

Synthesis and characterization of alternating copolymers containing bipyridine and phenylene vinylene for fluorescent chemosensors

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ABSTRACT: Alternating copolymers containing bipyridine and phenylene vinylene were synthesized through a Wittig condensation reaction of their corresponding diphosphonium salts and dialdehydes. The molecular weights of the resulting polymers were relatively low because of the low solubility in the reaction solvents. The optical properties of the polymers were substantially affected by the repeating units of phenylene vinylene. The absorption spectra of the copolymers in the solid state exhibited a bathochromic shift compared to those carried out in solution. The effective conjugation length could be extended with the addition of Cu^{2+} , Ni^{2+} , and Zn^{2+} ions into the polymer solutions in a 1 : 1 ratio of the bipyridine to the phenylene vinylene units. All of the polymer solutions behaved as a turn-off fluorescent chemosensor upon the addition of a variety of the metal ions. The sensing behavior to various metal ions revealed that the polymers were highly sensitive to the Cu^{2+} , Ni^{2+} , and Zn^{2+} ions. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42795.

KEYWORDS: copolymers; molecular recognition; optical properties; spectroscopy

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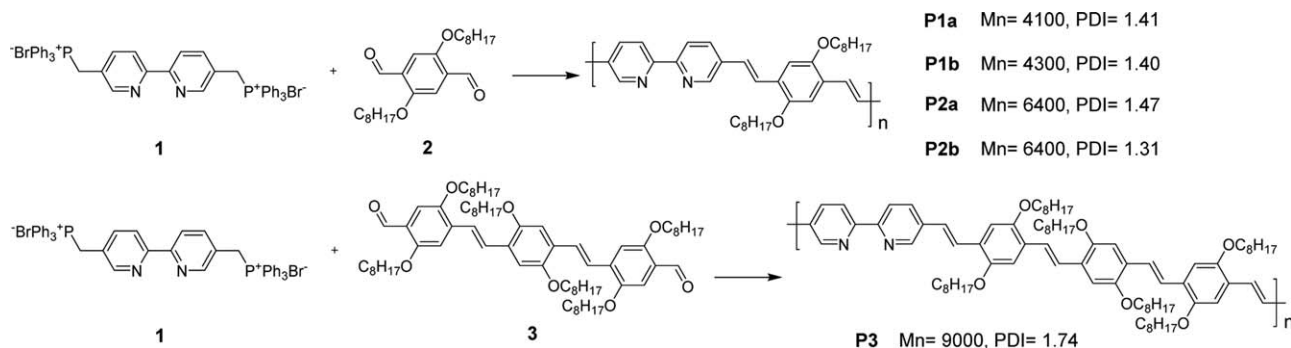
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INTRODUCTION

The development of synthetic materials for the sensing and recognition of environmentally and biologically hazardous metal ions has been investigated in recent years.^{1–4} Depending on the system response upon recognition or transduction, the sensory materials can be defined as chemomechanical sensors, colorimetric sensors, electrochemical sensors, and fluorescence sensors.⁵ The changes in the fluorescence signal upon the addition of the metal ions can be referred to as *fluorescent chemosensors*, which are currently of critical importance.^{6,7} Conjugated polymers displaying both a high sensitivity and high selectivity for the detection of a variety of the metal ions have been considered for potential use in fluorescent chemosensors and have attracted much attention in recent years^{8,9} for facile detection technics compared to numerous complex analytical methods, such as flame photometry, atomic absorption spectrometry, ion-sensitive electrodes, and electron microprobe analysis, which require sophisticated instruments and are time consuming. When metal ions are added to the polymer solution, the photo-physical characteristics of the polymer solution, such as the fluorescence intensity and emission wavelength, change, and such a change provides a signal that indicates the interaction between the metal ions and the polymers. The determination of the photo-physical response to the polymer interacting with metal ions

has been widely used as a popular methodology for chemical, biological, and medical applications because of its simplicity, high detection limit, nondestruction, and high-throughput screening applications.^{10,11} In addition, fluorescent polymers incorporating molecular recognition moieties are preferable for detecting the metal ions because fluorescent signals are rapidly obtained and can quantify a variety of metal ions.

