Triphenylamine-Based Fluorescent Conjugated Copolymers with Pendant Terpyridyl Ligands as Chemosensors for Metal Ions

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Received 6 October 2009; accepted 15 December 2009 DOI: 10.1002/pola.23890 Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Two well-defined triphenylamine-based fluorescent conjugated copolymers with pendant terpyridyl ligands were synthesized through Suzuki coupling polymerization and were further characterized by ¹H-NMR, ¹³C-NMR, gel permeation chromatography, Infrared, and UV-vis spectra. Polymer **P-1**, terpyridine-bearing poly(triphenylamine-*alt*-fluorene) with a high fluorescence quantum yield (62%) shows much higher sensitivities toward Fe³⁺, Ni²⁺, and Cu²⁺ as compared with the other metal ions investigated. Especially, Fe³⁺ can lead to an almost complete fluorescence quenching of polymer P-1. Whereas, the analogous polymer P-2, in which *N*-ethylcarbazole repeat units replace the fluorene units in P-1, shows a very poor selectivity. It demonstrates that polymers with a same receptor may show different sensitivity to analytes owing to their different type of backbones. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1310–1316, 2010

KEYWORDS: chemosensor; conjugated polymers; fluorescence; metal-polymer complexes; terpyridine; triphenylamine

INTRODUCTION With high efficiencies in both photoluminescence and electroluminescence, fluorescent conjugated polymers (FCPs) have attracted much attention as versatile sensory materials during the past decade owing to their high sensitivity, flexibility in synthesis, and ease in measurement.¹⁻⁴ FCPs are referred to as amplifying fluorescent polymers associated with an efficient electronic communication along the main backbone, and as the concept of molecular wire, which was first established by Zhou and Swager.^{5,6} Analyte-binding with the polymer can happen in a very short time, so a real-time detection as well as a trace detection will be achieved due to their high sensitivity. Therefore, FCPs provide a unique platform for exploiting novel chemo- and biosensors.^{7–12}

The toxicity of certain metal ions has been a constant concern of environmental problems. Thirteen transition-metal ions, such as beryllium, chromium, manganese, cobalt, copper, zinc, molybdenum, thallium, silver, mercury, cadmium, lead, and nickel have been listed as "priority pollutants" by the Environmental Protection Agency.¹³ Fe³⁺ is an essential trace element, which plays a significant role in chemical and biological processes. Fe³⁺ deficiency in the body leads to anemia, and Fe³⁺ excess causes liver and kidney damage. Furthermore, deficiency and overload of Fe³⁺ may induce various disorders of most organisms.^{14,15} Therefore, high sensitivity chemosensor for Fe³⁺ should be developed.

By introducing specific ligands such as bipyridine,¹⁶⁻¹⁸ terpyridine,¹⁹⁻²³ quinoline,²⁴ and dipyrrolylquinoxaline²⁵ to the main backbones or side chains, conjugated polymers have been widely employed for the metal ion detection owing to the characteristic metal-to-ligand charge transfer. In addition, terpyridine possesses a superb ability to coordinate a large number of transition-metal ions and forms stable terpyridine-metal ion complexes, so it is an important building block for designation of sensory materials to detect some transition-metal ions. Pang's group reported that the polymer of poly(phenylenevinylene) with terpyridyl ligand shows the potential for Cu²⁺ and Zn²⁺ detection.²⁶

We have reported the synthesis of various FCPs with pendant carbohydrates and their interactions with lectins or DNA.^{27–29} To extend the potential application of FCPs in chemo- and biosensing, herein, two well-defined triphenylamine-based conjugated polymers containing terpyridyl ligands were synthesized (Scheme 1) and well characterized using ¹H-NMR, ¹³C-NMR, Infrared (IR), and UV-vis spectra. The polymers take advantage of the effective π -conjugation and strong luminescence properties of the triphenylamine

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 48, 1310–1316 (2010) © 2010 Wiley Periodicals, Inc.



SCHEME 1 Synthetic routes to monomers and copolymers.

and metal ion-coordinating ability of terpyridine to develop a highly effective chemosensor for transition-metal ions. It is found that one of the synthesized polymers, polymer **P-1**, shows higher sensitivities and selectivities for Fe^{3+} , Ni^{2+} , and Cu^{2+} compared with the other metal ions investigated, such as Al^{3+} , Mn^{2+} , Cr^{3+} , Pb^{2+} , Zn^{2+} , Co^{2+} , and Fe^{2+} . We believe it will provide some clues for elucidation of the influence on the selectivity to metal ions owing to the structure of the main backbone of the polymers.

