Synthesis and Structure/Property Correlation of Fully Functionalized Photorefractive Polymers

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ABSTRACT: This paper describes the synthesis and physical study of several new photorefractive polymers. The Heck reaction was successfully applied in the synthesis of these multifunctional polymers. These polymers are conjugated poly(phenylenevinylene)s copolymerized with a small amount of macrocyclic zinc complexes as the photosensitizers. Nonlinear optical chromophores were incorporated as the pendant groups. Both electron-rich and electron-deficient PPV backbones were synthesized. Experimental results showed that when an electron-rich photosensitizer is used, the electron-deficient component for charge transport (CN-PPV) enhances photorefractive performance and reduces the response time.

Introduction

The photorefractive (PR) effect refers to reversible, spatial modulation of the index of refraction due to photoinduced charge redistribution in an optically nonlinear material.[1,2] Photorefractive polymers are multifunctional materials that combine two distinctive physical properties, photoconductivity and electrooptic effect, to manifest the photorefractive effect.[3−8] These multifunctional materials, therefore, must contain the appropriate functional moieties providing photosensitivity, photoconductivity, and electrooptical (EO) response, either by means of composite materials or fully functionalized polymers.[10−19] Our group has developed a series of fully functionalized PR materials; typical resultant PR polymers utilize conjugated polymer backbones as the photoconductive component because of their good photoconductivity and wide range of structural variation, which permits chemical modification and functionalization.[4,7,8] Numerous novel PR materials have been synthesized, such as high-T_g conjugated PR polymers containing transition-metal complexes, low-T_g PR polymers bearing tris(bipyridyl)ruthenium(II) complexes as photosensitizers, and low-T_g conjugated PR polymers containing metalloporphyrin (polymer **1**) or metallophthalocyanine (polymer **2,** Scheme 1).[9,16−19] Our previous results indicated that, among these polymers, polymers **1** and **2** exhibit the best PR performances. However, their performances are still pale compared with our small molecular systems.[19] For example, a monolithic methine dye PR material exhibits a net optical gain of larger than 200 cm^{-1} and a diffraction efficiency of 80%. These polymers show a net optical gain of around 80 cm^{-1} and a diffraction efficiency of 20%.[9]

Electrochemical studies found that there is an energy mismatch between the LUMO of photosensitizers and the LUMO of poly(phenylenevinylene) (PPV) backbones. It is well-known that PPV is a good conductor for holes. To achieve the charge transporting and separation, electrons in the HOMO of photosensitizers must be promoted to the LUMO via photoexcitation. If the excited electrons are then transferred to the LUMO of the backbone under the assistance of a certain electric field, the generated charge carriers will be electrons that cannot be effectively transported away along PPV backbone. Moreover, the HOMO energy of PPV is lower than that of photosensitizers, which makes the hole transfer from photosensitizer to PPV backbone very difficult. However, we reasoned that if the energy level of LUMO of PPV backbone can be lowered by introducing electron-deficient groups, the substituted PPV could be made a good electronic conductor (see Table 1). The excited electrons in photosensitizers will experience a stronger driving force for charge migration and separation. The dominant charge carriers will also become electrons. Better photorefractive performance could be achieved by tackling this energy mismatch. As shown in Figure 1, PPV substituted with cyano groups on the vinyl position exhibit a lower energy level of both LUMO and HOMO.[20,21] These are also reinforced by theoretical calculation for energy levels of bother CN-PPV(I) and CN-PPV(II).[22] These are the rationales for the polymers synthesized in this work, which contain cyano substituents on the PPV backbone. PPV with CN substituents on vinyl groups is well-known.[23] However, the reaction condition for the preparation of vinyl-CN-PPV(I) is not compatible with the preparation of our multifunctional polymer structures.[24] Thus, we decided to introduce the CN groups onto the aromatic rings. Additionally, to utilize the "orientational enhancement effect",[25] the polymer was designed to exhibit a low glass transition temperature (T_g). We have successfully developed such a polymer system (polymer **4** in Scheme 5), and an excellent PR performance was observed for this polymer system as expected. In this paper, we describe the detailed synthesis of three photorefractive polymers containing macrocyclic zinc complexes in their backbone and pendant NLO chromophores. Detailed physical studies of these polymers yielded very insightful information about the design principles of new photorefractive materials.

Results and Discussion

Synthesis of Monomers and Polymers. One of the key monomers for the polymerization is dicyanodivinylbenzene (monomer **A**). Several plausible approaches

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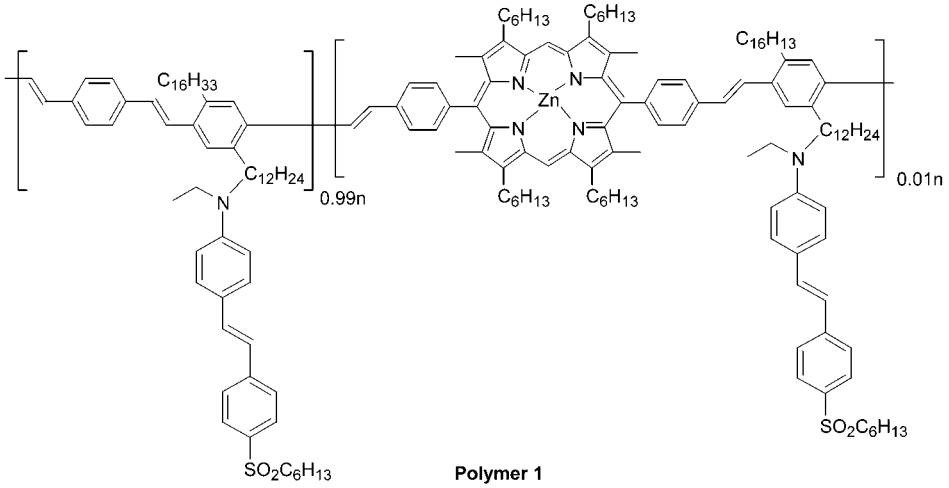
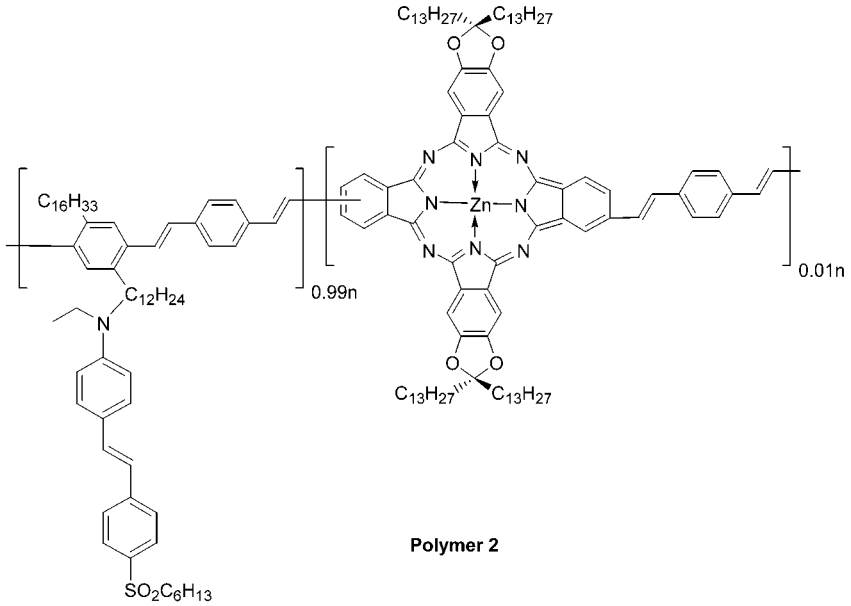
Scheme 1



