi U-3010 and Hitachi F-4500 spectrometer,

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respectively. Gel permeation chromatography (GPC) analyses were conducted with either Walter 2410 Model 515 HPLC or PL-GPC-210 system using polystyrene as the standard and THF as the eluant. Thermal gravimetric analyses (TGA) were carried out using Perkin–Elmer 7 series thermal analysis system. Cyclic voltammograms were recorded on a CHI voltametric analyzer at room temperature in CH_2Cl_2 containing tetrabutylammonium hexafluorophosphate ($TBAPF_6$) with a scan rate of 50 mV s^{-1}.

2.2. Synthesis of 1,4-bis(bromomethyl)-2,5-bis(pentoxy)-benzene **2**

To a mixture of compound **1** (3.8 g, 15.1 mmol) and paraformaldehyde (0.93 g, 31 mmol) in 50 ml of acetic acid, 33 wt% HBr in acetic acid (5.5 ml, 32.2 mmol) was added dropwise under stirring. Subsequently, the mixture was stirred at 60–70 °C for 2 h, and then cooled to room temperature. The resulting solution was poured into 400 ml of H_2O, and saturated solution of K_2CO_3 was added to adjust pH value in the range of 5–6. After filtration, washing with H_2O and recrystallization from EtOH, slight yellow crystal of 5.03 g was obtained (76.0%, mp 79–80 °C). FT-IR (KBr pellet, cm^{-1}): 2953, 2930, 2870, 1511, 1230; ^1H NMR ($CDCl_3$, ppm): δ 6.85 (s, 2H), 4.53 (s, 4H), 3.98 (t, 4H), 1.81 (q, 4H), 1.47 (m, 4H), 1.36 (m, 4H), 0.93 (t, 6H); MS (EI): 434 (M); Anal. calcd for $C_{18}H_{28}Br_2O_2$: C, 49.56; H, 6.47. Found: C, 49.57; H, 6.55%.

2.3. Synthesis of 1,4-bis(triphenylphosphonionmethyl)-2,5-bis(pentoxy)-benzene dibromide **3**

A solution of 325.5 mg (0.75 mmol) of compound **2** and 393 mg (1.5 mmol) of PPh_3 in 10 ml of toluene was refluxed for 6 h. The precipitate formed was filtered off and dried at vacuum at room temperature for 6 h to give 567 mg of white powder (78.9%). FT-IR (KBr pellet, cm^{-1}): 2951, 2864, 1510, 1437, 1220, 1111; ^1H NMR ($CDCl_3$, ppm): δ 7.57–7.78 (br, 32H), 5.21 (d, $J = 12.15$ Hz, 4H), 2.98 (t, $J = 5.13$ Hz, 4H), 1.02–1.21 (m, 12H), 0.82 (t, $J = 7.26$ Hz, 6H); MS (MALDI-TOF): 798 (M-2Br); Anal. calcd for $C_{54}H_{58}Br_2P_2O_2{\cdot}2H_2O$: C, 66.80; H, 6.02. Found: C, 66.76; H, 5.79%.

2.4. Synthesis of N-(3-chloropropyl)-3,6-diformyl-carbazole **5**

To 19.1 g (0.26 mol) of *N*,*N*-dimethylformamide cooled to 0 °C, 19.8 g (0.13 mol) phosphoryl chloride were added dropwise, and then the mixture was kept in room temperature to react for 1 h. To the stirred mixture, 1.92 g (6.7 mmol) of *N*-(3-bromopropyl)-carbazole **4** were added. After standing for 36 h at 90 °C, the mixture was poured into 150 ml of water, the precipitate was filtered off. The crude product was recrystallized from chloroform/*n*-hexane to give a yellow powder of 1.0 g, yield 50.0%. FT-IR (KBr pellet, cm^{-1}): 2961, 2821, 1683, 1593, 1488; ^1H NMR ($CDCl_3$, ppm): δ 10.17 (s, 2H), 8.72 (s, 2H), 8.12 (d, $J = 8.37$ Hz, 2H), 7.66 (d, $J = 8.58$ Hz, 2H), 4.63 (t, $J = 6.60$ Hz, 2H), 3.55 (q, $J = 5.67$ Hz, 2H), 2.38 (m, 2H); MS (EI): 299 (M); Anal. calcd for $C_{17}H_{14}ClNO_2{\cdot}0.33H_2O$: C, 66.78; H, 4.81; N, 4.58. Found: C, 66.79; H, 4.48; N, 4.38%.

