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Synthesis and Fluorescent Properties of a Chiral Conjugated Polymer Based on (*S*)-2,2′-Binaphtho-20-crown-6

Hui Huang,[1] Qian Miao,*[2] Yixiong Kang,[1] Xiaobo Huang,[1,2] Jinqian Xu,[1] and Yixiang Cheng*[1]

[1]Key Lab of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering,
Nanjing University, Nanjing 210093, P. R. China

[2]College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325027, P. R. China

Received February 8, 2008; E-mail: yxcheng@nju.edu.cn

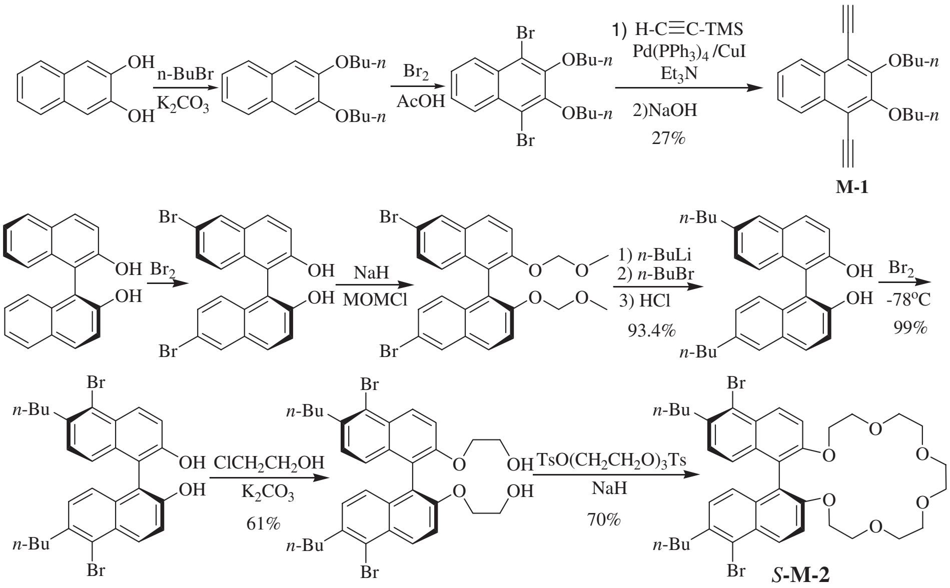
Linear conjugated polymer was obtained by the polymerization of 2,3-dibutoxy-1,4-diethynylnaphthalene (**M-1**) and (*S*)-5,5′-dibromo-6,6′-dibutyl-2,2′-binaphtho-20-crown-6 (*S*-**M-2**) via Pd-catalyzed Sonogashira reaction. The conjugated polymer shows strong green-blue fluorescence due to the extended π-electronic structure between the chiral repeating unit (*S*)-6,6′-dibutyl-2,2′-binaphtho-20-crown-6 and the conjugated linker 2,3-dibutoxynaphthyl group via acetylene bridge. The responsive properties of the chiral polymer on K^+, Pb^{2+}, Hg^{2+}, and As^{III} were investigated by fluorescent spectra. The results show that Hg^{2+} and As^{III} can cause effective fluorescent quenching of the polymer, whereas, K^+ and Pb^{2+} do not produce obvious changes in the polymer fluorescence. The obvious fluorescent influence shows that the 2,2′-binaphtho-20-crown-6 moiety plays an important role in fluorescent recognition for Hg^{2+} and As^{III} due to the effective photoinduced electron transfer (PET) and charge transfer (PCT) between the conjugated polymer backbone and receptor species.

Optically active 1,1′-bi-2-naphthol (BINOL) and its derivatives have attracted particular interest because their versatile backbone can be systematically modified by the introduction of functional groups based on steric and electronic properties.[1–11] In the last decade, Pu and other research groups reported a series of chiral polymers based on (*R*)- or (*S*)-1,1′-bi-2-naphthol as the starting material. These rigid and regular chiral binaphthyl-based polymers exhibit excellent fluorescent materials with good fluorescence quantum efficiencies and represent a new generation of materials for potential applications in areas such as fluorescent sensors in chiral molecule recognition, electro-optical materials.[3,4,12–23] According to the reported literature, the skeletal structure of BINOL can be selectively halogenated at the 3,3′- or 6,6′-positions of binaphthyl, leading to a variety of binaphthyl derivatives.[24–29] But so far there have been few reports on the halogenation of BINOL at the 5,5′-positions except that our group reported the facile synthesis of 5,5′-dibromo-6,6′-dialkyl-1,1′-bi-2-naphthol, and Pirkle and Schreiner described the synthesis and chiral resolution of racemic 5,5′-dibromo-6,6′,7,7′-tetramethyl-1,1′-bi-2-naphthol.[30–34] Based on our current study, (*S*)-BINOL can be specifically brominated at 5,5′-positions under mild conditions to afford a pure product in an excellent yield when 6,6′-positions are occupied by *n*-butyl groups. 5,5′-Dibromo-6,6′-dialkyl-1,1′-bi-2-naphthol can further be used as an entry into a wide range of other derivatives by strategic placement of substituents at the well-defined molecular level.

Polybinaphthyl hosts developed for molecular recognition purposes are mainly focused on crown ethers and cyclic amides. (*R*)- or (*S*)-2,2′-binaphtho-20-crown-6 and its derivatives used in molecular recognition devices have been extensively studied by Cram et al.[35–37] BINOL-derived chiral crown ethers have been recognized as efficient selectors for the separation of chiral amines or α-amino acids by chiral HPLC, and as useful chiral ligands in highly selective chiral luminescent sensors. Shinbo et al. employed 3,3′-dibenzo-2,2′-binaphtho-20-crown-6 as chromatographic packing for the separation of racemic amino acids. The results indicate that the chiral crown ether-coating packing is very powerful for the optical resolution of a variety of amino acids and optically active amines.[38] The Japanese company Daicel has successfully used the chromatographically stable phase Crownpak CR (+)™ and CR (−)™ for the resolution of amino acids and compounds with a primary amino group with an asymmetric center. But linear chiral polymers incorporating a 2,2′-binaphtho-20-crown-6 moiety at 5,5′-positions of conjugated polybinaphthyls have not been reported so far. In this paper, we report the synthesis and fluorescent properties of a linear conjugated polymer incorporating optically active 6,6′-dibutyl-2,2′-binaphtho-20-crown-6. The conjugated polymer shows strong green-blue fluorescence with high PL efficiency. Based on the responsive fluorescent properties of the chiral polymer, K^+, Pb^{2+}, Hg^{2+}, and As^{III}, Hg^{2+} and As^{III} cause effective fluorescent quenching of the polymer, whereas K^+ and Pb^{2+} do not produce obvious change in polymer fluorescence or UV–vis absorption spectra. The obvious fluorescence changes show that the 2,2′-binaphtho-20-crown-6 moiety in the polymer main chain backbone plays an important role in fluorescent recognition for Hg^{2+} and As^{III} due to effective photoinduced electron transfer and charge transfer between the conjugated polymer backbone and receptor species.