Polymer 1



Polymer 2

Table 1. Energy Level for Different Polymers and Photosensitizers

	E_{ox}^{onset} (V)	E_{re}^{onset} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)
PPV(MEH)[a]	0.68	−1.49	−5.07[d]	−2.90	2.17
CN-PPV(I)[a]	1.24	−0.90	−5.63[d]	−3.49	2.14
CN-PPV(II)[b]	0.75	−1.26	−5.55[e]	−3.54	2.01
porphyrin[c]	0.462	NA	−4.64	−2.57	2.07
phthalocyanine[c]	0.425	NA	−4.60	−2.90	1.70

[a] The values are referred to Ag.[20] [b] The values are based on the Fc/Fc^+ redox couple as the internal reference. [c] The values are based on the Ag/AgCl as the reference and are reported as $E^{1/2}$. [d] Calculated from $E_{HOMO} = -(E_{ox}^{onset} + 4.39)$ eV and $E_{LUMO} = -(E_{re}^{onset} + 4.39)$ eV.[20] [e] Calculated from $E_{HOMO} = -(E_{ox}^{onset} + 4.8)$ eV and $E_{LUMO} = -(E_{re}^{onset} + 4.8)$ eV.[29,30]

were attempted to synthesize this compound, and the one outlined in Scheme 2 worked best. The 1,4-dibromo-*p*-xylene was oxidized into 2,5-dibromoterephthaldehyde (**2**) by using CrO_3 and mixed acid.[26] Compound **2** was further transformed to 1,4-dicyano-2,5-dibromobenzene (compound **3**) in high yield. The Stille coupling of **3** with tributylvinyltin yielded monomer **A**.[27] The reaction conditions are not optimized, and the overall yield is rather low. Monomers **B** and **C** were synthesized according to the same scheme (Scheme 3) with moderate overall yield.

Zinc porphyrin was synthesized according to the procedure developed in our group.[28] The synthesis of zinc phthalocyanine was achieved according to a modified literature approach (Scheme 4). It is known that phthalocyanine (Pc) has a strong tendency to form columnar assemblies due to its aromatic planar macrocycle ($\pi-\pi$ stacking). To prevent the undesirable aggregation and enhance its solubility, two spiro centers with long alkyl chains were introduced into the Pc via ketal **13** that could undergo further transformation to afford one of the key molecules **15**, 2′,2′-bis(tridecyl)-5,6-(1′,3′-dioxole)-1,3-diiminoisoindole. Another key molecule for the formation of Pc ring is compound **11**, 6/7-iodo-1,3,3-trichloroisoindolenine, which was synthesized by reacting compound **10** with PCl_5. The phthalocyanine ring was formed by the coupling reaction of **11** and **15** in dry THF. Upon oxidation with quinone and metalation with zinc acetate dihydrate in a 1:3 mixture of methanol and chloroform, zinc Pc, a green compound, was obtained in moderate yield.

Polymers were synthesized by utilizing the palladium-catalyzed Heck polycondensation. The polymerization

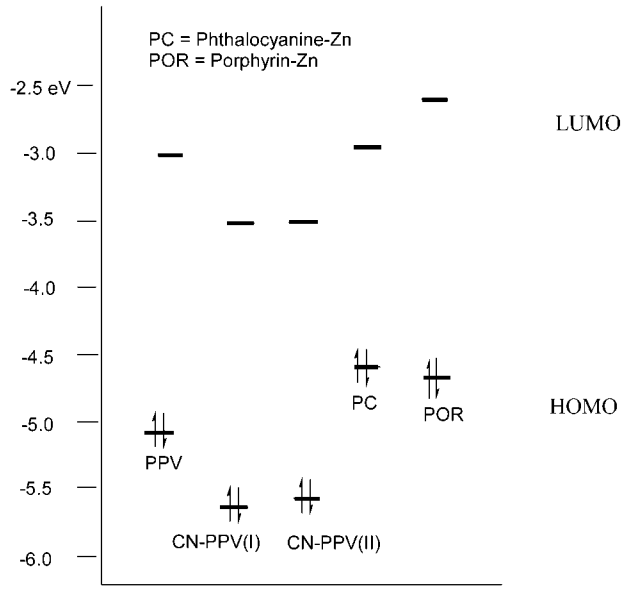


Figure 1. Energy diagram for polymer backbones and photosensitizers (PPV for MEH-PPV, CN-PPV(I) for cyano group in the double bond, CN-PPV(II) for cyano group in the aromatic ring, POR for zinc porphyrin, PC for zinc phthalocyanine).[9,20,21]

was carried out according to Scheme 4, using a catalytic system composed of $Pd(OAc)_2$/P(*o*-tolyl)$_3$/*n*-Bu_3N (4%/20%/250%, molar ratio vs monomer). Aprotic polar solvents, such as DMF and NMP, worked well as the polymerization solvent. NMP was found to generate CN-PPV polymers with better yield (polymers **3** and **4**). Initially, PR polymer was synthesized by using monomers **A** and **C** (structures shown in Schemes 2 and 3) and zinc porphyrin monomer. The resulting polymer exhibited poor solubility in common organic solvents (such as THF, chloroform, tetrachloroethane, and DMF), and it is not possible to prepare thick films (>100 μm) for physical studies. To enhance the solubility, longer alkyl chains were introduced to the chromophore (monomer **B** in Scheme 3), which lead to not only enhancement in the solubility but also lowering in glass transition temperature of resultant polymers. A polymer bearing no NLO chromophores was also synthesized as a model polymer to investigate electrical properties. These polymers now exhibit good solubility in common solvents, such as chloroform, THF, and DMF. Polymers **1** and **2** were obtained in high yields when divinylbenzene was used with two different zinc complexes. GPC measurement in THF with polystyrene standard indicated the relative number-averaged molecular weight (M_n) of approximately 14 000 and 20 000 for polymers **3** and **4.** Polymers **1** and **2** exhibit higher molecular weights (polymer **1**: M_w = 29 000, PDI = 1.55; polymer **2**: M_w = 72 000, PDI = 2.74) than polymers **1** and **2**, probably due to less steric hindrance in the divinyl monomers than monomer **A**.

The structures of polymers **1**, **2**, and **4** were confirmed by ^{1}H NMR study, elemental analysis, and UV−vis spectroscopy. For example, the ^{1}H NMR spectrum of polymer **4** (Figure 2) shows the characteristic chemical shifts for the NLO chromophore and the electron-deficient PPV backbone. For example, chemical shift around 8.01 ppm corresponds to the hydrogen in the cyano-substituted aromatic ring (hydrogen 11 in Figure 2). Q-band absorption at 574 nm was observed in polymer solution, indicating the incorporation of zinc porphyrin. Elemental analysis further confirmed this observation.

