

Novel Porphyrin-Grafted Poly(Phenylene Vinylene) Derivatives: Synthesis and Photovoltaic Properties

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ABSTRACT: A series of novel porphyrin-grafted poly(phenylene vinylene) derivatives, Porp-RO-PPV, were synthesized by a simple two-step method. These copolymers contain conjugated poly(phenylene vinylene) derivatives as polymer backbone and covalently linked porphyrin units as side chain, which were confirmed by FTIR and ¹H NMR, and used for photovoltaic devices. The thermal, optical properties and sensitizing effect, and photovoltaic properties have been investigated. The emission spectra of Porp-RO-PPV copolymers revealed the existence of

strong energy transfer from PPV backbone to porphyrin units. The energy conversion efficiency (η_c) of photovoltaic devices based on Porp-RO-PPV+PCBM reached 0.33% (78.2 mW/cm², AM1.5) and porphyrin units in the copolymers showed good sensitizing effect at low concentration. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2283–2290, 2008

Key words: porphyrin; poly(phenylene vinylene); derivatives synthesis; photovoltaic properties

INTRODUCTION

Polymer photovoltaic cells have been regarded as a prospective field because of their good properties such as cheap cost, good mechanical flexibility, and easy chemical tailoring.^{1–3} Especially, since the discovery of ultrafast photoinduced electron transfer from conjugated poly(phenylene vinylene)s to fullerene (C₆₀), by blending functionalized fullerenes with conjugated polymers, the energy conversion efficiencies of polymeric solar cells have improved by 1–2 orders of magnitude.^{4–6} Until now, the maximum energy conversion efficiency (ECE) is still very low. One of the limiting parameters is the mismatch of their absorption to the terrestrial solar spectrum, and the introduction of the dyes^{7,8} or conjugated polymers with wide range absorptions^{9,10} has been seen as a viable route to expand the spectral region of bulk heterojunction solar cells.

Porphyrins, which play an important role in the photosynthesis of plants, are preferable photosensitizers for utilizing solar energy.^{11,12} Inspired by the natural light-harvesting system, various kinds of porphyrin arrays consisting of porphyrin units and

energy-donating units, such as conducting polymer blocks,^{13–15} carbazole,¹⁶ and fluorine¹⁷ have been synthesized and revealed efficient energy transfer to porphyrin units. Meanwhile, efficient electron separation and transfer have been also reported between porphyrins and fullerene derivatives.^{18–20} And an enhanced photocurrent and energy transfer efficiency were reported for polythiophene (PTh)/free base porphyrin (H₂TPP)²¹ and poly(*N*-vinylcarbazole) (PVK)/metallo-porphyrin (ZnTPP)²² devices.

In this work, a series of porphyrin-grafted conjugated poly(phenylene vinylene) derivatives (Porp-RO-PPV) were synthesized. Their thermal, optical properties and sensitizing effect, and photovoltaic properties have been investigated. Porphyrin units in the copolymer could be regarded as good sensitizers of polymer photovoltaic solar cells at low concentration.

EXPERIMENTAL

Measurements

FTIR spectra were recorded on a Bruker Vector 22 IR spectrometer. ¹H NMR measurements were carried out on Advance DMX500, 500 MHz spectrometer (solvent: CDCl₃, internal standard: tetramethylsilane). The elemental analyses were performed on ThermoFinnigan Instrument Flash EA1112. The UV-vis spectrum was recorded on a Shimadzu 3101 UV-vis-NIR spectrophotometer. Photoluminescence (PL)

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spectra were measured with a Hitachi F-4500 Fluorescence spectrophotometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer series TGA7 thermal analysis system under N₂ at a heating rate of 20°C/min.

Fabrication of photovoltaic devices

Photovoltaic devices were fabricated by spin-coating the active layer from chlorobenzene at 1500 rpm onto ITO-substrates covered with PEDOT-PSS, poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonic acid), following a procedure described.^{23,24} Active layer consists of 100-nm thick composite films with a weight ratio of Porp-RO-PPV to PCBM (PCBM: 6,6-phenyl-C₆₁-butyric acid methyl ester) equal to 1/4 in all cases. The devices structures were ITO/PEDOT-PSS/Porp-RO-PPV+PCBM (1/4, w/w)/Ba/Al. Current density-voltage characteristic of devices were measured with a Keithley 236 source-measure unit. Photocurrent was measured under illumination (78.2 mW/cm², AM1.5) with a tungsten lamp.

Materials

All the solvents used were purified according to standard methods prior to use. All other chemicals were of reagent grade and were used as purchased without further purification. 1,4-Bis(chloromethyl)-2-(2'-ethylhexyloxy)-5-methoxybenzene (BCM-EHO-MOB) was synthesized and purified according to methods described in the literature.²⁵ All of the following reactions were carried out under argon atmosphere.

