A New Class of Conjugated Polyacetylenes Having Perylene Bisimide Units and Pendant Fullerene or Porphyrin Groups

Yang Liu,^{†,‡} Ning Wang,^{†,‡} Yongjun Li,^{†,‡} Huibiao Liu,[†] Yuliang Li,^{*,†} Jinchong Xiao,^{†,‡} Xinhe Xu,^{†,‡} Changshui Huang,^{†,‡} Shuang Cui,^{†,‡} and Daoben Zhu[†]

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

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ABSTRACT: A new class of conjugated polyacetylenes having perylene bisimide units and pendant fullerene or porphyrin groups were synthesized and characterized. SEM images displayed the aggregation superstructures of two polymers. The poly($\mathbf{5}_{0.1}$ -co- $\mathbf{4}_{0.9}$) can form a large quantity of spherical nanoparticles in chloroform because [60]fullerene derivatives have high aggregation tendency due to the $\pi - \pi^*$ stacking of the carbon cage. Furthermore, poly($\mathbf{6}_{0.1}$ -co- $\mathbf{4}_{0.9}$) can form different aggregation structures in chloroform with the addition of 4,4'-bipyridine (Bipy). In particular, when poly($\mathbf{6}_{0.1}$ -co- $\mathbf{4}_{0.9}$) was mixed with 2 equiv of Bipy, a uniform cottonlike superstructure was observed. These results indicated that the axial coordination of zinc porphyrin and Bipy played an important role in controlling the aggregation morphologies of poly($\mathbf{6}_{0.1}$ -co- $\mathbf{4}_{0.9}$) in CHCl₃ with the addition of Bipy. More interestingly, the photocurrent measurement showed that the films of these polyacetylenes could produce steady and rapid cathodic photocurrent responses, indicating that efficient charge transfer took place in two donor-acceptor polymers.

Introduction

In recent years, the synthesis of polymers containing C_{60} with a well-defined structure has attracted great interest due to their possible applications in the fields of materials¹ and biological sciences.² Fullerene C_{60} , as a novel three-dimensional acceptor, has been extensively studied for the construction of efficient electron-transfer model systems.³ It has been well established that fullerenes have the ability of remarkable acceleration of photoinduced charge separation and deceleration of charge recombination in donor-fullerene systems.⁴ Various kinds of porphyrin arrays, with their importance in artificial photosynthesis and molecular devices, have been demonstrated.⁵ Porphyrin-based polymers and oligomers have been actively pursued due to their potential applications in solar energy conversion, charge storage and transport, and nonlinear optical materials.⁶ Recently, red dyes based on perylene bisimides have attracted considerable attention⁷⁻¹⁰ and have been employed in various applications such as optical switching,¹¹ photovoltaic devices,¹² and dve lasers¹³ due to their excellent chemical, thermal, and photochemical stability. Perylene bisimides are potential candidates as electron-accepting materials.¹⁴ Sometimes peryelene bisimides can be also used as electron-donor materials.^{10a} Polyacetylene derivatives exhibit unique properties such as semiconductivity, high gas permeability, helix inversion, and nonlinear optical properties.¹⁵ Therefore, there has been an increasing interest in design and synthesis of polyacetylene derivatives having functional groups.¹⁶ It is expected that attaching side groups, such as fullerene, porphyrin, and perylene, to the well-defined π -conjugated backbone¹⁷ will improve the light-harvesting capacity and charge separation efficiency for poten-

[‡] Graduate School of Chinese Academy of Sciences.

* Corresponding author. E-mail: ylli@iccas.ac.cn.

tial application in solar cells based on synergistic actions of pendants and main-chain conjugation.

Here, we report the synthesis of a new class of polyacetylenes having perylene bisimides. The bissubstituted acetylene with perylene unit and monosubstituted acetylenes with [60]fullerene or porphyrin group were copolymerized with transition metal catalyst [Rh(nbd)Cl]₂ in CHCl₃. Copolymerized reactions were proved to be successful by FT-IR, ¹H NMR, and UVvis measurements. In this work we also studied the morphologies of polymers, especially how the axial coordination of zinc porphyrin and 4,4'-bipyridine effected the superstructure of polyacetylene having pervlene bisimide and zinc porphyrin group. In addition, photocurrent response measurements showed that efficient electron transfer took place in these polymer systems. It is expected that such polyacetylenes having pervlene bisimide units can improve charge separation efficiency for potential application in solar cells.

