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A New Class of Conjugated Polymers Having Porphyrin, Poly(*p*-phenylenevinylene), and Fullerene Units for Efficient Electron Transfer

Changshui Huang,[†,‡] Ning Wang,[†,‡] Yuliang Li,*[,†] Cuihong Li,[†,‡] Junbo Li,[†,‡]
Huibiao Liu,[†] and Daoben Zhu[†]

CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Science,
Beijing 100080, P. R. China, and Graduate School of Chinese Academy of Sciences,
Beijing 100080, P. R. China

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ABSTRACT: A series of new polymers containing porphyrin, poly(*p*-phenylenevinylene) (PPV), and/or a pendant fullerene unit has been synthesized. The cyclic voltammetry showed us a good candidate for a photoinduced electron-transfer system. More important, the photocurrent measurement revealed an interesting phenomenon that the photocurrent increased with the contents of the fullerene in the polymers increased. SEM images displayed the aggregation superstructures of three polymers. Nanobriquetting, nanofiber, and hierarchical porous structure were observed, respectively. The results indicated that the axial coordination of metal porphyrin and Bipy was very important to control the aggregation morphologies of the polymers.

Introduction

In recent years, various kinds of porphyrin arrays, with their importance in artificial photosynthesis[1−3] and molecular devices,[4−6] have been demonstrated. Porphyrin-based polymers and oligomers have been actively pursued due to their potential applications in solar energy conversion,[7] charge storage and transport,[8] and nonlinear optical materials.[9] Since the observation of electroluminescence in a poly(*p*-phenylenevinylene) (PPV) based diode first reported 15 years ago,[10] this field has expanded due to their high luminescence, easy modification of the chemical structure[11−15] and optoelectronic properties.[16] C_{60} has emerged as a novel three-dimensional acceptor and has been extensively studied for the construction of efficient electron-transfer model systems.[17] The small reorganization energy for C_{60} in electron process leads to significant acceleration of charge separation step and effective deceleration of energy wasting charge recombination step.[18] Extensive efforts have been devoted toward the development of donor−acceptor (D−A) multicomponent molecular systems, the exploring of a class of useful candidates to build molecular electronic devices[19−21] and artificial light energy harvesting systems. So far, the D−A system based on fullerene and PPV or that based on porphyrin and PPV have been observed.[22] However, little attention was paid to the synthesis of polymers containing porphyrin, PPV, and/or pendant fullerene, especially the direct N-alkylation of the readily available N-unsubstituted fulleropyrrolidines for further functionalization and control of the polymers morphologies for efficient improvement of optoelectronic properties.

Here, we present the synthesis and characterization of new polymers containing porphyrin, PPV, and/or pendant fullerene moieties. The properties of these new polymers have been investigated by UV−vis spectroscopy, fluorescence spectroscopy, and cyclic voltammetry. We also studied the relationships of the morphologies and photocurrent response of three polymers by using a scanning electron microscope (SEM) and the photoelectrochemical system.

Experimental Section

Materials. Unless otherwise stated, reagents were commercially obtained and used without further purification. Compounds **1a**, **1b′**, **1d**, **1e**, and **4** were prepared according to literature procedures.[23−25]

Characterization. Column chromatography (CC) used SiO_2 (200−300 mesh). UV−vis spectra were measured on a Hitachi U-3010 spectrometer. FT-IR spectra were recorded as KBr pellets on a Perkin-Elmer System 2000 spectrometer. ^{1}H NMR spectra were recorded on Bruker ARX300/400 spectrometers. MALDI−TOF mass spectrometric measurements were performed on Bruker Biflex III MALDITOF (both positive and negative ion reflector mode). The molecular weights of polymers were determined by gel permeation chromatography (GPC) on a Waters Breeze system equipped with polystyrene gel column, using tetrahydrofuran (THF) as eluant. Cyclic voltammograms (CV) and photocurrent were recorded on CHI660B voltammetric analyzer (CH Instruments).

Synthesis of 2-(2,2-Diethoxyethoxy)-1,4-dimethylbenzene (1). 2,5-Dimethylphenol (6.11 g, 0.05 mol) and NaOH (2.02 g, 0.055 mol) were dissolved in water (75 mL), and tetrabutylammonium (0.65 g, 2.5 mmol) and bromoacetaldehyde diethyl acetal (10.84 g, 0.055 mol) were added. The solution was heated at reflux for 24 h. After the reaction, the mixture was extracted with diethyl ether (2 × 50 mL). The combined diethyl ether extract was washed with an aqueous solution of NaOH (5%, 25 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified on a silica gel using a mixture of petroleum ether and ethyl acetate (100:1, v:v) as eluent ($R_f = 0.2$), giving 9.31 g (yield 71%) of compound **1**. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.25$ (t, $J = 7.5$ Hz, 6H, $-CH_3$), 2.19 (s, 3H, Ph$-CH_3$), 2.30 (s, 3H, Ph$-CH_3$), 3.72 (m, 4H, $-OCH_2-$), 4.00 (d, $J = 6.0$ Hz, 2H, PhO$-CH_2-$), 4.85 (t, $J = 4.5$ Hz, 1H, CH), 6.64 (s, 1H, phenyl), 6.68 (d, $J = 6.0$ Hz, 1H, phenyl), 7.00 (d, $J = 9.0$ Hz, 1H, phenyl). FT-IR (KBr): $\upsilon = 1296, 1270, 1000$ cm^{-1}. EI-MS: m/z 238.

Synthesis of 2-(2,2-diethoxyethoxy)-1,4-bis(bromomethyl)-benzene (2). To a solution of compound **1** (2.38 g, 0.01 mol) in carbon tetrachloride (50 mL) were added NBS (3.74 g, 0.021 mol) and azobis (isobutyronitrile) as an initiator. The reaction mixture was heated at reflux for 6 h under N_2. The completion of the reaction was indicated by the appearance of succinimide on the

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* Corresponding author. E-mail: ylli@iccas.ac.cn.
[†] CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Science.
[‡] Graduate School of Chinese Academy of Sciences.