Synthesis of monomers

5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin (HO-TPP)

To a solution of *p*-hydroxybenzaldehyde (3.978 g, 32.5 mmol) and benzaldehyde (10.347 g, 97.5 mmol) in 350 mL of propionic acid, pyrrole (8.722 g, 130 mmol) in 10 mL of propionic acid were added dropwise with vigorous stirring near boiling temperature. The solution was refluxed for 40 min, and then most of the propionic acid was distilled away under reduced pressure. After cooled to room temperature, ethanol was added. Then kept in refrigerator overnight, the black precipitate was collected by filtration and washed with ethanol. The purple precipitation obtained was further purified by silica-gel column chromatography using petroleum ether and THF as the eluent. The second fraction provided purple crystalline, 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin (HO-TPP) (yield: 6.0%). FTIR (KBr pellet,

cm⁻¹): 3520.46 (versus, OH), 3314.83 (s, N—H), 3052.60 (s, phenyl), 1593.17, 1553.13, 1511.81, and 1469.91 (m, C=C), 1348.94 (m, C=N), 1265.59 (m, OH), 1216.94, 1777.33, 1150.37, 1073.44, 1000.72, 961.68 (m, porphyrin), 875.01, 847.59, 798.49, 726.49, 699.58. ¹H NMR (CDCl₃, ppm): δ 8.88–8.85 (8H, β-H, pyrrole); 8.22–8.21 (6H, α-H, phenyl); 8.07–8.05 (2H, α-H, *p*-hydroxybenzyl); 7.78–7.74 (9H, β-H, phenyl); 7.17–7.16 (2H, β-H, *p*-hydroxybenzyl); 5.08 (1H, —OH); −2.77 (2H, N—H, pyrrole). Anal. Calcd. for C₄₄H₃₀N₄O : C, 83.78; H, 4.79; N, 8.88. Found: C, 83.69; H, 4.53; N, 8.80.

4-(3'-Bromopropoxy)anisole (2)

A solution of 1,3-dibromopropane (70.662 g, 0.35 mol) in 100 mL of dry ethanol was stirred and heated to 65°C, and then the solution of *p*-hydroxyanisole (24.828 g, 0.20 mol) and sodium methoxide (10.804 g, 0.20 mol) in 80 mL of dry ethanol was added dropwise. The mixture was refluxed for 6 h. After the reaction was completed, the solution was concentrated by a rotatory evaporator. The resulting mixture was then extracted with 200 mL of dichloromethane. The organic layer was washed with water and dried with anhydrous magnesium sulfate. After the solvent was removed by rotary evaporation, the residue was purified by silica-gel column chromatography using petroleum ether as the eluent. The product was a colorless liquid (yield: 90%). FTIR (film on NaCl, cm⁻¹): 3043.89, 2998.27, 2951.54, 2874.17, 2832.44, 1591.92, 1507.96, 1467.55, 1433.69, 1387.42, 1291.84, 1231.63, 1180.78, 1107.29, 1040.58, 932.38, 852.38, 812.35, 740.37. ¹H NMR (CDCl₃, ppm): δ 6.83 (4H, C—H, C₆H₄); 4.02–4.06 (2H, —OCH₂—); 3.74–3.76 (3H, —OCH₃); 3.57–3.60 (2H, —CH₂Br); 2.34 (2H, —CH₂—).

1,4-Bis(bromomethyl)-2-(3'-bromopropoxy)-5-methoxybenzene (3)

To a mixture of compound 2 (24.521 g, 0.10 mol) and paraformaldehyde (6.160 g, 0.2 mol) in 330 mL of acetic acid, the mixture of 31.2 mL HBr aqueous solution with 40 wt %, and 8.7 mL of acetic acid was added dropwise under stirring. The mixture was stirred at 60–70°C for 4 h, and then cooled to room temperature. The resulting solution was poured into 800 mL of water, and then its pH value was adjusted with a saturated solution of potassium carbonate to reach in the range of 5–6. After filtration, washing with water and dried under vacuum. The crude product was recrystallized from ethanol, and white powder was obtained (yield: 42%). ¹H NMR (CDCl₃, ppm): δ 6.86–6.89 (2H, C₆H₂); 4.51–4.53 (4H, Ar—CH₂Br); 4.13–4.17 (2H, —OCH₂—); 3.87 (3H,

—OCH₃); 3.66–3.70 (2H, —CH₂Br); 3.35–3.38 (2H, —CH₂—).