Experimental Section

Measurements. Column chromatography (CC): SiO₂ (160-200 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. ¹H NMR spectra were recorded on a Bruker ARX400 spectrometer. MALDI-TOF mass spectrometric measurements were performed on Bruker Biflex III MALDI-TOF (both positive and negative ion reflector mode). Elemental analyses were carried out on a Carlo Erba 1106 elemental analyzer. The molecular weights of polymers were determined by gel permeation chromatography (GPC) on a Waters Breeze system equipped with polystyrene gel columns, using tetrahydrofuran (THF) as eluent. Thermal gravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA-7 under nitrogen. Photocurrent response was recorded on CHI660B voltammetric analyzer (CH Instruments). Scanning electron micrographs (SEM) were recorded on a JSM 6700F NT instrument.

Materials. Unless otherwise stated, reagents were commercially obtained and used without further purification. 1,7-

[†] Chinese Academy of Sciences.

Dibromo-N,N'-(2,6-diisopropylphenyl)perylene-3,4,9,10-tetracarboxylic acid bisimide (1) was synthesized according to the literature.¹⁸ The solvents for polymerization were purified according to the standard methods.

1,7-Di(4-iodophenoxy)-N,N'-(2,6-diisopropylphenyl)perylene-3,4,9,10-tetracarboxylic Acid Bisimide (2). A mixture of 4-iodophenol (440 mg, 2 mmol), anhydrous potassium carbonate (138 mg, 1 mmol), and 18-crown-6 (528 mg, 2 mmol) was stirred in toluene (15 mL) at room temperature. Then compound 1 (430 mg, 0.5 mmol) was added. The reaction mixture was refluxed under nitrogen with stirring for 20 min. After cooling to room temperature, the reaction mixture was poured into the saturated solution of potassium carbonate. The organic phase was collected and washed by the distilled water for three times, dried by anhydrous sodium sulfate, and filtered. The solvent was removed by reduced pressure, and the residue was dried by vacuum to give the crude product. Purification was accomplished by column chromatography on silica with CH₂Cl₂ to afford 2 (397 mg, 69%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 9.55 (d, 2H, J = 7.6 Hz), 8.71 (d, 2H, J= 7.6 Hz), 8.41 (s, 2H), 7.75 (d, 4H, J = 8.2 Hz), 7.48 (t, 2H, J= 7.6 Hz), 7.34 (d, 4H, J = 7.6 Hz), 6.94 (d, 4H, J = 8.2 Hz), 2.74 (m, 4H), 1.14 (d, 24H, J = 6.5 Hz); UV/vis (CHCl₃): λ_{max} 535 nm, 503 nm, 405 nm. Fluorescence (CHCl₃): λ_{max} 571 nm. FT-IR (KBr), v [cm⁻¹]: 2963, 1709, 1670, 1597, 1479, 1406, 1337, 1260, 1201, 1006, 911, 837, 813, 738. MS (MALDI-TOF): 1146.5 (M⁻). Elemental analysis calcd (%) for C₆₀H₄₈-N₂O₆I₂ (1146.2): C, 62.84; H, 4.22; N, 2.44. Found: C, 62.89; H, 4.85; N, 2.48.

1,7-Di[4-(trimethylsilylethylnyl)phenoxy]-N,N'-(2,6-diisopropylphenyl)perylene-3,4,9,10-tetracarboxylic Acid Bisimide (3). Compound 2 (150 mg, 0.13 mmol) was dissolved in a mixture of dried triethylamine (10 mL) and absolute THF (15 mL) under nitrogen. Palladium acetate (18. 5 mg, 0.07 mmol), CuI (13.4 mg, 0.07 mmol), and PPh₃ (34 mg, 0.13 mmol) were added. Then trimethylsilvlethyne (88 mg, 0.9 mmol) was added under a flow of nitrogen. The reaction mixture was stirred for 78 h at room temperature and then poured into an equal volume of dichloromethane and filtered. Hydrochloric acid (6 M) was added to the filtrate until the aqueous phase became slightly acidic (pH < 5). Then the organic phase was collected and washed by a saturated solution of ammonium chloride. Then the organic phase was washed several times by the distilled water and dried by anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica with CH₂Cl₂/petroleum ether (1/2, v/v) to give 3 (119 mg, 84%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 9.57 (d, 2H, J = 9.0 Hz), 8.73 (d, 2H, J = 9.0 Hz), 8.42 (s, 2H), 7.55 (d, 4H, J= 9.0 Hz), 7.49 (t, 2H, J = 9.0 Hz), 7.34 (d, 4H, J = 9.0 Hz), 7.11 (d, 4H, J = 9.0 Hz), 2.75 (m, 4H), 1.18 (d, 24H, J = 6.7Hz), 0.26 (s, 18H). UV/vis (CHCl₃): λ_{max} 535 nm, 502 nm. Fluorescence (CHCl₃): λ_{max} 568 nm. FT-IR (KBr), ν [cm⁻¹]: 2962, 2159, 1710, 1672, 1594, 1498, 1406, 1336, 1258, 1201, 863, 760, 539. MS (MALDI-TOF): 1086.2 (M⁻). Elemental analysis calcd (%) for C₇₀H₆₆N₂O₆Si₂ (1086.5): C, 77.31; H, 6.12; N, 2.58. Found: C, 76.79; H, 6.29; N, 2.69.