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surface of the reaction solution. The latter was filtered and the filtrate was concentrated. The concentrated mixture was diluted with diethyl ether (100 mL) and washed with water for several times. The extract was dried over $MgSO_4$, evaporated under reduced pressure. The residue was purified on a silica gel using a mixture of petroleum ether and ethyl acetate (50:1, v:v) as eluent ($R_f = 0.1$). This afforded 1.94 g (yield 49%) of compound **2**. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.25$ (t, $J = 7.1$ Hz, 6H, $-CH_3$), 3.75 (m, 4H, $-OCH_2-$), 4.09 (d, $J = 5.1$ Hz, 2H, Ph$-OCH_2-$), 4.44 (s, 2H, Ph$-CH_2-$), 4.46 (s, 2H, Ph$-CH_2-$), 4.91 (t, $J = 5.1$ Hz, 1H, CH), 6.92 (s, 1H, phenyl), 6.95 (d, $J = 7.8$ Hz, 1H, phenyl), 7.29 (d, $J = 7.5$ Hz, 1H, phenyl). FT-IR (KBr): $\upsilon = 1296$, 1270, 1000 cm^{-1}. EI-MS: *m/z* 396.

Synthesis of (2,5-Bis(bromomethyl)phenoxy)acetaldehyde (3). Compound **2** (0.85 g, 2.15 mmol), *p*-TsOH (40.7 mg, 0.215 mol) and water (215 μL) were dissolved in EtOAc (10.75 mL). The solution was heated to 60 °C for 45 min; an aqueous solution of $NaHCO_3$ (10%, 2.15 mL) was then added. The EtOAc layer was separated, dried with $MgSO_4$ and filtered. After evaporaton under reduced pressure, the crude product was purified on silica gel, and 0.62 g. (yield 90%) of the compound **3** was obtained. ^{1}H NMR 300 MHz, $CDCl_3$): $\delta = 4.43$ (d, $J = 6.0$ Hz, 2H, PhO$-CH_2-$), 4.60 (s, 2H, Ph$-CH_2-$), 4.69 (s, 2H, Ph$-CH_2-$), 6.62 (s, 1H, phenyl), 7.03 (d, $J = 7.8$ Hz, 2H, phenyl), 7.35 (d, $J = 7.8$ Hz, 1H, phenyl), 9.90 (t, $J = 4.3$ Hz, 1H, CHO). FT-IR (KBr): $\upsilon =$ 2730, 1722, 1582, 1270, 1142 cm^{-1}. EI-MS: *m/z* 322.

Synthesis of *N*-(1,4-Bis(bromomethyl)-2-ethoxybenzene)-2,2-dimethyl-3,4-fulleropyrrolidine (1c) Compound **4** (158.4 mg, 0.2 mmol) and compound **3** were dissolved in dichloromethane and toluene (6:1, v:v), then sodium triacetoborohydride (424 mg, 2 mmol) was added under stirring, and glacial acetic acid (120 μL, 2 mmol) was added dropwise. The mixture was stirred at room temperature for 2 h. The reaction was quenched by added saturated aqueous solution of $NaHCO_3$, and the product was extracted with dichloromethane. The extract was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was purified on silica gel using toluene as eluent ($R_f = 0.2$), affording 114 mg (yield 51.5%) of compound **1c**. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.03$ (s, 6H, $-CH_3$), 3.53 (t, $J = 5.1$ Hz, 2H, NCH_2-), 4.51 (s, 2H, Ph$-CH_2-$), 4.58 (t, $J = 5.4$ Hz, 2H, $-OCH_2-$), 4.68 (s, 2H, Ph$-CH_2-$), 4.82 (s, 2H, $-CH_2-$), 7.00 (d, $J = 7.7$ Hz, 1H, phenyl), 7.11 (s, 1H, phenyl), 7.35 (d, $J = 7.7$ Hz, 1H, phenyl). FT-IR (KBr): $\upsilon = 2962$, 2924, 1582, 1426, 1262, 1165, 528 cm^{-1}. MALDI$-$TOF MS: *m/z* 1097 M$^-$.

Synthesis of Polymer (PP). A suspension of compound **1a** (177 mg, 0.2 mmol) and triphenylphosphine (110 mg, 0.42 mmol) in 50 mL of anhydrous toluene was heated at reflux for 12 h. The solvent was filtered. The resulting residue was washed with toluene several times and dried. Thus we obtained compound **1a′** (226 mg). A mixture of compound **1a′** (71 mg, 0.05 mmol) and compound **1b** (25 mg, 0.05 mmol) in 25 mL of anhydrous chloroform and ethanol (4:1, v:v) was stirred at room temperature under a nitrogen atmosphere. A freshly prepared solution of sodium ethoxide in anhydrous ethanol (3 M excess) was added dropwise to the mixture during 2 h. After the mixture was stirred at room temperature for 24 h, the solution was concentrated in a vacuum and added dropwise to methanol at room temperature with stirring to precipitate the polymer. The polymer was purified by repeatedly precipitation from chloroform into methanol, washing with absolute diethyl ether and then dried under vacuum. This gave 33 mg (yield 60%) of the polymer **PP** as a brown powder. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -2.56$ (br, 2H), 0.86 (br, 6H), 1.19$-$1.68 (br, 36H), 1.89 (br, 16H), 2.64 (br, 6H), 4.26 (br, 4H), 7.17$-$7.39 (br, 10H), 7.56 (br), 7.78$-$8.26 (br, 8H), 8.71$-$8.91 (br, 8H). FT-IR (KBr): $\upsilon = 3040$, 2922, 2851, 1467,1426, 1206, 967, 800, cm^{-1}.