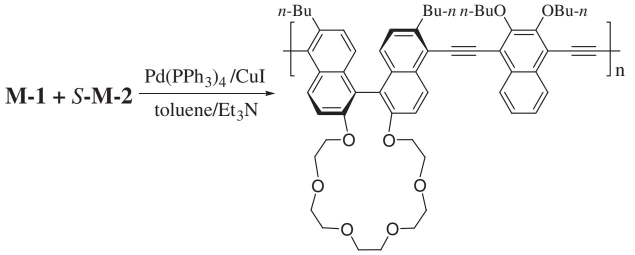
Results and Discussion

Syntheses and Features of Monomers and the Chiral Polymer. 2,3-Dibutoxy-1,4-diethynylnaphthalene (**M-1**) was obtained via Pd-catalyzed Sonogashira reaction from the



Scheme 1. Synthesis procedures of **M-1** and *S*-**M-2**.

starting material 1,4-dibromo-2,3-dibutoxynaphthalene, which was synthesized according to the literature (Scheme 1).[39] Sonogashira coupling is one of the most important C–C coupling reactions in synthetic organic chemistry.[40–44] Normally the reactivity order of organic halides for Sonogashira coupling is vinyl iodide ≈ vinyl triflate > vinyl bromide > vinyl chloride > aryl iodide > aryl bromide ≥ aryl chloride, and employs $Pd(PPh_3)_4 > Pd(PPh_3)_2Cl_2 > Pd(AcO)_2$ as catalyst. Herein, we chose $Pd(PPh_3)_4$ as a catalyst and CuI as a cocatalyst. Even at high temperature and long reaction time, **M-1** was obtained in a low yield due to the enhanced electron density of butoxy group at the 2,3-positions of naphthalene.



Scheme 2. Synthesis procedure of the chiral polymer.

The chiral monomer (*S*)-5,5′-dibromo-6,6′-dibutyl-2,2′-binaphtho-20-crown-6 (*S*-**M-2**) was prepared from starting material (*S*)-BINOL as in the reported literature,[31,45] which was different from the traditional synthesis routes by Cram (Scheme 1).[35,36,46,47] Triethylene glycol ditosylate [$TsO(CH_2CH_2O)_3Ts$] was synthesized according to the literature.[48] In all cases, the hydroxy group of (*S*)-BINOL was first transformed to an ether with 2-chloroethanol, and then the 2,2′-binaphtho-20-crown-6 can be directly obtained by coupling with $Ts(OCH_2CH_2)_3OTs$ in an overall yield of 44%. Optically active 1,1′-bi-2-naphthol (BINOL) derivatives have often been used as the starting materials for the preparation of conjugated polymers that have a chiral main-chain configuration. But so far there have been very few reports on halogenation of BINOL at the 5,5′-positions.[30,31] Based on Lin et al.[49–51] and Pu et al.,[52] with (*S*)-6,6′-dichloro-2,2′-diethoxy-1,1′-binaphthyl was chosen as the starting material, bromination occurred at the 4,4′-positions in CH_2Cl_2 at −78 °C with 10 equiv of bromine to afford a pure product 4,4′-dibromo-6,6′-dichloro-2,2′-diethoxy-1,1′-binaphthyl in a very high yield of 98%. And according to Chan et al., the bromination occurred at the 6,6′-positions at −78 °C when 4,4′-dibromo-BINOL was chosen as the starting material.[53,54] Pu et al. also reported preparation of (*R*)- or (*S*)-4,4′,6,6′-tetrabromo-2,2′-dihexyloxy-1,1′-binaphthyl in AcOH at room temperature with 10 equiv of bromine when optically pure 2,2′-dihexyloxy-1,1′-binaphthyl was used as a starting material.[55] Herein, (*R*)-BINOL can be specifically brominated at 5,5′-positions at low temperature to directly afford a pure product in an excellent yield of 99% when the 6,6′-positions are occupied by *n*-butyl groups. Starting from the BINOL derivatives brominated at the 5,5′-positions, we can further design and synthesize a series of novel binaphthyl-based chiral ligands by strategic placement of substituents within the framework of a given BINOL derivative. In this paper, a chiral conjugated polymer was obtained by the polymerization of 2,3-dibutoxy-1,4-diethynylnaphthalene (**M-1**) with (*S*)-5,5′-dibromo-6,6′-dibutyl-2,2′-binaphtho-20-crown-6 (*S*-**M-2**) via Pd-catalyzed Sonogashira reaction (Scheme 2). Sonogashira cross coupling was carried out in toluene solution in the presence of $Pd(PPh_3)_4$ (5 mol %), CuI (20 mol %), and n-$BuNH_2$ under a N_2 atmosphere at 80 °C. The resulting polymer was obtained in moderate yield. The molecular weight was determined by gel permeation chromatography (GPC): $M_w = 6030$, $M_n = 4200$, PDI = 1.44. The GPC result indicates that the polymer shows moderate molecular weight. The alkyl group and crown ether substituents on the naphthyl ring side chains of the polymer not only modify the electronic properties and conjugated structure of the linear polymer, but also improve solubility dramatically in common organic solvents. The chiral conjugated polymer exhibits strong green-blue fluorescence with high PL efficiency due to the extended π-electronic structure between the chiral repeating unit and the conjugated unit via ethynyl linker, which improves the electron-transporting properties of the chiral conjugated polymer within the conjugated polymer backbone. Furthermore, this kind of ethynyl bridge can reduce steric hindrance between backbone rings and groups, and also has a beneficial effect on the corresponding polymer stability.