1,7-Di(4-ethylnylphenoxy)-N,N'-(2,6-diisopropylphenyl)perylene-3,4,9,10-tetracarboxylic Acid Bisimide (4). Compound 3 (108.6 mg, 0.1 mmol) was dissolved in dry THF (10 mL) under nitrogen. A 0.8 mL solution of ⁿBu₄NF in THF (1 M) was added. The mixture was stirred for 20 min at room temperature. The solution was diluted with dichloromethane and washed by 6 M hydrochloric acid. The organic phase was collected, washed by distilled water, and dried over sodium sulfate. The solvent was removed by reduced pressure, and the crude product was purified by column chromatography on silica gel (eluent: CH₂Cl₂) to give 5 (45 mg, 48%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 9.57 (d, 2H, J = 8.0 Hz), 8.71 (d, 2H, J = 8.0 Hz), 8.43 (s, 2H), 7.57 (d, 4H, J = 8.0 Hz), 7.49 (t, 2H, J = 8.0 Hz), 7.34 (d, 4H, J = 8.0 Hz), 7.12 (d, 4H, J = 8.0Hz), 3.09 (s, 2H), 2.73 (m, 4H), 1.14 (d, 24H). UV/vis (CHCl₃): λ_{max} 533 nm, 502 nm, 405 nm. Fluorescence (CHCl₃): λ_{max} 568 nm. FT-IR (KBr), ν [cm⁻¹]: 3295, 2962, 2109, 1708, 1669, 1595, 1498, 1407, 1339, 1260, 1203, 1017, 912, 837, 812, 740, 550. MS (MALDI–TOF): 942.3 (M⁻). Elemental analysis calcd (%) for $C_{64}H_{50}N_2O_6$ (942.4): C, 81.51; H, 5.34; N, 2.97. Found: C, 81.18; H, 5.45; N, 3.12.

Poly(50,1-co-40.9). A dry flask was evacuated on a vacuum line and flushed with dry nitrogen. This evacuation-flush procedure was repeated for three times. Compound 4 (47 mg, 0.05 mmol) and compound 5 (5 mg, 0.0056 mmol) were dissolved in dry CHCl₃. The solution was injected into the dry flask with a syringe. To this was added a solution of a [Rh- $(nbd)Cl]_2$ catalyst in CHCl₃ and triethylamine (40 μ L). After 48 h, the resulting polymer was precipitated into a large amount of methanol. The product was collected by centrifugation, washed with methanol, and dried in a vacuum to give a dark solid (17.3 mg). ¹H NMR (400 MHz, CDCl₃/CS₂, 25 °C): δ 9.58 (br, 2H), 8.69 (br, 2H), 8.41 (br, 2H), 7.57-7.00 (br, 14H), 5.30 (s, 1H), 3.73 (d, 2H), 3.09 (s, 1H), 2.68 (br, 4H), 2.36 (s, 1H), 2.18 (s, 1H), 2.05 (s, 1H), 1.14 (br, 24H). UV/vis (CHCl₃): λ_{max} 540 nm, 510 nm. FT-IR (KBr), ν [cm⁻¹]: 2962, 1709, 1672, 1594, 1499, 1405, 1337, 1260, 1202, 1095, 1014, 910, 809, 739, 528. GPC (THF, g/mol): M_n, 3523; M_w, 5902; M_z, 13155. PDI: 1.68