Synthesis of polymers

Br-RO-PPV (1/3) (4a)

Monomer (3) (0.173 g, 0.4 mmol), 1,4-bis(chloromethyl)-2-(2'-ethylhexyloxy)-5-methoxybenzene (0.400 g, 1.2 mmol), and 0.095 mL of benzyl bromide were dissolved in 40 mL of dry THF and cooled in an ice-cooled water. Then, a solution of potassium *tert*-butoxide (1.614 g, 14.4 mol) in 30 mL of THF was added dropwise under stirring. The reaction mixture was stirred at ambient temperature for 4 h. After completion of the polymerization, the mixture was precipitated from methanol. The precipitate was filtered and washed with methanol and deionized water, extracted with hot methanol in a Soxhlet apparatus, and then dried in a vacuum oven at 40°C for 12 h. A red solid was obtained (yield: 50%). FTIR (KBr pellet, cm⁻¹): 3055.48, 2928.99, 2864.15, 2827.37, 1730.82, 1672.51, 1594.33, 1501.22, 1461.50, 1410.02, 1349.24, 114.27, 1204.36, 1176.63, 1087.19, 1035.74, 963.90, 922.00, 852.28, 694.03. ¹H NMR (CDCl₃, ppm): δ 7.50–7.46 (m, 4H, Ar—H); 7.29–7.14 (s, 4H, Ar—H and vinyl proton); 3.94–3.70 (b, 13H); 3.33–3.31 (m, 6H); 2.41–2.12 (m, 4H); 1.06–0.76 (m, 6H).

Br-RO-PPV (1/2) (4b)

The procedure was the same as for **4a**. Red precipitate was obtained (yield: 38%). FTIR (KBr pellet, cm⁻¹): 3056.99, 2958.31, 291.64, 2857.04, 1730.70, 1589.88, 1502.77, 1460.47, 1410.36, 1439.99, 114.12, 1204.32, 1178.00, 1090.04, 1038.61, 964.26, 919.98, 854.37, 699.72. ¹H NMR (CDCl₃, ppm): δ 7.50–7.46 (m, Ar—H); 7.29–7.14 (s, Ar—H and vinyl proton); 3.94–3.70 (b, OCH₂ and CH₂Br); 3.33–3.31 (m, OCH₃); 2.41–2.12 (m, CH₂); 1.06–0.76 (m, CH₃).

Br-RO-PPV (1/1) (4c)

The procedure was the same as for **4a**. Red precipitate was obtained (yield: 34%). FTIR (KBr pellet, cm⁻¹): 3057.24, 2958.37, 291.54, 2856.88, 1737.70, 1589.64, 1503.22, 1460.02, 1411.02, 1439.87, 114.77, 1204.29, 1178.26, 1114.07, 1038.35, 964.19, 919.76, 854.30, 700.47. ¹H NMR (CDCl₃, ppm): δ 7.50–7.46 (m, Ar—H); 7.29–7.14 (s, Ar—H and vinyl proton); 3.94–3.70 (b, OCH₂ and CH₂Br); 3.33–3.31 (m, OCH₃); 2.41–2.12 (m, CH₂); 1.06–0.76 (m, CH₃).

Br-RO-PPV (1/0) (4d)

The procedure was the same as for **4a**. Red precipitate was obtained (yield: 42%). FTIR (KBr pellet,

cm⁻¹): 3057.00, 2958.24, 2926.14, 2856.28, 1736.30, 1589.64, 1502.35, 1460.32, 1411.32, 1439.67, 115.07, 1204.49, 1178.20, 1110.91, 1038.35, 964.19, 919.36, 854.60, 698.67. ¹H NMR (CDCl₃, ppm): δ 7.60–7.36 (m, 2H, Ar—H); 7.29–7.14 (s, 2H, vinyl proton); 4.03–3.56 (m, 4H); 3.36–3.12 (s, 2H); 2.43–2.34 (m, 3H, CH₃).

Porp-RO-PPV (1/3) (5a)