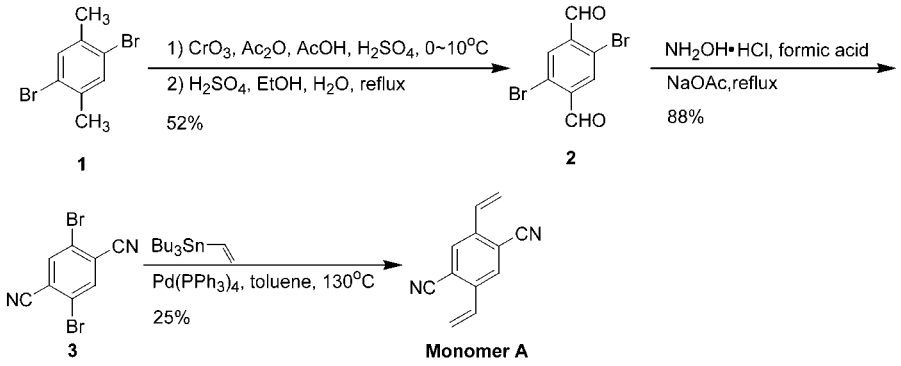
Thermal Properties. To exhibit large photorefractive effect, low-T_g materials are needed in order to utilize the "orientational enhancement effect".[25] Differential scanning calorimetry (DSC) studies indicated that the four polymers (polymers **1**, **2**, **3**, and **4)** exhibit low glass transition temperatures, 16, 16, 9.8, and 4.8 °C, respectively. These low T_g values are due to incorporation of long alkyl chains on both the polymer backbones and the NLO chromophores. Therefore, the NLO chromophores in these polymer films can be reoriented in response to photoinduced space-charge field under ambient temperature.

Optical Properties. The optical properties of these polymers were studied by UV−vis absorption spectroscopy (see Figure 3). For polymer **3**, which is only electron-deficient PPV, the maximum absorption λ_{max} appears at 443 nm, red-shifted from the absorption band around 400 nm of the conventional alkyl-substituted PPV without cyano susbtituents. PR polymer **4** shows a strong absorption at 411 nm of λ_{max}. The strong intensity at 411 nm can be ascribed to the absorption of the NLO chromophore incorporated in the polymer backbone. The shoulder around 440 nm can be attributed to the absorption of polymer backbone. The Q-band at 574 nm was observed due to the incorporation of zinc porphyrin. The Q-band is the most interesting feature for the optical measurement, because it permits the selective photoexcitation of polymers through the photosensitizer (zinc porphyrin in polymer **4**) by using a He−Ne laser (632.8 nm), far away from the maximum absorption of the NLO chromophore and PPV backbone. Polymers **1** and **2** exhibit typical absorption due to either porphyrin or phthalocyanine zinc complexes (inset of Figure 3).

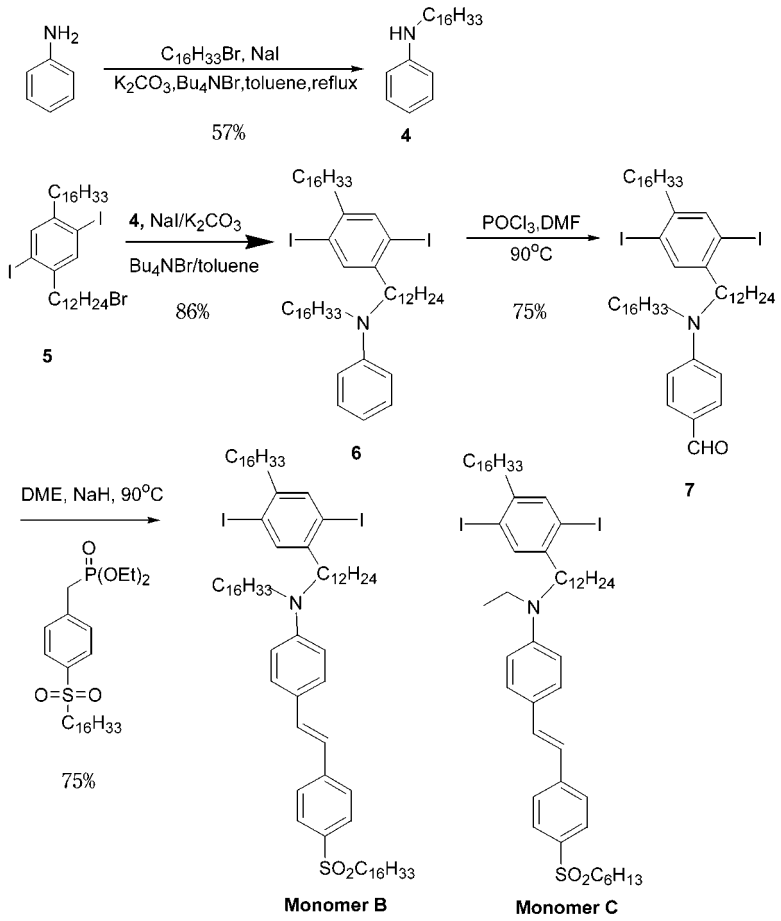
Redox Properties. The redox properties of polymers **3** and **4** were investigated by using cyclic voltammetry (CV). Under the assumption that the energy level of ferrocene/ferrocenium is 4.8 eV below vacuum, we can calculate the LUMO and HOMO energy levels according to $E_{HOMO} = -(E_{ox}^{onset} + 4.8)$ eV and $E_{LUMO} = -(E_{re}^{onset} + 4.8)$ eV.[29,30] The onset reduction potential for **3** appeared at −1.27 V (vs Fc/Fc^+), which was used to infer the energy level of LUMO for CN-PPV (−3.53 eV). This value is more negative than that for the LUMO of MEH-PPV (−2.90 eV). Clearly, the introduction of cyano groups lowers the energy level of LUMO of electron-deficient PPV backbone, which supports our previous assumption. For the PR polymer **4**, the reduction potential was determined to be −1.26 V (vs Fc/Fc^+), corresponding to a LUMO energy level of −3.54 eV (vs vacuum). On the basis of these data and the UV/vis absorption spectroscopic results, an energy diagram can be drawn (see Figure 1). Figure 1 indicates that there is driving force for the transfer of electrons from LUMO of photosensitizer to LUMO of polymer **4**, which is beneficial in terms of improving PR properties.

Photorefractive Properties. To investigate the photorefractive properties, thick polymer films (>100 μm) were prepared from concentrated polymer solutions and were sandwiched between two transparent ITO glasses. Two-beam coupling (2BC) experiments were performed to determine the PR nature of the polymers. Two coherent laser beams with equal intensity (632.8 nm, p-polarized, 2 × 1.6 mW/cm^2) were intersected inside the polymer films. The asymmetric energy change