Poly(60.1-co-40.9). A dry flask was evacuated on a vacuum line and flushed with dry nitrogen. This evacuation-flush procedure was repeated for three times. Compound 4 (47 mg, 0.05 mmol) and compound 6 (5.6 mg, 0.0056 mmol) were dissolved in dry CHCl₃. The solution was injected into the dry flask with a syringe. To this was added a solution of a [Rh-(nbd)Cl]₂ catalyst in CHCl₃ and triethylamine (40 μ L). After 48 h, the resulting polymer was precipitated into a large amount of methanol. The product was collected by centrifugation, washed with methanol, and dried in a vacuum to give a dark solid (10.6 mg). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 9.54 (br, 2H), 9.06 (br, 2H), 8.70 (br, 2H), 8.43 (br, 2H), 7.55-7.00 (br, 20H), 5.30 (s, 1H), 4.19 (br, 1H), 3.96 (br, 2H), 3.71 (br, 1H), 3.08 (s, 1H), 2.69 (br, 4H), 2.17 (s, 1H), 1.14 (br, 24H). UV/vis (CHCl₃): λ_{max} 542 nm, 508 nm, 427 nm. FT-IR (KBr), ν [cm⁻¹]: 2963, 1710, 1672, 1595, 1500, 1406, 1339, 1260, 1203, 1167, 1096, 1015, 911, 863, 809, 739. GPC (THF, g/mol): M_n, 4428; Mw, 6473; Mz, 10265. PDI: 1.46.

Results and Discussion

Scheme 1 showed the synthetic route of bis-substituted acetylene 4 with perylene bisimide unit. Briefly, compound 2 was prepared by the nucleophilic substitution of the two bromine atoms of compound 1 using 4-iodophenol. Subsequently, compound 2 was doubly heterocoupled with trimethylsilylethyne in triethylamine with the palladium catalyst, at room temperature, to give compound 3 in a good yield. Then compound 4 was obtained by desilylation using "Bu₄NF in dry THF. These perylene bisimides were mixtures of 1,7 and 1,6 regioisomers rather than isomerically pure compounds,¹⁹ and there was no way of separating the isomers on a larger scale so the isomeric mixtures were used as such.¹⁸

Two other monomers, 2-(4-ethynyloxy-phenyl)-3,4fulleropyrrolidine (**5**) and 5-(4-prop-2-ynyloxyphenyl)-10,15,20-tris(3,4,5-trimethoxyphenyl)-21*H*,23*H*-porphyrine zinc (**6**), were synthesized according to the literature.^{16d} The acetylene-containing monomers were copolymerized in the presence of a rhodium catalyst in anhydrous chloroform at room temperature for 48 h, as shown in Scheme 2. The rhodium catalyst [Rh(nbd)Cl]₂ has been reported to be effective for the polymerization of monosubstituted acetylenes to afford high molecular weight stereoregular polymers with the cis C=C backbone.²⁰

 $Poly(\mathbf{6}_{0.1}$ -co- $\mathbf{4}_{0.9})$ has a better solubility than $poly(\mathbf{5}_{0.1}$ -co- $\mathbf{4}_{0.9})$ in common organic solvents such as chloroform and toluene because zinc porphyrin derivative **6** is more soluble than fullerene derivative **5**. Table 1 displayed





^a Reaction conditions: (a) 4-iodophenol, K₂CO₃, 18-crown-6, toluene, nitrogen, reflux, 20 min, 69%; (b) PPh₃, Pd(OAc)₂, CuI, trimethylsilylethyne, dried Et₃N, absolute THF, nitrogen, rt, 78 h, 84%; (c) ⁿBu₄NF, absolute THF, rt, 20 min, 48%.

 Table 1. Polymerization Results and Molecular Weights

 of Polyacetylenes^a

copolymers	$M_{\rm n}$ (g/mol)	$M_{ m w}$ (g/mol)	M_z (g/mol)	PDI	yield (%)					
$\begin{array}{c} \text{poly}(5_{0.1}\text{-}co\text{-}4_{0.9})\\ \text{poly}(6_{0.1}\text{-}co\text{-}4_{0.9}) \end{array}$	$\begin{array}{c} 3523\\ 4428 \end{array}$	$\begin{array}{c} 5902 \\ 6473 \end{array}$	$\frac{13}{10} \frac{155}{265}$	$\begin{array}{c} 1.68\\ 1.46\end{array}$	33 20					
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^a GPC in THF using polystyrene standards.