2.5. N-(3-azidopropyl)-3,6-diformyl-carbazole **6**

To a solution of 32.5 mg (0.5 mmol) of NaN_3 in 10 ml of DMSO, 149.5 mg (0.5 mmol) of compound **5** was added. After refluxing for 12 h at 60 °C, the mixture was poured into 30 ml of water, the precipitate was filtered off. The crude product was recrystallized from EtOH to give a yellow powder of 120.0 mg, yield 65.4%. FT-IR (KBr pellet, cm^{-1}): 2934, 2824, 2098, 1682, 1627, 1595, 1486; ^1H NMR ($CDCl_3$, ppm): δ 10.16 (s, 2H), 8.70 (s, 2H), 8.11 (d, $J = 8.61$ Hz, 2H), 7.60 (d, $J = 8.58$ Hz, 2H), 4.51 (t, $J = 6.64$ Hz, 2H), 3.35 (t, $J = 6.15$ Hz, 2H), 2.18 (t, $J = 6.54$ Hz, 2H); MS (EI): 306 (M); Anal. calcd for $C_{17}H_{14}N_4O_2$: C, 66.65; H, 4.61; N, 18.29. Found: C, 66.31; H, 4.68; N, 17.93%.

2.6. Synthesis of PPV-ACAR (**I**)

To a solution of 30.6 mg (0.1 mmol) of compound **6** and 96 mg (0.1 mmol) of compound **3** in 15 ml of EtOH and 20 ml of $CHCl_3$, excess fresh EtONa/EtOH was added. The mixture was stirred at room temperature for 24 h. The resulting precipitate was filtered off. The crude product was redissolved in 5 ml of $CHCl_3$ and poured into 30 ml of methanol. The precipitate was filtered off and dried at room temperature for 6 h to give 25.8 mg of yellow powder (46.9%). FT-IR (KBr pellet, cm^{-1}): 2931, 2869, 2097, 1597, 1489, 966; ^1H NMR ($CDCl_3$, ppm): δ 7.73–8.26 (br, 2H), 7.21–7.51 (br, 8H), 6.55–7.05 (br, 2H), 3.83–4.40 (br, 6H), 3.12–3.33 (br, 2H), 1.88–2.16 (br, 8H), 1.33–1.72 (br, 6H), 0.82–1.01 (br, 6H); ^{13}C NMR ($CDCl_3$, ppm): 144.3, 135.0, 133.3, 132.2, 130.0, 128.6, 128.1, 127.5, 124.1, 109.3, 108.9, 69.6, 48.3, 40.1, 29.6, 28.9, 28.1, 22.5, 14.1; GPC (THF): M_w 2360, M_n 1730, M_z 3380, PDI 1.36; UV–vis λ_{max} ($CHCl_3$, nm): 241, 276, 299, 345; FL λ_{max} ($CHCl_3$, nm): 469, 491.

2.7. Synthesis of PPV-AFCAR (**I**)

A solution of 5.6 mg of PPV-ACAR (**I**) and 7.2 mg (0.01 mmol) of C_{60} in 20 ml of chlorobenzene was refluxed for 24 h. After removal of the solvent, the crude reaction mixture was redissolved in dichloroethane and filtered to remove unreacted C_{60}. Precipitation into hexane afforded 6.5 mg of C_{60}-polymer PPV-AFCAR as dark brown powders with a yield of 50.8%. FT-IR (KBr pellet, cm^{-1}): 2923, 2852, 1597, 1491, 966, 527; ^1H NMR ($(CD)_2Cl_4$, ppm): δ 7.19–8.24 (br, 12H), 3.10–4.55 (br, 8H), 0.78–2.08 (br, 20H); GPC (THF): M_w 2300, M_n 1130, M_z 4980,

PDI 2.03; UV–vis λ_{max} ($CHCl_3$, nm): 228, 260, 329, 345; FL λ_{max} ($CHCl_3$, nm): 469, 491.