Fluorescent polymers in combination with receptors such as crown ether, terpyridine, bi-imidazole, and bipyridine have been demonstrated to show several advantages for sensing applications compared to small molecules.^{12–15} Nitrogen-based ligands such as 2,2'-bipyridine and other multidentate ligands have been used extensively as metal-chelating ligands because of their effective coordination with a variety of metal ions.^{16–18} The emission intensity of fluorescent conjugated polymers dramatically decreases as a turn-off sensor under photon irradiation if the exciton can rapidly migrate along the polymer backbone to the 2,2'-bipyridine site. Fluorescence changes in response to the conformation of the polymer backbone upon the addition of a variety of metal ions were reported by Wang and Wasielewski.¹⁹ A bipyridyl group with a dihedral angle of about 20° between the two pyridine planes in the 2,2'-bipyridine system was introduced into the polymer backbone. When metal ions were chelated by a bipyridyl site, the conformation of the bipyridine



Scheme 1. Synthetic routes to polymers P1a, P1b, P2a, P2b, and P3.

units were forced into a planar structure. The conformational change of the bipyridine moiety results in an increase in the conjugation length; this could be determined by absorption and photoluminescence (PL) spectroscopy.

Phenylene vinylene derived polymers are ideal building blocks for fluorescent chemosensors because of their moderately high fluorescence quantum yield and tunable electronic properties by structural variation; these are one of the most promising polymers for chemosensor applications.^{20–22} Polymers containing phenylene vinylene and 2,2-bipyridyl units have been demonstrated to display fluorescence quenching upon interaction with a wide range of transition-metal ions. When phenylene vinylene incorporating 2,2-bipyridyl moieties interacts and forms complexes with metal ions, the structural perturbations and electron density changes within the polymer main chain give rise to a high sensitivity and selectivity.

Herein, we report the synthesis and characterization of alternating copolymers containing bipyridine and phenylene vinylene moieties. The bipyridine unit was placed in the polymer main chain. Therefore, the resonance interaction from the bipyridine ring was fully transmitted to the all of polymer backbone. The molecular design, therefore, maximized the resonance interaction between bipyridine and phenylene vinylene. This chelating ability and chelating mode should have allowed individual metal ions or a combination of them as input with fluorescence output in terms of both intensity and wavelength. This was expected to couple with the bipyridine ring to form *N,N*-bidentate chelation for metal ions; this would alter the conformation of the polymer backbone and, hence, show the differences in the optical properties between metal-free polymers and metal-chelating polymers.

EXPERIMENTAL

Instrumentation

¹H-NMR spectra were recorded in deuterated chloroform on a Bruker 600-MHz NMR spectrometer (in NMR data, the following abbreviations are used: s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad). The chemical shifts (δ s) were expressed in parts per million with the residual solvent as an internal standard. Electron impact mass spectra and fast atom bombardment mass spectra were determined on a Micromass TRIO-2000 gas chromatograph/mass spectrometer. Electrospray ionization mass spectra were obtained on a Bruker high-resolution liquid chromatography tandem mass spectrometer (Impact HD). The molecular weights of the polymers were determined by gel permeation chromatography with a Waters ACQUITY advanced polymer chromatograph with a refractive-index detector in a tetrahydrofuran (THF) solution calibrated with narrow polydispersity polystyrene standards. Ultraviolet–visible absorption spectra were recorded on a Jasco V-670 ultraviolet–visible–near infrared spectrophotometer. PL measurements were carried out on a Jasco FP-8500 fluorescence spectrophotometer. Polymer thin films were spin-coated on a glass slide from THF solution at 600 rpm for 60 s.

