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Novel polyfluorene copolymers containing porphyrin and thiophene moieties with broad absorption and efficient charge transfer and separation

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Summary

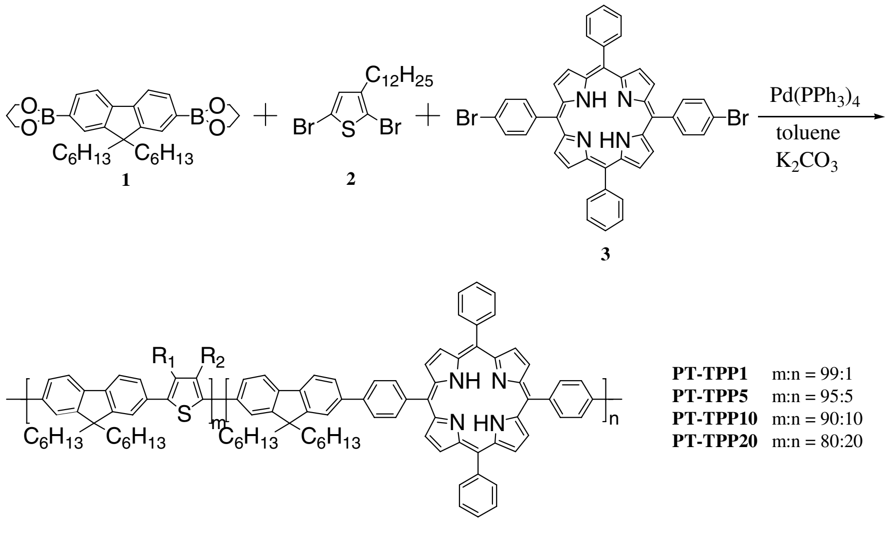
A novel series of soluble conjugated polyfluorene copolymers comprised of porphyrin and thiophene moieties were synthesized by palladium-catalyzed Suzuki coupling reactions with various feed ratios. Chemical structures of the copolymers were characterized by ^{1}H NMR and IR. All of the polyfluorene copolymers demonstrated good thermal stability, relatively high glass transition temperatures, and strong absorption over 600 nm and nearly cover 400~700 nm visible region. It was revealed by cyclic voltammetry that the bandgaps of copolymers were between 1.96 and 2.03 eV. And the polymer:TiO_2 bulk-heterojunction films were made from mixtures of polymer and titanium isopropoxide ($Ti(OC_3H_7)_4$) via hydrolysis in air. The photoluminescence (PL) at 380~800 nm of the blend film of PT-TPP20:TiO_2 bulk-heterojunction in the 20% $Ti(OC_3H_7)_4$ blend film was decreased compared to that of a pristine copolymer film. PL was significantly quenched in the 50% $Ti(OC_3H_7)_4$ blend film, indicative of rapid and efficient separation of photoinduced electron-hole pairs with electrons on the TiO_2 and holes on the polymer.

Introduction

Conjugated polymers solar cells were becoming increasingly attractive because they showed many potential advantages over traditional inorganic solar cells[1-5]. But the main limitations of polymers solar cells to their application were narrow spectral coverage, poor mobility of charge carriers and instability of polymer materials compared to inorganic solar cells.

Polyfluorenes, which were developed as organic optoelectronic materials, were characterized by good thermal and chemical stability, and hole-transporting properties[6,7]. However, the large bandgap and blue shifted absorption range had made most polyfluorene copolymers less suited for use in solar cells, where the low bandgap and large coverage of the solar spectrum were desirable. Porphyrin and its derivatives were characterized by excellent absorption at 400~700 nm visible region. Some polymers containing porphyrin moieties were designed and synthesized. The polymers containing porphyrin moiety in the side chains were prepared by Morgado et al.[8]. The red electrophosphorescence polymers containing porphyrin moiety in the main chains were synthesized by Hou et al.[9]. The utilization of thiophene moiety was attractive because polythiophene had good thermal and environmental stability, and good hole accepting and transporting properties[3].