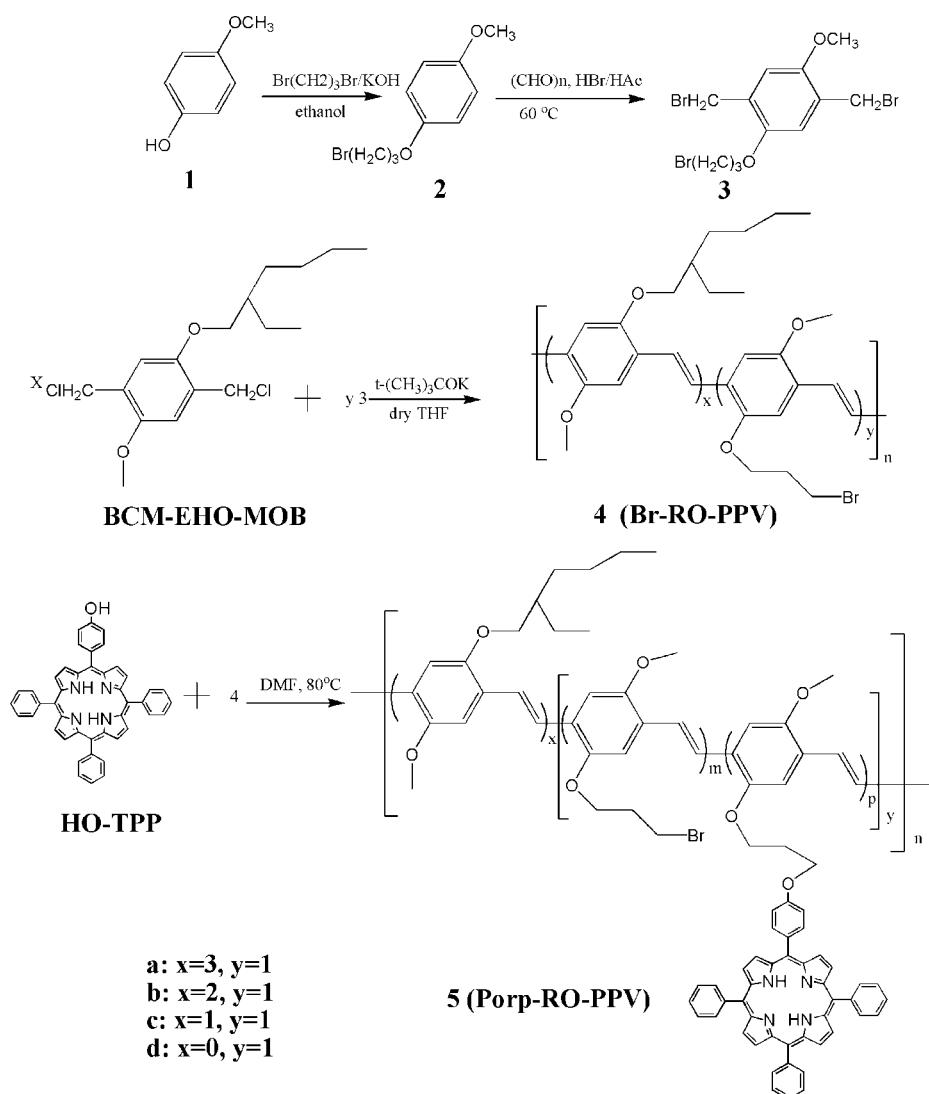
To a solution of HO-TPP (0.095 g, 0.15 mmol) and KOH (0.020 g, 0.36 mmol) in 15 mL of dimethylformamide, Br-RO-PPV (0.157 g, 0.6 mmol) was added. Then the mixture was heated to 80–85°C and reacted for 30 h. The mixture was precipitated from methanol. The precipitate was filtered and washed with methanol, ethanol, and deionized water, respectively. The crude product was extracted with hot methanol and ethanol in a Soxhlet apparatus, respectively, until the purple disappeared, and then dried in a vacuum oven at 60°C for 12 h. A deep red solid was obtained (yield: 74%). FTIR (KBr pellet, cm⁻¹): 3055.51, 2958.13, 291.05, 2856.41, 1730.55, 1667.20, 1590.30, 1502.60, 1461.14, 1410.48, 1381.03, 1349.41, 113.33, 1204.16, 1115.22, 1039.13, 965.90, 855.90, 797.90, 700.61. ¹H NMR (CDCl₃, ppm): δ 8.84–8.79 (m, β-H, pyrrole); 8.23–8.21 (m), 8.17–8.05 (s), 7.79–7.72 (b), and 7.69–7.46 (m) (Ar porphyrin); 7.13–6.65 (m, Ar—H and vinyl proton); 3.83–3.69 (m, OCH₂ and OCH₃); 2.33–2.16 and 1.87–1.83 (m, CH₂); 1.26–0.74 (m, CH₃), -2.78 (s, N—H, pyrrole).

Porp-RO-PPV (1/2) (5b)

To a solution of HO-TPP (0.120 g, 0.19 mmol) and KOH (0.027 g, 0.48 mmol) in 15 mL of dimethylformamide, **4b** (0.158 g, 0.6 mmol) was added. The other procedure was the same as for **5a**. A deep red solid was obtained (yield: 74%). FTIR (KBr pellet, cm⁻¹): 3056.27, 2958.27, 291.32, 2857.31, 1730.74, 1636.44, 1590.61, 1503.10, 1461.08, 1410.30, 1350.43, 113.88, 1204.37, 1038.70, 964.22, 923.21, 854.73, 801.71, 728.67, 701.41. ¹H NMR (CDCl₃, ppm): δ 8.84–8.79 (m, β-H, pyrrole); 8.23–8.21 (m), 8.17–8.05 (s), 7.79–7.72 (b), and 7.69–7.46 (m) (Ar porphyrin); 7.13–6.65 (m, Ar—H and vinyl proton); 3.83–3.69 (m, OCH₂ and OCH₃); 2.33–2.16 and 1.87–1.83 (m, CH₂); 1.26–0.74 (m, CH₃), -2.78 (s, N—H, pyrrole).