polymerization results and molecular weights of two polyacetylenes. The number-average and weight-average molecular weights for $poly(5_{0.1}-co-4_{0.9})$ were 3523 and 5902, respectively, whereas those for $poly(\mathbf{6}_{0.1}$ -co- $4_{0.9}$) were 4428 and 6473, respectively. In fact, two copolymers were partially soluble in THF, their actual molecular weights should be higher than the measured values because the insoluble parts possessed higher molecular weights. Thermal properties of two polyacetylenes were measured by TGA measurement (Figure 1). Thermal gravimetric analysis showed that both of two polymers exhibited good thermal stability. The weight loss of $poly(\mathbf{5}_{0.1}$ -co- $\mathbf{4}_{0.9})$ was less than 5% on heating to about 328 °C. However, the temperature for 5% weight loss of poly(60.1-co-40.9) was around 368 °C. This indicated that $poly(\mathbf{6}_{0,1}$ -co- $\mathbf{4}_{0,9})$ has a better thermal stability than $poly(\mathbf{5}_{0,1}-co-\mathbf{4}_{0,9})$.

The FT-IR spectrum of compound **4** (Figure 2a) showed the characteristic absorption peaks of acetylene group at 3295 and 2108 cm⁻¹, responding to $\nu_{C=H}$ and $\nu_{C=C}$, respectively. After polymerization, the FT-IR spectra of poly(**5**_{0.1}-*co*-**4**_{0.9}) and poly(**6**_{0.1}-*co*-**4**_{0.9}) exhibited no absorption at 3295 and 2108 cm⁻¹ (Figure 2b,c). Moreover, the spectra of poly(**5**_{0.1}-*co*-**4**_{0.9}) showed a



Figure 1. TGA spectra of $poly(5_{0.1}-co-4_{0.9})$ and $poly(6_{0.1}-co-4_{0.9})$.

characteristic absorption peak of [60] fullerene unit at 528 cm^{-1} . These results indicated that the polymerized reactions were successful.

The ¹H NMR characteristic peaks of monomer 4 at δ 9.57, 8.71, and 8.43 ppm were due to the resonance of protons on perylene ring, but the peaks at δ 7.57–7.12 ppm and the single peak at δ 3.09 ppm were due to the resonance of protons on aromatic rings and acetylene groups, respectively. However, the ¹H NMR spectra of polymers displayed apparent changes that the peaks of polymers were broader than those of monomer 4. Moreover, the new peak at δ 5.30 ppm appeared,

Scheme 2. Synthesis of Polyacetylenes^a



^a Polymerization conditions: [Rh(nbd)Cl]₂, anhydrous CHCl₃, dry Et₃N, nitrogen, rt, 48 h.



Figure 2. FT-IR spectra of monomer 4 (a), $poly(5_{0.1}-co-4_{0.9})$ (b), and $poly(6_{0.1}-co-4_{0.9})$ (c).

responding to the resonance of the main-chain cis olefinic protons, which indicated cis-transoidal structure. 16d,21

The UV-vis absorption spectra of monomers and polymers in CHCl₃ are shown in Figure 3. The main absorption band of pure compound **4** showed a peak at 533 nm. After polymerization, the absorption maximum of poly($\mathbf{5}_{0.1}$ -co- $\mathbf{4}_{0.9}$) and poly($\mathbf{6}_{0.1}$ -co- $\mathbf{4}_{0.9}$) were red-shifted by 8 and 9 nm, respectively. This is similar to the phenomenon that perylene bisimides exhibit a red shift upon aggregation.²² Moreover, poly($\mathbf{5}_{0.1}$ -co- $\mathbf{4}_{0.9}$) exhibited no obvious absorption at 430 nm, where monomer **5** showed an characteristic absorption of [60]fullerene (Figure 3a). When the zinc porphyrin was introduced to the π -conjugated polyacetylene backbone, as in the case of poly($\mathbf{6}_{0,1}$ -co- $\mathbf{4}_{0,9}$), the Q-band at 595 nm disappeared compared with monomer $\mathbf{6}$ and the Q-band at 552 nm may be overlapped by the absorption of monomer $\mathbf{4}$ (Figure 3b). These results indicated the interaction of the pendants and backbone.^{16d}

Figure 4 showed the fluorescence spectra of monomers and polymers in chloroform at excitation wavelength 430 nm. Pure monomer **4** showed intense fluorescence, whereas the fluorescence of two polymers showed strong quenching due to introducing fullerene and porphyrin units into polymers (Figure 4a,b). As shown in Figure 4c, the fluorescence of poly(**6**_{0.1}-co-**4**_{0.9}) showed stronger quenching than that of poly(**5**_{0.1}-co-**4**_{0.9}). Significant quenching of the emission in two polymers indicated charge transfer at excitation wavelength.