The polymer is an air stable solid with brown color and shows good solubility in THF, CH_2Cl_2, $CHCl_3$, and DMF due to attachment of the flexible butoxy and 6,6′-dibutyl-2,2′-binaphtho-20-crown-6 group substitutents in the side of the chiral polymer. The polymer does not show glass-transition temperature (T_g). Thermogravimetric analysis (TGA) of the polymer was carried out under a N_2 atmosphere at a heating rate of 10 °C min^{-1}. According to Figure 1, the polymer shows high thermal stability, there is no weight loss before 250 °C. An apparently one-step degradation was observed at temperature ranging from 280 to 675 °C. The polymer tends toward complete decomposition at 720 °C. A total loss of about 46% is observed when heated to 720 °C.

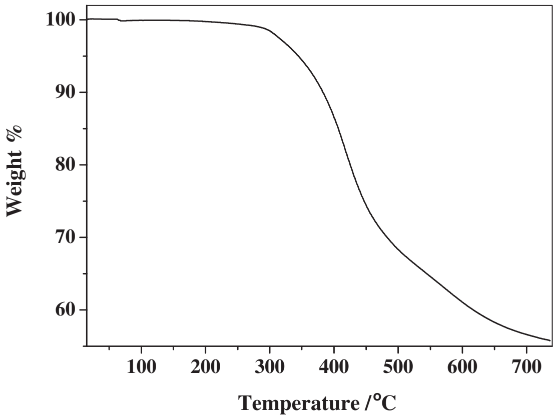


Figure 1. TGA curve of the chiral polymer.

Optical Properties. Figures 2 and 3 illustrate the UV–vis absorption and fluorescent spectra of 2,3-dibutoxy-1,4-diethynylnaphthalene (**M-1**), (*S*)-5,5′-dibromo-6,6′-dibutyl-2,2′-binaphtho-20-crown-6 (*S*-**M-2**), and the chiral polymer. Optical data of **M-1**, *S*-**M-2**, and the polymer are summarized in Table 1. UV–vis spectra of the polymer are similar in THF, CH_2Cl_2, acetone, and DMF. It can be concluded that solvent has no effect on the conjugation structure of the chain backbone. Compared to **M-1** and *S*-**M-2**, UV–vis absorption spectrum of the chiral polymer displays a large red shift. UV absorption maxima λ_{max} of **M-1** and *S*-**M-2** appear at 240 and 243 nm, respectively. The absorption maxima λ_{max} of the polymer appears in a broad region from 375 to 500 nm, which shows that a large red shift can be ascribed to the effective π–π^*-conjugated segment in the polybinaphthyl main chain.[15,20,56,57]

The polymer emits green-blue light under ultraviolet light (254 or 365 nm) or sunlight even at low concentration

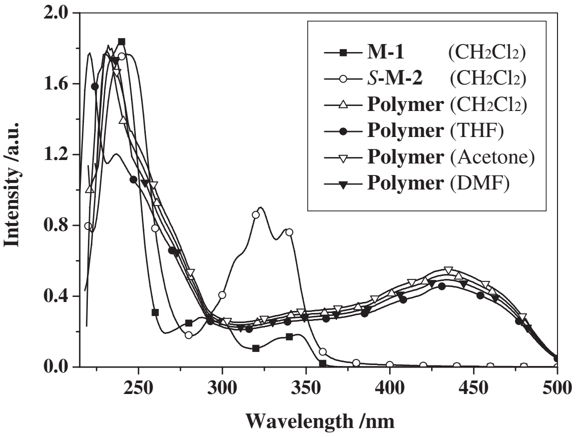


Figure 2. UV–vis spectra of **M-1**, *S*-**M-2**, and the chiral polymer.

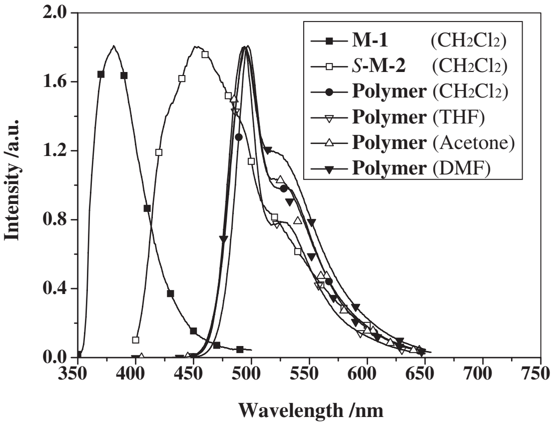


Figure 3. Fluorescent spectra of **M-1**, *S*-**M-2**, and the chiral polymer.

Table 1. Optical Properties of **M-1**, *S*-**M-2**, and the Chiral Polymer

	UV–vis (λ_{max})/nm	PL (λ_{max})/nm		Stokes shift/nm[e)]	Φ_{PL}[f)]
		λ_{ex}	λ_{em}		
M-1[a)]	243, 323	403	454		
S-**M-2**[a)]	240	360	382		
Polymer[a)]	434	366	494, 526(sh)	60	0.61
Polymer[b)]	434	366	497, 529(sh)	63	
Polymer[c)]	434	366	494, 526(sh)	60	
Polymer[d)]	434	366	494, 527(sh)	60	

a) Determined in CH_2Cl_2 solution. b) Determined in THF solution. c) Determined in acetone solution. d) Determined in DMF solution. e) Stokes shift = PL λ_{max} (nm) − UV–vis λ_{max} (nm). f) These values were estimated by using a quinine sulfate solution (ca. 1.1×10^{-5} mol L^{-1}) in 0.5 mol L^{-1} H_2SO_4 ($\Phi_f = 55\%$) as a standard.