Porp-RO-PPV (1/1) (5c)

To a solution of HO-TPP (0.120 g, 0.19 mmol) and KOH (0.027 g, 0.48 mmol) in 15 mL of dimethylformamide, **4c** (0.105 g, 0.4 mmol) was added. The other procedure was the same as for **5a**. A deep red solid was obtained (yield: 74%). FTIR (KBr pellet,



Scheme 1 Synthetic routes of monomers and Porp-RO-PPV.

cm^{-1}): 3316.63, 3053.32, 2956.53, 2924.67, 1667.40, 1599.66, 1501.82, 1467.79, 1441.09, 1407.34, 1348.69, 1245.10, 1204.11, 1176.08, 1107.38, 1032.24, 962.87, 873.10, 847.73, 798.63, 728.78, 728.73, 700.05. $^1\text{H NMR}$ (CDCl_3 , ppm): δ 8.84–8.79 (m, β -H, pyrrole); 8.23–8.21 (m), 8.17–8.05 (s), 7.79–7.72 (b), and 7.69–7.46 (m) (Ar porphyrin); 7.13–6.65 (m, Ar–H and vinyl proton); 3.83–3.69 (m, OCH_2 and OCH_3); 2.33–2.16 and 1.87–1.83 (m, CH_2); 1.26–0.74 (m, CH_3), -2.78 (s, N–H, pyrrole).

1554.70, 1501.68, 1468.55, 1440.37, 1407.14, 1348.99, 1246.01, 1205.69, 1177.14, 1030.94, 963.90, 875.35, 848.09, 799.72, 728.99, 701.03. $^1\text{H NMR}$ (CDCl_3 , ppm): δ 8.85–8.80 (m, β -H, pyrrole); 8.23–8.07 (m), 7.80–7.73 (m), 7.80–7.73 (m), and 7.56 (s) (Ar porphyrin); 7.13–6.65 (m, Ar–H and vinyl proton); 3.76–3.73 (m, OCH_2 and OCH_3); 1.87–1.84 and 1.56 (m, CH_2); -2.77 (s, N–H, pyrrole).

RESULTS AND DISCUSSION

Synthesis and structural characterization of the copolymers

The porphyrin-containing copolymers (Porp-RO-PPV) were prepared by a simple two-step method, as shown in Scheme 1. First, the conjugated PPV copolymers containing alkyl bromide side groups were synthesized according to the well-known Gilch method.¹⁴ Then, porphyrin units were introduced

Porp-RO-PPV (1/0) (5d)

To a solution of HO-TPP (0.177 g, 0.28 mmol) and KOH (0.039 g, 0.70 mmol) in 15 mL of dimethylformamide, **4d** (0.081 g, 0.30 mmol) was added. The other procedure was the same as for **5a**. A deep red solid was obtained (yield: 74%). FTIR (KBr pellet, cm^{-1}): 3316.42, 3054.16, 2927.30, 1675.53, 1599.53,

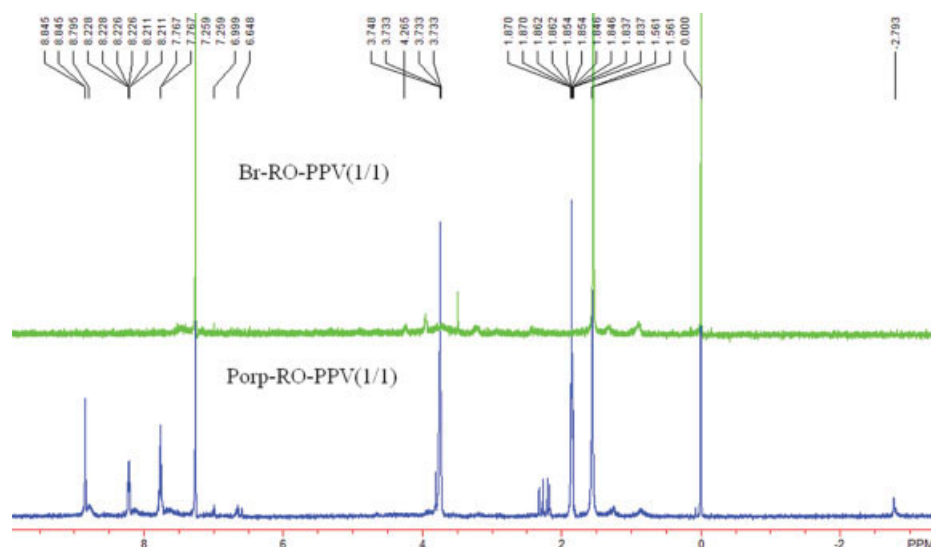


Figure 1 ^1H NMR spectra of Br-RO-PPV(1/1) and Porp-RO-PPV(1/1). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