For the first time the synthesis and characterization of polyfluorenes containing tetraphenylporphyrin and thiophene moieties in main chain is reported. The tetraphenylporphyrin moieties were introduced into the main chain of polyfluorene to extend the spectral coverage of copolymers and to make the most of solar spectrum, and thiophene moieties were introduced into the main chain of polyfluorene to enhance the thermal and environmental stability and to improve the hole accepting and transporting of copolymers. The hybrid donor-acceptor bulk-heterojunctions based on the hole accepting and transporting properties of copolymer and the electron transporting properties of TiO_2 could lead to an efficient transfer and separation of photogenerated electron-hole pairs with electrons on the TiO_2 and holes on the polymer.



PT-TPP1 m:n = 99:1
PT-TPP5 m:n = 95:5
PT-TPP10 m:n = 90:10
PT-TPP20 m:n = 80:20

$R_1 = H$, $R_2 = C_{12}H_{25}$ or $R_1 = C_{12}H_{25}$, $R_2 = H$

Scheme 1 Synthetic routes of polyfluorene copolymers

Experimental

Materials

All the chemicals were purchased from Aldrich or Fluka company and were used without any further purification. Solvents such as $CHCl_3$, THF, and toluene were dried with appropriate drying agents, then distilled under reduced pressure. 9,9-dihexylfluorene-2,7-bis(trimethyleneboronates)**1**[10],2,5-dibromo-3-dodecylthiophene **2** [11,12], and 5,15-bis (4-bromophenyl)-10,20-bis(phenyl)porphyrin **3** [13], were prepared following the already published procedures.

Measurements

^{1}H NMR were recorded on a Bruker AVANCE AV II-400MHz and a Varian Unity INOVA-400MHz spectrometer. The FT-IR spectra were obtained on a Perkin-Elmer 2000 infrared spectrometer as KBr pellets. UV-vis spectra of the copolymers in solutions were taken on a Suhimadzu UV2100 UV-vis recording spectrometer. Photoluminesence (PL) spectra of the copolymers in the thin films were measured on a Hitachi 850 fluorescence spectrometer. Thermal gravimetric analysis (TGA) measurements were performed on America TGA Q500 thermal analysis system under N_2 at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC II under N_2 at a heating rate of 10°C/min. The weight-average molecular weights (M_w) and polydispersity indices of the copolymers were measured on a PL-GPC model 210 chromatograph at 25°C, using THF as the eluent and standard polystyrene as the reference. Cyclic voltammetry (CV) were measured on a Autolab PGSTAT30 electrochemical workstation (Eco Chemie Company, Netherlands) at a scan rate of 50 mV/s with a solution of 0.1 mol/L tetrabutyl ammonium perchlorate (Bu_4NClO_4) in acetonitrile (CH_3CN) with platinum and AgCl(0.1 mol/L)/Ag as the working and reference electrodes, respectively. The deposition of the copolymer on the electrode was done by the evaporation of a dilute THF solution.

Polymerization

A typical procedure was as follows. To a mixture of **1** (0.502 g, 1 mmol), **2** (0.328 g, 0.80 mmol), **3** (0.154 g, 0.20 mmol) and $Pd(PPh_3)_4$ (12 mg, 1 mmol) were added a mixture of toluene (5 mL) and 2M potassium carbonate (5 mL). The mixture was stirred and refluxed for 72 h under argon. Then the solution was poured into the mixture of methanol and water (v:v = 9:1). A solid was obtained by filtration. The solid was washed with methanol, water. And the solid was purified by washing with acetone in a Soxhlet apparatus for 24 h. Copolymer **PT-TPP20** was obtained as a brown solid with yield of 70% after drying under a vacuum[2]. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.84~8.81 (m, 8H), 8.20~7.40 (m, 30H, ArH), 7.30 (s, 1H), 2.10~0.50 (m, 77H), -2.87 (s, 2H). IR (KBr, cm^{-1}): 3473 (N-H), 3058 (ph-H), 2900 (C-H), 1400 (C-H), 750 (ph-H).