EXPERIMENTAL

Materials and Measurements

All chemical reagents were commercially available and used as received unless otherwise stated. Aldehyde **1** and terpyridyl-benzyl phosphonate ester **3** (Scheme 1) were prepared according to reported methods.^{19,30}

The ¹H- and ¹³C-NMR spectra were recorded on a Bruker DMX 300 NMR spectrometer. The optical rotations were measured with a JASCO DIP-1000 digital polarimeter. Mass spectra were recorded with a VG PLATFORM mass spectrometer using the ESI technique. The molecular weight and polydispersity index (PDI) of the polymers were determined by an Agilent 1100 gel permeation chromatography (GPC) system in tetrahydrofuran (THF). The number-average and weight-average molecular weights (M_n and M_w) were estimated by using a calibration curve of polystyrene standards. Infrared (IR) spectra were recorded using a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Ultraviolet-visible (UV-vis) spectra were measured using a Perkin-Elmer Lamda 900 UV-vis-NIR spectrophotometer and quartz cells with 1 cm path length. The fluorescence spectra were measured using a Perkin-Elmer LS55 luminescence spectrometer in a conventional quartz cell with 1 cm path length. Thermogravimetric analyses (TGA) were performed on a Pyris Diamond thermogravimetric/differential thermal analysis instrument (10 °C min⁻¹, nitrogen).

Synthesis of Monomer and Polymers *Monomer 4*

To the mixture of terpyridyl-benzyl phosphonate ester **3** (0.930 g, 2.15 mmol) and aldehyde **1** (1.13 g, 2.15 mmol) in dry THF (20 mL) under argon, *t*-BuOK (1.12 g, excess) was added slowly in portions. A yellow colored mixture was obtained and became warm. The mixture was stirred under argon for 24 h. After completion of the reaction (monitored by TLC), the mixture was dispersed in ethanol (100 mL). The residual solid was filtered and recrystallized from

anhydrous dichloromethane–ethanol, to give yellow crystals 4 (1.3 g, yield 75%). ¹H-NMR (300 MHz, CDCl₃): δ = 8.75 (d, J = 12.0 Hz, 4H), 8.68 (d, J = 7.2 Hz, 2H), 7.94–7.80 (m, 4H), 7.63 (d, J = 8.4 Hz, 2H), 7.57–7.52 (m, 4H), 7.44 (d, J = 8.7Hz, 2H), 7.38–7.34 (m, 2H), 7.18 (d, J = 8.4 Hz, 1H), 7.15 (d, J = 8.7 Hz, 1H), 7.12 (d, J = 8.7 Hz, 1H), 6.94–6.84(m, 5H). ¹³C-NMR (75 MHz, CDCl₃): δ = 155.3, 155.0, 154.9, 148.1, 145.8, 137.3, 135.8, 129.1, 128.3, 126.7, 126.6, 126.2, 126.1, 125.9, 125.2, 125.0, 123.3, 122.8, 122.6, 120.3, 117.6, 117.5, 85.2. ESI(+)-MS: calcd. for C₄₁H₂₈I₂N₄: 830.5 (M); found 831.4 (M+1)⁺.

General Procedure for Suzuki Coupling Polymerization

Under a nitrogen atmosphere, monomer **4** (0.3 mmol), diborate **5** or **6** (0.33 mmol), Pd(PPh₃)₄ (80 mg), and potassium carbonate (0.5 g, 3.6 mmol) were placed in a 50 mL roundbottom flask, and then THF-H₂O (20 mL, 2/1, v/v) was added. The mixture was stirred at 70 °C for 48 h under a nitrogen atmosphere. The resulting product was purified by precipitation with methanol and washed with methanol-acetone in a Soxhlet apparatus for 48 h.

P-1 was obtained as a gray powder with a yield of 85%. ¹H-NMR (300 MHz, CDCl₃): $\delta = 8.74$ -8.68 (m, 6H), 7.87-7.80 (m, 6H), 7.78-7.40 (m, 10H), 7.39-6.98 (m, 12H), 2.06-1.85 (m, 4H), 1.06 (br, 12H), 0.73 (br, 10H). ¹³C-NMR (75 MHz, CDCl₃): $\delta = 156.3$, 156.0, 149.1, 136.9, 136.8, 129.3, 128.0, 127.9, 127.6, 127.5, 127.2, 127.0, 126.8, 124.8, 123.9, 123.8, 121.4, 121.0, 118.6, 118.5, 118.4, 117.6, 31.5, 29.7, 23.8, 22.6, 22.5, 14.0.