Table 2. CD Spectra Data of *S*-**M-2** and the Chiral Polymer

	$[\theta]$ ($\lambda_{\max}$ in nm)
S-**M-2** × 10^5 (CH_2Cl_2)	−3.69 (229.5), +5.47 (242.2)
Polymer × 10^5 (CH_2Cl_2)	−14.35 (223.0), +10.23 (250.6), −2.03 (327.3)
Polymer × 10^5 (THF)	−14.01 (222.4), +9.84 (250.6), −2.00 (327.3)

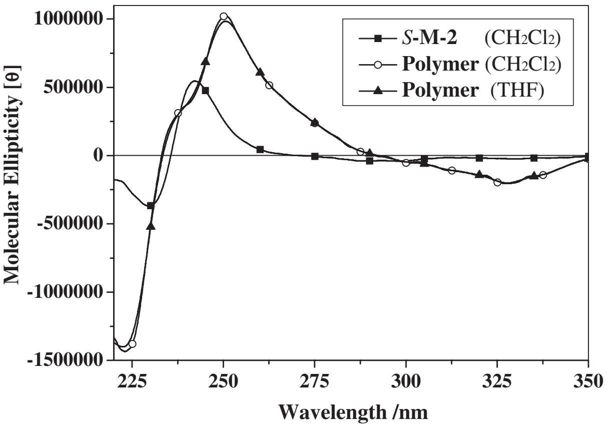


Figure 4. CD spectra of *S*-**M-2** and the chiral polymer.

(1.0×10^{-4} mol L^{-1}). According to Figure 3, the maximum fluorescent wavelengths $\lambda^{F}{}_{\max}$ of **M-1** and *S*-**M-2** show photoluminescent bands at 454 and 382 nm in CH_2Cl_2, respectively. The chiral conjugated polymer shows two bands at 494 and 526 nm in CH_2Cl_2, acetone and DMF. But the polymer shows 3 nm of red shift in THF, and the fluorescent wavelengths $\lambda^{F}{}_{\max}$ appear at 497 and 529 nm. The PL efficiency (Φ_{PL}) of the polymer is 0.61. The polymer shows strong fluorescence with high PL efficiency due to the extended π-electronic structure between the chiral repeating unit and the conjugated linker via ethynyl linker.[58,59] The greatly enhanced fluorescence of the conjugated polymer incorporating 6,6′-dibutyl-2,2′-binaphtho-20-crown-6 moiety is expected to have potential application in polarized light-emitting materials and fluorescent sensors for the sensitive detection of various metal ions and enantiomeric recognition of chiral amines, chiral amino acids, and amino esters.

CD Spectra. The specific rotation value ($[\alpha]_D^{25}$) of *S*-**M-2** is −56.1 (*c* 0.25, CH_2Cl_2), and of the conjugated polymer is −170.6 (*c* 0.17, THF). Both *S*-**M-2** and the chiral conjugated polymer exhibit intense CD signals with negative and positive Cotton effects in their CD spectra (Figure 4). CD spectral data of *S*-**M-2** and polymer are listed in Table 2. The ^1L_a and ^1B_b band intensity and position of the polymer are similar in CH_2Cl_2 and THF. But the ^1L_a and ^1B_b band intensity and position of the polymer are different from that of *S*-**M-2**. CD intensity of the polymer is stronger than that of *S*-**M-2**. Moreover, the ^1L_a bands of the CD spectrum of the polymer show about 5 nm of red shift compared to *S*-**M-2**, and ^1B_b bands of the CD spectrum of the polymer show about 7 nm of blue shift relative to *S*-**M-2**. The chiral polymer exhibits a weaker Cotton effect at about 327 nm. The chiral conjugated polymer adopts a linear backbone configuration due to the main chain backbone at 5,5′-positions of 1,1′-binaphthyl,[30] which has a chain backbone similar to the chiral polymer at the 4,4′-positions of 1,1′-binaphthyl.[60]

Table 3. The Quenching Ratios of Metal Ions to the Chiral Polymer

	n_{Polymer}:n_{ion}					
	1:1	1:2	1:5	1:10	1:20	1:50
K^+	4.29	5.16	5.89	7.63	6.81	7.93
Pb^{2+}	3.01	4.94	5.72	3.31	5.55	7.45
Hg^{2+}	4.82	6.08	12.66	19.76	29.22	58.13
As^{III}	3.87	7.95	9.32	14.23	21.97	44.96

Responsive Fluorescence Properties of the Chiral Polymer towards Metal Ions. Most fluorescent chemosensors for cations are composed of a cation recognition unit (ionophore) together with a fluorogenic unit (fluorophore) and are called fluoroionophores. An effective fluorescence chemosensor must convert the event of cation recognition by the ionophore into an easily monitored and highly sensitive optical signal from the fluorophore.[61–67] Fluorescent conjugated polymers have several advantages over small molecule sensors due to enhancements associated with electronic communication between receptors along the polymer backbone, processability, and ease of structural modification.[68]

Conjugated polymers incorporating molecular recognition moieties can show high sensitivity of fluorescent chemosensors to external structural perturbations and to electron density changes within the conjugated polymer main backbone when they interact with metal ions to form complexes. One effective group of fluorescent chemosensors for alkali metal, alkaline earth metal, and heavy metal ions involves chromophores having covalently linked crown ether substituents.[69–74] These sensors are known to form complexes with various metal cations. Fluorescent sensing often involves changes in luminescence via PET, PCT, and excimer formation after the crown ether coordinates the analyte. In this paper, 2,2′-binaphtho-20-crown-6 substituents can orient in a well-defined spatial arrangement in the main chain backbone of linear conjugated polymer. Based on the size of the metal ion and crown ether cavity, we chose the conjugated polymer as fluorescent chemosensor for the recognition of K^+, Pb^{2+}, Hg^{2+}, and As^{III}. These cations or groups can fit well into the 20-crown-6 cavity to form the corresponding polymer complexes, which may lead to optical signal changes of the polymer.