Bulk-heterojunction

Bulk-heterojunction films of copolymer **PT-TPP20** and TiO_2 were made by spin-casting a solution of copolymer **PT-TPP20** (5 mg/mL) and $Ti(OC_3H_7)_4$ (80 µL/mL) (v:v = 1:0, 1:0.25, 1:1) in dry THF on the quartz substrate. To allow $Ti(OC_3H_7)_4$ to react with moisture, the samples were kept in the dark, in air overnight[4].

Results and Discussion

As shown in Scheme 1, a series of novel polyfluorene copolymers derived from monmers **1**, **2**, and **3** were synthesized via the palladium-catalyzed Suzuki coupling reaction. The comonomer feed molar ratios of thiophene to porphyrin were respectively 99:1 (**PT-TPP1**), 95:5 (**PT-TPP5**), 90:10 (**PT-TPP10**), and 80:20 (**PT-TPP20**). Yield: 70~75%. The resulting polyfluorene copolymers were readily soluble in common organic solvents, such as CH_2Cl_2, $CHCl_3$, and THF. The molecular weight measurements were performed by gel permeation chromatography (GPC) in eluent THF using the calibration curve of polystyrene standards. The weight-average molecular weights (M_w) of copolymers were 5300 (**PT-TPP20**), 6000 (**PT-TPP10**), 8800 (**PT-TPP5**), and 12000 (**PT-TPP1**). The polydispersity indices of copolymers were 1.65 (**PT-TPP20**), 1.66 (**PT-TPP10**), 1.67 (**PT-TPP5**), and 1.7 (**PT-TPP1**).

Polyfluorene copolymers were characterized by their ^{1}H NMR and FT-IR. The ^{1}H NMR spectrum of polymer **PT-TPP20** as a representative polymer was shown in Figure 1. In the ^{1}H NMR spectrum of polymer **PT-TPP20** in $CDCl_3$, the signal of the 4-position of thiophene at about 7.30 ppm, and the N-H of porphyrin at -2.87 ppm. The signals of the pyrrole-H of the porphyrin unit dominated in the region of 8.81~8.84 ppm, the alkyl chains appeared at 0.50~2.10 ppm, and other aromatic protons were between 7.40 and 8.20 ppm. The ^{1}H NMR spectra of polyfluorene copolymers **PT-TPP1**, **PT-TPP5**, and **PT-TPP10** were similar to copolymer **PT-TPP20** and were not shown. The polyfluorene copolymers were characterized by IR spectra, strong absorptions were observed at 3473, 3058 cm^{-1}, which were characteric of the nitrogen-hydrogen of porphyrin and carbon-hydrogen of aromatic ring respectively.

The thermal properties of the polyfluorene copolymers had been investigated using TGA and DSC. The results were shown in Table 1, Figure 2, and Figure 3, respectively. All copolymers showed highly thermal stabilities with the initial decomposition temperatures of 398~429°C under nitrogen, and little weight loss was observed at lower temperature. After the temperature increased above 400°C, the curves fall rapidly, indicating the decomposition of the copolymers backbone. The glass transition temperatures of polyfluorene copolymers ranged from 117°C to 152°C. These T_g values were much higher in compared to those of typical poly(9, 9-dialkylfluorene) (about 50°C), indicating that the thiophene and porphyrin moieties