Materials

All chemicals and reagents were purchased from commercial sources (TCI, Alfa Aesar, Sigma Aldrich) and were used without further purification unless otherwise noted. The solvents used for spectroscopic measurements were spectrograde. THF was distilled under a nitrogen atmosphere over sodium/benzophenone. Most of the reactions were monitored by thin-layer chromatography carried out on silica gel plates. Preparative separations were performed by column chromatography on

Table I. Polymerization Conditions and Molecular Weights of Polymers P1a, P1b, P2a, P2b, and P3

Polymer	Solvent	Temperature and time	M_n^a	M_w^a	Polydispersity ^a	Yield (%) ^b
P1a	Toluene	110°C, 7 h	4,100	5,800	1.41	48
P1b	Toluene	110°C, 17 h	4,300	6,000	1.40	34
P2a	DMF	110°C, 7 h	6,400	9,400	1.47	56
P2b	DMF	110°C, 17 h	6,400	8,400	1.31	44
P3	DMF	110°C, 17 h	9,000	15,700	1.74	56

^a Determined by gel permeation chromatography in a THF solution with refractive-index detection.

^b After Soxhlet extraction.

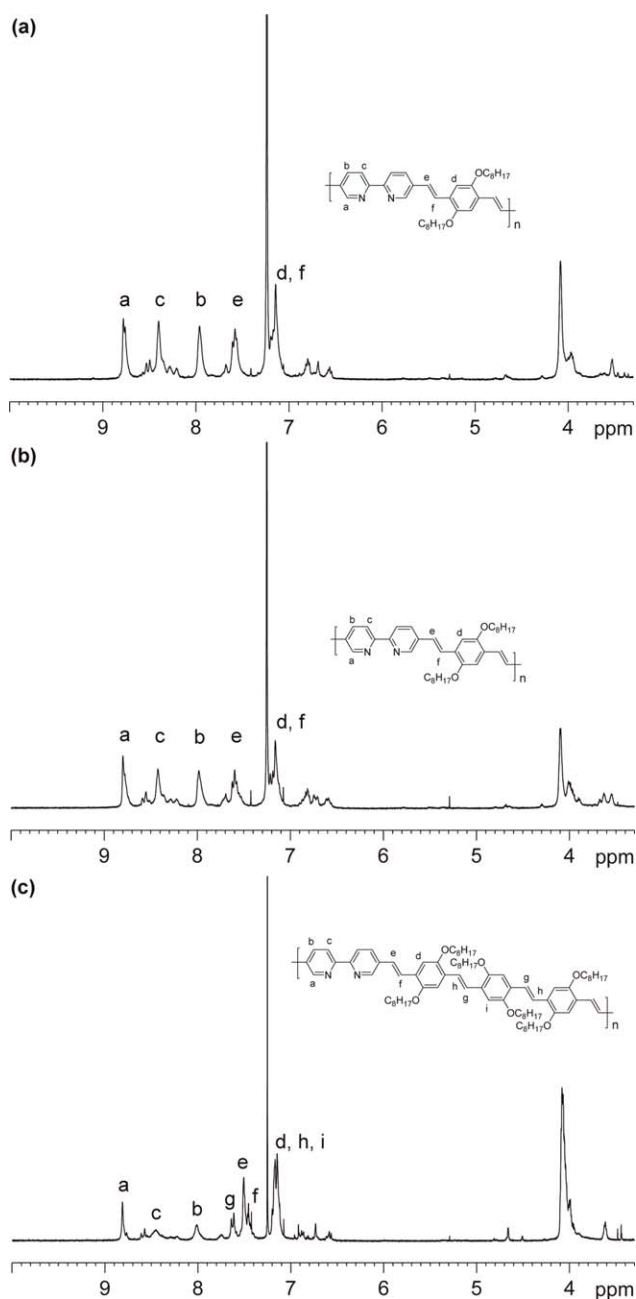


Figure 1. $^1\text{H-NMR}$ spectra of polymers in CDCl_3 : (a) **P1b**, (b) **P2b**, and (c) **P3**. The region below 3 ppm was omitted for clarity.