2.8. Synthesis of PPV-ACAR (*II*)

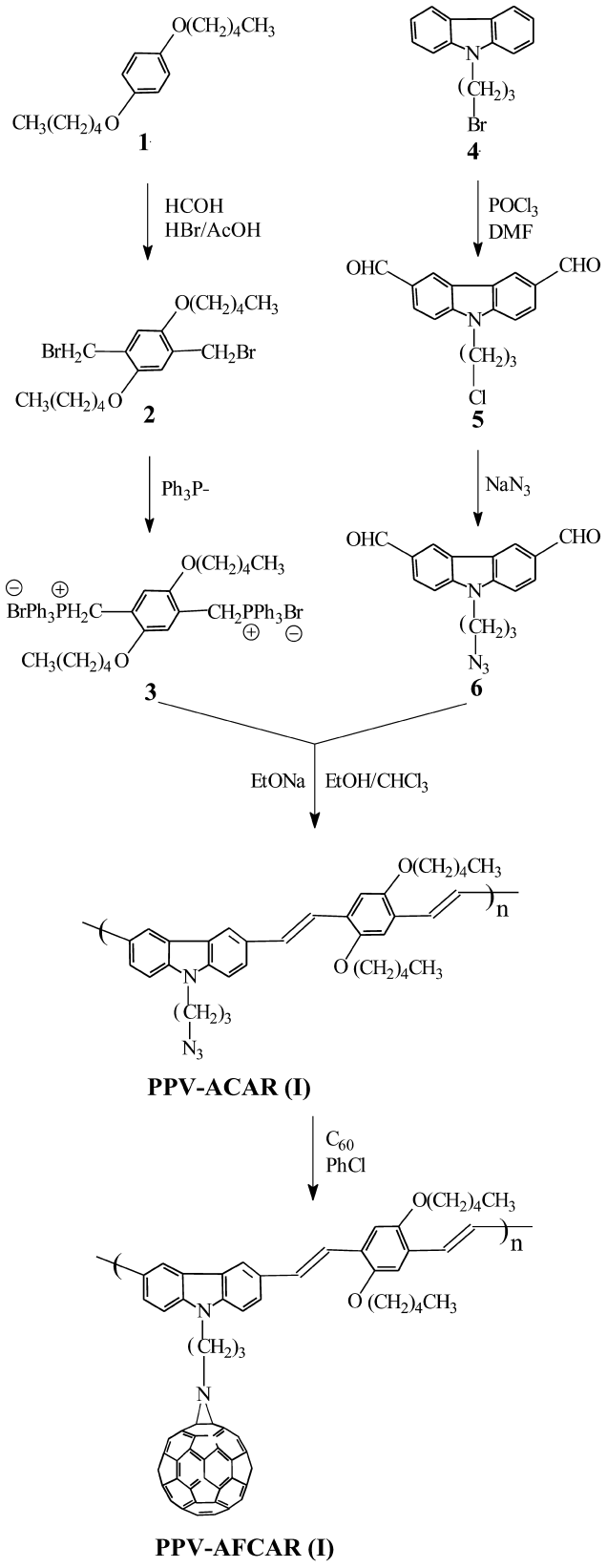
To a solution of 0.2 mmol of compound **3**, 0.04 mmol of compound **6** and 0.16 mmol of terephthalaldehyde in 10 ml of EtOH and 30 ml of $CHCl_3$, excess fresh EtONa/EtOH was added. The mixture was stirred at room temperature for 24 h. The solvent was removed. The crude product was redissolved in 1 ml of $CHCl_3$ and poured into 10 ml of methanol. The precipitate was filtered off and dried at room temperature for 6 h to give 45.0 mg of yellow powder (54.9%). FT-IR (KBr pellet, cm^{-1}): 2954, 2931, 2096, 1494, 1204, 966, 805; ^1H NMR ($CDCl_3$, ppm): δ 6.85–8.15 (br), 6.40–6.80 (br), 3.82–4.30 (br), 3.40–3.80 (br), 1.20–2.20 (br), 0.80–1.10 (br); GPC (THF): M_w 4220, M_n 1820, M_z 8620, PDI 2.32; UV–vis λ_{max} ($CHCl_3$, nm): 449; FL λ_{max} ($CHCl_3$, nm): 516, 550.