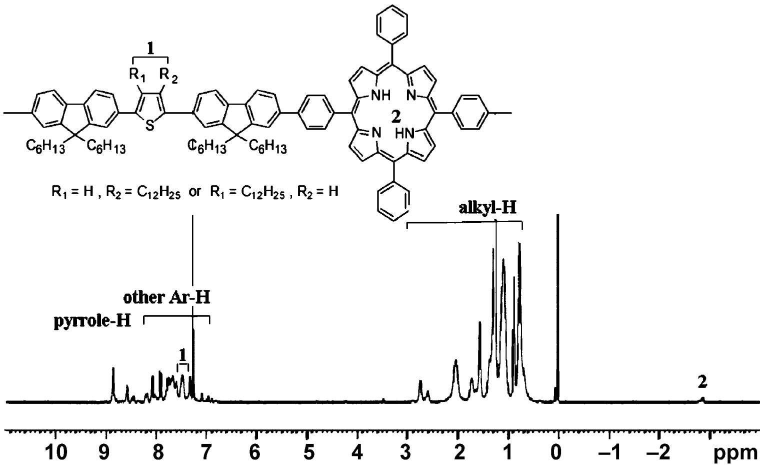


Figure 1. ^{1}H NMR spectrum of polyfluorene copolymer **PT-TPP20** in $CDCl_3$

significantly enhanced the thermal stability of the copolymers. This was very important for such types of polymers used as solar cell materials.

Table 1. TGA and DSC parameters of the polyfluorene copolymers

	PT-TPP1	**PT-TPP5**	**PT-TPP10**	**PT-TPP20**
T_d^a/°C	398	412	419	429
T_g^b/°C	117	135	152	149

^{a}TGA and ^{b}DSC under N_2 at a heating rate of 10°C/min.

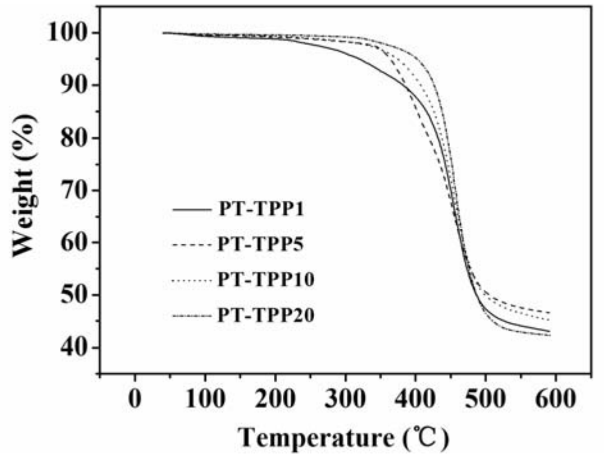


Figure 2. Thermal gravimetric analysis (TGA) curves of the polyfluorene copolymers under nitrogen (10°C/min)

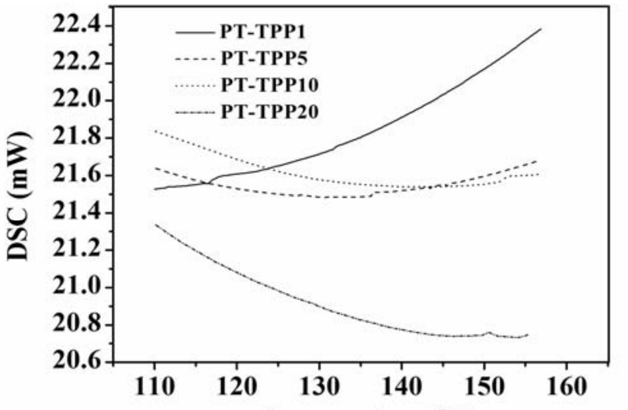


Figure 3. Differential scanning calorimetry (DSC) curves of the polyfluorene copolymers under nitrogen (10°C/min)

The UV-vis absorption spectra of polyfluorene copolymers and TPP monomer were shown in Figure 4. The UV-vis spectra of these copolymers showed two absorption bands at 400~500 nm and at about 516, 552, 590, 647 nm, which were from the Soret-band and Q-band of TPP moiety respectively. The absorption peaks of fluorene and thiophene at around 400 nm. So copolymers appeared redshifted absorption in comparison with fluorene and thiophene obviously, and nearly cover 400~700 nm visible region. The spectra of copolymers were similar to that of TPP above 450 nm, indicating that TPP moiety had been introduced into the main chains of copolymers, and fluorene and thiophene moieties in the polymers had no influence on the absorption of the TPP moiety. Absorption peaks and absorption coefficient of copolymers and porphyrin monomer were shown in Table 2. As TPP feed composition in the copolymers increased, the absorption peaks were not different obviously, the absorption coefficient of copolymers decreased significantly.