into the polymer side chain by alkyl substitution reaction with 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin (HO-TPP). The resulting copolymers were purified through dissolving/reprecipitation in THF/methanol for three times and Soxhlet extraction, and no spot of porphyrin was detected by thin layer chromatography (TLC). All the copolymers were soluble in common organic solvents such as chloroform, tetrahydrofuran, and chlorobenzene. Their chemical structures were confirmed by FTIR and ^1H NMR spectroscopy. In FTIR spectra, the characteristic band of hydroxyl group at 3520 cm^{-1} disappeared, and new band at 3316 cm^{-1} ($\nu_{\text{N-H}}$)

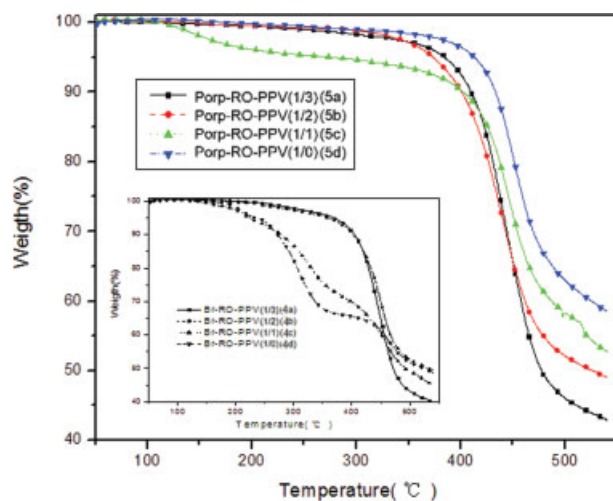


Figure 2 TGA curves of porphyrin-grafted copolymers Porp-RO-PPV and copolymers Br-RO-PPV without porphyrin (inner figure). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

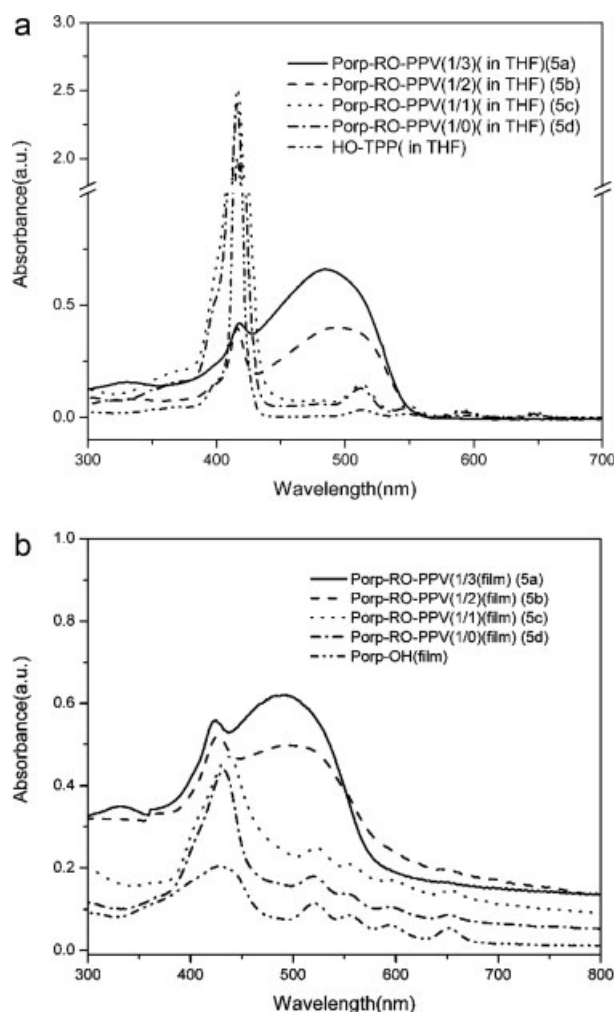


Figure 3 UV-Vis spectra of porphyrin-grafted copolymers Porp-RO-PPV and HO-TPP in THF (a) and as solid films (b).