The responsive fluorescent changes of a conjugated polymer incorporating (*S*)-2,2′-binaphtho-20-crown-6 on K^+, Pb^{2+}, Hg^{2+}, and As^{III} have been investigated. The concentration of the polymer was fixed at 4.6×10^{-5} mol L^{-1} corresponding to 2,2′-binaphtho-20-crown-6 receptor moiety in THF. Aqueous nitrate or acetate salts were used at a concentration of 4.3×10^{-2} mol L^{-1}. The influences of metal ions on the fluorescent emission response of the polymer are shown in Table 3. As is evident from Figures 5 and 6, an effective fluorescence quenching can be detected upon the various molar

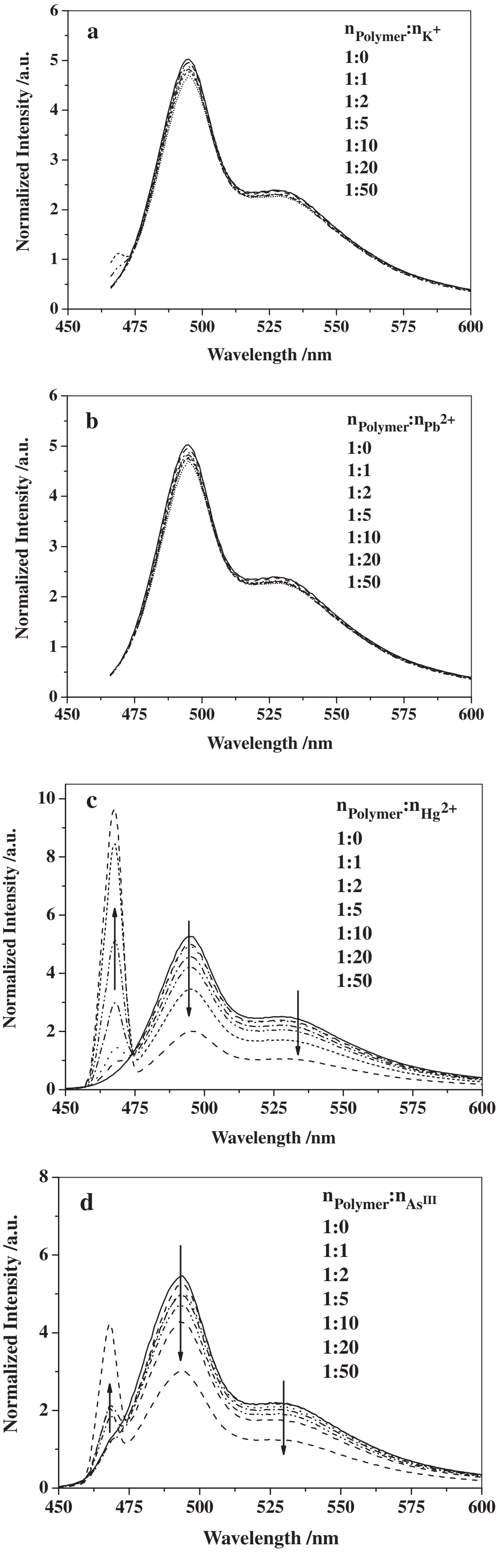


Figure 5. Fluorescent titration curves of the chiral polymer on K$^+$ (a), Pb^{2+} (b), Hg^{2+} (c), and As^{III} (d) (λ_{ex} = 366 nm).

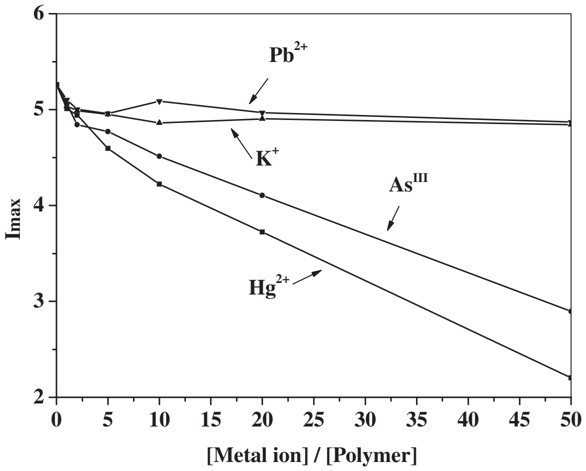


Figure 6. The fluorescent quenching effect of the polymer on K$^+$, Pb^{2+}, Hg^{2+}, and As^{III}.

ratio additions of Hg^{2+} and As^{III} from 1:1 to 1:50, whereas, there is no obvious fluorescence change for K$^+$ and Pb^{2+}. It can also be seen that the emission wavelengths of the metal–polymer complexes do not show an obvious difference from metal-free polymer at the maximum fluorescent wavelengths $\lambda^{\mathrm{F}}{}_{\mathrm{max}}$. But the polymer complexes display a new emission wavelength at 468 nm, and its intensity is gradually enhanced with the increase of Hg^{2+} or As^{III} solution concentration. The emission intensities of the complexes were significantly quenched by the addition of Hg^{2+} and As^{III} (50 equiv) with a reduction of ca. 45% and 58%, respectively. Fluorescence changes of the chiral polymer in response to Hg^{2+} and As^{III} can be regarded as effective intramolecular photoinduced electron transfer (PET) and photoinduced charge transfer (PCT) along the extended π-conjugated structure after the crown ether group coordinates with the metal ions.

UV–vis absorption spectra changes of the conjugated polymer in response to K$^+$, Pb^{2+}, Hg^{2+}, and As^{III} are shown in Figure 7. According to Figures 7a and 7b, UV–vis spectra of the polymer exhibit nearly no change upon addition of K$^+$ or Pb^{2+}. On the contrary, UV–vis absorption spectra of the polymer exhibit obvious changes upon addition of Hg^{2+} or As^{III} (Figures 7c and 7d). The UV–vis absorption intensities of the polymer in response to Hg^{2+} and As^{III} show a pronounced increase upon molar ratio additions from 1:5 to 1:20, but the absorption positions are similar to the free-metal polymer. The 434 nm absorption wavelength arising from the conjugated structure of the polymer backbone exhibits slight enhancement. Moreover, the absorption intensity of the polymer at about 228 nm which is regarded as the absorption band of the naphthyl group exhibits dramatic enhancement with the increase of Hg^{2+} or As^{III} concentration.

Conclusion

Linear conjugated polymer were obtained by the polymerization of 2,3-dibutoxy-1,4-diethynylnaphthalene and (*S*)-5,5′-dibromo-6,6′-dibutyl-2,2′-binaphtho-20-crown-6 via Pd-catalyzed Sonogashira reaction. The conjugated polymer shows strong green-blue fluorescence due to the extended π-electronic structure between the chiral repeating unit (*S*)-

6,6′-dibutyl-2,2′-binaphtho-20-crown-6 and the conjugated linker 2,3-dibutoxynaphthyl group via ethynyl bridge. Based on the responsive fluorescent properties of the chiral polymer to K^+, Pb^{2+}, Hg^{2+}, and As^{III}, Hg^{2+} and As^{III} cause effective fluorescent quenching of the polymer, whereas, Pb^{2+} and K^+ do not produce obvious change of the polymer fluorescence and absorption spectra. The obvious fluorescence influence shows that the 2,2′-binaphtho-20-crown-6 moiety plays an important role in fluorescent recognition for Hg^{2+} and As^{III} due to the effective photoinduced electron transfer and charge transfer between the conjugated polymer backbone and receptor species.