Synthesis of Polymer (P4P5F1). A suspension of compound **1c** (110 mg, 0.1 mmol) and triphenylphosphine (55 mg, 0.21 mmol) in 60 mL of anhydrous toluene and anhydrous DMF (1:1, v:v) was heated at reflux for 12 h. The solvent was removed from the resulting clear solution under reduced pressure. The resulting residue was washed with toluene several times and filtered. Thus we obtained compound **1c′** (137 mg). A mixture of compound **1a′** (56 mg, 0.04 mmol), compound **1b** (25 mg, 0.05 mmol), and compound **1c′** (16 mg, 0.01 mmol) in 25 mL of anhydrous chloroform and ethanol (4:1, v:v) was stirred at room temperature under a nitrogen atmosphere. A freshly prepared solution of sodium ethoxide in anhydrous ethanol (3 M excess) was added dropwise to the mixture during 2 h. After the mixture stirred at room temperature for 24 h, the solution was concentrated in a vacuum and added dropwise to methanol at room temperature with stirring to precipitate the polymer. The polymer was purified by repeatedly precipitation from chloroform into methanol, washing with absolute diethyl ether and then dried under vacuum. This gave 32 mg (yield 51%) of the polymer **P4P5F1** as dark brown powder. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -2.57$ (br), 0.78$-$0.89 (br), 0.99$-$1.30 (br), 1.43$-$1.85 (br), 2.20$-$2.35 (br), 2.51$-$2.63 (br), 3.49 (br), 4.12$-$4.37 (br), 6.99$-$7.45 (br), 7.52 (br), 7.94$-$8.23 (br), 8.70$-$8.85 (br). FT-IR (KBr): $\upsilon = 2922$, 2851, 1719, 1659, 1458, 1378, 1076, 968, 527 cm^{-1}.

Synthesis of Polymer (P1P2F1). A mixture of compound **1a′** (42 mg, 0.03 mmol), compound **1b** (30 mg, 0.06 mmol), and compound **1c′** (49 mg, 0.03 mmol) in 25 mL of anhydrous chloroform and ethanol (4:1, v:v) was stirred at room temperature under a nitrogen atmosphere. The general procedure described above gave 33 mg (yield 42%) of polymer **P1P2F1**. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -2.57$ (br), 0.80$-$0.96 (br), 1.09$-$1.31 (br), 1.43$-$2.03 (br), 2.12$-$2.36 (br), 2.52$-$2.64 (br), 3.49 (br), 4.13$-$4.35 (br),7.00$-$7.53 (br), 7.55 (br), 7.717$-$8.26 (br), 8.71 (br). FT-IR (KBr): $\upsilon = 2921$, 2851, 1719, 1660, 1378, 1066, 968, 527 cm^{-1}.

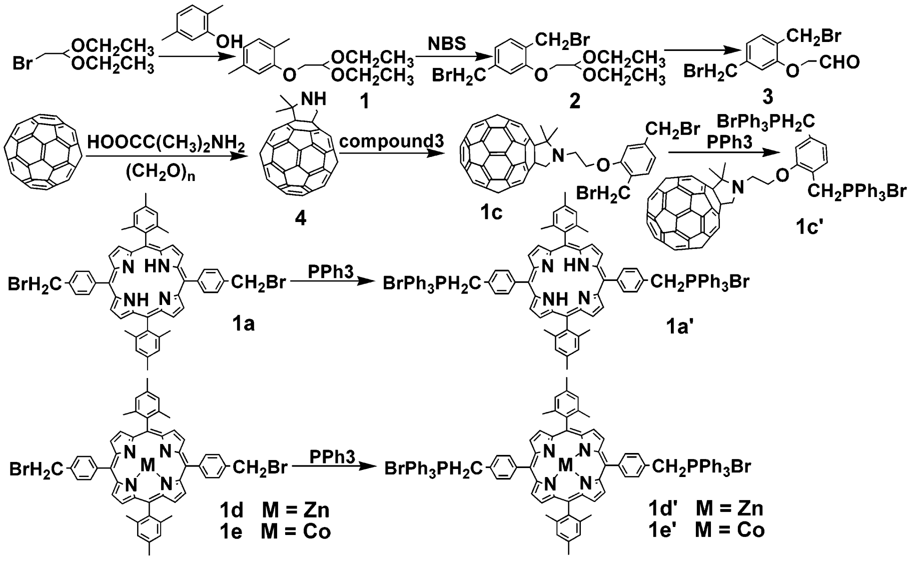
Synthesis of Polymer (ZnP4P5F1). A suspension of compound **1d** (95 mg, 0.1 mmol) and triphenylphosphine (55 mg, 0.21 mmol) in 50 mL of anhydrous toluene was heated at reflux for 12 h. The solvent was filtered. The resulting residue was washed with toluene several times and dried. Thus we obtained compound **1d′** (119 mg). A mixture of compound **1d′** (59 mg, 0.04 mmol), compound **1b** (25 mg, 0.05 mmol), and compound **1c′** (16 mg, 0.01 mmol) in 25 mL of anhydrous chloroform and ethanol (4:1, v:v) was stirred at room temperature under a nitrogen atmosphere. The general procedure described above gave 30 mg (yield 47%) of polymer **ZnP4P5F1**. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.84$$-$1.04 (br), 1.06$-$1.31 (br,), 1.42$-$2.00 (br), 2.35 (br), 2.62 (br), 3.49 (br), 4.08$-$4.40 (br), 6.97$-$7.45 (br), 7.51 (br), 7.70$-$8.26 (br), 8.70 (br). FT-IR (KBr): $\upsilon = 2921$, 2851, 1721, 1663, 1459, 1377, 1226, 969, 527 cm^{-1}.

