Synthesis and Chemical Properties of Conjugated Polyacetylenes Having Pendant Fullerene and/or Porphyrin Units

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ABSTRACT: Conjugated polyacetylenes having pendant fullerene and/or porphyrin groups were prepared by copolymerization in the presence of $[Rh(nbd)Cl]_2$−NEt_3 in $CHCl_3$. The photochemical and electrochemical properties of the polymers were studied by UV−vis spectroscopy and voltammetry. The photoinduced charge-transfer properties of the monolayer films were also measured by a three-electrode cell technique. More importantly, poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$) shows a high capacity to form a photoinduced charge-separated state and to produce steady and prompt photocurrent at the irradiation of 21.2 mW cm^{-2} white light. We estimate an aerobic IPCE value of 0.15% for a true monolayer coverage of poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$) at its peak absorption around 440 nm (the maximum of the Soret band).

Introduction

Photosynthesis, which converts solar energy into chemical energy, is one of the most elaborate processes in nature. Photoinduced electron transfer has so far been widely studied to mimic the natural photosynthetic reaction center and to investigate its potential use in solar cells using donor−acceptor linked molecules or equivalents.[1]

Recently, fullerene C_{60}, containing six delocalized π electrons, has emerged as a novel three-dimensional acceptor and has been extensively studied for the construction of efficient electron-transfer model systems.[2] The small reorganization energy for C_{60} in electron process leads to a significant acceleration of charge separation step and a effective deceleration of energy wasting charge recombination step.[3] On the other hand, the rich and extensive absorption features of porphyrinoid systems guarantee increased absorption cross sections and an efficient use of the solar spectrum.[4] Therefore, porphyrins are the most frequently employed building blocks as electron donors and sensitizers in artificial photosynthetic models for solar energy conversion.[5] So far, photoinduced electron-transfer systems based on fullerenes and porphyrins have accomplished for revealing basic electron-transfer processes.[6] Polyacetylene derivatives exhibit unique properties such as semiconductivity, high gas permeability, helix inversion, and nonlinear optical properties.[7] It is expected that attaching side groups, such as fullerene and porphyrin, to the well-defined π conjugated backbone[8] will improve the light-harvesting capacity and charge separation efficiency for potential application in solar cells based on synergistic actions of pendants and main-chain conjugation.

Here, we report the synthesis of new monosubstituted acetylene with fullerene and porphyrin. The monomers were copolymerized in the presence of transition metal catalyst $[Rh(nbd)Cl]_2$ in $CHCl_3$. Investigation of the polymers and their films provided optical and electrochemical information on such macromolecules.

Experimental Section

Measurements. Column chromatography (CC): SiO_2 (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 and ^{13}C NMR spectra were recorded on Bruker ARX400 and AV600 spectrometers, respectively. 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 column, using tetrahydrofuran (THF) as eluent. Thermal gravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA-7 under nitrogen. Cyclic voltammograms (CV) and photocurrent were recorded on CHI660B voltammetric analyzer (CH Instruments).

Materials. Unless otherwise stated, reagents were commercially obtained and used without further purification. 2-*tert*-Butoxycarbonylamino-3-(4-prop-2-ynyloxyphenyl)propionic acid prop-2-ynyl ester (**2**) was synthesized according to the literature.[9] The solvents for polymerization were purified according to the standard methods.

4-Prop-2-ynyloxybenzaldehyde. *p*-Hydroxybenzaldehyde (611.6 mg, 5 mmol) and K_2CO_3 (1.038 g, 7.5 mmol) were suspended in acetone (30 mL), propargyl bromide (647 μL, 6 mmol, 80% solution in toluene) was slowly added, and the reaction mixture was stirred and maintained reflux under nitrogen for 6 h. After cooling to room temperature, water (100 mL) and dichloromethane (100 mL) were added, the layers were separated, and the aqueous phase was extracted with dichloromethane (100 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was purified on silica gel column using petroleum ether/ethyl acetate (3/1 (v/v), $R_f = 0.5$). The product was obtained as white solid (720 mg, 90%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.93$ (s, 1H), 7.89 (d, $J = 8.7$ Hz, 2H), 7.12 (d, $J = 8.7$ Hz, 2H), 4.80 (s, 2H), 2.59 (s, 1H). FT-IR (KBr): $\nu = 3210$, 2835, 2753, 2121, 1682, 1603, 1576, 1250, 1171, 1019, 833. EI-MS: *m*/*z* 160.

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2-(4-Ethynyloxy-phenyl)-3,4-fulleropyrrolidine (1a). Glycine (75 mg, 1 mmol), 4-prop-2-ynyloxybenzaldehyde (400 mg, 2.5 mmol), and C_{60} (360 mg, 0.5 mmol) were dissolved in chlorobenzene, and the mixture was refluxed for 6 h under stirring. After cooling, the solvent was evaporated under reduced pressure. The crude solid was purified on silica gel column using toluene as the eluent ($R_f = 0.1$), yielding a black powder (178 mg, 40%). ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta =$ 7.73 (d, $J = 8.6$ Hz, 2H), 7.03 (d, $J = 8.6$ Hz, 2H), 5.76 (s, 1H), 5.09 (d, $J = 10.4$ Hz, 1H), 4.87 (d, $J = 10.4$ Hz, 1H), 4.70 (s, 2H), 3.26 (s, 1H), 2.51 (s, 1H). ^{13}C NMR (600 MHz, C_6D_6): $\delta =$ 157.39, 155.96, 153.62, 153.44, 153.04, 146.65, 146.41, 146.06, 145.83, 145.78, 145.73, 145.63, 145.58, 145.42, 145.21, 145.04, 144.98, 144.87, 144.84, 144.80, 144.77, 144.71, 144.21, 144.04, 143.94, 143.90, 142.77, 142.62, 142.27, 142.16, 142.07, 141.92, 141.89, 141.73, 141.69, 141.63, 141.55, 141.49, 141.45, 141.24, 141.04, 139.69, 139.51, 139.25, 136.19, 135.79, 135.46, 128.87, 114.79, 77.99, 76.84, 76.11, 74.91, 60.75, 54.89. FT-IR (KBr): $\nu =$ 3295, 2914, 2809, 2121, 1609, 1560, 1428, 1221, 1028, 825, 527. MALDI−TOF MS: m/z 894 $[M + H]^+$. Anal. Calcd for $C_{71}H_{11}NO$: C, 95.41; H, 1.24; N, 1.57. Found: C, 94.94; H, 1.06; N, 1.49.