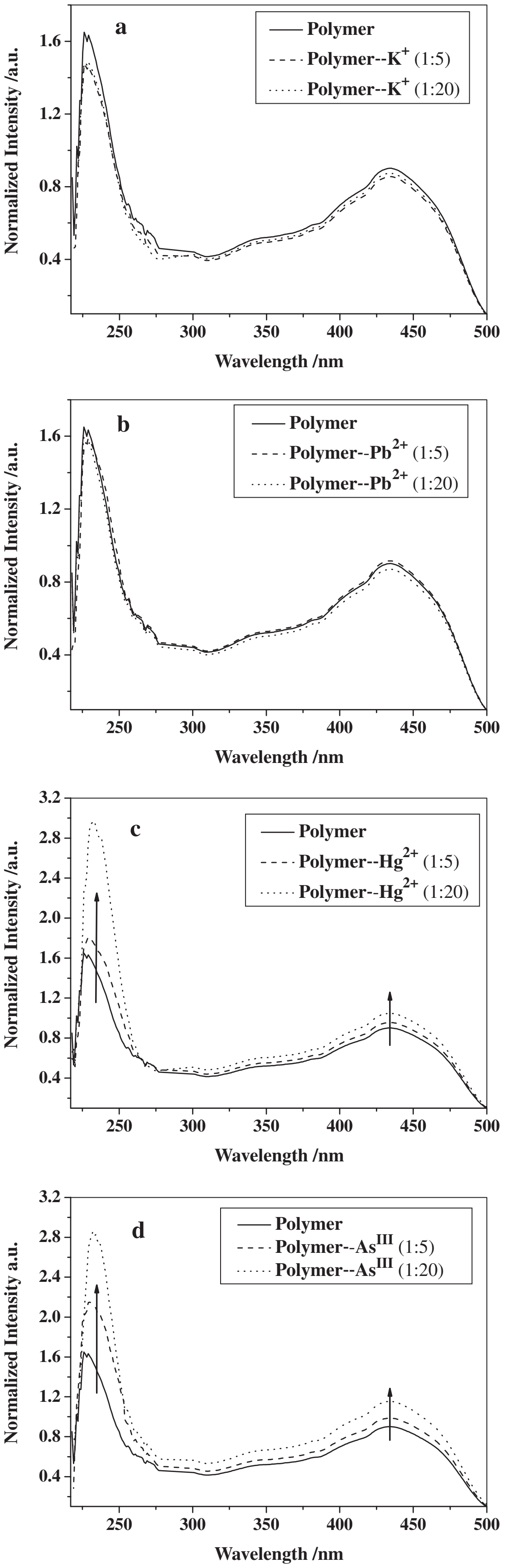


Figure 7. UV–vis spectra of the polymer on K^+ (a), Pb^{2+} (b), Hg^{2+} (c), and As^{III} (d).

Experimental

General Methods. ^1H and ^{13}C NMR spectra measurements (all in $CDCl_3$) were recorded on a 300-Bruker spectrometer with TMS as an internal standard. FTIR spectra were recorded on a Nexus 870 FTIR spectrometer. UV–vis spectra were obtained with a Perkin-Elmer Lambda 25 spectrometer. DSC-TGA was performed on a Perkin-Elmer Pyris-1 instrument under a N_2 atmosphere. Fluorescent spectra were obtained with a 48000 DSCF spectrometer. Mass spectrometry (MS) was determined on a Micromass GCT. C, H, and N elemental analyses were performed on an Elementar Vario MICRO analyzer. The circular dichroism (CD) spectrum was determined with a JASCO J-810 spectropolarimeter. Molecular weight was determined by gel permeation chromatography (GPC) relative to polystyrene standards with a Waters-244 HPLC pump and THF was used as solvent. All solvents and reagents were commercially available A.R. grade. (*S*)-1,1′-Bi-2-naphthol (BINOL) were purchased from Aldrich and used directly without purification. All reactions were performed under a N_2 atmosphere using Schlenk tube techniques. THF and Et_3N were purified by distillation from sodium in the presence of benzophenone. CH_2Cl_2 and CH_3CN were distilled from P_2O_5.

Metal Ion Titration. Each metal ion titration experiment was started with 3.0 mL of polymer in THF solution with known concentration (4.6×10^{-5} mol L^{-1}). Aqueous nitrate or acetate salts (4.3×10^{-2} mol L^{-1}) were used for the titration. Polymer complexes were produced by adding aliquots of a solution of the selected analyte to a THF solution of the chiral polymer (3.0 mL). The mixture was stirred constantly during the titration. Steady-state fluorescence spectra were monitored 15 min after addition of aqueous analyte to the polymer solution. Distilled water was monitored as a blank.

Synthesis of 2,3-Dibutoxy-1,4-diethynylnaphthalene (M-1) (Scheme 1). 1,4-Dibromo-2,3-dibutoxynaphthalene (2.13 g, 4.9 mmol), $Pd(PPh_3)_4$ (283 mg, 0.25 mmol), and CuI (186.6 mg, 0.98 mmol) were mixed and dissolved in 20 mL of *n*-$BuNH_2$, and trimethylsilylethyne (1.44 g, 13.8 mmol) was added via syringe to the above solution. The reaction mixture was stirred and refluxed for 72 h. After the mixture was cooled to room temperature, the solution was filtered through a short column of silica gel with ethyl acetate as eluent. After removal of solvent, the crude product 1,4-di(trimethylsilylethynyl)-2,3-dibutoxynaphthalene was dissolved in 100 mL of a mixed solvents of THF–MeOH (4:1 v/v). The solution was bubbled with N_2 for 10 min, and aqueous NaOH (0.78 g and 1 mL water) was added to the above solution. The mixture was stirred for 2 h at room temperature and then the solvent was removed under reduced pressure. The residual solid was extracted with CH_2Cl_2 (2×100 mL) and washed with saturated brine twice. The combined organic layers were dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the crude product was purified on a silica column using petroleum ether as the eluent to afford a brown viscous product in a yield of 27% (0.42 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (dd, 2H, $J = 6.6$, 3.3 Hz), 7.53 (dd, 2H, $J = 6.6$, 3.3 Hz), 4.23 (t, 4H, $J = 6.6$ Hz), 3.75 (s, 2H), 1.89–1.80 (m, 4H), 1.64–1.51 (m, 4H), 1.00 (t, 6H, $J = 7.2$ Hz). ^{13}C NMR ($CDCl_3$): δ 155.1, 131.3, 126.8, 126.2, 114.8, 88.0, 78.1, 74.9, 32.8, 19.6, 14.3. GC-MS: 320 *m*/*z* (M).