P-2 was obtained as a yellow powder with a yield of 78%. ¹H-NMR (300 MHz, CDCl₃): $\delta = 8.75-8.69$ (m, 6H), 8.26-8.21(m, 2H), 7.90-7.81 (m, 4H), 7.78-7.63 (m, 6H), 7.61-7.46(m, 6H), 7.42-7.01 (m, 10H), 4.41-4.30(br, 2H), 1.45 (br, 3H). ¹³C-NMR (75 MHz, CDCl₃): $\delta = 156.4$, 155.9, 149.5, 136.9, 133.2, 129.5, 128.2, 127.9, 127.6, 126.7, 124.8, 123.7, 122.4, 121.6, 120.3, 118.6, 117.7, 115.6, 111.5, 51.2, 13.5.

Fluorescence Spectra of Polymer P-1 in the Presence of Different Metal Ions

A solution of **P-1** (1.0 μ M) was prepared in THF. The solutions of various metal ions (5.0 mM) were prepared in distilled water. A solution of **P-1** (3.0 mL) was placed in a quartz cell (1 cm width), and the fluorescence spectrum was recorded. Different metal ion solutions were introduced (3.0 μ L) into the polymer solution and the fluorescence intensity was recorded at room temperature (excitation wavelength: 384 nm).

Spectrofluorometric Titration of Polymer P-1 with Fe^{3+} Ion

Aliquots of Fe³⁺ ion in aqueous solution were added to a solution of polymer **P-1** in THF. The final concentration of polymer **P-1** is 0.5 μ M, corresponding to the repeating unit. After each addition, the sample was allowed to equilibrate for 30 min before recording a spectrum. Addition of the Fe³⁺ ion was continued until no change in the fluorescence signal was observed. The excitation wavelength was 384 nm, and the emission scan ranged from 400 to 750 nm.

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

The synthetic routes to the monomers and copolymers are outlined in Scheme 1. Through the Horner-Wadsworth-Emmons (HWE) reaction (also called the Horner-Wittig reaction),³¹ the known aldehyde $\mathbf{1}$ was coupled with terpyridylbenzyl phosphonate ester 3 (prepared from methylphenyl terpyridine 2) to afford monomer 4. The vinylene group in the side chain formed from the HWE reaction of 1 and 3 can facilitate the electronic communication between triphenylamine backbone and terpyridine side chain. A palladium-catalyzed Suzuki coupling polymerization of the monomer 4 with corresponding diboronate $(5, 6)^{32}$ furnished two welldefined copolymers, poly(triphenylamine-alt-fluorene) and poly(triphenylamine-alt-N-ethylcarbazole) bearing terpyridyl ligands (P-1, P-2), respectively. Figure 1 shows the ¹H-NMR spectra of monomer 4, polymers P-1, and P-2 in CDCl₃ solution. We can find that the signal peaks of protons in pyridyl (δ = 8.8–8.5 ppm), which derived from both **P-1** and **P-2**. Ethyl ($\delta = 4.41$ -4.30 and 1.45 ppm) and hexyl ($\delta = 2.06$ -1.85, 1.06, and 0.73 ppm) groups derived from P-1 and P-2, respectively. The successful polymerization is also confirmed by FT-IR spectra of the monomer and polymers as shown in Figure 2. Compared with monomer 4, the absorption bands at 2850–2950 cm^{-1} on the FT-IR spectra of polymers P-1 and P-2 indicate the C-H stretching of alkyl chains from diboronate monomers (5, 6). Both P-1 and P-2 show the same characteristic absorption profiles in the range of 1425-1570 cm⁻¹ for terpyridine and benzene rings.

The number-average molecular weight and distribution were obtained by GPC with polystyrene standards in THF to be $M_n = 20950$ with PDI = 1.25 for **P-1**, and $M_n = 18700$ with PDI = 1.06 for **P-2**. Both polymers **P-1** and **P-2** are easily soluble in THF, DMF, and chloroform. The thermal stability of the polymer **P-1** was characterized by TGA. A slight mass loss of 5% was observed from 300 to 340 °C, and a main mass loss of **P-1** occurred at the temperature of around 425 °C. The other data for physical properties of the polymers are shown in Table 1.