Scheme 2. Synthesis of 1,4-Dicyano-2,5-divinylbenzene



Scheme 3



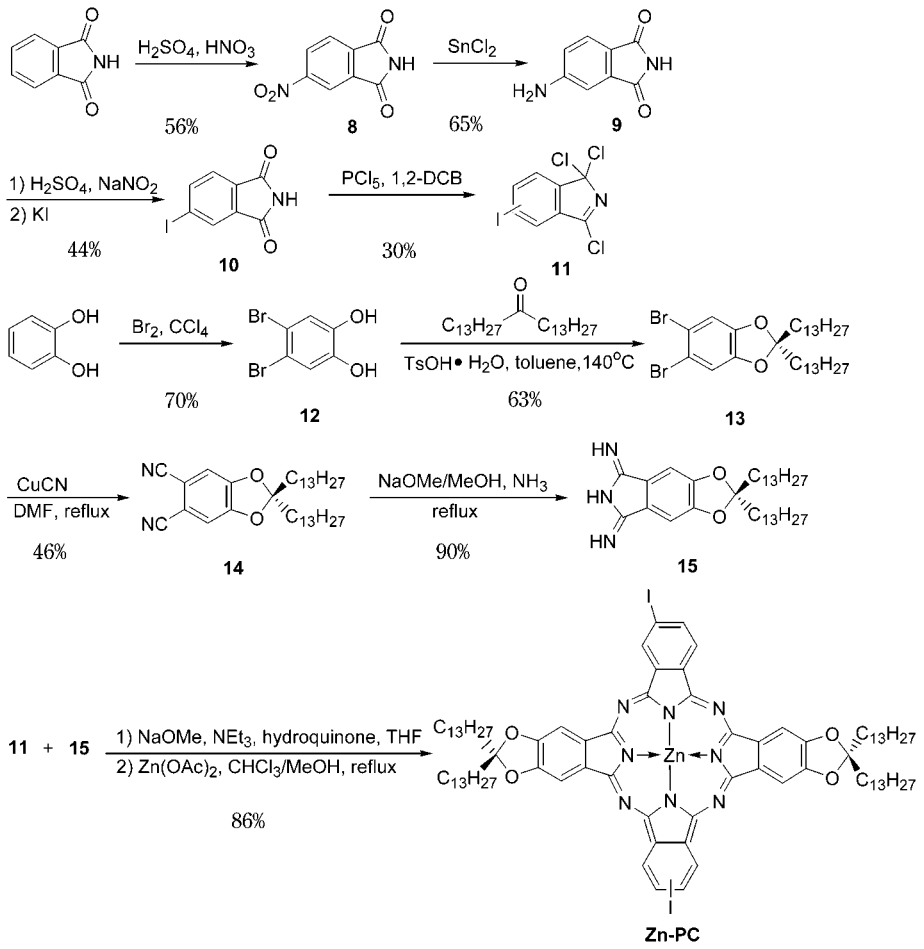
between the two beams was clearly observed due to the phase shift between the incident light intensity and the refractive index modulation. (The refractive index was measured to be 1.72 for polymer **4**.) The 2BC gain coefficient (Γ) was calculated according to the following equation:

$$\Gamma = \frac{1}{L}\ln\left(\frac{1+\alpha}{1-\beta\alpha}\right)$$

where α is the intensity modulation of the signal beam, β is the intensity ratio of the two incident writing beams, and L is the optical path length of the beam with gain. As shown in Figure 4, the gain coefficients for all three polymers (polymers **1**, **2**, and **4**) increase with the applied field, and polymer **4** shows the highest gain coefficient with 93.6 cm^{-1} at a relatively low field of 45 V/mm. At the same field, polymer **1** exhibits a gain coefficient of 47.7 cm^{-1} and polymer **2**, 54.2 cm^{-1}. While the absorption coefficients (α) for polymers **1**, **2**, and **4** were determined to be 12.4, 37, and 10.3 cm^{-1}, respectively, the net optical gain coefficient (Γ − α) are 35.3, 17.2, and 83.3 cm^{-1} for polymers **1**, **2**, and **4,** individually, at this low field. Thus, polymer **4** is superior to polymers **1** and **2** in terms of both gain coefficient and net gain coefficient.

To further investigate the PR properties for these polymers, degenerate four-wave mixing (DFWM) experiments were performed, in which two s-polarized laser beams were used to write the PR grating and a weak p-polarized, counterpropagating beam served to probe the grating. All of these polymers show high diffraction efficiency between 10 and 23%. However, polymer **4** consistently shows higher diffraction efficiency. This provides additional evidence to show that

Scheme 4



our initial design idea works. Because of the favored charge separation process in these polymer systems, the response time of the photorefractive effect should also be shortened. It was determined that the response times for polymers **1**, **2**, and **4** were 4.7, 0.45, and 0.094 s, respectively, at a field strength of about 60 V/μm (Figure 6). Clearly, polymer **4** exhibits the fastest response time among three polymers.

Conclusion

Several fully functionalized photorefractive polymers containing conjugated backbones, and macrocyclic metal complexes have been synthesized. All of the PR polymers exhibit net optical gain under certain external field. It was found that, in order to obtain high PR performance, energy levels between photosensitizers and transporting moieties should be carefully designed to optimize the driving force for charge transfer. When an electron-rich photosensitizer is used, the electron-deficient charge transporting component both enhances photorefractive performance and reduces the response time.

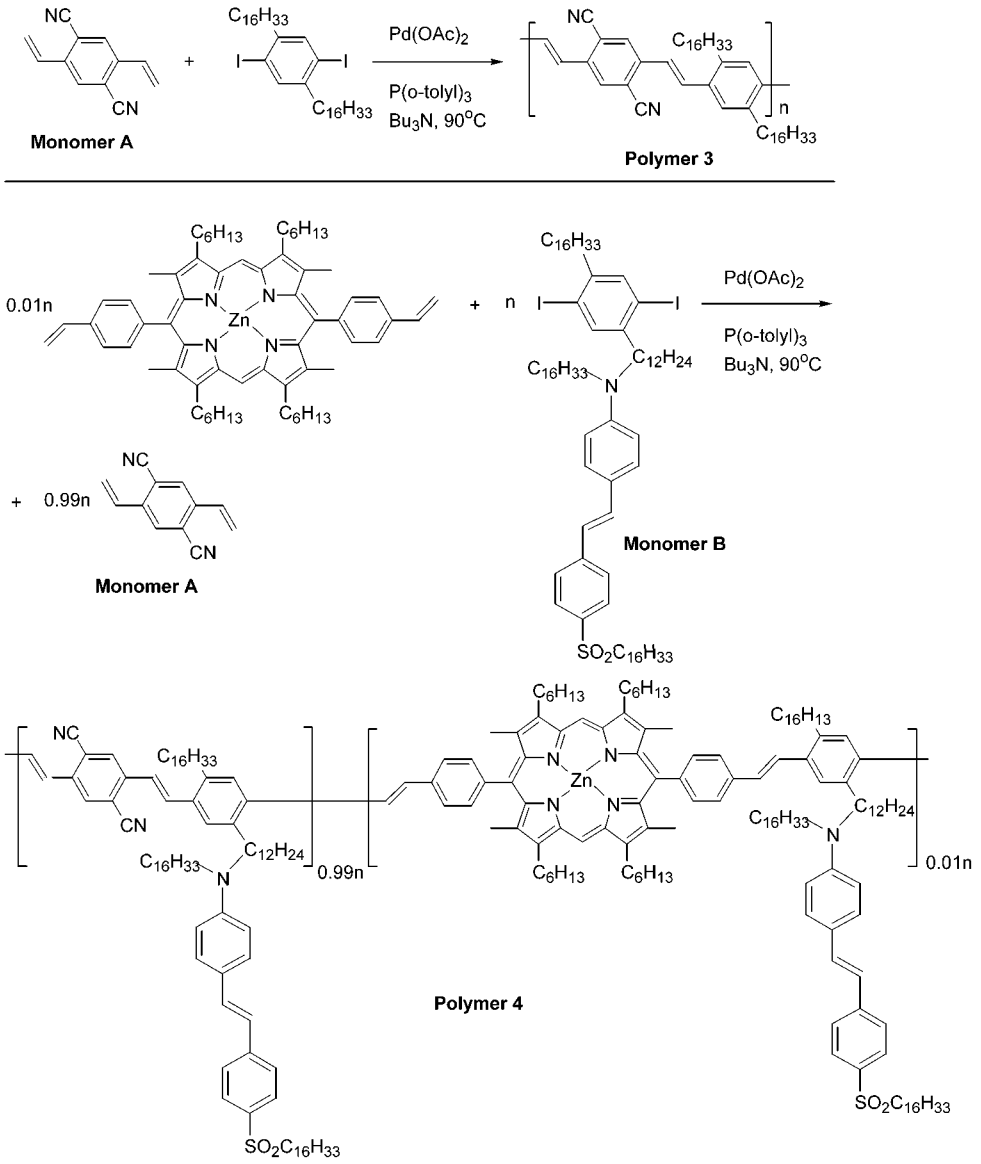
Experimental Section

Materials. All chemicals were purchased from commercial suppliers and used as received unless otherwise specified. All reactions were carried out under a nitrogen atmosphere unless otherwise noted. Tetrahydrofuran (THF) was distilled over sodium and benzophenone. Zinc porphyrin, compound **2**, and compound **5** were synthesized according to the literature.[17,26,28]