2.9. Synthesis of PPV-AFCAR (*II*)

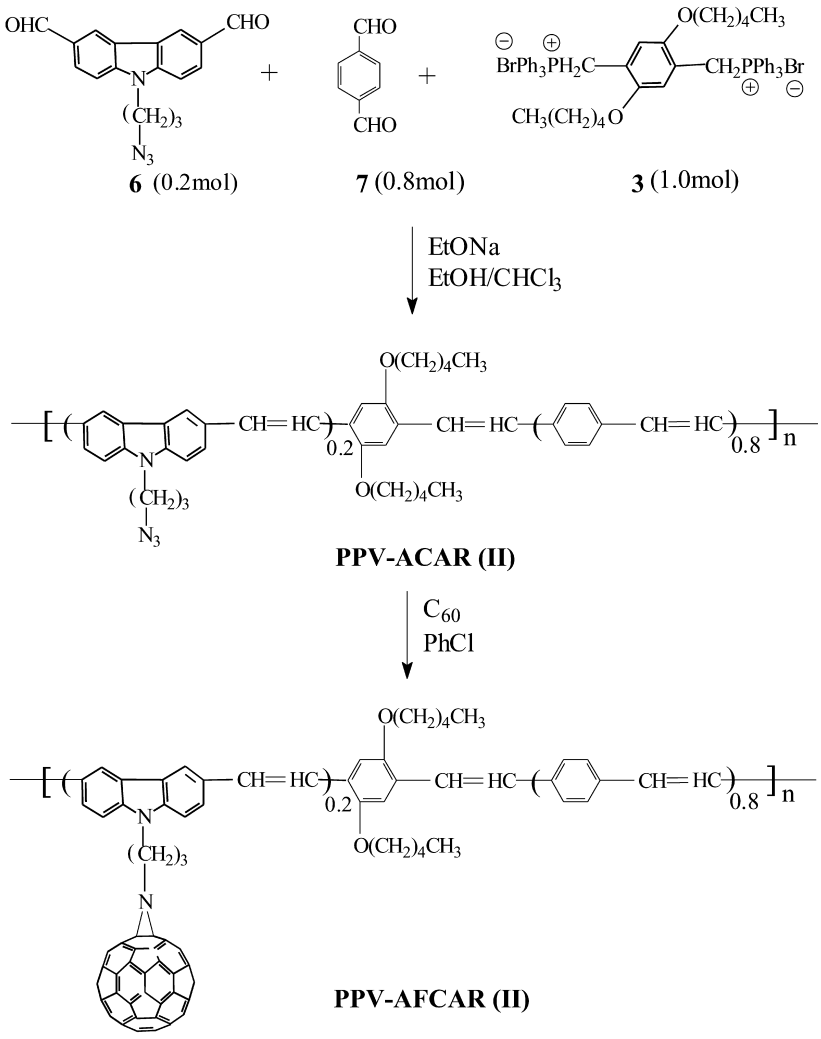
A solution of 20.5 mg of PPV-ACAR (**II**) and 7.2 mg (0.01 mmol) of C_{60} in 30 ml of chlorobenzene was refluxed for 24 h. After removal of the solvent, the crude reaction mixture was redissolved in dichloroethane and filtered to remove unreacted C_{60}. Precipitation into hexane afforded 15.0 mg of C_{60}-polymer PPV-AFCAR (**II**) as dark brown powders with a yield of 54.0%. FT-IR (KBr pellet, cm^{-1}): 2952, 2926, 1493, 1203, 964, 527; ^1H NMR ($CDCl_3$, ppm): δ 6.90–7.80 (br), 6.30–6.80 (br), 3.90–4.15 (br), 3.40–3.80 (br), 1.37–2.20 (br), 0.80–1.05 (br); GPC(THF): M_w 3810, M_n 1860, M_z 6770, PDI 2.05; UV–vis λ_{max} ($CHCl_3$, nm): 330, 444; FL λ_{max} ($CHCl_3$, nm): 516, 550.