Synthesis of Polymer (CoP4P5F1). A suspension of compound **1e** (94 mg, 0.1 mmol) and triphenylphosphine (55 mg, 0.21 mmol) in 50 mL of anhydrous toluene was heated at reflux for 12 h. The solvent was filtered. The resulting residue was washed with toluene several times and dried. Thus we obtained compound **1e′** (110 mg). A mixture of compound **1e′** (59 mg, 0.04 mmol), compound **1b** (25 mg, 0.05 mmol), and compound **1c′** (16 mg, 0.01 mmol) in 25 mL of anhydrous chloroform and ethanol (4:1, v:v) was stirred at room temperature under a nitrogen atmosphere. The general procedure described above gave 29 mg (yield 45%) of polymer **CoP4P5F1**. FT-IR (KBr): $\upsilon = 2922$, 2852, 1725, 1663, 1460, 1377, 1075, 968, 526 cm^{-1}.

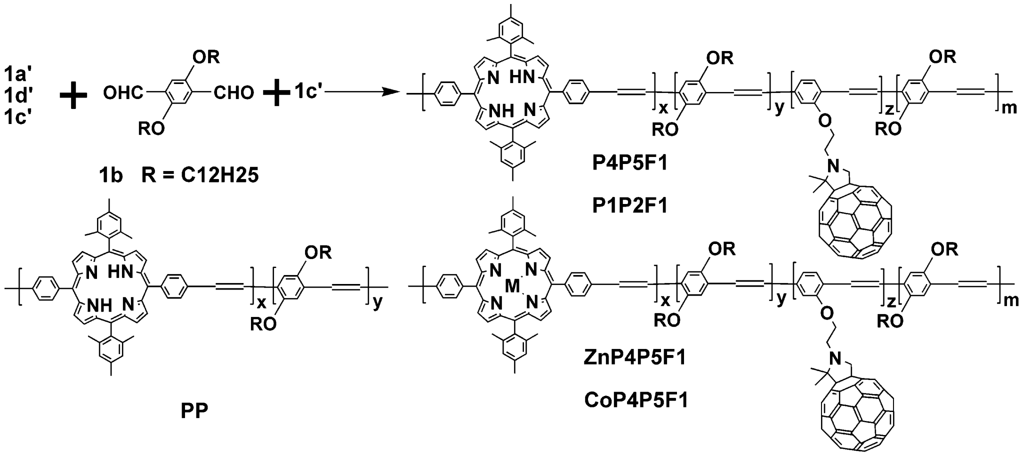
Results and Discussion

Synthesis of Monomers and Polymers. The synthetic methods for the novel monomers were illustrated in Scheme 1, and Scheme 2 outlined the structures and synthetic routes to the five polymers. To protect the aldehyde, bromoacetaldehyde diethyl acetal was used as a starting material for the synthesis of 2-(2,2-diethoxyethoxy)-1,4-bis(bromomethyl)benzene **2.** *N*-(1,4-bis(bromomethyl)-2-ethoxy-benzene)-2,2-dimethyl-3,4-fulleropyrrolidine (**1c**) was synthesized from compound **4** by using a facile method of reductive amination of compound **3** in high yield.[21] The compound **1c** was converted to the triphenylphosphonium salt before the polymerization, using both

Scheme 1. Synthesis of the Monomers



Scheme 2. Polymerization



toluene and DMF as solvent to provide reasonable solubility. The triphenylphosphonium salt was washed with dried toluene for purifying. Polymerization reaction was carried out by Wittig condensation at room temperature using sodium ethoxide in chloroform/ethanol (4:1, v:v). The volume ratio of chloroform/ethanol was controlled to provide reasonable reaction rates and solubility. The polymers were purified by precipitation from chloroform into methanol and washing with diethyl ether. The structure of the polymers **PP**, **P4P5F1**, **P1P2F1, ZnP4P5F1**, and **CoP4P5F1** were confirmed by ^{1}H NMR and FT-IR spectra.

The ^{1}H NMR spectra of the polymers showed no detectable peaks at δ 10.45[22] and 9.99[23] ppm which attributed to the aldehyde of compound **1b** indicated no existence of compound **1b**. The characteristic peaks at $\delta = 8.91-8.70$, $8.26-7.70$, and -2.57 ppm are attributed to the resonance of protons on porphyrin. The ^{1}H NMR signals in the olefinic regions showed peaks at $\delta = 7.62-7.50$ ppm, typical for *trans*-stilbene moieties.[24] The ^{1}H NMR spectra of the polymers showed broader peaks than those of monomers.

The FT-IR spectra of the dialdehyde compound **1b** showed the characteristic absorption peaks of aldehyde group at about 2730 cm^{-1}. While the absorption peaks at 2730 cm^{-1} disappeared in the FT-IR spectra of the polymers. At the same time, a weak absorption peak at 970−968 cm^{-1} corresponding to the out-of-plane bending mode of the *trans*-vinylene groups appeared, and no detectable peaks attributed to the cis isomer in the 730−670 cm^{-1} region could be found, confirming that the generated double bonds are mainly the trans configuration.

Table 1. Polymerization Results and Molecular Weights of Polymers PP, P4P5F1, P1P2F1, ZnP4P5F1, and CoP4P5F1[a]

polymers	M_n (g/mol)	M_w (g/mol)	PDI	yield (%)
PP	8422	13182	1.57	60
P4P5F1	7126	8432	1.18	51
P1P2F1	5592	5680	1.02	42
ZnP4P5F1	5134	9116	1.78	47
CoP4P5F1	7869	19473	2.47	45

[a] GPC in THF using polystyrene standards

The polymerization results determined by GPC were displayed in Table 1. GPC analysis used THF as eluent and polystyrene standards for calibration. In fact, all those four polymers were lowly soluble in THF, therefore, their actual molecular weights should be higher than the measured values because the insoluble parts possessed higher molecular weights.

Optical Properties. Figure 1 showed the UV−vis absorption spectra of the monomers and the polymers in chloroform (10 μmol/L). Characteristic visible absorptions of the porphyrins appear in the 420 nm region for the B-band $\pi-\pi^*$ transitions. Additional electronic transitions appear as sets of peaks in the 500−600 nm regions of the spectra, consistent with Q-band transitions. The main absorption band of the compound **1a** showed peaks at 419 nm, while the absorption of the polymers attributed to the unit red-shifted by 2 and 4 nm in Figure 1A.