***N*-Dodecyl-2-(4-ethynyloxy-phenyl)-3,4-fulleropyrrolidine (1b).** Compound **1a** (134 mg, 0.15 mmol) and dodecanal (138 mg, 0.75 mmol) were mixed in dichloromethane (50 mL) and then treated with sodium triacetoborohydride (159 mg, 0.75 mmol) and AcOH (35 μL). The mixture was stirred at room temperature under a N_2 atmosphere for 12 h until the reactants were consumed as determined by TLC analysis. The reaction mixture was quenched by adding aqueous saturated $NaHCO_3$ solution, and the product was extracted with dichloromethane. The extract was dried over $MgSO_4$, and the solvent was evaporated. The crude product was purified on silica gel using petroleum ether/toluene (10/1 (v/v), $R_f = 0.6$); yield: 127 mg, 80%. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.74$ (bs, 2H), 7.02 (d, $J = 8.6$ Hz, 2H), 5.09 (d, $J = 9.1$ Hz, 1H), 5.02 (s, 1H), 4.69 (s, 2H), 4.12 (d, $J = 9.2$ Hz, 1H), 3.20 (m, 1H), 2.52 (m, 1H), 2.17 (s, 1H), 1.86−1.90 (m, 2H), 1.67−1.29 (m, 18H), 0.89 (t, $J = 6.72$ Hz, 3H). ^{13}C NMR (600 MHz, $CDCl_3$): $\delta =$ 157.62, 156.72, 154.43, 153.71, 147.31, 146.81, 146.52, 146.31, 146.27, 146.22, 146.14, 146.11, 145.93, 145.76, 145.55, 145.48, 145.32, 145.28, 145.24, 145.21, 145.15, 144.74, 144.65, 144.41, 143.19, 143.03, 142.68, 142.56, 142.37, 142.30, 142.12, 142.01, 141.98, 141.83, 141.68, 141.52, 140.17, 140.13, 139.90, 139.51, 136.84, 136.59, 135.81, 135.74, 130.60, 130.40, 114.91, 82.04, 78.50, 75.63, 68.87, 66.87, 55.92, 53.12, 31.98, 29.78, 29.74, 29.58, 29.52, 29.43, 28.39, 27.60, 22.75, 14.19. FT-IR (KBr): 3301, 2921, 2850, 2126, 1609, 1508, 1428, 1219, 1030, 833, 527. MALDI−TOF MS: m/z 1062 $(M + H)^+$. Anal. Calcd for $C_{83}H_{35}NO$: C, 93.87; H, 3.30; N, 1.32. Found: C, 93.19; H, 3.38; N, 1.03.

5-(4-Prop-2-ynyloxyphenyl)-10,15,20-tris(3,4,5-trimethoxyphenyl)porphyrine (4). 4-[10,15,20-Tris(3,4,5-trimethoxyphenyl)porphyrin-5-yl]phenol (**3**) (364 mg, 0.4 mmol) and K_2CO_3 (138 mg, 1 mmol) were suspended in acetone (50 mL), propargyl bromide (86 μL, 0.8 mmol, 80 wt % solution in toluene) was slowly added, and the reaction mixture was stirred and maintained reflux for 10 h. After cooling to room temperature, the mixture was concentrated. Water (100 mL) and dichloromethane (100 mL) were added, the layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was purified on silica gel column using chloroform as eluent ($R_f = 0.2$) (330.5 mg, 88%). ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 8.96$ (s, 4H), 8.95 (d, $J = 5.1$ Hz, 2H), 8.96 (d, $J = 4.7$ Hz, 2H), 8.15 (d, $J = 8.6$ Hz, 2H), 7.47 (s, 6H), 7.38 (d, $J = 8.6$ Hz, 2H), 4.99 (s, 2H), 4.18 (s, 9H), 3.97 (s, 18H), 2.71 (s, 1H), −2.78 (s, 2H). FT-IR (KBr): $\nu =$ 3316, 2928, 2853, 1581, 1503, 1464, 1409, 1357, 1235, 1127, 803. MALDI−TOF MS: m/z 939 $[M + H]^+$. Anal. Calcd for $C_{56}H_{50}N_4O_{10}$: C, 71.63; H, 5.37; N, 5.97. Found: C, 71.34; H, 5.23; N, 5.68.

5-(4-Prop-2-ynyloxyphenyl)-10,15,20-tris(3,4,5-trimethoxyphenyl)-21*H*,23*H*-porphyrine Zinc (5). Saturated zinc acetate−methanol solution (3 mL) was added to a solution of compound **4** (198 mg, 0.2 mmol) in chloroform (30 mL). The mixture was stirred at room temperature for 3 h and then was washed with water and dried over anhydrous $NaSO_4$. The solvent was removed in vacuo. ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 9.06$ (s, 4H), 9.05 (d, $J = 5.2$ Hz, 2H), 9.00 (d, $J = 4.7$ Hz, 2H), 8.14 (d, $J = 8.5$ Hz, 2H), 7.47 (s, 6H), 7.36 (d, $J = 8.5$ Hz, 2H), 4.98 (s, 2H), 4.17 (s, 9H), 3.95 (s, 18H), 2.70 (s, 1H). ^{13}C NMR (600 MHz, $CDCl_3$): $\delta =$ 157.36, 151.26, 150.64, 150.30, 150.25, 150.23, 138.31, 137.71, 136.00, 135.33, 132.16, 132.06, 132.02, 121.00, 120.88, 113.11, 112.82, 78.71, 75.88, 61.27, 56.38, 56.17. FT-IR (KBr): $\nu =$ 3278, 2939, 2831, 2127, 1579, 1492, 1459, 1348, 1235, 1126, 1000, 799. MALDI−TOF MS: m/z 1001 $[M + H]^+$. Anal. Calcd for $C_{56}H_{48}N_4O_{10}Zn$: C, 67.10; H, 4.83; N, 5.59. Found: C, 66.73; H, 4.96; N, 5.84.

Polymerization. Polymerization was carried out in a dry glass ampule under a N_2 atmosphere using $[Rh(nbd)Cl]_2$ as catalyst. A typical polymerization procedure is described below.