Synthesis of Monomers: Compound 3. Compound **2** (7.01 g, 24 mmol), hydroxyamine hydrochloride (8.34 g, 120 mmol), sodium acetate (11.81 g, 144 mmol), and formic acid (70 mL, 99%) were mixed into a 250 mL two-necked round-bottom flask. The mixture was heated to reflux overnight. Then it was poured into water (250 mL) and extracted with chloroform. The organic layer was washed with diluted $NH_3 \cdot H_2O$ solution and water and dried over $MgSO_4$. After removing the solvent, compound **3** was obtained as a pale-yellow/brown solid (6.00 g, 88%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.95 (s, 2H, aromatic proton). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 114.53, 121.13, 124.23, 137.87. mp: 234−240 °C.

Monomer A. Stille coupling reaction was used to prepare the final monomer **A**.[27] Compound **3** (2.00 g, 7 mmol), tributylvinyltin (5.1 mL, 17 mmol), and one portion of the catalyst $Pd(PPh_3)_4$ (0.24 g, 0.2 mmol), plus a few crystals of 2,6-di-*tert*-butyl-4-methylphenol, were put into 50 mL two-necked RB flask. The system was flushed with N_2, and dry toluene (20 mL) was then added. The mixture was kept at reflux for 4 h, and another portion of the same catalyst 0.24 g was then added into the flask. The solution was kept at reflux for another 4 h. The mixture was diluted with ether and treated with KF solution (10%). The resulting solution was stirred and followed by suction filtration to remove the insoluble solid. The yellow organic layer was separated and dried. After removing the solvents, a yellow/orange solid was collected. The solid was dissolved into 100 mL of hexane followed by suction filtration to provide the pale-yellow solid (0.72 g). Recrystallization with hexane/chloroform gave a pure white crystal (0.31 g, 25%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.68 (d, J = 11 Hz, 2H), 6.02 (d, J = 17 Hz, 2H), 7.03 (dd, J_1 = 17 Hz, J_2 = 11 Hz, 2H), 7.91 (s, 1H, aromatic proton). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 115.19, 116.17, 121.18, 129.93, 130.89, 139.72. MS *m/z* calcd from $C_{12}H_8N_2$ (M^+): 180.21. Found: 181.1 ($M + 1^+$). Anal. Calcd for $C_{12}H_8N_2$: C, 79.98; H, 4.47; N, 15.54. Found: C, 79.68; H, 4.35; N, 15.29.

Scheme 5



Compound 4. A mixture of aniline (9.2 mL, 100 mmol), 1-bromohexadecane (15.5 mL, 50 mmol), tetrabutylammonium bromide (1.61 g, 5 mmol), sodium iodide (0.075 g, 0.5 mmol), and potassium carbonate (20.73, 150 mmol) with toluene (100 mL) was kept at reflux for 2 days. The mixture was poured into water and extracted with ether. The organic layer was washed with water and dried over $MgSO_4$. After removing the solvent under reduced pressure, the residue was distilled under reduced pressure (0.2 mmHg, 130−150 °C) to afford compound **12** (almost white solid, 9.0 g, 57%). Further purification could be achieved by recrystallization with ethanol. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 0.88 (t, J = 7 Hz, 3H, $-CH_3$), 1.22−1.29 (m, 24H, alkyl protons), 1.59−1.63 (m, 4H, alkyl protons), 3.09 (t, J = 7 Hz, 2H, $-NCH_2-$), 6.60 (d, J = 8 Hz, 2H, aromatic protons), 6.68 (t, J = 7 Hz, 1H, aromatic protons), 7.17 (m, 2H, aromatic proton). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 14.11, 22.69, 27.17, 29.36, 29.45, 29.57, 29.60, 29.65, 29.67, 29.68, 31.92, 43.98, 112.66, 117.04, 129.19, 148.53. mp: 45−46 °C.

Compound 6. A mixture of compound **5** (2.88 g, 3.6 mmol), compound **12** (2.28 g, 7.2 mmol), tetrabutylammonium bromide (0.115 g, 0.36 mmol), sodium iodide (0.004 g, 0.024 mmol), and potassium carbonate (1.50 g, 10.8 mmol) with toluene (10 mL) was kept at reflux for 2 days. The mixture was poured into water and extracted with CH_2Cl_2, and the organic extract was dried over $MgSO_4$. After removing the solvent under reduced pressure, the residue was purified by flash chromatography on silica gel (hexane:CH_2Cl_2 = 6:1 v/v) to afford compound **6** (white solid, 3.23 g, 86%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 0.88 (t, J = 7 Hz, 6H, $-CH_3$), 1.26−1.31 (m, 66H, alkyl protons), 1.50−1.56 (m, 10H, alkyl protons), 2.58 (t, J = 8 Hz, 4H, benzyl protons), 3.24 (t, J = 8 Hz, 4H, $-CH_2NCH_2-$), 6.60−6.64 (m, 3H, aromatic protons), 7.19 (m, 2H, aromatic proton), 7.59 (s, 2H, aromatic protons). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 14.12, 22.69, 27.20, 29.30, 29.36, 29.39, 29.55, 29.69, 30.18, 31.92, 39.82, 51.03, 100.32, 110.60, 114.98, 129.16, 139.27, 144.81, 148.14. mp: 43.5−45.5 °C.

Compound 7. Phosphorus oxychloride (0.4 mL, 4.3 mmol) was added dropwise into a flame-dried 50 mL two-necked RB flask loaded with anhydrous DMF (2 mL) in an ice bath. The mixture was kept stirring for 1 h at 0 °C and another hour at room temperature. Then, a mixture of compound **6** (3.08 g, 2.97 mmol) with 8 mL of anhydrous DMF was dropwise added into the flask. The mixture was then kept at 90 °C overnight. After cooling to room temperature, the mixture was poured into water and neutralized with sodium acetate and followed by extraction with CH_2Cl_2. The organic extract was washed with water and dried. After removing the solvent under reduced pressure, the residue was purified by flash chromatography on a silica gel column (hexane:ether = 6:1, then 4:1 v/v) to afford compound **7** (pale yellow/white solid, 2.38 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 0.88 (t, J = 7 Hz, 6H, $-CH_3$), 1.26−1.33 (m, 66H, alkyl protons), 1.50−1.55 (m, 10H, alkyl protons), 2.58 (t, J = 8 Hz, 4H, benzyl protons), 3.33 (t,