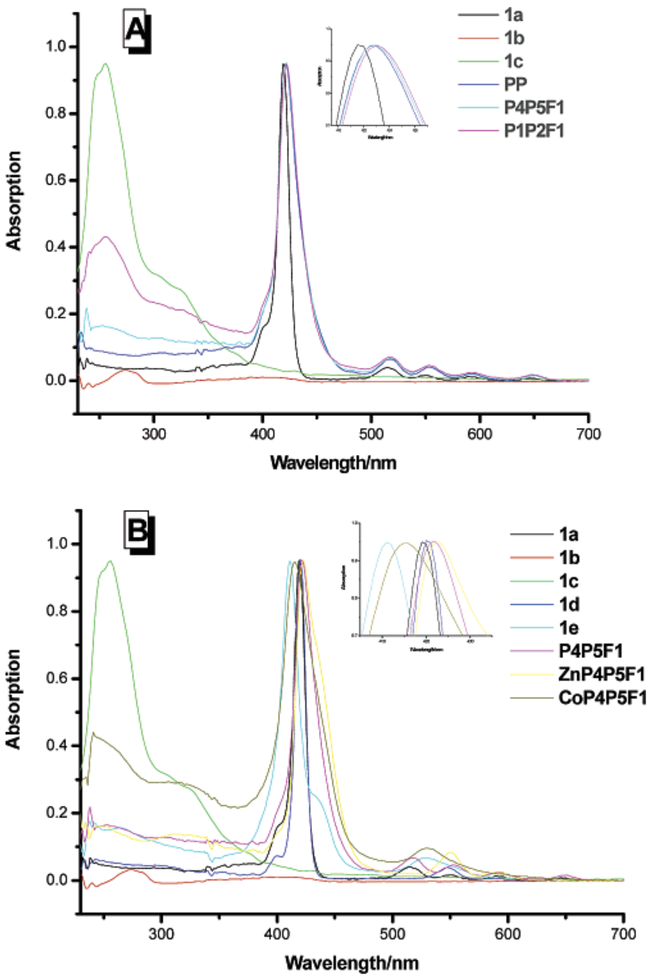


Figure 1. (A) UV−vis absorbance spectra of compound **1a**, compound **1b**, compound **1c**, **PP**, **P4P5F1**, and **P1P2F1** in chloroform. (B) UV−vis absorbance spectra of compound **1a**, compound **1b**, compound **1c**, compound **1d**, compound **1e**, **P4P5F1**, **ZnP4P5F1**, and **CoP4P5F1** in chloroform.

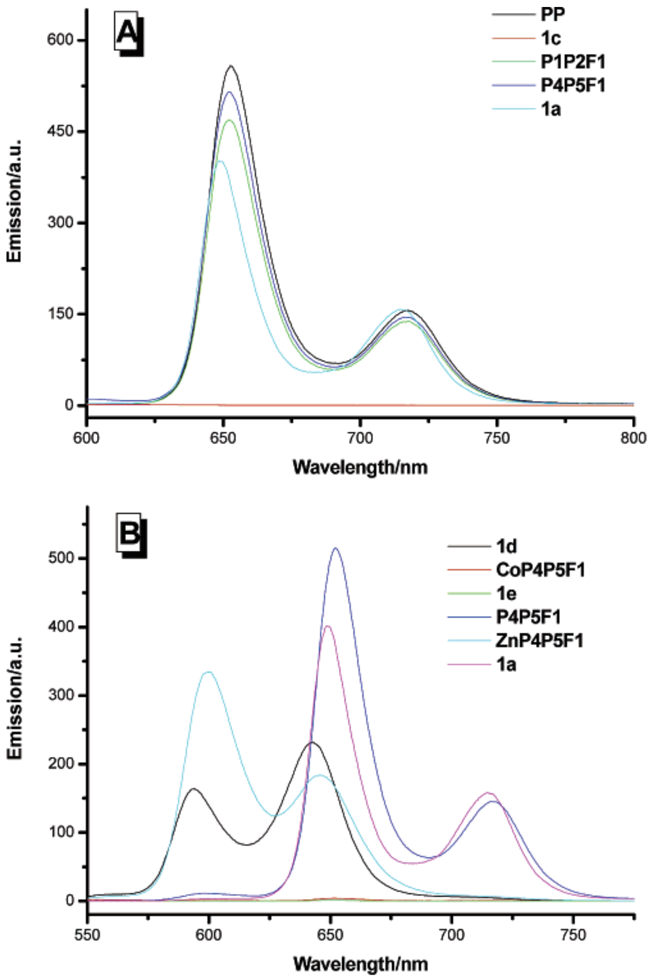


Figure 2. (A) Fluorescence spectra of compound **1a**, compound **1c**, **PP**, **P4P5F1**, and **P1P2F1** in chloroform. (B) Fluorescence spectra of compound **1a**, compound **1d**, compound **1e**, **P4P5F1**, **ZnP4P5F1**, and **CoP4P5F1** in chloroform. Excitation wavelength = 421 nm; concentration = 10^{-6} mol/L

Meanwhile, the absorption of the polymers red-shifted gradually with the content of the fullerene in the polymers increased. The main absorption band of the compound **1d** showed peaks at 420 nm, while the absorption of the polymer **ZnP4P5F1** attributed to the unit red-shifted by 3 nm in Figure 1B. The main absorption band of the compound **1e** showed peaks at 411 nm, while the absorption of the polymer **CoP4P5F1** attributed to the unit red-shifted by 4 nm in Figure 1B. The polymers attributed to the PPV structure was broader at around 400 nm due to the $\pi-\pi^*$ transition of the PPV conjugated backbone.[26]