3. Results and discussion

Scheme 1 describes the chemical structure and synthetic route of the dopant PPV-AFCAR (**I**). The synthetic approach to prepare PPV-AFCAR (**I**) relied on the cycloaddition reaction of azide group with C_{60}, pioneered by the Wudl group [17,18]. This methodology had proven to be a simple and versatile method for the synthesis of polymers containing fullerene moiety due to the ease of preparation of azide-containing polymers, the lack of cross-linking and the retention of the fullerenes electronic properties [19]. The starting azido-polymer poly{(2,5-di-pentoxyl-phenylene)-1,4-diylvinylene-3,6-[9-(1-azido-propyl)carbazolenevinylene]} [PPV-ACAR (**I**)] was synthesized by the well-known Wittig reaction of compound **3** with compound **6** under sodium ethoxide in chloroform/ethanol. Then, a mixture of PPV-ACAR (**I**) and 1 equiv. of C_{60} were reacted in chlorobenzene at reflux to afford the PPV-AFCAR (**I**) as a dark brown powder. In order to obtain the polymer PPV-AFCAR (**II**) containing different percentage of C_{60}, the azido-polymer PPV-ACAR (**II**) was synthesized as shown



Scheme 1.



Scheme 2.

in Scheme 2, with the percentage of azido unit being controlled by the initial feed ratio.

The PPV-AFCAR (**I**) and (**II**) were partially soluble in common organic solvents such as $CHCl_3$ and THF, and completely soluble in tetrachloroethane. The solubility behaviors were similar to precursor polymers PPV-ACAR (**I**) and (**II**) unlike C_{60}. This made them good processability for fabricating devices.

Compared with the PPV-ACAR (**I**), the FT-IR spectroscopy of PPV-AFCAR (**I**) showed that a strong band at 2097 cm^{-1} for the azide group had completely disappeared and a new strong absorption at 527 cm^{-1} for the C_{60} appeared. The molecular weights of PPV-ACAR (**I**) and PPV-AFCAR (**I**) were determined by a waters 2410 GPC instrument with polystyrene as standard, and those of PPV-ACAR (**II**) and PPV-AFCAR (**II**) were determined by a waters 2410 GPC instrument. The weight-average molecular weight (M_w) were 2357 and 2307 for PPV-ACAR (**I**) and PPV-AFCAR (**I**), and 4220 and 3810 for PPV-ACAR (**II**) and PPV-AFCAR (**II**), respectively (Fig. 1). As can be seen, almost no shift in the peak maximum occurred comparing PPV-ACAR (**I**) to PPV-AFCAR (**I**) and PPV-ACAR (**II**) to PPV-AFCAR (**II**). The molecular weights of polymers containing C_{60} were lower than those of precursor polymer without C_{60}. In fact, polymers PPV-AFCAR (**I**) and (**II**) were partially soluble in THF, their actual molecular weights should be higher than the measured values because the insoluble parts possessed higher molecular weights.

The weight percentage of C_{60} in PPV-AFCAR (**I**) and (**II**) were obtained using the quantitative UV–vis method (comparing PPV-ACAR (**I**) and (**II**) with pure C_{60}), which were found to be 68.8% for PPV-AFCAR (**I**) and 19.9% for PPV-AFCAR (**II**) (Fig. 2). The thermal properties of PPV-AFCAR (**I**) and (**II**) were investigated by TGA, which showed good thermal stability up to 350 °C, a small amount of weight loss occurred in the 380–460 °C.

The UV–vis spectra of PPV-AFCAR (**I**) corresponded to the two components of C_{60} moiety and PPV unit and showing the three characteristic absorption bands in the range of 200–330 nm as well as a very weak band at