Synthesis of (*S*)-5,5′-Dibromo-6,6′-dibutyl-2,2′-binaphtho-20-crown-6 (*S*-M-2) (Scheme 1). Synthesis of (*S*)-6,6′-Dibutyl-1,1′-bi-2-naphthol: (*S*)-6,6′-Dibromo-2,2′-di(methoxymethoxy)-1,1′-binaphthyl (2.0 g, 3.8 mmol) was dissolved in 30.0 mL of anhydrous THF. 3.8 mL of *n*-BuLi (9.5 mmol, 2.5 mol L^{-1} in hexane) was added by syringe injection at −78 °C under a N_2 atmosphere. After the reaction mixture was stirred for 10 min, *n*-C_4H_9Br (2.1 g, 15.2 mmol) was added to the above solution at −78 °C under a N_2 atmosphere. The reaction mixture was gradually warmed to room temperature and stirred overnight. The mixture was extracted with ethyl acetate (2×50 mL). The combined organic layers were washed with water and brine, and then dried over anhydrous Na_2SO_4. After removal of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/ethyl acetate) (30:1 v/v) to afford a colorless viscous product (0.93 g, 51% yield). The product was dissolved in 10 mL of THF. A mixture of 10 mL of methanol and 15 mL of hydrochloric acid (12 mol L^{-1}) was added to the above solution, and the mixed solution was stirred at room temperature for 12 h. After removal of all solvents under reduced pressure, the residue was extracted with ethyl acetate (2×30 mL). The combined organic layers were washed with 2 mol L^{-1} $NaHCO_3$ solution and brine twice, and then dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography on silica gel using the mixed solvents of petroleum ether/ethyl acetate (20:1 v/v) to afford a white solid product in a yield of 93.4% (0.71 g). Mp: 72–74 °C. $[\alpha]_D^{25} = -82.9$ (*c* 0.31, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (d, 2H, $J = 9.0$ Hz), 7.69 (s, 2H), 7.36 (d, 2H, $J = 9.0$ Hz), 7.19 (d, 2H, $J = 8.4$ Hz), 7.12 (d, 2H, $J = 8.4$ Hz), 5.01 (s, 2H), 2.76 (t, 4H, $J = 7.8$ Hz), 1.74–1.64 (m, 4H), 1.49–1.36 (m, 4H), 0.97 (t, 6H, $J = 7.2$ Hz). ^{13}C NMR ($CDCl_3$): δ 152.5, 139.0, 132.1, 131.2, 130.0, 129.4, 127.3, 124.6, 118.0, 111.3, 35.9, 33.9, 22.8, 14.4. FTIR (KBr, cm^{-1}): 3503.4, 3421.9, 2950.1, 2921.8, 1598.1, 1507.3, 1474.1, 1363.7, 1214.1, 1142.6, 1124.5, 952.2, 880.6, 827.1.

Synthesis of (*S*)-5,5′-Dibromo-6,6′-dibutyl-1,1′-bi-2-naphthol: 0.14 mL of bromine (2.8 mmol in 5 mL of CH_2Cl_2) was slowly added to a solution of (*S*)-6,6′-dibutyl-1,1′-bi-2-naphthol (0.52 g, 1.33 mmol) in CH_2Cl_2 (10 mL) at −78 °C over 1 h. The solution was stirred overnight and gradually warmed to room temperature. The reaction was quenched with 15 mL of saturated $NaHSO_3$ solution. The mixture was extracted with CH_2Cl_2 (2×30 mL). The combined organic layers were washed with water and saturated brine, and then dried over anhydrous Na_2SO_4. After removal of solvent, a pure solid product was directly obtained in a yield of 99% (0.73 g) without further purification. Mp: 48–50 °C. $[\alpha]_D^{25} = -13.3$ (*c* 0.23, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 (d, 2H, $J = 9.0$ Hz), 7.46 (d, 2H, $J = 9.6$ Hz), 7.17 (d, 2H, $J = 8.4$ Hz), 7.01 (d, 2H, $J = 8.7$ Hz), 5.04 (s, 2H), 2.93–2.92 (m, 4H), 1.67–1.62 (m, 4H), 1.49–1.42 (m, 4H), 0.99–0.94 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 153.1, 139.1, 133.4, 131.5, 130.2, 128.9, 124.6, 124.0, 119.2, 111.3, 37.3, 32.7, 23.0, 14.3. ESI-MS: 554.4 *m*/*z* (M + 1). Anal. Calcd for $C_{28}H_{28}Br_2O_2$: C, 60.45; H, 5.07%. Found: C, 60.41; H, 5.11%. FTIR (KBr, cm^{-1}): 3530.2, 3027.4, 2956.5, 2928.9, 1597.9, 1567.3, 1467.1, 1367.7, 1248.7, 1212.0, 1154.1, 1132.9, 970.7, 819.2.