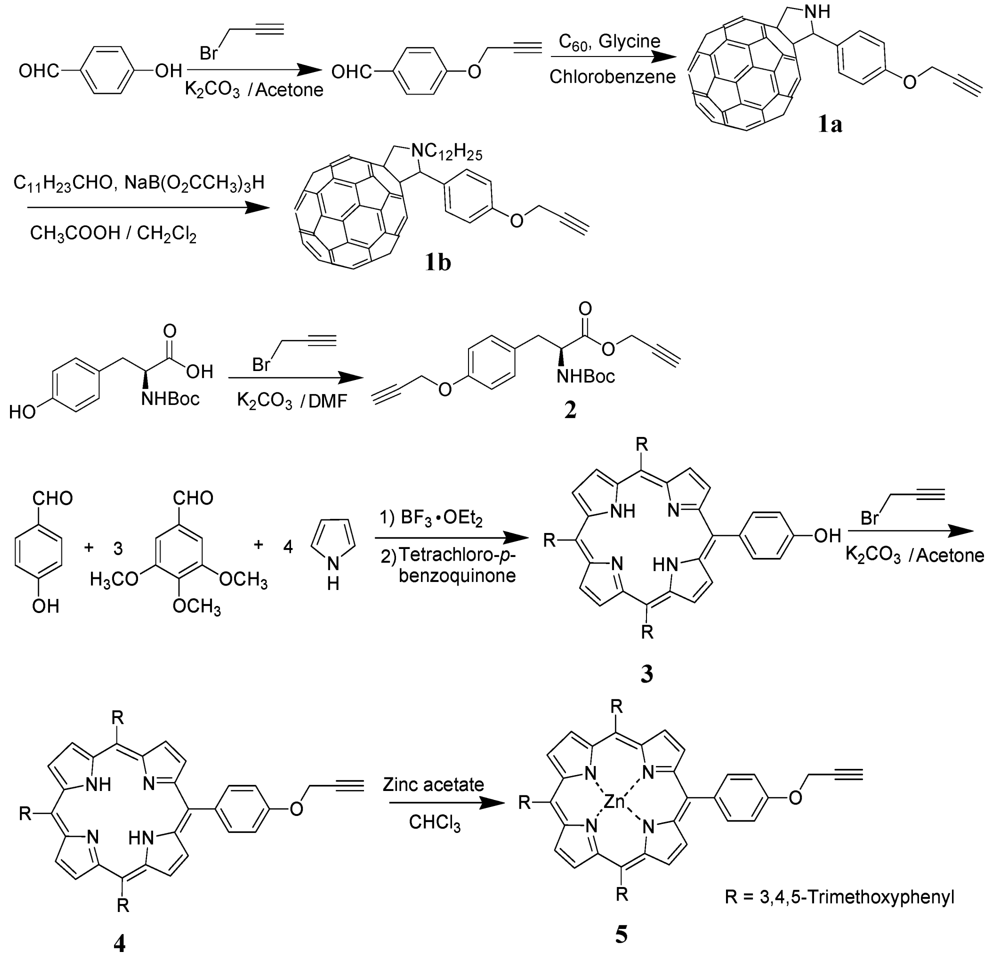
Monomer **1a** (26.8 mg, 0.03 mmol) and monomer **5** (107.1 mg, 0.279 mmol) were placed in a dry ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation−flush procedure was repeated three times, a three-way stopcock was attached to the ampule, and dry chloroform (6.7 mL) and triethylamine (40 μL) were added with a syringe. To this was added a solution of a rhodium catalyst in chloroform (0.3 mL) at 30 °C. The concentrations of the monomer and the rhodium catalyst were 4.3 and 0.86 mM, respectively. After 24 h, the resulting polymer poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$) was precipitated into a large amount of methanol, collected by centrifugation, washed with methanol, and dried in vacuo at room temperature for 10 h.

Spectroscopic Data of the Polymers. Poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$): ^1H NMR (400 MHz, $CDCl_3/C_6D_6CD_3$, TMS): $\delta = 9.0−8.8$ (broad s), 8.2−7.9 (broad s), 7.6−7.3 (broad s), 5.5−5.3 (broad s, $-CH{=}C$), 5.0−4.8 (broad s), 4.2−3.3 (broad d). FT-IR (KBr): $\nu =$ 2959.9, 2831.6, 1579.7, 1503.0, 1348.8, 1258.8, 1126.9, 1004.1, 801.2, 527.5. Poly($\mathbf{5}_{0.2}$-*co*-$\mathbf{2}_{0.8}$): ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 9.1$ (s), 8.2−8.0 (broad s), 7.5 (s), 7.1−6.8 (broad s), 5.3−4.9 (broad m), 4.7−4.3 (broad m), 4.2 (s), 4.0 (s), 3.0−2.8 (broad m), 2.0−1.9 (broad s), 1.6−1.3 (broad s). FT-IR (KBr): $\nu =$ 2976.1, 2934.6, 1715.1, 1507.6, 1237.3, 1167.0, 1002.0. Poly(**1b**): ^1H NMR (400 MHz, $CDCl_3/CS_2$, TMS): $\delta = 7.7−7.5$ (broad s, 2H), 6.9−6.5 (broad s, 2H), 5.3 (broad s, 1H, $-CH{=}C$), 5.2−5.0 (broad s, 2H), 4.8−4.6 (broad s, 2H), 4.2−4.1 (broad s, 1H), 3.3−3.1 (broad s, 1H), 2.6−2.4 (broad s, 1H) 2.1−1.7 (broad m, 2H), 1.6−1.3 (m, 18H), 0.9 (t, 3H). FT-IR (KBr): $\nu =$ 2920.6, 2849.4, 1607.6, 1507.1, 1175.1, 1109.9, 1015.5, 526.9. Poly($\mathbf{1a}_{0.1}$-*co*-$\mathbf{2}_{0.9}$): FT-IR (KBr): $\nu =$ 2964.3, 1718.2, 1509.2, 1260.9, 1096.9, 1019.7, 802.9, 527.1.

Results and Discussion

Scheme 1 illustrates the synthetic routes for the novel monomers containing monosubstituted acetylene. 4-[10,15,20-Tris(3,4,5-trimethoxyphenyl)porphyrin-5-yl]phenol was prepared by condensation of *p*-hydroxybenzaldehyde, 3,4,5-trimethoxybenzaldehyde, and pyrrole (1:3:4, molar ratio) involving $(C_2H_5)_2O{\cdot}BF_3$ catalysis, followed by oxidation with tetrachloro-*p*-benzoquinone in $CHCl_3$.[10] In our strategy, 4-[10,15,20-tris(3,4,5-trimethoxyphenyl)porphyrin-5-yl]phenol was chosen for two reasons. First, methoxy groups would undoubtedly lead to polymers having a pronounced solubility. Second, the electron-donor character of the tetrapyrrolic macrocycle was enhanced by the presence of methoxy groups in a para position on the peripheral phenyl rings.[11] Compounds **2** and **4** were synthesized by alkylation of 4-[10,15,20-tris(3,4,5-trimethoxyphenyl)porphyrin-5-yl]phenol and *N*-(*tert*-butoxycarbonyl)-L-tyrosine with propargyl bromide in high yields, respectively. 2-(4-Ethynyloxyphenyl)-3,4-fulleropyrrolidine (**1a**) was synthesized from glycine and 4-prop-2-ynyloxybenzaldehyde, based on the 1,3-dipolar cycloaddition of azomethine ylides to C_{60}.[12a] To improve the solubility of polymers, we synthesized *N*-dodecyl-2-(4-ethynyloxyphenyl)-3,4-fulleropyrrolidine (**1b**) from (**1a**) by using a facile

Scheme 1. Synthesis of the Monomers



method of reductive amination of dodecanal in high yield.[12b] The monomers were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, MS spectra, and elemental analysis data.