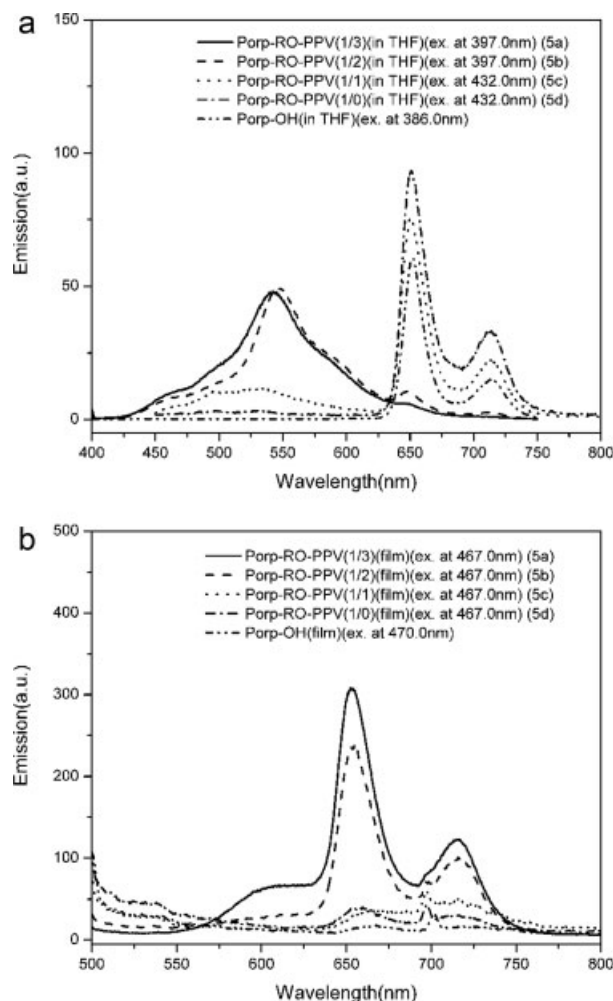


Figure 4 Normalized emission spectra of porphyrin-grafted copolymers Porp-RO-PPV and HO-TPP in THF (a) and as solid films (b).

appeared, and the band at 963 cm^{-1} (γ_{C-C} , porphyrin) became much stronger. In the ^1H NMR spectra (^1H NMR spectra of Br-RO-PPV(1/1) and Porp-RO-PPV(1/1) as an example shown in Fig. 1), obvious characteristic chemical shift of porphyrin at 8.85–8.80, 8.23–8.21, and -2.77 ppm were observed.

The thermal properties of the copolymers Porp-RO-PPV were analyzed by thermal gravimetric analysis (TGA) (Fig. 2). The decomposition temperatures were about 320°C for all the copolymers. Compared to free porphyrin copolymers Br-RO-PPV, these porphyrin-containing copolymers were much more stable, and had less 5% weight loss till 400°C .

Optical properties

Figure 3 shows the UV–vis absorption spectra of four porphyrin-containing copolymers (Porp-RO-PPV: 5a, 5b, 5c, 5d) and HO-TPP in THF and as films. It revealed obvious dependence with porphy-

rin concentration, that is, the content of porphyrin units in the copolymer. When porphyrin concentration was relatively high, such as for 5c and 5d samples, the absorption spectra of the copolymer were dominated by that of porphyrin units, with an intense B-band at around 420 nm, and four weak Q-bands between 500 and 700 nm. When porphyrin concentration was low, such as for 5a and 5b samples, the absorption spectra of the copolymers were dominated by that of conjugated PPV backbone at 480–500 nm, together with one small shoulder at around 420 nm. Compared to the absorption spectra of the copolymers in THF solution, the maximum absorption of copolymer films was all slightly broadened and red shifted due to π – π stacking effects in the solid state. Otherwise, no splitting of the Soret bands was observed, suggesting that there might be limited electronic interaction in the ground state between the porphyrin units and conjugated backbone in solution and as film.⁷

Fluorescence (PL) spectra of the copolymers both in dilute THF solution and as films revealed strong energy transfer process, as shown in Figure 4. The low energy bands at around 650 and 715 nm were attributed to the porphyrin subunits, and the high energy emission bands around 540 nm were attributed to conjugated PPV backbone. In THF, the emission peaks changed from high energy bands to low energy bands with the increase of porphyrin content in copolymers. While spin-coated as films, the thin-film emission spectra of the copolymers were dominated by that of porphyrin units in the copolymer, when exciting at 467 nm, with an intense emission peak around 655 nm and a shoulder at 716 nm, and no emission of PPV backbone was found. These observations revealed that there was an intensive

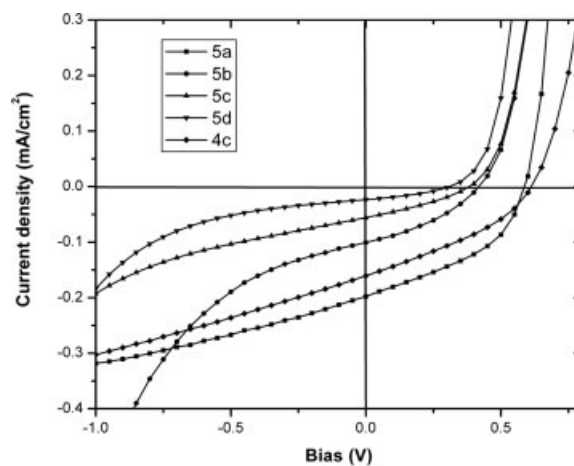


Figure 5 Current density- voltage characterization of photovoltaic devices based on Porp-RO-PPV (Br-RO-PPV)+PCBM(1/4, w/w) under illumination of 78.2 mw/cm^2 at AM1.5. Ambient temperature. Porp-RO-PPV (1/3, 5a;1/2, 5b;1/1, 5c;1/0, 5d) and Br-RO-PPV (1/1, 4c).