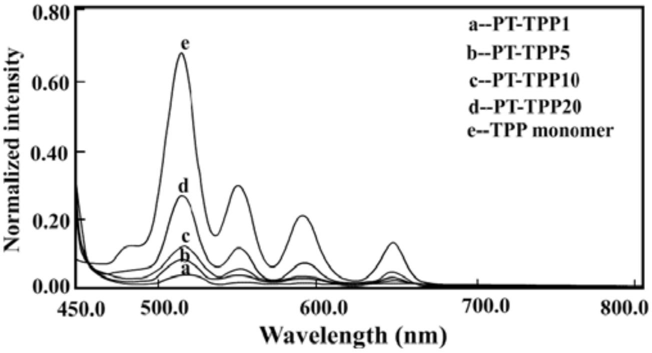


Figure 4. UV-vis absorption spectra of polyfluorene copolymers and TPP monomer

Table 2. Absorption peaks and absorption coefficient of copolymers and porphyrin monomer

	λ_{max} (nm)^a	E_{max} (1×10^3)^b
PT-TPP1	517.80, 552.80, 590.00, 647.00	4.86, 2.32, 1.28, 0.90
PT-TPP5	516.60, 551.60, 590.60, 646.40	9.05, 4.52, 2.97, 2.19
PT-TPP10	516.40, 552.00, 589.80, 646.20	12.49, 6.09, 4.03, 2.98
PT-TPP20	516.00, 551.00, 590.00, 646.50	27.13, 12.10, 7.84, 5.30
TPP monomer	515.50, 550.50, 590.00, 645.50	69.04, 29.99, 21.06, 13.75

[a] Absorption spectra were record in dilute $CHCl_3$ solution at room temperature. [b] Absorption coefficients were calculated by formula (E_{max} = A/cL), c = 1×10^{-5} mol/L, L = 1 cm

As shown in Figure 5, Cyclic voltammetry (CV) was employed to investigate the redox behaviors of the copolymers and to estimate the bandgaps of polymers. The onsets of reduction processes of the copolymers were between -1.16 and -1.11 V, and the onsets of oxidation processes of the copolymers were between 0.85 and 0.89 V. HOMO (highest occupied moleclar orbital) and LUMO (lowest unoccupied moleclar orbital) levels were calculated according to empirical formulas (E_{HOMO} = IP = $-e$ ($E_{oxonset}$ + 4.4) eV and E_{LUMO} = EA = $-e$ ($E_{redonset}$+ 4.4) eV)[14]. The resulting HOMO and LUMO levels of copolymers were listed in Table 3. As the tetraphenylporphyrin moieties in the copolymers increased, The bandgaps of copolymers calculated decreased from 2.03 eV (**PT-TPP1**) to 1.96 eV (**PT-TPP20**).