The fluorescence spectra of monomers **1a** and **1c** and polymers **PP**, **P4P5F1**, and **P1P2F1** in chloroform at excitation wavelength 421 nm are shown in Figure 2A. The fluorescence of porphyrin is enhanced in polymers **PP**, **P4P5F1**, and **P1P2F1**. However, fluorescence is quenched after introducing fullerene into the polymers. That resulted from the discrepancy of push−pull electron properties between porphyrin units, PPV units and fullerene units. Figure 2A also shows that the more contents of the fullerene unit the polymer had the stronger the fluorescent quenching of the polymer would be. The compound **1c** almost had no fluorescence. The fluorescence spectra of monomers **1a**, **1d**, and **1e** and polymers **P4P5F1**, **ZnP4P5F1**, and **CoP4P5F1** in chloroform at excitation wavelength 421 nm are shown in Figure 2B. As shown in Figure 2B, the fluorescence maximum and shape of the polymers are obviously different from the monomers. Co^{II} has a d^7 electronic configuration. The unpaired electron in the $d_{x^2-y^2}$ orbital couples with the normal porphyrin (π, π^*) excited states to form the singdoublet, ^{2}Q (π, π^*), the tridoublet, ^{2}T (π, π^*), and the quartet, ^{4}T (π, π^*). These complexes do not exhibit the typical fluorescence of closed-shell metalloporphyrins. So the monomers **1e** and polymer **CoP4P5F1** almost had no fluorescence.

Cyclic Voltammetry. The redox properties of the monomers and the polymers were studied by cyclic voltammetry (CV). CV experiments were performed at room temperature in anhydrous *o*-dichlorobenzene solution containing 0.04 M $TBAPF_6$ as electrolyte. The CV data of the monomers and the polymers were displayed in Table 2. As shown in Table 2A, the electrochemical reduction of polymer **PP** shows four one-electronprocesses at −1.23, −1.37, −1.73 and −1.65 V, corresponding to producing monoanion, dianion and trianion of the porphyrin unit, and anion of PPV unit, respectively. The electrochemical oxidations of the polymers **PP** at 1.67, 1.22, 1.47, and 1.05 V correspond to producing the monocation and dication of the porphyrin unit and the monocation and dication of the PPV unit, respectively. The phenomena of the polymer **P4P5F1** and the polymer **P1P2F1** were similar to that of the polymer **PP**. It should be pointed out that the reduction potentials of fullerene attached to the conjugated backbone are decreased compared to the corresponding reduction process of the compound **1c,** which indicates better electron-accepting ability. The first reduction potential of the polymers decreased with

Table 2. Cyclic Voltammetry Data of the Monomers and Polymers

Part A

compound	peak potential[a]/V										
	E_{ox}^{a2}	E_{ox}^{a1}	E_{ox}^{b2}	E_{ox}^{b1}	E_{red}^{a1}	E_{red}^{a2}	E_{red}^{a3}	E_{red}^{b1}	E_{red}^{c1}	E_{red}^{c2}	E_{red}^{c3}
1a	1.70	1.21			−1.23	−1.37	−1.74				
1b			1.52	1.05				−1.66			
1c									−0.82	−1.26	−1.81
PP	1.67	1.22	1.47	1.05	−1.23	−1.37	−1.73	−1.66			
P4P5F1	1.74	1.26	1.42	1.03	−1.23	−1.33	−1.72	−1.62	−0.65	−1.24	−1.76
P1P2F1	1.67	1.30	1.40	1.03	−1.20	−1.31	−1.71	−1.61	−0.59	−1.22	−1.74

Part B

compound	peak potential[a]/V												
	E_{ox}^{b2}	E_{ox}^{b1}	E_{ox}^{d2}	E_{ox}^{d1}	E_{ox}^{e3}	E_{ox}^{e2}	E_{ox}^{e1}	E_{red}^{b1}	E_{red}^{c1}	E_{red}^{c2}	E_{red}^{c3}	E_{red}^{d1}	E_{red}^{e1}
1b	1.52	1.05						−1.66					
1c									−0.82	−1.26	−1.81		
1d			1.25	0.57								−1.70	
1e					1.54	1.35	1.06						−0.85
ZnP4P5F1	1.26	1.03	1.09	0.54				−1.64	−0.73	−1.21	−1.78	−1.67	
CoP4P5F1	1.49	1.03			1.40	1.32	1.04	−1.56	−0.80	−1.20	−1.76		−0.82

[a] Versus Ag wire. The scan rate was 50 mV/s

the content of the fullerene unit in the polymers increased. Although the first oxidation potential of the polymers are bigger than the corresponding oxidation peak potential of the fullerene, the potential gaps between the first oxidation peak potential and reduction peak potential of the polymers are gradually decreased with the content of the fullerene in the polymers increased. The results show that the polymer with pendent fullerene, porphyrin and PPV units is a good candidate for the photoinduced electron-transfer system. Table 2B showed us the phenomena of polymers **ZnP4P5F1** and **CoP4P5F1** which were similar to the polymer **P4P5F1**.

Photocurrent Generation. A conventional three-electrode cell was used to measure the photoelectrochemical properties of the monolayer film deposited on indium−tin oxide (ITO) glass. The electrolyte solution selected in all measurements was 0.5 M KCl. A platinum wire was used as a counter electrode, a saturated calomel electrode was used as a reference electrode, and the ITO glass modified with polymer was used as a working electrode. The photocurrent of the polymers monolayer film deposited on ITO electrode was measured separately at white light irradiation of 20.7 mW cm^{-2}. As shown in Figure 3A, a steady and rapid photocurrent response was produced when the irradiation of the monolayer film was switched on and off. The polymer **PP** monolayer film engendered cathodic photocurrent of 0.086 μA cm^{-2}. However, the polymers **P4P5F1,** and **P1P2F1** films engendered cathodic photocurrents of 0.149 and 0.152 μA cm^{-2}, respectively. More interestingly, the photocurrent enhanced with the content of the fullerene unit in the polymers increased. This was due to the increase of the component of fullerene electron acceptor in the polymers. As shown in Figure 3B, the polymer **ZnP4P5F1** monolayer film engendered a cathodic photocurrent of 0.196 μA cm^{-2}, while the polymer **CoP4P5F1** monolayer film engendered a cathodic photocurrent of 0.095 μA cm^{-2}.