The redox properties of the monomers and polymers were studied by cyclic voltammetry (CV). CV experiments were performed at room temperature in dried o-dichlorobenzene solutions containing 0.04 M TBAPF₆ as a supporting electrolyte. A three-electrode configuration consisting of a glassy carbon working electrode, a Pt counter electrode, and an Ag wire quasireference electrode was used. Table 2 showed the cyclic voltammogram data of the samples. For perylene bisimide 4, two reversible reductions at -0.82 and -1.07 V and one reversible oxidation at 1.68 V were found. The electrochemical reduction of $poly(5_{0,1}-co-4_{0,9})$ showed three oneelectron processes at -0.81, -1.06, and -1.20 V, corresponding to the formation of anions of perylene bisimide unit and fullerene moiety, respectively. Moreover, the oxidation peak of $poly(5_{0,1}-co-4_{0,9})$ was at 1.63 V, corresponding to the perylene bisimide cation. However, the oxidation peaks of $poly(\mathbf{6}_{0,1}$ -co- $\mathbf{4}_{0,9})$ were at 0.73



Figure 3. UV-vis absorption spectra of 4, 5, 6, $poly(5_{0,1}-co-4_{0,9})$, and $poly(6_{0,1}-co-4_{0,9})$ in CHCl₃. Concentration = 2×10^{-5} M.



Figure 4. Fluorescence spectra of 4, 6, poly($\mathbf{5}_{0.1}$ -co- $\mathbf{4}_{0.9}$), and poly($\mathbf{6}_{0.1}$ -co- $\mathbf{4}_{0.9}$) in CHCl₃. $\lambda_{ex} = 430$ nm; concentration = 2×10^{-5} M.

Table 2. Electrochemical Data for the Monomers and Copolymers

		peak potential ^a /V								
compound	$E_{ m ox}^{ m PO3}$	$E_{ m ox}{}^{ m PO2}$	$E_{ m ox}{}^{ m PO1}$	$E_{ m ox}{}^{ m PE}$	${E}_{ m red}{}^1$	${E}_{ m red}{}^2$	${E}_{ m red}{}^3$	$E_{ m red}^{ m PO}$		
4 (PE)				1.68	-0.82	-1.07				
5^{b}					-0.98	-1.33	-1.88			
$6^{b}(\mathrm{PO})$	1.74	1.02	0.80					-1.71		
$poly(5_{0.1}-co-4_{0.9})$				1.63	-0.81	-1.06	-1.20			
$poly(6_{0.1}-co-4_{0.9})$			0.73	1.56	-0.80	-1.05		-1.22		

^a Versus Ag wire. The scan rate was 50 mV/s. ^b The electrochemical data of compound **5** and **6** were obtained directly from the literature.^{16d}

and 1.56 V, corresponding to the porphyrin cation and perylene bisimide cation, respectively. Furthermore, the reduction of $poly(\mathbf{6}_{0.1}$ -co- $\mathbf{4}_{0.9})$ showed three one-electron processes at -0.80, -1.05, and -1.22 V, corresponding to the formation of perylene bisimide unit anion and porphyrin anion, respectively. For $poly(\mathbf{5}_{0.1}$ -co- $\mathbf{4}_{0.9})$, the reduction potential was decreased by 170 mV relative to the corresponding reduction process of monomer $\mathbf{5}$, indicating a better electron-accepting ability. And the perylene bisimide unit of $poly(\mathbf{5}_{0.1}$ -co- $\mathbf{4}_{0.9})$ was 50 mV easier to oxidize than the perylene bisimide monomer $\mathbf{4}$ according to the oxidation peak potential. For poly- $(\mathbf{6}_{0.1}$ -co- $\mathbf{4}_{0.9})$, the reduction potential was decreased by 20 mV compared to that of monomer $\mathbf{4}$, indicating an

electron-accepting ability. The porphyrin moiety of poly-($\mathbf{6}_{0.1}$ -co- $\mathbf{4}_{0.9}$) was 70 mV easier to oxidize than the porphyrin monomer **6** according to the first oxidation peak potential. It is assumed that the electron-donating and -withdrawing nature of the pendants is influenced by the conjugated backbone. Therefore, both poly($\mathbf{5}_{0.1}$ co- $\mathbf{4}_{0.9}$) with perylene bisimide and pendent fullerene units and poly($\mathbf{6}_{0.1}$ -co- $\mathbf{4}_{0.9}$) with perylene bisimide and pendent porphyrin units were good candidates for photoinduced electron-transfer systems.