grade 60 silica gel (0.040–0.063 mm) from Merck. The monomers 5,5'-bis(triphenyl phosphonium methyl)-2,2'-bipyridine dibromide (**1**), 2,5-bis(octyloxy)benzene-1,4-dialdehyde (**2**), and 2,5-Bis(octyloxy)-1,4-bis[(2,5-dioctyloxy-4-formyl)phenylene vinylene]benzene (**3**) were synthesized by the modification of established procedures that were reported previously.¹⁹

Synthesis of 1

5,5'-Bis(bromomethyl)-2,2'-bipyridine (1.37 g, 4.0 mmol) and triphenyl phosphine (2.11 g, 8.0 mmol) were dissolved in anhydrous *N,N*-dimethylformamide (DMF; 40 mL). The mixture was heated to 100°C for 3 h, during which a white precipitate

formed from the reaction. The resulting white precipitate was quickly filtered, washed with a copious amount of hexane, and then dried *in vacuo* to give a fine white solid at a yield of 93%.

$^1\text{H-NMR}$ (600 MHz, CDCl_3 , δ): 8.41 (s, 2H), 7.88–7.91 (m, 12H), 7.77 (s, 2H), 7.70–7.73 (m, 6H), 7.65 (s, 2H), 7.58–7.61 (m, 12H), 6.35 (d, 4H, $J = 16.2$ Hz). Mass spectroscopy (electrospray ionization, mass to charge ratio): 705.2 [M]⁺.

Synthesis of 2

1,4-Dibromo-2,5-bis(octyloxy)benzene (10 g, 20 mmol) was dissolved in anhydrous THF (200 mL) and stirred under an argon atmosphere. The mixture was cooled to -78°C and *n*-butyl lithium (33 mL, 1.6M) was added dropwise and kept cool at -78°C for 1 h. Anhydrous DMF (10 mL, 130 mmol) was added all at once to the reaction mixture at -78°C . The solution was stirred at -78°C for an additional 1 h before the mixture was warmed up to room temperature. The solution was then extracted several times with dilute aqueous hydrochloric acid and dichloromethane. The organic layer was combined, washed with brine, and dried over anhydrous magnesium sulfate. After filtration and evaporation of the solvent, the residue was purified by column chromatography (dichloromethane/hexane = 4 : 6 v/v). The major fraction was collected to give a fluorescent yellow solid at a yield of 50%.

$^1\text{H-NMR}$ (600 MHz, CDCl_3 , δ): 10.52 (s, 2H), 7.43 (s, 2H), 4.08 (t, 4H, $J = 6.6$ Hz), 1.81–1.85 (m, 4H), 1.36–1.48 (m, 4H), 1.28–1.35 (m, 16H), 0.89 (t, 6H, $J = 6.6$ Hz). Mass spectroscopy (electron impact, m/z): 390.4 [M]⁺.

Synthesis of 3

2,5-Dioctyloxy-1,4-xylene bis(triphenyl phosphonium bromide) (1.04 g, 1 mmol) and **2** (0.78 g, 2 mmol) were dissolved in dichloromethane (50 mL) at room temperature. To this solution was added potassium *tert*-butoxide (0.28 g, 2.5 mmol), and then, the solution was stirred for 1 h. The solution was then extracted with dilute aqueous hydrochloric acid and dichloromethane several times. The organic layer was combined, washed with brine, and dried over anhydrous magnesium sulfate. After filtration and evaporation of the solvent, the residue contained