SEM. We studied the morphologies of three polymers by scanning electron microscope (SEM). Samples were prepared by casting thin films of polymers from chloroform onto silicon slices. Parts A−C of Figure 4 showed that polymers **P4P5F1**, **ZnP4P5F1,** and **CoP4P5F1** in $CHCl_3$ (10^{-4} M) could form the aggregation nanobriquetting, because C_{60} derivatives were easy to gather together to form spherical particles through the $\pi-\pi^*$ stacking interacting of carbon cage.[27] This could be also confirmed by the SEM image of polymers **PP, P4P5F1** and **P1P2F1** in $CHCl_3$ (10^{-4} M) (see Supporting Information Figure 1s). Parts D−F of Figure 4 showed that polymers **P4P5F1**, **ZnP4P5F1,** and **CoP4P5F1** in $CHCl_3$ (10^{-4} M) with the addition of 4,4′-bipyridine (Bipy) at 1:1 molar radio could form the nanofiber. The average width and the average length of the nanofiber of polymer **P4P5F1** were about 85 nm and about 400 nm, respectively, while those of polymer **ZnP4P5F1** were about

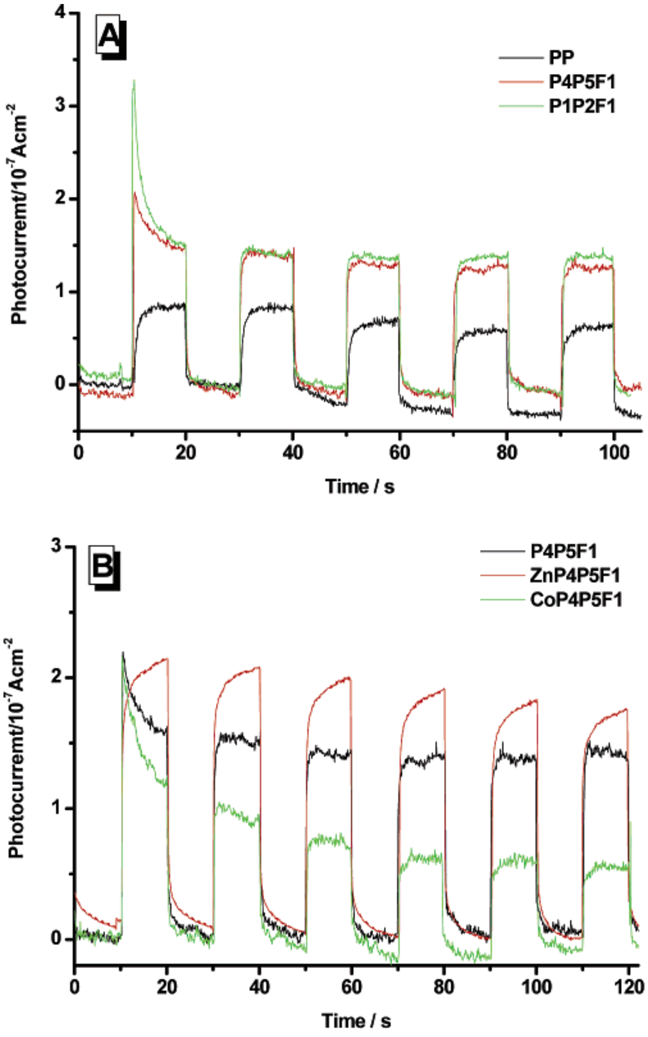


Figure 3. Photocurrent generation of the monolayer films upon the irradiation of 20.7 $mWcm^{-2}$ white light in 0.5 M KCl solution.