To investigate the photocurrent response of two polymers, the photocurrent measurement was performed on a model CHI660B voltammetric analyzer (CH Instruments). A conventional three-electrode cell was



Figure 5. Time dependence of the photocurrent responses of the self-assembled $poly(\mathbf{5}_{0.1}-co-\mathbf{4}_{0.9})$ and $poly(\mathbf{6}_{0.1}-co-\mathbf{4}_{0.9})$ films upon the irradiation of 70 mW cm⁻² white light in 0.5 M KCl solution.

used to measure the photoelectrochemical properties of two polymers. A platinum wire was used as a counter electrode and the saturated calomel electrode as a reference electrode. A solution of 0.5 M KCl was selected as the supporting electrolyte in measurement. The indium-tin oxide (ITO) glass modified with polymer

monolayer film was used as a working electrode. The polymer monolayer film was prepared by immersing ITO glass into chloroform solution of polymer overnight and depositing on ITO glass. The cathodic photocurrent responses of 1.39 and 1.72 μ A cm⁻² at 70 mW cm⁻² white light irradiation were produced as the irradiations of the $poly(5_{0,1}-co-4_{0,9})$ and $poly(6_{0,1}-co-4_{0,9})$ films were switched on and off, respectively. The responses to on/ off cycling were prompt and reproducible; four cycles are shown in Figure 5. The photocurrent stabilities in two polymers were good in the monitored time. These results indicated that charge transfer took place in two donoracceptor polymers. As for $poly(\mathbf{5}_{0.1}$ -co- $\mathbf{4}_{0.9})$, C₆₀ is an acceptor and pervlene is a donor, but as for $poly(6_{0,1})$ $co-4_{0,9}$), perylene is an acceptor and porphyrin is a donor. There was charge transfer from perylene to C_{60} and from porphyrin to perylene in two polymers systems, respectively.

We studied the morphologies of two polymers by scanning electron microscope (SEM). Samples were prepared by casting thin films of polymers from chloroform solution onto silicon slices. Figure 6A showed that poly($\mathbf{5}_{0.1}$ -co- $\mathbf{4}_{0.9}$) in CHCl₃ (10^{-4} M) could form the aggregation nanostructure having a large quantity of nanoparticles with diameters in the range of 10-36 nm because C₆₀ derivatives were easy to gather together to form spherical particles through the $\pi-\pi^*$ stacking



Figure 6. (A) SEM image of $poly(\mathbf{5}_{0.1}-co-\mathbf{4}_{0.9})$ in CHCl₃. (B) SEM image of $poly(\mathbf{6}_{0.1}-co-\mathbf{4}_{0.9})$ in CHCl₃ with 4,4'-bipyridine (Bipy), 1:1 stoichiometry. (C) 1:2 stoichiometry. (D, E) Magnified SEM images of (C). (F) 1:4 stoichiometry.



Figure 7. UV–vis absorption spectra of poly($\mathbf{6}_{0,1}$ -co- $\mathbf{4}_{0,9}$) with the addition of 4,4'-bipyridine at different molar ratios in CHCl₃. The concentration of poly($\mathbf{6}_{0,1}$ -co- $\mathbf{4}_{0,9}$) was kept constant at 2×10^{-5} M.