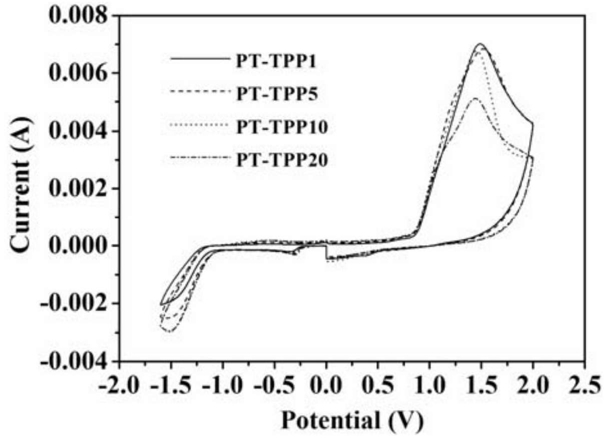


Figure 5. Cyclic voltammograms of polyfluorene copolymers

Table 3. Electrochemical parameters of the polyfluorene copolymers

Polymer	$E_{redonset}$ (V)	$E_{oxonset}$ (V)	LUMO (eV)[a]	HOMO (eV)[b]	E_g (eV)[c]
PT-TPP1	−1.16	0.87	−3.24	−5.27	2.03
PT-TPP5	−1.12	0.89	−3.28	−5.29	2.01
PT-TPP10	−1.11	0.87	−3.29	−5.27	1.98
PT-TPP20	−1.11	0.85	−3.29	−5.25	1.96

[a] Calculated according to LUMO = $-e$ ($E_{redonset}$+ 4.4). [b] Calculated according to HOMO = $-e$ ($E_{oxonset}$ + 4.4). [c] Calculated according to E_g = LUMO – HOMO.

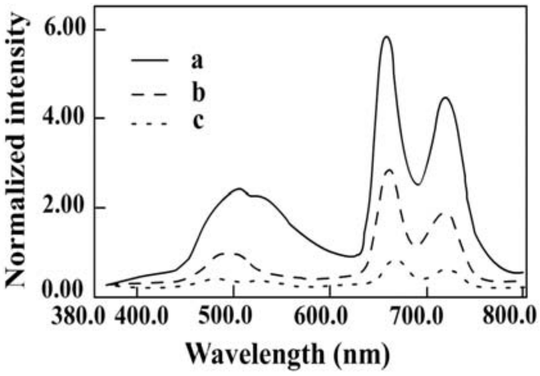


Figure 6. PL spectra of PT-TPP20:TiO_2 bulk-heterojunctions with varying amounts of $Ti(OC_3H_7)_4$ (**a** : $V_{PT-TPP20}$:$V_{Ti(OC3H7)4}$ = 1: 0, **b** : $V_{PT-TPP20}$:$V_{Ti(OC3H7)4}$ = 1: 0.25, **c** : $V_{PT-TPP20}$: $V_{Ti(OC3H7)4}$ = 1: 1)

The PL spectra of PT-TPP20:TiO_2 bulk-heterojunctions with varying amounts of $Ti(OC_3H_7)_4$ were displayed in Figure 6. The PL spectrum of **PT-TPP20** (**a**) showed two main emission bands at 508 nm corresponding to fluorene and thiophene moieties and 660 nm with a shoulder peak at 720 nm corresponding to TPP moiety in the copolymers. The intensity of the emission of fluorene and thiophene moieties were weaker than that of the TPP moiety emission, indicating the intramolecular energy transfer from fluorene and thiophene moieties to the TPP moiety. The PL of bulk-heterojunction was decreased with increasing amount of $Ti(OC_3H_7)_4$ compared to that of a pristine copolymer film, and was significantly quenched in the 50% blend, which suggested that rapid and efficient separation of photoinduced electron-hole pairs with electrons on the TiO_2 and holes on the polymer.

Conclusion

Novel polyfluorene copolymers containing porphyrin and thiophene moieties were prepared by Suzuki coupling reactions. These copolymers were soluble in common organic solvents. These polyfluorene copolymers were found to be thermally stable with initial decomposition temperatures over 398°C and together with high glass transition temperatures (117~152°C), which may improve the operating lifetime of the solar cells. Cyclic voltammetry studies revealed that the bandgaps of copolymers were between 1.96 and 2.03 eV. The copolymers had strong absorption over 600 nm and nearly cover 400~700 nm visible region. The Photoluminesence spectra was significantly quenched in the 50% $Ti(OC_3H_7)_4$ blend film of Polymer:TiO_2 bulk-heterojunction film, indicative of rapid and efficient separation of photoinduced electron-hole pairs with electrons on the TiO_2 and holes on the polymer. Futher studies on their application as the polymer solar cell materials are now in progress.

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