The acetylene-containing monomers were copolymerized in hydrous $CHCl_3$ at 30 °C for 24 h (Scheme 2). Table 1 summarizes the results of copolymerization reaction. 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.[13] The ^{1}H NMR spectra of the polymers exhibited a signal assignable to the main-chain cis olefinic protons at 5.3 ppm, indicating cis−transoidal structure.[14] However, the singlet for the main-chain protons showed a broad line width. It is assumed that the large pendant fullerene and porphyrin units distort the stereoregularity of the main chains.

The IR spectra of the polymers exhibited no absorption due to $\nu_{C\equiv C}$ at 2100−2150 cm^{-1}, which were observed in the monomers. In a similar fashion, the polymers exhibited no IR absorption due to $\nu_{\equiv C-H}$ at 3220−3300 cm^{-1}.

Poly($\mathbf{1a}_{0.1}$-*co*-$\mathbf{2}_{0.9}$) and poly(**1b**) had very low solubility in common solvents such as THF, $CHCl_3$, and toluene. It is quite interesting that poly(**1b**) was soluble in CS_2 very well, while poly($\mathbf{1a}_{0.1}$-*co*-$\mathbf{2}_{0.9}$) was insoluble in this solvent. On the other hand, poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$) and poly($\mathbf{5}_{0.2}$-*co*-$\mathbf{2}_{0.8}$) were soluble in common organic solvents such as THF, $CHCl_3$, and toluene.

The molecular weights determined by GPC of poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$) and poly($\mathbf{5}_{0.2}$-*co*-$\mathbf{2}_{0.8}$) were much larger than those of poly($\mathbf{1a}_{0.1}$-*co*-$\mathbf{2}_{0.9}$) and poly(**1b**). The difference in molecular weight between the polymers may be responsible for the different solubility. First, the molecular weight was influenced by the precipitation of the insoluble product during the polymerization process. Second, only the THF-soluble fraction could be analyzed by GPC, which would underestimate the absolute molecular weight of the polymer.

Thermal gravimetric analysis shows that the temperatures for 5% weight of the polymers were around 300 °C under nitrogen. The weight loss of the poly($\mathbf{5}_{0.2}$-*co*-$\mathbf{2}_{0.8}$) proceeded faster than other present polymers, which may be attributable to the instability of compound **2**.

Optical Properties. Figure 1 and Figure 2 depict the UV−vis spectra of the polymers. For comparison, the absorption spectra of the monomers are also shown. When the zinc porphyrin is introduced to the π-conjugated polyacetylene backbone, as in the case of polymers poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$) and poly($\mathbf{5}_{0.2}$-*co*-$\mathbf{2}_{0.8}$), the Soret and Q-bands were 1−5 nm red-shifted relative to the monomers, which indicates the interaction of the pendants and backbone.

As shown in the Figure 3 and Figure 4, the fluorescence maximum and shape of the polymers are obviously different from the monomers. Fluorescence is quenched after introducing fullerene into the polymers. Especially, the fluorescence of porphyrin is enhanced in poly($\mathbf{5}_{0.2}$-*co*-$\mathbf{2}_{0.8}$) while it is apparently quenched in its counterpart poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$). That resulted from the discrepancy of push−pull electron properties between porphyrin units and fullerene units.

Scheme 2. Schematic Structures of Polymers

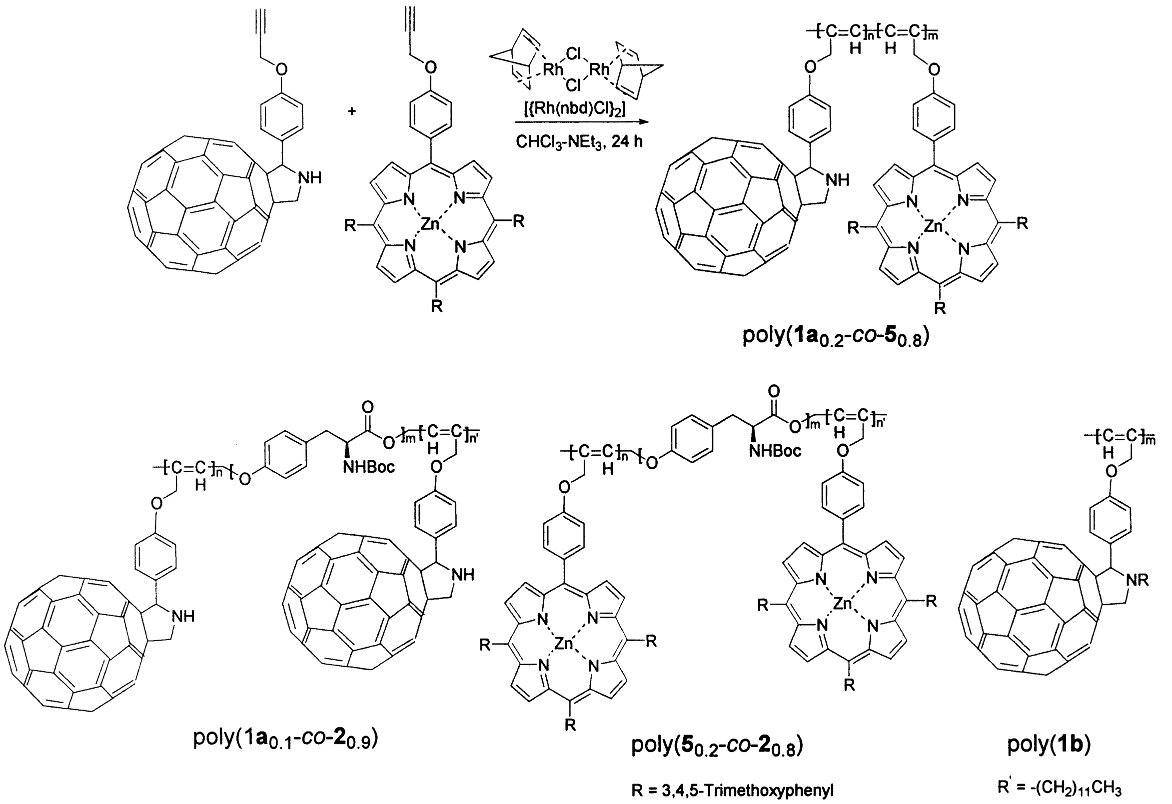


Table 1. Copolymerization of Acetylene Monomers with $[Rh(nbd)Cl]_2$-Net_3 in $CHCl_3$ at 30 °C[a]

				polymer			
run	M_1	M_2	M_2/M_1 (molar ratio)	yield (%)[b]	M_n	M_w	M_w/M_n
1	**1a**	**2**	9/1	75	8 100	12 400	1.53
2	**1a**	**5**	8/2	74	40 200	52 300	1.3
3	**5**	**2**	8/2	52[c]	24 300	49 300	2.0
4	**1b**	**1b**	1	56	10 100	15 300	1.52

[a] $[M_1 + M_2] = 43$ mM, [Rh] = 0.86 mM. [b] Methanol-insoluble fraction. [c] Ether-insoluble fraction.