interaction of carbon cage.²³ From the photocurrent response measurements, $poly(\mathbf{6}_{0.1}$ -co- $\mathbf{4}_{0.9})$ could produce stronger photocurrent than $poly(\mathbf{5}_{0.1}$ -co- $\mathbf{4}_{0.9})$ under the same conditions. This was due to the fact that $poly(\mathbf{6}_{0.1})$ $co-4_{0.9}$) was able to form a uniform membrane for improving photoelectronic property. These results indicated that the different membrane morphologies of polymers could be of importance for affecting photoinduced electron-transfer properties. It should be pointed out that $poly(6_{0,1}-co-4_{0,9})$ in CHCl₃ (10⁻⁴ M), with the addition of 4,4'-bipyridine (Bipy) at different molar radios, displayed the different aggregation structure. It was likely that this was driven by phase transitions in the drying process and would depend on the solvent, substrate, and environment. But it was probably mainly caused due to the axial coordination of zinc porphyrin and Bipy and the $\pi - \pi^*$ interaction of perylene rings. As can be seen in Figure 6B, $poly(\mathbf{6}_{0,1}-co-\mathbf{4}_{0,9})$ with 1 equiv of Bipy in CHCl₃ can form a hierarchical porous structure, which was not observed without the addition of Bipy. Figure 6C showed a uniform cottonlike aggregation superstructure of $poly(\mathbf{6}_{0,1}$ -co- $\mathbf{4}_{0,9})$ with 2 equiv of Bipy. Both Figure 6D and Figure 6E were magnified SEM images of Figure 6C. Figure 6D displayed that the cotton ball has a mean diameter of about 1 μ m. Interestingly, many convex hulls were observed clearly on the surface of these cotton balls as shown in Figure 6E. Nevertheless, when $poly(\mathbf{6}_{0.1}$ -co- $\mathbf{4}_{0.9})$ in CHCl₃ was mixed with 4 equiv of Bipy, the cottonlike structure was not observed, and Figure 6F showed agglomerate aggregation structure. These results indicated that the axial coordination of zinc porphyrin and Bipy played an important role in controlling the aggregation morphologies of $poly(\mathbf{6}_{0,1}$ -co- $\mathbf{4}_{0,9})$ in CHCl₃ with the addition of Bipy.

We also studied the absorption spectra of $poly(\mathbf{6}_{0.1}$ $co-\mathbf{4}_{0.9})$ in CHCl₃ with the addition of Bipy (Figure 7). The Soret band of $poly(\mathbf{6}_{0.1}$ - $co-\mathbf{4}_{0.9})$ without Bipy were at 427 nm. However, the Soret band weakened and was red-shifted slightly by 2 nm with the addition of 4 equiv of Bipy. Moreover, the main absorption band of perylene unit in $poly(\mathbf{6}_{0.1}$ - $co-\mathbf{4}_{0.9})$ was blue-shifted slightly by 3 nm from 542 to 539 nm after the addition of 4 equiv of Bipy. These changes of absorption spectra of $poly(\mathbf{6}_{0.1}$ $co-\mathbf{4}_{0.9})$ were consistent with their different morphologies with the addition of Bipy. In theory, there are a perylene unit and two pendant zinc porphyrin units in a unit of poly($\mathbf{6}_{0.1}$ -co- $\mathbf{4}_{0.9}$). While poly($\mathbf{6}_{0.1}$ -co- $\mathbf{4}_{0.9}$) was mixed with 1 equiv of Bipy, a hierarchical structure was easily formed. Furthermore, some cavities, which can form porous structure, appeared possibly due to the shortage of Bipy. When poly($\mathbf{6}_{0.1}$ -co- $\mathbf{4}_{0.9}$) was mixed with 2 equiv of Bipy, a uniform cottonlike structure was formed through strong axial coordination and π - π * stacking interaction. However, with the addition of 4 equiv of Bipy, the axial coordination became stronger so that the aggregation structure of poly($\mathbf{6}_{0.1}$ -co- $\mathbf{4}_{0.9}$) generated agglomeration.

Conclusions

In summary, a new class of conjugated polyacetylenes having perylene bisimide units and pendant fullerene or porphyrin groups were synthesized and characterized. SEM images displayed the aggregation superstructures of two polymers. In chloroform $poly(\mathbf{5}_{0,1}$ -co- $\mathbf{4}_{0,9})$ can form a large quantity of spherical nanoparticles and $poly(\mathbf{6}_{0,1}$ -co- $\mathbf{4}_{0,9})$ with the addition of Bipy can form different aggregation superstructures. In particular, when $poly(\mathbf{6}_{0,1}$ -co- $\mathbf{4}_{0,9})$ was mixed with 2 equiv of Bipy, a uniform cottonlike superstructure was observed. The results indicated that the axial coordination of zinc porphyrin and Bipy was very important to control the aggregation morphologies of $poly(\mathbf{6}_{0,1}-co-\mathbf{4}_{0,9})$. Interestingly, the photocurrent measurement showed that the monolayer films of polymers could produce steady and rapid cathodic photocurrent responses, indicating efficient charge transfer in two donor-acceptor polymers. It is expected that these novel polyacetylenes having perylene bisimide unit have a potential application in the field of organic photovoltaic solar cells.

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Supporting Information Available: FT-IR spectra, ¹H NMR spectra, and mass spectra for compounds **2**–**4** and two polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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