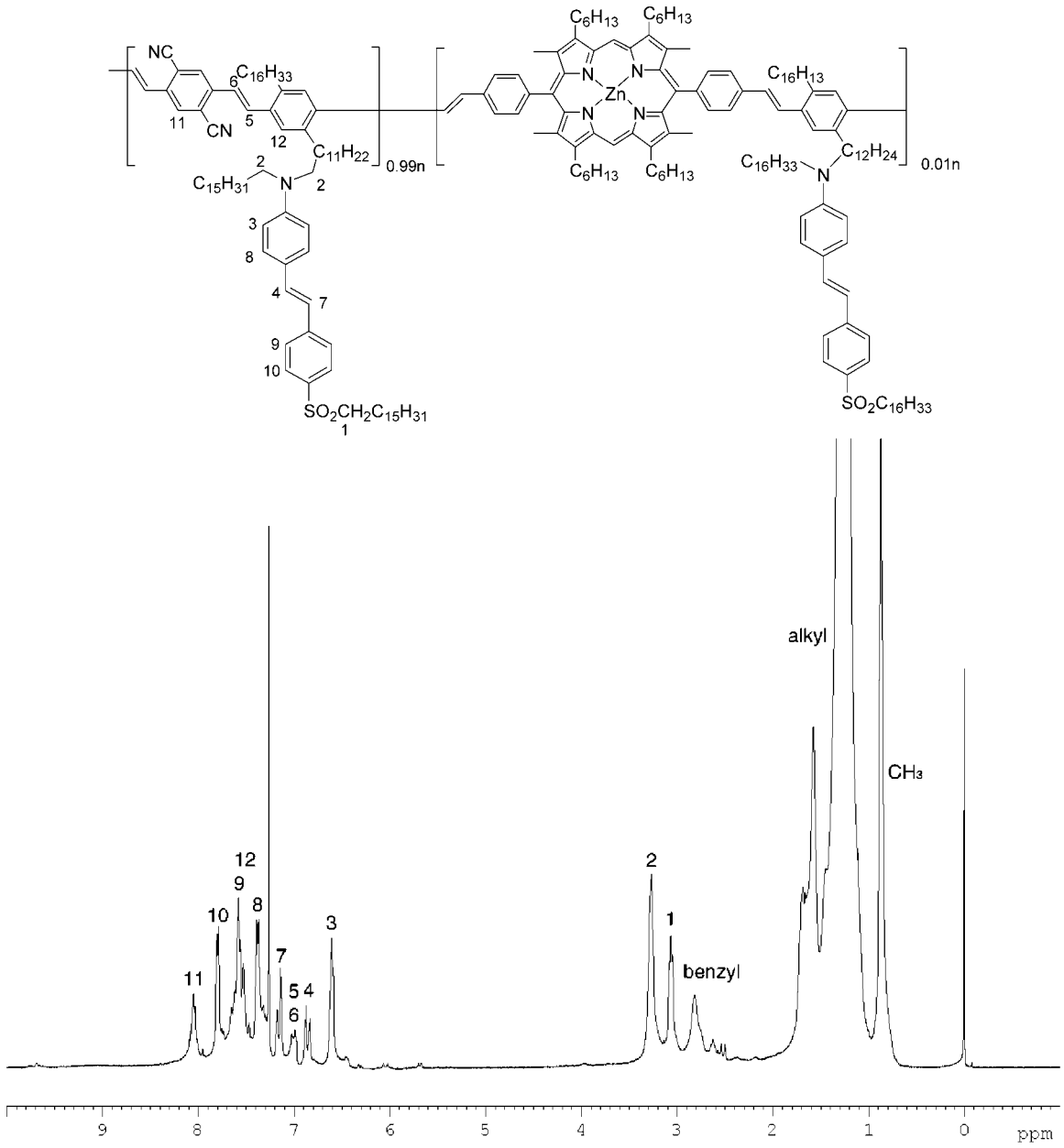


Figure 2. ^{1}H NMR spectrum for polymer **4**.

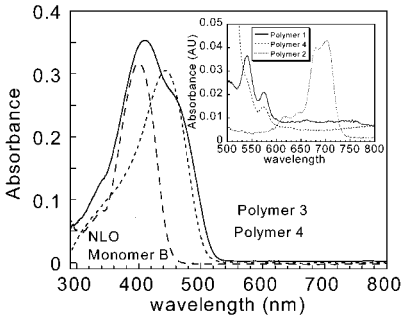


Figure 3. UV−vis spectra of different polymers in chloroform ($c = 1 \times 10^{-5}$ mol L^{-1}). Inset: Q-bands for incorporation of metal complexes in polymers.

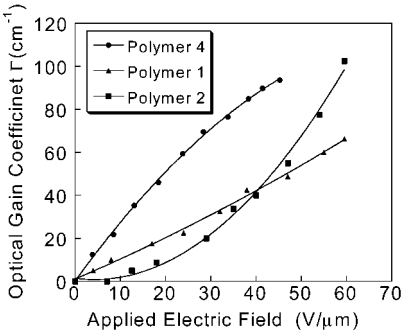


Figure 4. Optical gain coefficients of polymers **1, 2**, and **4** as a function of applied field.

$J = 8$ Hz, 4H, $-CH_2NCH_2-$), 6.63 (d, $J = 9$ Hz, 2H, aromatic protons), 7.59 (s, 2H, aromatic protons), 7.69 (d, $J = 9$ Hz, 2H, aromatic proton), 9.69 (s, 1H, aldehyde proton). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 14.12, 22.69, 27.08, 29.29, 29.36, 29.45, 29.50, 29.55, 29.58, 29.60, 29.68, 30.18, 31.91, 39.81, 51.10, 100.32, 110.62, 124.43, 132.26, 139.26, 144.80, 152.56, 189.95. mp: 59.0−62.0 °C.

Monomer B. Compound **7** (1.99 g, 1.86 mmol) was mixed with 10 mL of dry DME into 50 mL two-necked RB flask, followed by adding NaH (0.085 g, 3.52 mmol). The suspension was stirred at room temperature for 20 min. A solution of

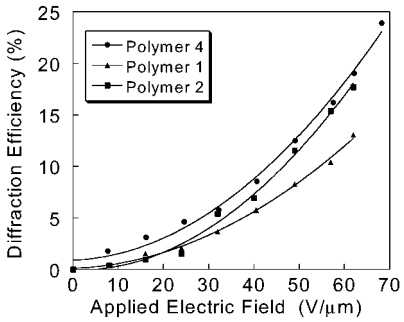


Figure 5. Diffraction efficiency of polymers **1, 2**, and **4** as a function of applied field.