TABLE I
Photovoltaic Parameters of Photovoltaic Devices Based on Porp-RO-PPV (1/3; 1/2; 1/1; 1/0) (Br-RO-PPV, 1/1) + PCBM (1/4, w/w) Under Illumination of 78.2 mW/cm² at AM 1.5

Active layer	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η_e (%)
Porp-RO-PPV(1/3) : PCBM(1/4 w/w)	0.198	0.60	0.41	0.325
Porp-RO-PPV(1/2) : PCBM(1/4 w/w)	0.101	0.40	0.38	0.101
Porp-RO-PPV(1/1) : PCBM(1/4 w/w)	0.056	0.40	0.30	0.045
Porp-RO-PPV(1/0) : PCBM(1/4 w/w)	0.024	0.30	0.36	0.017
Br-RO-PPV(1/1) : PCBM(1/4 w/w)	0.161	0.60	0.36	0.229

J_{sc} : short-circuit current density, V_{oc} : open-circuit voltage, FF: fill factor, η_e : energy conversion efficiency.

energy transfer in solid film from PPV backbone to porphyrin subunits, although there existed some photoluminescence quenching for 5c and 5d due to the aggregation of porphyrin units in films.

Photovoltaic properties

Figure 5 shows the current density-voltage characterization of bulk heterojunction photovoltaic devices under illumination of 78.2 mW/cm² at AM1.5. Their photovoltaic parameters are given in Table I. The device structures were ITO/PEDOT-PSS/Porp-RO-PPV+PCBM (1/4, w/w)/Ba/Al. The active layers were fabricated by spin coating from a solution of Porp-RO-PPV and PCBM blends in chlorobenzene (weight ratio of Porp-RO-PPV to PCBM equal to 1/4). It is seen from Table I that ITO/PEDOT-PSS/Porp-RO-PPV (1/3)+PCBM/Ba/Al device exhibits the maximum energy conversion efficiency (η_e) of 0.33%, open-circuit voltage (V_{oc}) of 0.6 V, short circuit current density (J_{sc}) of 0.198 mA/cm², and fill factor (FF) of 0.41. However, with the increase of porphyrin content in copolymers, the energy conversion efficiency (η_e) and short circuit current density (J_{sc}) decreased. According to the emission spectra of porphyrin-grafted copolymers as film, it could be deduced that due to strong energy transfer from PPV backbone to porphyrin units, the resulting energy and electron transfer process in active layer would almost be in the direction of PPV backbone to porphyrin side chain then to PCBM, and therefore, to some extent, the charge separation and energy transfer between PPV backbone and PCBM might decrease. Considering that two-step transfer processes have less efficient than one process, the increase of porphyrin concentration means the increases of two-step transfer process in whole energy and electron transfer process, and then result in low energy conversion efficiency. However, when compared with the device based on Br-RO-PPV (1/1)+PCBM without porphyrin units, the device based on Porp-RO-PPV (3/1)+PCBM revealed higher energy conversion efficiency (η_e). These observations indicated that porphyrin units in the copolymer

could be regarded as good sensitizers of polymer photovoltaic solar cells at low concentration.

CONCLUSIONS

A series of novel porphyrin-grafted poly(phenylene vinylene) derivatives (Porp-RO-PPV) have been synthesized by a simple two-step method. They are soluble in common organic solvents, easily spin-coated as films, and highly thermostable. These copolymers showed strong energy transfer from PPV backbone to porphyrin subunits in their emission spectra. Porp-RO-PPV+PCBM composite can be used as the active layer material for photovoltaic devices. The device based on Porp-RO-PPV+PCBM composite, ITO/PEDOT-PSS/Porp-RO-PPV+PCBM (1/4, w/w)/Ba/Al, shows photovoltaic effect. Its maximum energy conversion efficiency (η_e) reached 0.33% at 78.2 mW/cm² (AM 1.5) with open-circuit voltage (V_{oc}) of 0.6V, short-circuit current density (J_{sc}) of 0.198 mA/cm², and fill factor (FF) of 0.41. The η_e of their photovoltaic devices increased with the decrease of porphyrin content in the copolymer, which is related to strong energy transfer from PPV backbone to porphyrin units. Porphyrin units in the copolymer could be regarded as good sensitizer of polymer photovoltaic solar cells at low concentration. Further investigations of bulk heterojunction photovoltaic devices based on porphyrin-containing copolymers are in progress.

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