Cyclic Voltammetry. To evaluate the energy of the charge-separated state, it is necessary to know both the reduction potential of fullerene and the oxidation potential of the porphyrin moiety. 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 $TBAPF_6$ as a supporting electrolyte. A three-electrode configuration consisting of a glassy carbon working electrode, a Pt counter electrode, and an Ag wire quasi-reference electrode was used. Table 2 shows the cyclic voltammogram data of the samples. The electrochemical reduction of poly(**1a**$_{0.2}$-*co*-**5**$_{0.8}$) shows four one-electron processes at −0.89, −1.40, −1.81, and −1.20 V, corresponding to the formation of monoanion, dianion, and trianion of fullerene moiety and the formation of porphyrin anion, respectively. On the other hand, oxidation of the polymer takes place in the potential range between 0.78 and 1.68 V, corresponding to the porphyrin cation. It should be pointed out that the reduction potential of fullerene attached to the polyacetylene backbone is decreased relative to the corresponding reduction process of monomer **1a**, which indicates a better electron-accepting ability. Poly(**1b**) gives a similar result. At the same time, the porphyrin moiety of the polymer is 20 mV easier to oxidize than the porphyrin monomer **5** 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, poly(**1a**$_{0.2}$-*co*-**5**$_{0.8}$) with pendent fullerene and porphyrin units is a good candidate for a photoinduced electron-transfer system.

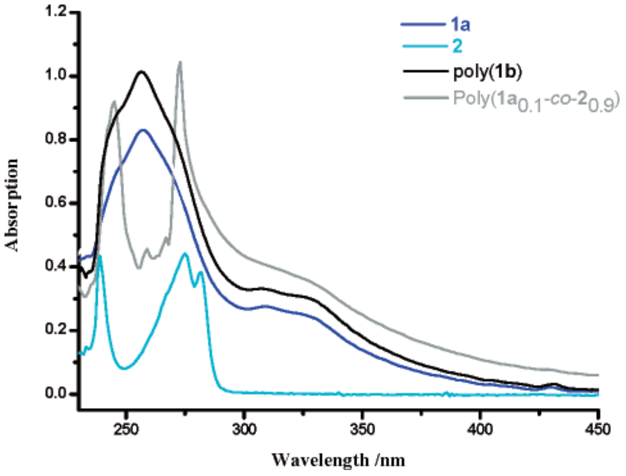


Figure 1. UV−vis absorption spectra of **1a**, **2,** poly(**1b**), and poly(**1a**$_{0.1}$-*co*-**2**$_{0.9}$) in $CHCl_3$.

Photocurrent Generation. Thin films were prepared by immersing the ITO glass into $CHCl_3$ solution (1 mg/mL) for 2 h. Poly(**1a**$_{0.2}$-*co*-**5**$_{0.8}$) and poly(**5**$_{0.2}$-*co*-**2**$_{0.8}$) afforded films with smooth surface suitable for optical and electrochemical analyses. As shown in Figure 6, the Soret band and Q-band absorption of the porphyrin are broadened, while those of fullerene are masked by ITO absorption at wavelengths <350 nm. Furthermore, the absorption position was shifted to

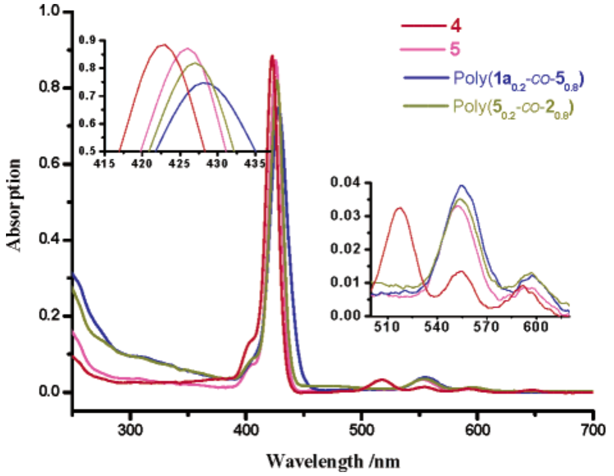


Figure 2. UV−vis spectra of **4**, **5,** poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$), and poly($\mathbf{5}_{0.2}$-*co*-$\mathbf{2}_{0.8}$) in $CHCl_3$.

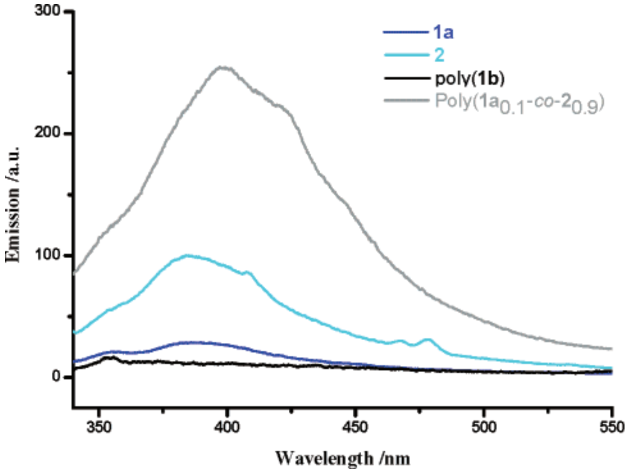


Figure 3. Fluorescence spectra of **1a**, **2**, poly(**1b**), and poly($\mathbf{1a}_{0.1}$-*co*-$\mathbf{2}_{0.9}$) in $CHCl_3$. Excitation wavelength = 320 nm; concentration = 10^{-6} mol/L.