Optical Properties of the Copolymers

The UV-vis absorption and photoluminescence spectra of polymers P-1 and P-2 in the THF solution (1.5 μ M) are shown in Figure 3. The polymer P-2 exhibits an absorption maximum peak at 355 nm and an emission maximum peak at 456 nm in THF solution, which are partly assigned to the π - π ^{*} transition of the conjugated polymer backbone. The stilbene-terpyridine side groups, which were reported to possess a main absorption around 380 nm,³³ definitely contribute to the aforementioned absorption peak. Compared with polymer P-2, red shifts in absorption and emission are observed for polymer P-1, which shows an absorption maximum peak at 384 nm and an emission maximum peak at 510 nm in THF solution. The red shifts are ascribed to the enhanced extent of π -orbital overlap and electron-donating effect due to the dihexylfluorene residues in the backbone of polymer P-1. Fluorescence quantum yields of the polymers



FIGURE 1 ¹H-NMR spectra of monomer 4, polymers P-1, and P-2.

were measured by a standard method using quinine bisulfate in a 0.1 N sulfuric acid as the reference absolute quantum efficiency (0.55). Polymer **P-1** possesses a high fluorescence quantum yield (0.62), however, polymer **P-2** shows a much lower fluorescence quantum yield (0.13), probably arising from the lower extent of π -orbital overlap effect of the carbazole residues in the backbone of polymer **P-2**.³⁴



FIGURE 2 FT-IR spectra of monomer 4, polymers P-1, and P-2.

Fluorescence Quenching by Various Transition-Metal Ions

The influence of various metal ions $(Ag^+, Cd^{2+}, Al^{3+}, Mn^{2+}, Cr^{3+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, and Fe^{2+})$ on the fluorescence emission of polymer **P-1** is shown in Figure 4. The concentration of **P-1** solution was fixed at 1.0 μ M. The metal ion solutions were used at a concentration of 5.0 μ M. As shown in Figure 4, Fe³⁺, Cu²⁺, and Ni²⁺ lead to an efficient fluorescence quenching of the conjugated polymer. Especially, nearly complete fluorescence quenching was observed when Fe³⁺ was added. Whereas, the other metal ions (Al³⁺, Mn²⁺, Cr³⁺, and Pb²⁺) result in a slight decrease

 TABLE 1 Physical and Optical Properties of Polymers P-1 and

 P-2

Polymer	<i>M</i> _n ^a	PDI	Absorbance (λ_{max}, nm)	Emission (λ_{max} , nm)	Quantum yield	7 _d ^b (°C)
P-1	20,950	1.25	384	510	0.62	340
P-2	18,700	1.06	355	456	0.13	308

^a The number-average molecular weight (M_n), and polydispersity index (PDI) were determined for **P-1** and **P-2** by GPC with polystyrene standards in THF.

 $^{\rm b}$ T_d was determined by TGA with heating rates of 10 °C min⁻¹ under nitrogen atmosphere.



FIGURE 3 UV-vis absorption and fluorescence spectra of polymers P-1 and P-2 in THF.

in the fluorescence emission of the polymer. This is consistent with the poor coordination of these cations with terpyridyl groups. The metal ions such as Zn^{2+} and Fe^{2+} cause a little heavier fluorescence quenching of **P-1**. The complexation of metal ions do not cause any shift of the emission peak. On the other hand, the addition of Zn^{2+} ions results in another broad emission peak from 575 to 700 nm, as shown in Figure 4. This phenomenon is consistent with the coordination of Zn^{2+} and terpyridine, which alters the electron density of the polymer backbone.²¹ The distinct cation-responsive behaviors reveal the different coordination abilities of transition-metal ions with terpyridyl receptors in the backbone of the polymer. A possible mechanism for the fluorescence quenching of **P-1** is attributed to its aggregation derived from **P-1**—metal ion complex formation.

The distinctly different response profiles of **P-1** upon the addition of various metal ions could be easily seen in Figure 5. The fluorescence quenching of **P-1** varied with different metal ions. Most cations such as Al^{3+} , Mn^{2+} , and Cr^{3+} result in a very limited influence on the polymer emission. How-



FIGURE 4 Fluorescence response profiles of copolymer **P-1** in THF upon addition of different metal ions.



FIGURE 5 Emission quenching response profiles for P-1 by different metal ions in THF.

ever, the addition of Fe^{3+} , Cu^{2+} , and Ni^{2+} ions into the solution of P-1 leads to a significant fluorescence quenching. Especially, nearly complete fluorescence quenching was observed when Fe³⁺ is added. This phenomenon shows that the varying chelating ability of terpyridine with different metal ions makes P-1 show a high sensitivity toward Fe³⁺, which can be attributable to the unique properties of Fe³⁺ and possible size-fit concept. For a d^5 ion such as Fe³⁺, the five electrons may be present as two orbitals occupied by pairs of electrons and one orbital having single occupancy. So it could form an inner-orbital complex, which is more stable than the other terpyridine-metal complexes.35 In addition, the higher charge and smaller size of Fe³⁺ result in high charge density, which make its electron-accepting easier, thus lead to form stable terpyridine—Fe³⁺ complex.³⁶ On the basis of these results, it is very likely that polymer P-1 is a highly sensitive and relatively selective chemosensor for Fe^{3+} in the THF solution.