Synthesis of (*S*)-5,5′-Dibromo-6,6′-dibutyl-2,2′-di(2-hydroxyethoxy)-1,1′-binaphthyl: A mixture of (*S*)-5,5′-dibromo-6,6′-dibutyl-1,1′-bi-2-naphthol (2.0 g, 3.6 mmol), $ClCH_2CH_2OH$ (1.16 g, 14.4 mmol), and K_2CO_3 (6.0 g, 43.2 mmol) in 23 mL of DMF was stirred at 130 °C for 24 h. The mixture was poured into 100 mL of aqueous NaOH (1 mol L^{-1}) and the crude product precipitated. The solid was filtered and dissolved with CH_2Cl_2, and the solution was washed with water to pH 7. The crude product was purified on a silica column with a mixed solvent of petroleum ether and ethyl acetate (2:1, v/v) as eluent to afford a pale yellow viscous product in a yield of 61% (1.4 g). Mp: 53–55 °C. $[\alpha]_D^{25} = -8.8$ (*c* 0.80, THF). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.50 (d, 2H, $J = 9.6$ Hz), 7.51 (d, 2H, $J = 9.6$ Hz), 7.10 (d, 2H, $J = 8.7$ Hz), 6.97 (d, 2H, $J = 8.7$ Hz), 4.28–4.22 (m, 2H), 4.09–4.03 (m, 2H), 3.65–3.60 (m, 4H), 2.91 (t, 4H, $J = 7.2$ Hz), 2.18 (s, 2H), 1.67–1.59 (m, 4H), 1.46–1.39 (m, 4H), 0.96 (t, 6H, $J = 7.2$ Hz). ^{13}C NMR ($CDCl_3$): δ 178.0, 169.4, 159.7, 155.1, 130.8, 120.5, 75.5, 72.0, 68.2, 67.4, 63.3, 62.9, 62.5, 58.5, 53.4, 38.4. FTIR (KBr, cm^{-1}): 3386.1, 2953.9, 2927.2, 2859.4, 1613.8, 1591.6, 1556.6, 1477.2, 1465.4, 1455.1, 1344.9, 1317.3, 1261.4, 1212.6, 1145.0, 1088.9, 1048.3, 990.1, 973.1, 896.9, 807.6. Anal. Calcd for $C_{32}H_{36}Br_2O_4$: C, 59.64; H, 5.63%. Found: C, 59.60; H, 5.70%.

Synthesis of (*S*)-5,5′-Dibromo-6,6′-dibutyl-2,2′-binaphtho-20-crown-6 (*S*-M-2): A solution of NaH (0.42 g, 17.5 mmol) and (*S*)-5,5′-dibromo-6,6′-dibutyl-2,2′-di(2-hydroxyethoxy)-1,1′-binaphthyl (1.13 g, 1.75 mmol) in 20 mL of THF was stirred and kept refluxing under a N_2 atmosphere. A solution of $TsO(CH_2CH_2O)_3Ts$ (0.88 g, 1.93 mmol in 5 mL of THF) was added dropwise. The mixture was refluxed for 24 h. After being cooled to room temperature and filtered, the resulting solution was evaporated to remove solvent under reduced pressure, and the residue was extracted with CH_2Cl_2 (2×40 mL). The solution was washed with brine three times and dried over anhydrous Na_2SO_4, and then the solvent was evaporated under reduced pressure to give a brown product. The crude product was purified on a silica column with mixed solvents of petroleum ether and ethyl acetate (2:1, v/v) as eluent to afford a colorless viscous product in a yield of 70% (0.93 g). $[\alpha]_D^{25} = -56.1$ (*c* 0.25, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.45 (d, 2H, $J = 9.3$ Hz), 7.53 (d, 2H, $J = 9.3$ Hz), 7.06 (d, 2H, $J = 8.7$ Hz), 6.98 (d, 2H, $J = 8.7$ Hz), 4.22–4.18 (m, 2H), 4.08–4.05 (m, 2H), 3.66–3.41 (m, 12H), 3.40–3.39 (m, 4H), 2.91 (t, 4H, $J = 7.5$ Hz), 1.67–1.59 (m, 4H), 1.46–1.39 (m, 4H), 0.95 (t, 6H, $J = 7.2$ Hz). ^{13}C NMR ($CDCl_3$): δ 154.8, 138.4, 134.1, 129.2, 129.0, 128.7, 125.2, 123.9, 120.6, 117.1, 71.3, 71.0, 70.9, 70.1, 70.0, 37.3, 32.7, 23.0, 14.3. Anal. Calcd for $C_{38}H_{46}Br_2O_6$: C, 60.17; H, 6.11%. Found: C, 59.11; H, 6.15%.

Synthesis of Polymer (Scheme 2). A mixture of **M-1** (106.3 mg, 0.332 mmol) and *S*-**M-2** (251.6 mg, 0.332 mmol) was dissolved in 7 mL of toluene, and then $Pd(PPh_3)_4$ (19.2 mg, 0.017 mmol), CuI (12.7 mg, 0.067 mmol), and 3 mL of *n*-$BuNH_2$ were added to the above solution. The solution was stirred and heated at 80 °C for 72 h under a N_2 atmosphere. After phenylacetylene (3.6 µL, 0.033 mmol) was added to the above solution, the solution was kept refluxing for an additional 2 h. Then bromobenzene (7 µL, 0.067 mmol) was added to the mixture, the solution continued to be refluxed for another 2 h. After the mixture was cooled down to room temperature, the mixture was filtered through a silica gel column into methanol (50 mL) to precipitate out the brown crude polymer. The crude polymer was obtained by centrifuge and washed with methanol several times. The polymer was dried in vacuo and collected in a yield of 35.2% (126 mg). GPC analysis result: $M_w = 6030$, $M_n = 4200$, PDI = 1.44. $[\alpha]_D^{25} = -170.6$ (c 0.17, THF). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44–8.41 (m, 2H), 7.53–7.50 (m, 4H), 7.05–7.02 (m, 2H), 6.97–6.95 (m, 2H), 4.32–4.31 (m, 4H), 3.60–3.47 (m, 16H), 3.39–3.37 (m, 4H), 2.89–2.88 (m, 4H), 0.93 (t, $J = 7.2$ Hz, 6H). FTIR (KBr, cm^{-1}): 3245.4, 2961.4, 2928.8, 2869.8, 1615.4, 1593.7, 1561.0, 1463.2, 1422.3, 1349.8, 1261.7, 1217.3, 1096.6, 1022.9, 863.9, 802.0, 759.6. Anal. Calcd for $C_{60}H_{68}O_8$: C, 78.57; H, 7.47%. Found: C, 77.14; H, 7.89%.

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