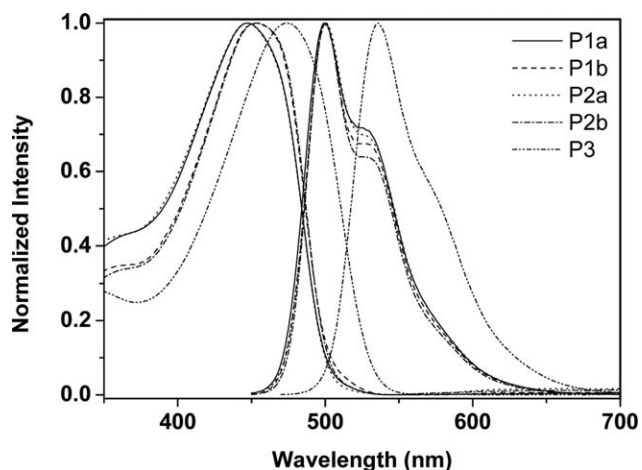


Figure 2. Normalized intensity of the solution ultraviolet–visible spectra and PL spectra of polymers **P1a**, **P1b**, **P2a**, **P2b**, and **P3**.

Table II. Optical Properties of Polymers **P1a**, **P1b**, **P2a**, **P2b**, and **P3**

Polymer	λ_{abs} (nm) ^a	PL _{max} (nm) ^a	λ_{abs} (nm) ^b	PL _{max} (nm) ^b	Stocks shift (nm)	Φ_{PL} ^c
P1a	447	500	471	601	53	0.30
P1b	453	500	471	601	47	0.39
P2a	449	500	472	602	51	0.28
P2b	457	500	472	602	43	0.27
P3	474	539	488	620	65	0.16

λ_{abs} : absorption maximum, PL_{max}: photoluminescence maximum, Φ_{PL} : photoluminescence quantum yield.

^aPolymer in a THF solution.

^bPolymer in the solid state.

^cQuantum yield of emission calculated with quinine sulfate in 0.1N H₂SO₄ ($\Phi_{\text{PL}} = 0.546$) as a standard and corrected for the refractive index of THF. The values have been estimated as ± 0.01 .

both E and Z isomers. A solution of this isomer mixture and iodine (500 mg) in dichloromethane was stirred at room temperature overnight. The dark solution was diluted with dichloromethane, washed with aqueous sodium thiosulfate, and dried over anhydrous magnesium sulfate. After the filtration and evaporation of the solvent, the residual was then purified by column chromatography (dichloromethane/hexane = 1 : 1 v/v). The major fraction was collected to give a fluorescent orange solid of pure compound at a yield of 62%.

¹H-NMR (600 MHz, CDCl₃, δ): 10.45 (s, 2H), 7.59 (d, 2H, $J = 16.8$ Hz), 7.50 (d, 2H, $J = 16.8$ Hz), 7.33 (s, 2H), 7.20 (s, 2H), 7.15 (s, 2H), 4.10–4.12 (t, 4H, $J = 6.0$ Hz), 4.02–4.08 (m, 8H), 1.84–1.89 (m, 12H), 1.48–1.56 (m, 12H), 0.85–0.90 (m, 18H). Mass spectroscopy (fast atom bombardment, m/z): 1108.0 [M + H]⁺.

Synthesis of the Alternating Copolymers **P1a** and **P1b**

A suspension of 5,5-bis(methyl triphenyl phosphonium bromide)-2,2-bipyridine (0.865 g, 1 mmol) and **2** (0.390 g, 1 mmol) in anhydrous toluene (20 mL) was heated to 110°C under an argon atmosphere. Potassium *tert*-butoxide (0.340 g, 3 mmol) was then added in one portion, and the reaction mixture was stirred for 7 or 17 h. The mixture was then concentrated and poured into methanol. The precipitate was collected by filtration. The crude compound was washed in the Soxhlet instrument with hot methanol and acetone for 24 h before it was washed out with hot chloroform. The residuals were then dried *in vacuo* to give the products at yields of 48% for **P1a** and 34% for **P1b**.