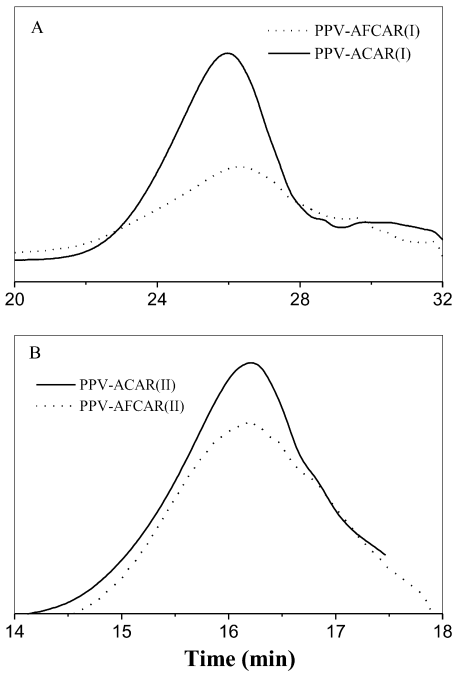


Fig. 1. The GPC traces for the PPV-AFCAR (**I**) and (**II**) and the starting azido-polymers PPV-ACAR (**I**) and (**II**) in THF.

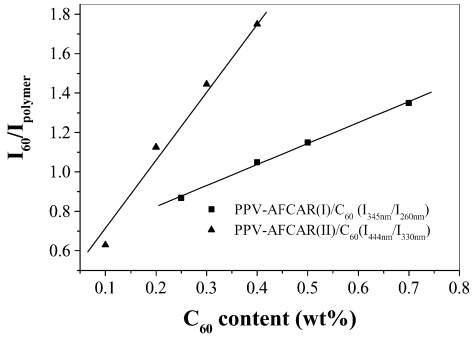


Fig. 2. Calibration curve for determining C_{60} contents of C_{60}-containing PPV-AFCAR (**I**) and (**II**) using the intensity ratios of the absorption bands of C_{60} and PPV unit.

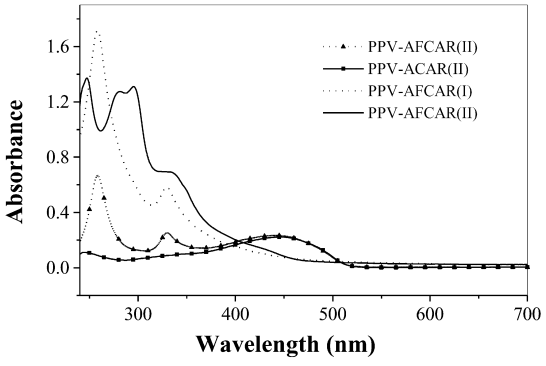


Fig. 3. The UV–vis spectra of the PPV-AFCAR (**I**) and (**II**) and the starting azido-polymers PPV-ACAR (**I**) and (**II**) in $CHCl_3$ (c: 1.0×10^{-5} M).

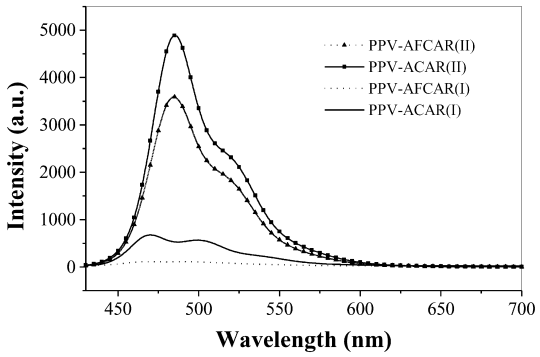


Fig. 4. The FL spectra of the PPV-AFCAR (**I**) and (**II**) and the starting azido-polymers PPV-ACAR (**I**) and (**II**) in $CHCl_3$ (c: 1.0×10^{-5} M).

345 nm corresponding to the $\pi-\pi^*$ transition of PPV conjugated unit. The UV–vis spectra of PPV-AFCAR (**II**) showed two absorption bands at 330 nm corresponding to C_{60} moiety and 444 nm corresponding to the $\pi-\pi^*$ transition of PPV conjugated unit (Fig. 3). In $CHCl_3$ solution, precursor PPV-ACAR (**I**) displayed fluorescence maximum at 469 and 491 nm, PPV-ACAR (**II**) displayed at 516 and 550 nm. The PPV-AFCAR (**I**) and (**II**) exhibited emission spectra with characteristic features of the PPV unit, however, the luminescence was strongly quenched. The related fluorescent quantum yield of precursor PPV-ACAR (**I**) was 0.444 and that of PPV-AFCAR (**I**) was 0.00551. This quenching was due to the photoinduced electron transfer from PPV unit to C_{60} moiety (Fig. 4).