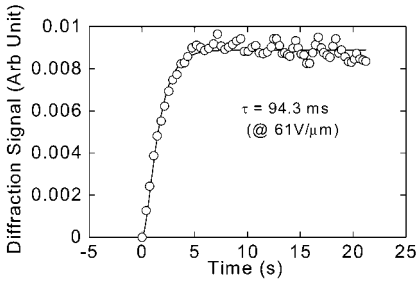


Figure 6. Response time of diffraction signal of polymer **4** at a field of 61 V/μm and 2 × 1.6 mW/cm^2.

compound **16** (1.45 g, 2.80 mmol) with 10 mL of anhydrous DME was added dropwise into the flask. The mixture was kept at 90 °C overnight. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The organic extract was washed with water and dried. After removing the solvent under reduced pressure, the residue was purified by flash chromatography on silica gel (hexane:ether = 8:1 v/v) to afford monomer **B** (greenish-yellow solid, 2.02 g, 75%). (Some residue of the cis isomer could be transformed to the trans isomer by iodine-assisted isomerization.) ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 0.88 (t, J = 7 Hz, 9H, $-CH_3$), 1.23−1.33 (m, 90H, alkyl protons), 1.54−1.60 (m, 12H, alkyl protons), 1.68−1.72 (m, 2H, alkyl protons), 2.58 (t, J = 8 Hz, 4H, benzyl protons), 3.07 (t, J = 8 Hz, 2H, $-SO_2CH_2-$), 3.29 (t, J = 8 Hz, 4H, $-CH_2NCH_2-$), 6.62 (d, J = 9 Hz, 2H, aromatic protons), 6.87 (d, J = 16 Hz, 1H, trans double bond), 7.16 (d, J = 16 Hz, 1H, trans double bond), 7.39 (d, J = 8 Hz, 2H, aromatic protons), 7.58 (m, 4H, aromatic protons), 7.81 (d, J = 8 Hz, 2H, aromatic proton). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 14.12, 22.69, 27.08, 29.29, 29.36, 29.45, 29.50, 29.55, 29.58, 29.60, 29.68, 30.18, 31.91, 39.81, 51.10, 100.32, 111.48, 121.08, 123.25, 126.12, 128.40, 132.87, 135.88, 139.26, 143.91, 144.77, 144.84. 148.48. mp: 53.0−57.0 °C. MS m/z calcd from $C_{80}H_{135}SO_2NI_2$ (M^+): 1428.82. Found: 1428.5. Anal. Calcd for $C_{80}H_{135}SO_2NI_2$: C, 67.25; H, 9.52; O, 2.24; N, 0.98; S, 2.24; I, 17.76. Found: C, 67.46; H, 9.56; O, 2.26; N, 0.98; S, 2.24; I, 17.36.

Compound 8. Fuming H_2SO_4 (20 mL, 20% SO_3) was mixed with fuming HNO_3 (5 mL), followed by adding phthalimide (4.00 g, 27.2 mmol) in portions over a 15 min interval with stirring. The temperature was raised slowly to 40−50 °C and kept at that range for 40 min. Then the mixture was cooled to 0 °C and slowly poured onto ice with stirring, followed by filtration to afford the crude product. The crude product was washed with water and purified by recrystallization with ethanol to afford compound **8** (2.90 g, 56%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.04 (d, J_1 = 8 Hz, J_2 = 0.5 Hz, 1H), 8.60 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 1H), 8.62 (dd, J_1 = 2 Hz, J_2 = 0.5 Hz, 1H).

Compound 9. $SnCl_2$ (8.4 g, 44.3 mmol) was mixed with HCl (saturated solution, 45 mL) and 15 mL of water to prepare the $SnCl_2$ solution. To this solution was added compound **8** (2.00 g, 10.4 mmol) slowly with stirring. The mixture was kept at 50 °C for 2 h until TLC showed completion of reaction. The mixture was cooled to 0 °C, followed by filtration to provide the crude product, which was washed by hot water to afford compound **9** (1.10 g, 65%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 6.35 (s, 2H), 6.75 (d, J = 8 Hz, 1H), 6.82 (s, 1H), 7.38 (d, J = 8 Hz, 1H).

Compound 10. Compound **9** (2.0 g, 12.3 mmol) was dissolved in a solution of concentrated H_2SO_4 (4 mL) and water (15 mL) at 0 °C. Then a solution of $NaNO_2$ (1.0 g, 14.5 mmol) mixed with 3 mL of water was added dropwise into the mixture. After stirring for 30 min, another solution of KI (3.5 g, 21.1 mmol) dissolved in 15 mL of water was added into the mixture. After another 1 h, the mixture was poured into ice water and extracted with CH_2Cl_2, and the organic layer was further washed with $Na_2S_2O_3$ solution. After removing the solvent at reduced pressure, the crude product was purified by flash chromatography on silica gel (CH_2Cl_2: ethyl acetate = 10:1, then 5:1 v/v) several times to afford compound **10** (1.5 g, 44%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 7.54 (d, J = 8 Hz, 1H), 8.08 (s, 1H), 8.15 (d, J = 8 Hz, 1H).

Compound 11. Compound **10** (1.7 g, 6.2 mmol) was mixed with PCl_5 (2.6 g, 12.5 mmol) and dry 1,2-dichlorobenzene (20 mL) in a 50 mL two-necked RB flask. The mixture was heated to 105 °C for 30 min until it was sufficiently liquidified to stir. The mixture was heated and stirred for a week. The mixture was cooled to room temperature, and the solvent and the byproduct were removed by vacuum distillation. The residue was distilled under high vacuum (bp ca. 140 °C for 0.1 Torr) to afford compound **11** (0.64 g, 30%, almost a 1:1 mxiture of two regio isomers). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.28 (d, J = 8 Hz, 1H), 7.94 (dd, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 8.17 (d, J = 1.5 Hz, 1H); 7.56 (d, J = 8 Hz, 1H), 7.90 (d, J = 1.5 Hz, 1H), 7.99 (dd, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H).

Compound 12. 1,2-Dihydroxybenzene (11.0 g, 99.9 mmol) was dissolved in 100 mL of CCl_4 at 0 °C. Then bromine (9.9 mL, 194.0 mmol) dissolved in 15 mL of CCl_4 was added dropwise into the mixture, followed by raising the temperature to room temperature. After keeping stirring for an hour, the solvent was removed at reduced pressure, and the residue was purified by recrystallization with ethanol to afford compound **12** (18.94 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.35 (s, 2H, OH), 7.14 (s, 2H, ArH).

Compound 13. Compound **12** (4.80 g, 17.9 mmol), heptacosanone (4.0 g, 10.2 mmol), and a catalytic amount of *p*-toluenesulfonic acid monohydrate (0.5 g, 2.6 mmol) were dissolved in 100 mL of toluene. The solution was kept at reflux until TLC showed the completion of reaction. The solvent was removed at reduced pressure, and the residue was purified by flash chromatography on silica gel (hexane as eluent) to afford compound **13** (4.12 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.86 (t, J = 7 Hz, 6H, $-CH_3$), 1.23−1.33 (m, 44H, alkyl protons), 1.81 (t, J = 7 Hz, 4H, O−C−CH_2-alkyl), 7.14 (s, 2H, ArH).

Compound 14. A mixture of compound **13** (7.0 g, 10.9 mmol), CuCN (3.00 g, 33.5 mmol), and DMF (80 mL) was kept at reflux for several hours until TLC showed the completion of reaction. The mixture was poured into NH_4OH solution (200 mL), followed by filtration, and the collected solid was washed with NH_4OH solution and water. The crude product was purified with flash chromatography on silica gel several times (first with CH_2Cl_2, then with CH_2Cl_2:hexane = 1:2 v/v) to afford compound **14** (2.7 g, 46%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 0.88 (t, J = 7 Hz, 6H, $-CH_3$), 1.25−1.35 (m, 44H, alkyl protons), 1.93 (t, J = 7 Hz, 4H, O−C−CH_2-alkyl), 7.02 (s, 2H, ArH).