¹H-NMR (600 MHz, CDCl₃, δ): 8.78 (2H), 8.42 (2H), 7.98 (2H), 7.59 (2H), 7.16 (4H), 3.99–4.12 (4H), 1.20–1.92 (24H), 0.89 (6H).

Synthesis of the Alternating Copolymers **P2a** and **P2b**

A suspension of 5,5-bis(methyl triphenyl phosphonium bromide)-2,2-bipyridine (0.865 g, 1 mmol) and **2** (0.390 g, 1 mmol) in anhydrous DMF (20 mL) was heated to 110°C under an argon atmosphere. Potassium *tert*-butoxide (0.340 g, 3 mmol) was then added in one portion, and the solution was stirred for 7 or 17 h. The solution was extracted with dichloromethane. The organic layer was combined, washed with brine, and dried over anhydrous magnesium sulfate. The residue was concentrated and poured into methanol. The solid was collected by filtration. The crude compound was then washed in the Soxhlet instrument with hot methanol and acetone for 24 h before it was dissolved in hot chloroform. The residuals were

then dried *in vacuo* to give the final product at yields of 56% for **P2a** and 44% for **P2b**.

¹H-NMR (600 MHz, CDCl₃, δ): 8.79 (2H), 8.42 (2H), 7.98 (2H), 7.59 (2H), 7.16 (4H), 3.99–4.12 (4H), 1.20–1.92 (24H), 0.89 (6H).

Synthesis of the Alternating Copolymer **P3**

A suspension of 5,5-bis(methyl triphenyl phosphonium bromide)-2,2-bipyridine (0.259 g, 0.3 mmol) and **3** (0.332 g, 0.3 mmol) in anhydrous DMF (6 mL) was heated to 110°C under an argon atmosphere. Potassium *tert*-butoxide (0.113 g, 1 mmol) was then added in one portion, and the mixture was stirred for 17 h. The solution was extracted with dichloromethane several times. The organic layer was combined, washed with brine, and dried over anhydrous magnesium sulfate. The solvent was concentrated and poured into methanol, and then, the precipitate was collected by filtration. The crude compound was washed by Soxhlet extraction with methanol and acetone for 24 h before being dissolved in hot chloroform. The residual was then dried *in vacuo* to give the final product at a yield of 56%.

¹H-NMR (600 MHz, CDCl₃, δ): 8.82 (2H), 8.45 (2H), 8.02 (2H), 7.62 (2H), 7.51 (2H), 7.46 (2H), 7.15 (8H), 4.00–4.10 (12H), 1.20–1.92 (72H), 0.88 (18H).

RESULTS AND DISCUSSION

Polymerization and Molecular Weights of the Polymers

Polymers **P1a**, **P1b**, **P2a**, and **P2b** were prepared by the reaction of **1** and **2** in the presence of 3 equiv of potassium *tert*-butoxide in anhydrous toluene or DMF under an argon atmosphere (Scheme 1). The mixture was then heated to 110°C, and 3 equiv of potassium *tert*-butoxide was then added in one portion with vigorous stirring for 7 or 17 h. After the removal of the solvent, the crude product was further purified by Soxhlet extraction in methanol and acetone for 24 h to remove the oligomers and byproduct before they were dissolved in hot chloroform. The resulting polymers **P1** and **P2** were soluble in common organic solvents, such as THF, dichloromethane, and chloroform. Polymers **P1a**, **P1b**, **P2a**, and **P2b** were obtained at yields of 48, 34, 56, and 44%, respectively. Polymer **P3** was prepared by the reaction of **1** and **3** in the presence of 3 equiv of potassium *tert*-butoxide in anhydrous DMF at 110°C for 17 h