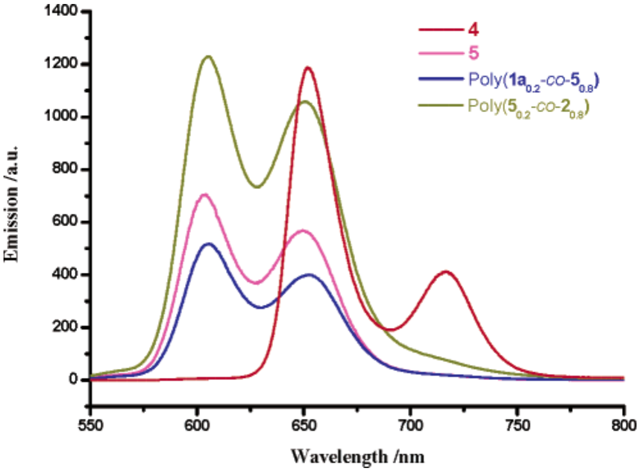


Figure 4. Fluorescence spectra of **4**, **5,** poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$), and poly($\mathbf{5}_{0.2}$-*co*-$\mathbf{2}_{0.8}$) in $CHCl_3$. Excitation wavelength = 423 nm; concentration = 10^{-6} mol/L.

longer wavelength (Figure 6). The broadening is probably due to the strong interaction occurring between individual molecules and light scattering in the densely packed films.[3c]

A conventional three-electrode cell was used to measure the photoelectrochemical properties of the monolayer film deposited on indium−tin oxide (ITO) glass. 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 all measurements. The ITO glass modified with polymer was used as a working electrode.

Table 2. Electrochemical Data for the Monomers and Polymers

compd	peak potential[a]/V						
	E_{ox}^{P3}	E_{ox}^{P2}	E_{ox}^{P1}	E_{red}^{F1}	E_{red}^{F2}	E_{red}^{F3}	E_{red}^{P}
5	1.74	1.02	0.80				−1.71
1a				−0.98	−1.33	−1.88	
1b				−0.97	−1.35	−1.88	
poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$)	1.68	1.09	0.78	−0.89	−1.40	−1.81	−1.20
poly(**1b**)				−0.90	−1.30	−1.82	

[a] Versus Ag wire. The scan rate was 20 mV/s.

The photocurrent of poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$) monolayer film deposited on ITO electrode was measured at 21.2 mW cm^{-2} white light irradiation. A steady and rapid cathodic 2.5 $\mu A\ cm^{-2}$ photocurrent response was produced when the irradiation of the monolayer film was switched on and off. Importantly, the response to on/off cycling is prompt and reproducible as shown in Figure 5A. The photocurrent stability in the systems was rather good during the monitor time. However, the photocurrent of poly($\mathbf{5}_{0.2}$-*co*-$\mathbf{2}_{0.8}$) monolayer film was 1 order lower under the same conditions than that of poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$). This was presumably resulted from the lack of fullerene electron acceptor. This phenomenon was also confirmed by poly(**1b**) monolayer film containing only fullerene gradient, which produced anodic 0.04 $\mu A\ cm^{-2}$ photocurrent (Figure 5B). The results show that the photocurrent generated from the combination of zinc porphyrin and fullerene C_{60} units in poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$) monolayer film.

With a change of the excitation of wavelength to 400−700 nm, a photocurrent action spectrum is obtained (Figure 6). The incident-photon-to-photocurrent efficiency (IPCE) was obtained through the measure of the generated photocurrent when the electrode was irradiated with monochromatic light by using the equation

$$\mathrm{IPCE}\ (\%) = 100(i_{sc} \times 1240)/(I_{inc}\lambda)$$

where i_{sc} is the short-circuit photocurrent (A cm^{-2}), I_{inc} is the incident light intensity (W cm^{-2}), and λ is the excitation wavelength (nm).[11,15] The photocurrent action spectrum closely matches the absorption spectrum of the poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$) modified electrode. This confirms the origin of the photocurrent, namely, that porphyrin moiety is the photoactive species. Therefore, photocurrent generation can be attributed to the excitation of the zinc porphyrin unit incorporated into the poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$) polymer. We estimate an aerobic IPCE value of 0.15% for a true monolayer coverage of poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$) at its peak absorption around 440 nm (the maximum of the Soret band).

Cyclic voltammogram allows us to estimate the relative HOMO and LUMO energies of the poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$). The oxidation process corresponds to the removal of electrons from the HOMO band, whereas the reduction process corresponds to the filling of electrons into the LUMO band. Therefore, the oxidation and reduction potential are closely related to the energies of the HOMO and LUMO levels of an organic molecule and can provide important information regarding the magnitude of the energy gap. The HOMO level of porphyrin moiety and the LUMO level of fullerene moiety are 0.78

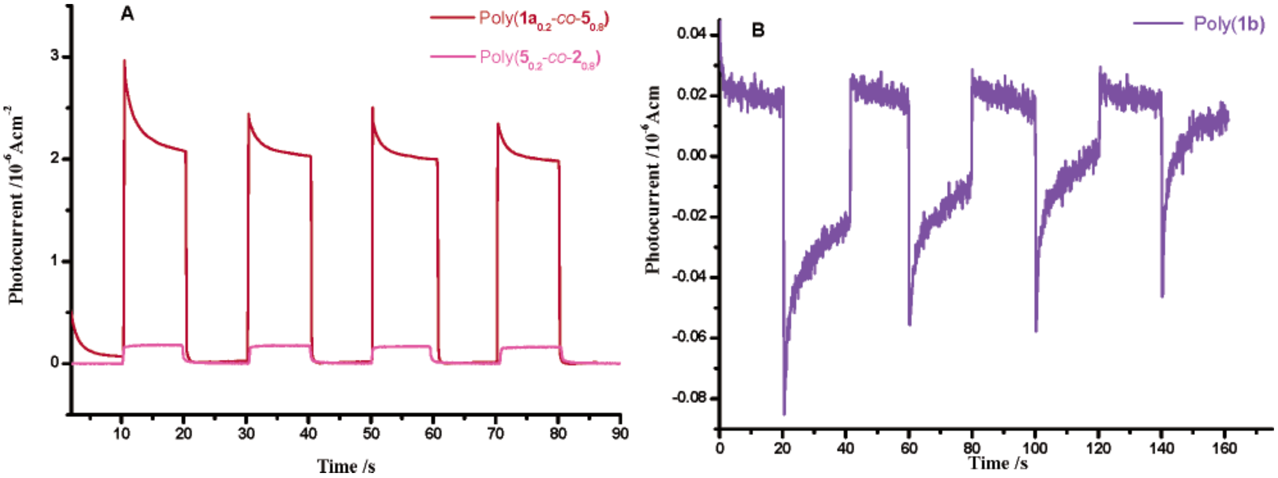


Figure 5. Photocurrent generation of the monolayer films upon the irradiation of 21.2 mW cm^{-2} white light in 0.5 M KCl solution.