Compound 15. CH_3ONa/CH_3OH was prepared by adding Na (0.1 g, 4.4 mmol) to 40 mL of dry CH_3OH. To this solution was added compound **14** (1.0 g, 1.8 mmol), followed by bubbling dry NH_3 (3 atm) through the solution. The solution was first kept stirring at room temperature for 1 h and then heated to reflux for another 3 h. The solution was then cooled and left overnight. After filtration and washed with cold methanol, compound **15** could be obtained (0.92 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.87 (t, J = 7 Hz, 6H, $-CH_3$), 1.24−1.40 (m, 44H, alkyl protons), 1.91 (t, J = 7 Hz, 4H, O−C−CH_2-alkyl), 6.99 (s, 2H, ArH).

Zinc Phthalocyanine. In a dried 100 mL RB flask were loaded compound **15** (0.41 g, 0.74 mmol) and triethylamine (0.161 g, 1.6 mmol). Dry nitrogen was passed through the flask by the two-needle method. 50 mL of dry THF was added into the flask by a syringe to dissolve compound **15**. Then the mixture was cooled to 0 °C by a salt/ice bath. A solution of compound **11** (0.26 g, 0.74 mmol) in 15 mL of dry THF was gradually added in the flask by a syringe over a period of 15 min. The reaction mixture was then stirred at 0 °C for about 1 h and allowed to warm to room temperature with stirring for another 6 h. After removing the salt by filtration, the reaction mixture was put back to the flask, followed by addition of hydroquinone (0.082 g, 0.74 mmol) and sodium methoxide (0.130 g, 2.39 mmol). The reaction mixture was refluxed under nitrogen for 6 h. After the mixture was cooled and filtered, the solvent was removed. The residue was washed with boiling water and filtered until the filtrate was clear and then washed with ethanol until filtrate was clear. After purification by flash chromatography with neutral alumina (column with heating) (first with CH_2Cl_2:hexane = 1:6, then adding some $CHCl_3$ to increase the polarity, until finally using pure $CHCl_3$), dihydrophthalocyanine (H_2Pc) could be obtained at 40% yield. The H_2Pc (0.030 g, 0.019 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (0.030 g, 0.14 mmol) were added into a mixed solvent of 15 mL of $CHCl_3$ and 5 mL of CH_3OH. The resulting mixture was heated to reflux for 1 day. After removing the solvent at reduced pressure, the residue was purified by flash chromatography in a basic alumina column (CH_2Cl_2:hexane = 1:6, then 1:4 v/v) to afford the zinc phthalocyanine (zinc Pc, 0.027 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.85 (s, br, 12H, $-CH_3$), 1.25−1.55 (m, br, 88H, alkyl protons), 1.84 (s, br, 8H), 2.34 (s, br, 8H), 7.50−7.74 (br, 4H), 8.07 (br, 4H), 8.65 (br, 2H).

Polymerization. A typical polymerization procedure is as follows: A mixture of monomer **A** (0.0812 g, 0.45 mmol), monomer **B** (0.6507 g, 0.455 mmol), and zinc porphyrin (0.0045 g, 0.0046 mmol) in 10 mL of NMP was added with tri-*n*-butylamine (0.27 mL, 1.13 mmol), palladium acetate (0.0045 g, 0.02 mmol), and tri-*o*-tolylphosphine (0.0287, 0.094 mmol). The mixture was kept stirring at 90 °C overnight and then poured into methanol. The resulting precipitate was collected, redissolved into chloroform, and filtered through Celite to remove the catalyst residue. The filtrate was concentrated and precipitated into methanol, followed again by redissolving the collected solid, filtration, and reprecipitation. The resulting polymer was further purified by extraction in a Soxhlet extractor with methanol for 24 h and then was dried under vacuum at 40 °C overnight.

Polymer **1**: Anal. Calcd for $C_{66.54}H_{95.68}N_{1.04}O_2S_1Zn_{0.01}$: C, 82.04; H, 9.82; N, 1.49; Zn, 0.067. Found: C, 81.27; H, 9.57; N, 1.52; Zn, 0.071.

Polymer **2**: Anal. Calcd for $C_{66.3}H_{95.31}N_{1.07}O_{2.02}S_{0.99}Zn_{0.01}$: C, 81.98; H, 9.81; N, 1.54; Zn, 0.067. Found: C, 81.04; H, 9.37; N, 1.49; Zn, 0.070.

Polymer **4**: Anal. Calcd for $C_{92.52}H_{143.7}N_{3.02}O_2S_1Zn_{0.01}$: C, 81.52; H, 10.63; N, 3.10; O, 2.35; S, 2.35; Zn, 0.048. Found: C, 81.26; H, 10.64; N, 3.14; O, 2.26; S, 2.29; Zn, 0.040.

Characterization. ^{1}H NMR spectra were collected at 400 or 500 MHz on a Brüker DRX-400 or DRX-500 spectrometer, respectively. ^{13}C NMR spectra at 125 MHz were obtained on a Brüker DRX-500. Melting points were collected by using a Mel-Temp II instrument. UV/vis spectra were recorded on a Shimazu UV-2401PC spectrometer. Thermal analyses were performed on Shimazu DSC-60 and TGA-50 under nitrogen atmosphere at a heating rate of 10 °C/min. Cyclic voltammetry was performed on a Bioanalytical Systems CA-50W with a three-electrode compartment cell (Bioanalytical Systems Inc.) equipped with a platinum disk as working electrode, a platinum wire as counter electrode, and a $Ag/AgNO_3$ electrode as reference electrode. The supporting electrolyte used was tetrabutylammonium hexafluorophosphate (0.1 M in methylene chloride). The scan rate was adjusted to 100 mV/s. All potentials were calibrated with ferrocene/ferrocenium (Fc/Fc^+) couple. All reported $E_{1/2}$ values are taken as the average of the anodic and cathodic peak potentials. Mass spectrometry was provided by Hewlett-Packard Agilent 1100 LCMSD. Elemental analyses were performed by Atlantic Microlab, Inc., except for the metal (zinc), which was collected by Galbraith Laboratories, Inc. Molecular weights and distributions were measured with a Waters RI and UV GPC system (Waters 410 differential refractometer and Waters 486 tunable absorbance detector) with polystyrene as the standard and THF as the eluent.

The films for two-beam coupling and four-wave mixing experiments were prepared by sandwiching the materials between two indium−tin oxide (ITO) covered glass substrates. The thickness of the film was maintained at 125 μm with the help of a polyimide spacer. Two-beam coupling experiments were performed using a He−Ne laser (632.8 nm, 30 mW) as the light source. The two split p-polarized laser beams with equal intensity (2×1.6 mW/cm^2) were intersected in the film with a cross-angle of 7.5° to generate the refractive index grating. The film normal was tilted an angle of 53° with respect to the symmetric axis of the two writing beams to provide a nonzero projection of the grating wave vector along the poling axis. The transmitted intensities of the two beams were monitored by two calibrated diode detectors. The diffraction efficiency was measured by degenerate four-wave mixing (DFWM) experiment, in which two s-polarized laser beams (632.8 nm) of equal intensity intersected in the film to write the index grating and a weak p-polarized beam (probe beam) counterpropagating to one of the writing beams was used to read the index grating formed in the material. The diffracted light intensity of the probe beam was detected by a photodiode and subsequently amplified with a lock-in amplifier. The diffraction efficiency η was calculated as the ratio of the intensities of the diffracted beam to the incident reading beam. Data were collected by a computer. The refractive indexes of the polymers were measured by using the Metricon model 2010 prism coupler at 632 and 780 nm. The refractive indexes at other wavelength were deduced from the corresponding Sellmyer relationship.

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