Figure 6 shows the fluorescence emission spectra of the P-1 in the absence and presence of Fe³⁺ ions at various concentrations. In these spectrofluorometric titration experiments, the concentration of **P-1** is 0.5 μ M. The fluorescent emission of the polymer gradually reduces with the increase in metal ion concentrations stepwise. At the very beginning, the Fe³⁺ concentration is only 0.1 μ M, which is only 20% of the polymer concentration, the fluorescence emission of P-1 is quenched to 78% of its original emission intensity. And then when the concentration of Fe³⁺ is 0.4 μ M, almost 55.0% of the emission of the polymer is quenched. At last, the emission was nearly completely quenched (98%) when the Fe^{3+} concentration increases to 0.9 μ M. In addition, there was a small blue shift in the emission peak, which suggested a shortening of the excitation migration distance in the backbone with increasing loading of quencher. Terpyridine possesses a superb ability to coordinate a large number of transition-metal ions and forms stable terpyridine-metal ion complexes of 2:1 stoichiometry.^{22,37} This makes terpyridine—Fe³⁺ complex as the bridge of the photoelectron energy transferring between the polymer backbones. Besides,



FIGURE 6 Fluorescence spectra and Stern–Volmer plot (inset) of **P-1** (0.5 μ M) in the absence and presence of different concentrations of Fe³⁺ in solution: Fe³⁺ concentrations from top to down are 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 μ M.

 Fe^{3+} may also bind to only one terpyridine ligand, where the photoelectron energy transferring is from the backbone to terpyridine—Fe³⁺ complex. Both of the two processes can induce the fluorescence quenching of the polymer. These results suggested that P-1 is a highly sensitive chemosensor for Fe³⁺ in the THF solution. No other metal ions showed such a significant response. It is interesting to note the nonlinear nature of the Stern-Volmer plot in Figure 6 (inset), suggesting that in this case the mechanism of the quenching process involves complexation rather than collisional deactivation. However, P-2 showed a poor selectivity to the metal ions, while $\text{Co}^{2+},\ \text{Ni}^{2+},\ \text{Zn}^{2+},$ and Fe^{2+} could cause nearly complete quenching of the polymer. The difference between P-1 and P-2 is the structure in the main backbones, which makes the two polymers possess completely different selectivity to the metal ions. The only difference between the molecular structures of polymers P-1 and P-2 is the second repeat unit (triphenylamine is defined as the first repeat unit), which is fluorene and carbazole, respectively. The side chain and the terminal terpyridine moiety are the same. We believe that the fluorene units play a dominant role for copolymer **P-1** in its high selectivity toward Fe³⁺. The fluorene moiety in **P-1**, poly(triphenylamine-*alt*-fluorene), is a better electron-donating group than the carbazole in P-2. Therefore, the photoelectron energy transferring from the backbone to the terpyridine-metal complex or photoelectron energy loss in P-1 between backbones would be easy. Furthermore, the π -orbital overlap extent in **P-1** is enhanced by the 2,7-linked fluorene unit as compared with P-2, poly(triphenylamine-alt-N-ethylcarbazole), in which carbazole units are 3,6-linked. Due to these reasons mentioned earlier, P-1 possesses a higher fluorescence quantum yield than P-2 and shows a higher sensitivity for Fe³⁺.

Kimura, Jones, and Bernd have reported different types of conjugated polymers with the same pendant terpyridyl ligands as chemosensors for different transition-metal ions.^{19,21,23} Different electron-donating groups in the main backbones make the polymers possess different selectivity to metal ions. Based on the results reported above and by us, it is believed that by selecting a proper type of the main backbone, the conjugated polymers with pendant terpyridyl ligands may show distinct selectivity to a certain transition-metal ion.

CONCLUSIONS

We have successfully designed and synthesized two welldefined triphenylamine-based FCPs with pendant terpyridyl ligands by Suzuki coupling polymerization. The polymers can be a chemosensor for transition-metal ions. Polymer **P-1** shows a significant sensitivity to transition-metal ions due to the enhanced electronic communication properties of the conjugated polymers. Especially, Fe^{3+} ion can lead to complete fluorescence quenching of **P-1**. It demonstrates that the polymers with a same receptor may show different sensitivity to analytes owing to their different structure in the main backbone.

The financial supports of the Ministry of Science and Technology of China (National Basic Research Program, Grant No. 2007CB808000) and National Science Foundation of China (Grant Nos. 20672025 and 20972035) is acknowledged.

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