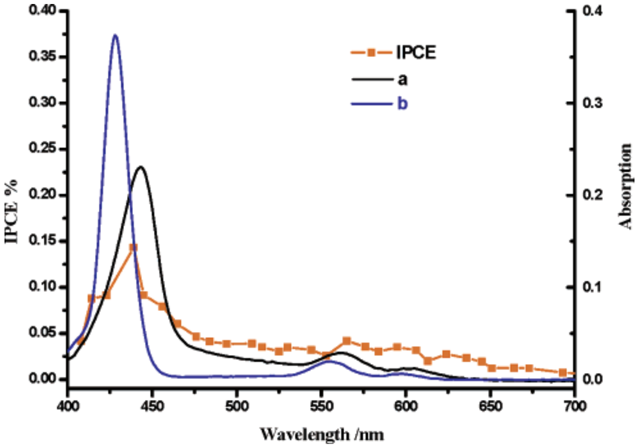


Figure 6. Photocurrent action spectrum (solid squares), absorption spectrum of ITO electrode modified by poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$) monolayer film (a), and absorption spectrum of poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$) in $CHCl_3$ (b).

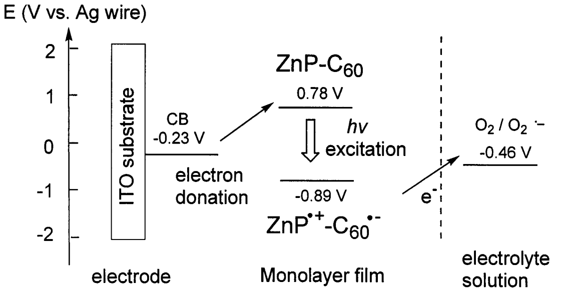


Figure 7. Schematic illustration of cathodic photocurrent generation.

and −0.89 V vs Ag wire, respectively. The band gap (1.66 V) for the ion pair state ($ZnP^{\bullet+}$−$C_{60}^{\bullet-}$) of poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$) was derived from the first oxidation potential of the porphyrin and the first reduction potential of the C_{60} moieties. The energy of the conduction band of ITO is estimated at −4.5 eV (∼−0.23 V vs Ag wire). Figure 7 shows a simplified picture of the photoinduced electrons pathway for the observed photocurrent.

Electrons transfer from the conduction band of ITO to the polymer layer. Upon illumination, the exciton forms, and electron transfer from porphyrin moiety to C_{60} occurs, forming a charge-separated state ($ZnP^{\bullet+}$−$C_{60}^{\bullet-}$). The $C_{60}^{\bullet-}$ moiety in the charge-separated state gives one electron to the electron carrier such as O_2 ($O_2/O_2^{\bullet-} = -0.46$ V)[3c,k,16] of the electrolyte solution, which is thermodynamically possible. And then, the electron flows from ITO through monolayer film to the electrolyte, resulting in the observed cathodic photocurrent.

In conclusion, conjugated polyacetylenes having pendant fullerene and/or porphyrin groups were prepared by copolymerization in the presence of $[Rh(nbd)Cl]_2$−NEt_3 in $CHCl_3$. The photochemical and electrochemical properties of the polymers were studied by UV−vis spectroscopy and voltammetry. The photoinduced charge-transfer properties of the monolayer films were also measured by a three-electrode cell technique. More importantly, poly($\mathbf{1a}_{0.2}$-*co*-$\mathbf{5}_{0.8}$) shows a high capacity to form a photoinduced charge-separated state and to produce steady and prompt photocurrent at the irradiation of white light. We believe that the polymers are expected to provide novel photonic or electronic functions that will lead us toward device applications.

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Supporting Information Available: Figures showing ^1H NMR data and TGA trances of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Verhoeven, J. W. In *Electron Transfer*; Jortner, J., Bixon, M., Eds.; Wiley: New York, 1999; Part 1. (b) Zerza, G.; Cravino, A.; Neugebauer, H.; Sariciftci, N. S.; Gomez, R.; Segura, J. L.; Martin, N.; Svensson, M.; Andersson, M. R. *J. Phys. Chem. A* **2001**, *105*, 4172. (c) D'Souza, F.; Deviprasad, G. R.; Rahman, M. S.; Choi, J. P. *Inorg. Chem.* **1999**, *38*, 8, 2157. (d) Tkachenko, N. V.; Rantala, L.; Tauber, A. Y.; Helaja, J.; Hynninen, P. H.; Lemmetyinen, H. *J. Am. Chem. Soc.* **1999**, *121*, 9378. (e) Imahori, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y. *J. Phys. Chem. B* **2000**, *104*, 2099. (f) Redmore, N. P.; Rubtsov, I. V.; Therien, M. J. *Inorg. Chem.* **2002**, *41*, 566. (g) Guldi, D. M.; Gonzalez, S.; Martin, N.; Anton, A. Garin, J.; Orduna, J. *J. Org. Chem.* **2000**, *65*, 1978. (h) Ikeda, A.; Hatano, T.; Shinkai, S.; Akiyama, T.; Yamada, S. *J. Am. Chem. Soc.* **2001**, *123*, 4855. (i) Kamat, P. V.; Barazzouk, S.; Hotchandani, S.; Thomas, K. G. *Chem.—Eur. J.* **2000**, *6*, 3914.

(2) For reviews, see: (a) Martin, N.; Sanchez, L.; Illescas, B.; Perez, I. *Chem. Rev.* **1998**, *98*, 2527. (b) Guldi, D. M.; Prato, M. *Acc. Chem. Res.* **2000**, *33*, 695. (c) Reed, C. A.; Bolskar, R. D. *Chem. Rev.* **2000**, *100*, 1075. (d) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40.

(3) (a) Imahori, H.; Sakata, Y. *Adv. Mater.* **1997**, *9*, 537. (b) Guldi, D. M. *Chem. Commun.* **2000**, 321. (c) Guldi, D. M.; Pellarini, F.; Prato, M.; Granito, C.; Troisi, L. *Nano Lett.* **2002**, *2*, 965.