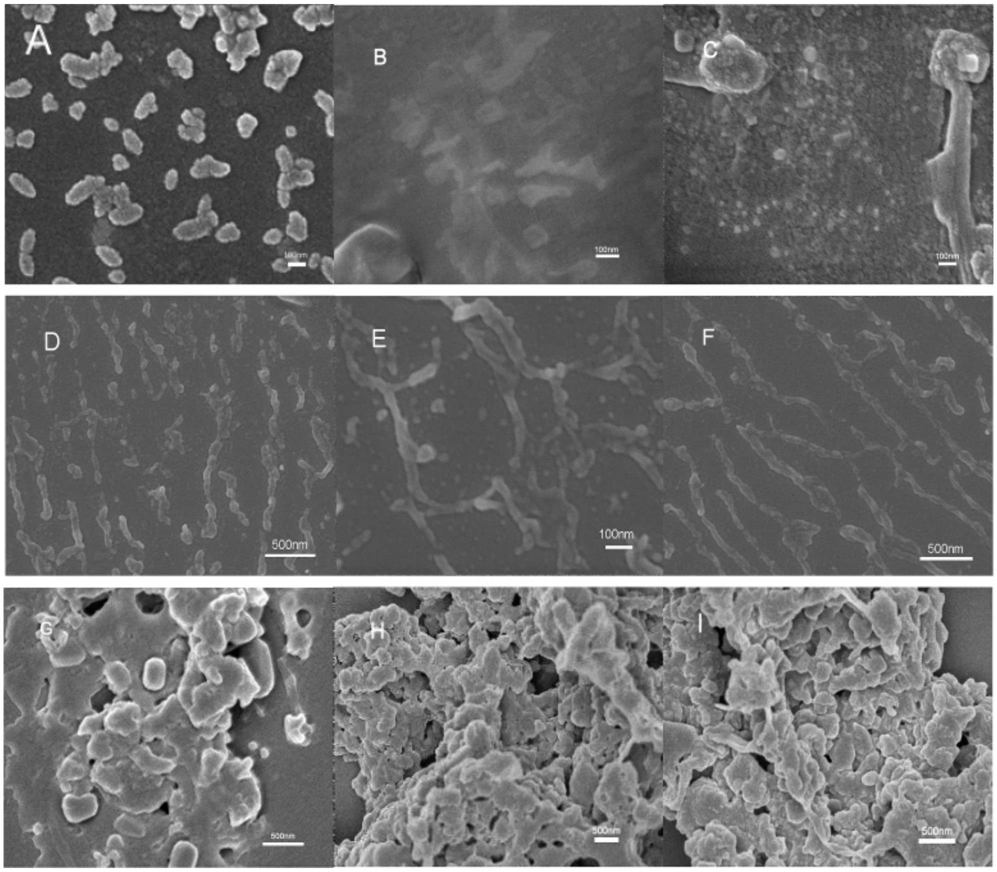


Figure 4. (A) SEM image of polymer **P4P5F1** in $CHCl_3$. (B) SEM image of polymer **ZnP4P5F1** in $CHCl_3$. (C) SEM image of polymer **CoP4P5F1** in $CHCl_3$. (D). SEM image of polymer **P4P5F1** in $CHCl_3$ with 4,4′-bipyridine (Bipy), 1:1 stoichiometry. (G) SEM image of polymer **P4P5F1** in $CHCl_3$ with 4,4′-bipyridine (Bipy), 1:5 stoichiometry. (E) SEM image of polymer **ZnP4P5F1** in $CHCl_3$ with 4,4′-bipyridine (Bipy), 1:1 stoichiometry. (H) SEM image of polymer **P4P5F1** in $CHCl_3$ with 4,4′-bipyridine (Bipy), 1:5 stoichiometry. (F) SEM image of polymer **CoP4P5F1** in $CHCl_3$ with 4,4′-bipyridine (Bipy), 1:1 stoichiometry. (I) SEM image of polymer **CoP4P5F1** in $CHCl_3$ with 4,4′-bipyridine (Bipy), 1:5 stoichiometry.

50 nm and about 800 nm, respectively, and those of polymer **CoP4P5F1** were about 50 nm and about 1200 nm, respectively. It was likely that this was driven by phase transitions in the drying process and would depend on the solvent, substrate, and environment. However, it was probably mainly caused due to the axial coordination of porphyrin and Bipy and the $\pi-\pi^*$ interaction of fullerene cage. This the nanofiber of the polymer **ZnP4P5F1** and **CoP4P5F1** was longer than the nanofiber of the polymer **P4P5F1** confirmed that the axial coordination of porphyrin and Bipy was the main reason. The hybridized orbital of the Zn^{II} was sp^3, while the hybridized orbital of the Co^{II} was dsp^2. So the axial coordination of polymer **CoP4P5F1** and Bipy was more stable than that of polymer **ZnP4P5F1** and Bipy, and the nanofiber of the polymer **ZnP4P5F1** was longer than the nanofiber of the polymer **CoP4P5F1**. Parts G−I of Figure 4 showed that polymers **P4P5F1**, **ZnP4P5F1,** and **CoP4P5F1** in $CHCl_3$ (10^{-4} M) with the addition of 4,4′-bipyridine (Bipy) at 1:5 molar radio could form the hierarchical porous structure. We presumed that this was both caused due to the axial coordination of porphyrin and Bipy and the $\pi-\pi^*$ interaction of fullerene cage and driven by phase transitions in the drying process, and it would depend on the solvent, substrate, and environment.

Conclusions

We have described the synthetic methods for fabricating the conjugated polymer systems having porphyrin, PPV and/or pendant fullerene units by means of the Wittig reaction. The polymers were characterized by ^1H NMR, FT-IR spectra, and GPC analysis. The optical properties of the polymers were studied by UV−vis and FL spectra. The cyclic voltammetry showed us a good candidate for a photoinduced electron-transfer system. The photocurrent revealed that the photocurrent increased with the content of the fullerene in the polymers increased. SEM images displayed the aggregation superstructures of three polymers. In chloroform polymers of **P4P5F1**, **ZnP4P5F1**, and **CoP4P5F1** can form nanobriquetting structures. When polymers of **P4P5F1**, **ZnP4P5F1**, and **CoP4P5F1** were mixed with 1 equiv of Bipy, the nanofiber was observed, while when polymers **P4P5F1**, **ZnP4P5F1**, and **CoP4P5F1** were mixed with 5 equiv of Bipy, the hierarchical porous structure was also observed. The results indicated that the axial coordination of metal porphyrin and Bipy was very important to control the aggregation morphologies of the three polymers.

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Supporting Information Available: Figure 1s, SEM images of polymer **PP**, **P4P5F1**, and **P1P2F1** in $CHCl_3$, Figure 2s, FT-IR spectrum of compound **1c**, Figure 3s, FT-IR spectrum of compound **1e**, Figure 4s, FT-IR spectrum of polymer **PP**, Figure 5s, FT-IR spectrum of polymer **P4P5F1**, Figure 6s, FT-IR spectrum of polymer **P1P2F1**, Figure 7s, FT-IR spectrum of polymer **ZnP4P5F1**, Figure 8s, FT-IR spectrum of polymer **CoP4P5F1**, Figure 9s, ^1H NMR spectrum of compound **1c**, Figure 10s, ^1H NMR spectrum of polymer **PP**, Figure 11s, ^1H NMR spectrum of polymer **P4P5F1**,

Figure 12s, ^{1}H NMR spectrum of polymer **P1P2F1**, Figure 13s, ^{1}H NMR spectrum of polymer **ZnP4P5F1**, Figure 14s, GPC spectrum of polymer **PP**, Figure 15s, GPC spectrum of polymer **P4P5F1**, Figure 16s, GPC spectrum of polymer **P1P2F1**, Figure 17s, GPC spectrum of polymer **ZnP4P5F1**, and Figure 18s, GPC spectrum of polymer **CoP4P5F1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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