Cyclic voltametric analysis (Fig. 5) in CH_2Cl_2 showed three reversible waves with cathodic potentials (E_{pc}) at −0.673, −1.066 and −1.511 V versus SCE for PPV-AFCAR (**I**), −0.656, −1.049 and −1.491 V for PPV-AFCAR (**II**) and −0.632, −1.027 and −1.484 V versus SCE for C_{60}. These reductions were all based on the fullerene core. The electrochemical reduction of PPV-AFCAR (**I**) and (**II**) were slightly negative than those of the corresponding reductions of C_{60} itself due to the donor ability of the PPV bone containing carbazole moiety. This showed the fullerenes electronic properties

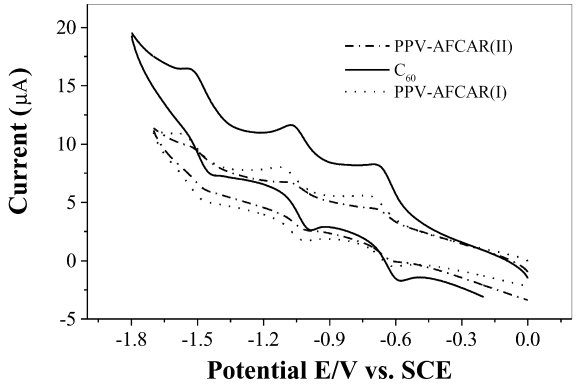


Fig. 5. Cyclic voltammograms in CH_2Cl_2 containing 1.0 M $TBAPF_6$ at room temperature of PPV-AFCAR (**I**) and (**II**) and C_{60}. Scan rate: 50 V s^{-1}.

were almost remained after it was connected to polymer by the cycloaddition reaction.

4. Conclusion

We have synthesized and characterized new C_{60} covalently linked PPV derivatives PPV-AFCAR (**I**) and (**II**). The works of time-dependent measurements and fabrication of photovoltaic cells are now underway.

Acknowledgements

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References

[1] Hirsch A. Adv Mater 1993;5:859.
[2] Echegoyen L, Echegoyen LE. Acc Chem Res 1998;31:593.
[3] Prato M. J Mater Chem 1997;7:1097.
[4] Li Y, Mao Z, Xu J, Yang J, Guo Z, Zhu D, Li J, Yin B. Chem Phys Lett 1997;265:361.
[5] Yu G, Gao J, Hummelen JC, Wudl F, Heeger AJ. Science 1995;270:1789.
[6] Roman LS, Andersson MR, Yohannes T, Ingänas O. Adv Mater 1997;9:1164.
[7] Kraabel B, Hummelen JC, Vacar D, Moses D, Sariciftci NS, Heeger AJ, Wudl F. J Chem Phys 1996;104:4267.
[8] Sariciftci NS, Braun D, Zhang C, Srdanov V, Heeger AJ, Stucky G, Wudl F. Appl Phys Lett 1993;62:585.
[9] Martin N, Sánchez L, Mescas B, Pérez I. Chem Rev 1998;98:2527.
[10] Nierengarten JF, Ecker JF, Nicoud JF, Ouali L, Krasnikov V, Hadziioannou G. Chem Commun 1999:617.
[11] Wang S, Hua W, Zhang F, Wang Y. Synth Met 1999;99:249.
[12] Kim HK, Ryu MK, Kim KD, Lee SM. Macromolecules 1998;31:1114.
[13] Wang Y. Nature 1992;356:585.
[14] Li F, Li Y, Guo Z, Long C, Bai F, Zhu D. J Appl Polym Sci 1999;72:209.
[15] Neubert ME, Laskos LS, Maurer LJ, Carlino LT, Ferrato JP. Mol Cryst Liq Cryst 1978;44:197.
[16] Haggquist GW, Katayama H, Tsuchida A, Ito S, Yamamoto M. J Phys Chem 1993;97:9270.
[17] Prato M, Li Q, Wudl F, Lucchini V. J Am Chem Soc 1993;115:1148.
[18] Grösser T, Prato M, Lucchini V, Hirsch A, Wudl F. Angew Chem Int Ed Engl 1995;34:1343.
[19] Hawker J. Macromolecules 1994;27:4836.