(d) Fukuzumi, S.; Guldi, D. M. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, Germany, 2001; Vol. 2, pp 270−326. (e) Page, C. C.; Moser, C. C.; Chen, X.; Dutton, P. L. *Nature (London)* **1999**, *402*, 47. (f) Gust, D.; Moore, T. A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic: San Diego, CA, 2000; Vol. 8, pp 153−190. (g) Gust, D.; Moore, T. A.; Moore, A. L. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, Germany, 2001; Vol. 3, pp 272−336. (h) Imahori, H.; Tamaki, K.; Guldi, D. M.; Luo, C.; Fujitsuka, M.; Ito, O.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 2607. (i) Luo, C.; Guldi, D. M.; Imahori, H.; Tamaki, K.; Sakata, Y. *J. Am. Chem. Soc.* **2000**, *122*, 6535. (j) Imahori, H.; El-Khouly, M. E.; Fujitsuka, M.; Ito, O.; Sakata, Y.; Fukuzumi, S. *J. Phys. Chem. A* **2001**, *105*, 325. (k) Li, H. M.; Li, Y. L.; Zhai, J.; Cui, G. L.; Liu, H. B.; Xiao, S. Q.; Liu, Y.; Lu, F. S.; Jiang, L.; Zhu, D. B. *Chem.*—*Eur. J.* **2003**, *9*, 6031.

(4) *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 1999.

(5) (a) Wennerstom, O.; Ericsson, H.; Raston, I.; Svensson, S.; Pimlott, W. *Tetrahedron Lett.* **1998**, *30*, 1129. (b) Anderson, H. L.; Anderson, J. K.; Sanders, M. *Acc. Chem. Res.* **1993**, *26*, 469. (c) Osuka, A.; Liu, B.; Maruyama, K. *Chem. Lett.* **1993**, 949. (d) Anderson, H. L. *Inorg. Chem.* **1994**, *3*, 972. (e) Lin, V. S.-Y.; DiMagnom, S. G.; Therein, M. J. *Science* **1994**, *264*, 1105. (f) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759. (g) Osuka, A.; Okada, T.; Taniguchi, S.; Nozaki, K.; Ohno, T.; Mataga, N. *Tetrahedron Lett.* **1995**, *36*, 5781. (h) Osuka, A.; Tanabe, N.; Nakajima, S.; Maruyama, K. *J. Chem. Soc., Perkin Trans. 2* **1996**, 199. (i) Hsiao, J.; Krueger, B. P.; Wagner, R. W.; Johnson, T. E.; Delaney, J. K.; Mauzerall, D. C.; Fleming, G. R.; Lindsey, J. S.; Bocian, D. F.; Donohoe, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 11181. (j) Seth, J.; Palaniappan, V.; Wagner, R. W.; Johson, T. E.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 11194. (k) Kuciauskas, D.; Liddell, P. A.; Lin, S.; Johnson, T. E.; Weghorn, S. J.; Lindsey, J. S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1999**, *121*, 8604.

(6) For reviews, see: Imahori, H.; Sakata, Y. *Eur. J. Org. Chem.* **1999**, 2445.

(7) For reviews, see: (a) Nagai, K.; Masuda, T.; Nakagawa, T.; Freeman, B. D.; Pinnau, I. *Prog. Polym. Sci.* **2001**, *26*, 721. (b) Masuda, T. Acetylenic Polymers. In *Polymeric Material Encyclopedia*; Salamone, J. C., Ed.; CRC: New York, 1996; Vol. 1, p 32.

(8) (a) Yashima, E.; Huang, S. L.; Matsushima, T.; Okamoto, Y. *Macromolecules* **1995**, *28*, 4184. (b) Teraguchi, M.; Masuda, T. *Macromolecules* **2000**, *33*, 240. (c) Sanda, F.; Kawaguchi, T.; Masuda, T.; Kobayashi, N. *Macromolecules* **2003**, *36*, 2224. (d) Nishimura, T.; Takatani, K.; Sakurai, S. I.; Maeda, K.; Yashima, E. *Angew. Chem., Int. Ed.* **2002**, *41*, 3602. (e) Konishi, T.; Ikeda, A.; Asai, M.; Hatano, T.; Shinkai, S.; Fujitsuka, M.; Ito, O.; Tsuchiya, Y.; Kikuchi, J. I. *J. Phys. Chem. B* **2003**, *107*, 11261. (f) Ikeda, A.; Hatano, T.; Shinkai, S.; Akiyama, T.; Yamada, S. *J. Am. Chem. Soc.* **2001**, *123*, 4855.

(9) Deiters, A.; Cropp, T. A.; Mukherji, M.; Chin, J. W.; Anderson, J. C.; Schultz, P. G. *J. Am. Chem. Soc.* **2003**, *125*, 11782.

(10) Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828.

(11) Milanesio, M. E.; Gervaldo, M.; Otero, L. A.; Sereno, L.; Silber, J. J.; Durantini, E. N. *J. Phys. Org. Chem.* **2002**, *15*, 844.

(12) (a) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798. (b) Xiao, S. Q.; Li, Y. J.; Li, Y. L.; Liu, H. B.; Li, H. M.; Zhuang, J. P.; Liu, Y.; Lu, F. S.; Zhang, D. Q.; Zhu, D. B. *Tetrahedron Lett.* **2004**, *45*, 3975.

(13) (a) Furlani, A.; Napoletano, C.; Russo, M.; Camus, A.; Marsich, N. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 75. (b) Tabata, M.; Yang, W.; Yokota, K. *Polym. J.* **1990**, *12*, 1105. (c) Yang, W.; Tabata, M.; Kobayashi, S.; Yokota, K.; Shimizu, A. *Polym. J.* **1991**, *23*, 1135. (d) Lindgren, M.; Lee, H. S.; Yang, W.; Tabata, M.; Yokota, K. *Polymer* **1991**, *32*, 1531. (e) Miura, Y.; Matsumoto, M.; Ushitani, Y. *Macromolecules* **1993**, *26*, 2628. (f) Miura, Y.; Matsumoto, M.; Ushitani, Y.; Teki, Y.; Yakui, T.; Itoh, K. *Macromolecules* **1993**, *26*, 6673. (g) Tabata, M.; Inaba, Y.; Yokota, K.; Nozaki, Y. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 465. (h) Tabata, M.; Yang, W.; Yokota, K. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1113.

(14) (a) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1994**, *116*, 12131. (b) Yang, W.; Tabata, M.; Kobayashi, S.; Yokota, K.; Shimizu, A. *Polym. J.* **1991**, *23*, 1135. (c) Furlani, A.; Napoletano, C.; Russo, M. V.; Feast, W. J. *Polym. Bull. (Berlin)* **1986**, *16*, 311.

(15) (a) Fungo, F.; Otero, L.; Durantini, E. N.; Silber, J. J.; Sereno, L. *J. Phys. Chem. B* **2000**, *104*, 7644. (b) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Buker, R.; Muller, E.; Liska, P.; Vlachopoulos, N.; Gratzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.

(16) (a) Imahori, H.; Norieda, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 100. (b) Kim, Y. S.; Liang, K.; Law, K. Y.; Whitten, D. G. *J. Phys. Chem.* **1994**, *98*, 984.

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