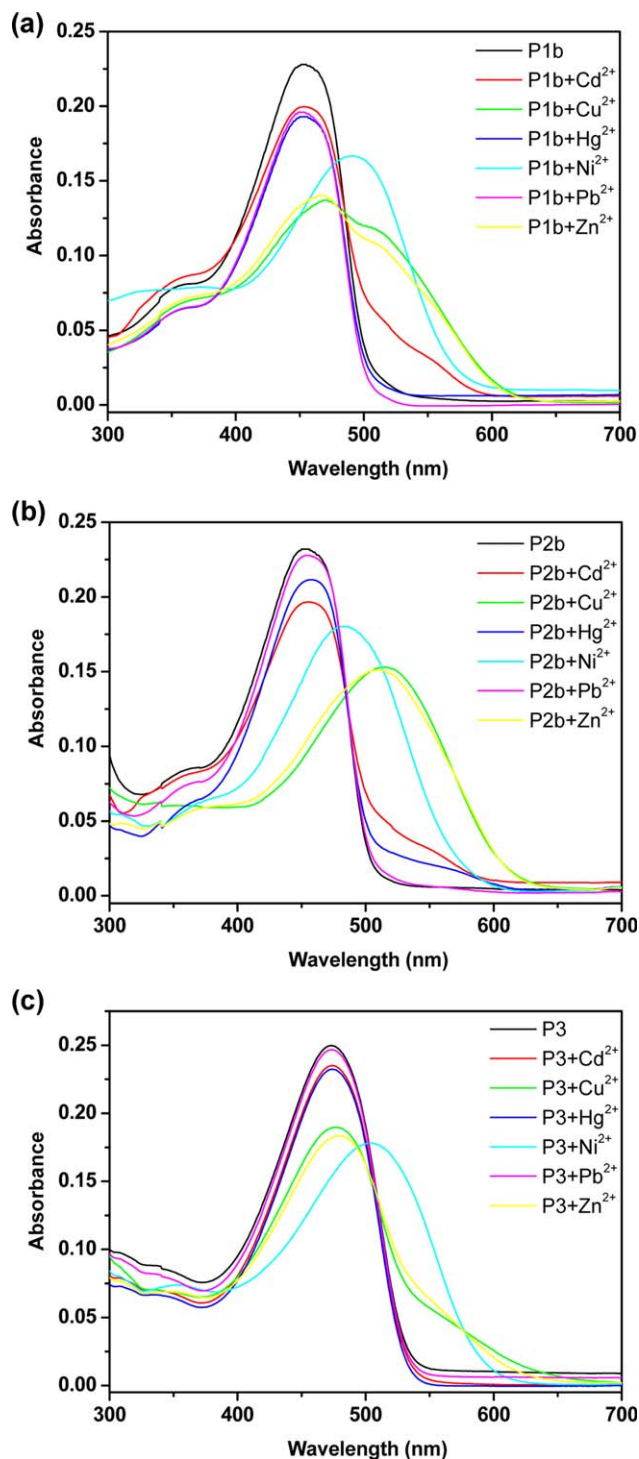


Figure 3. Solution ultraviolet–visible absorption spectra of polymers in the presence of 0.5 equiv of Cd^{2+} , Cu^{2+} , Hg^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} in a THF solution: (a) **P1b**, (b) **P2b**, and (c) **P3**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(Scheme 1). The resulting polymer **P3** was obtained at a yield of 56%.

The molecular weights of **P1a**, **P1b**, **P2a**, **P2b**, and **P3** were determined by gel permeation chromatography in THF solution, calibrated against narrow polydispersity index (PDI) polystyrene

standards with refractive-index detection. The number-average molecular weight (M_n), weight-average molecular weight (M_w), PDIs, and isolated yields of the resulting polymers are summarized in Table I. The polymer **P1a** had an M_n of 4100 and a PDI of 1.41. The polymer **P1b** had an M_n of 4300 and a PDI of 1.40. The polymer **P2a** had an M_n of 6400 and a PDI of 1.47. The polymer **P2b** had an M_n of 6400 and a PDI of 1.31. The polymer **P3** had an M_n of 9000 and a PDI of 1.74. All of the

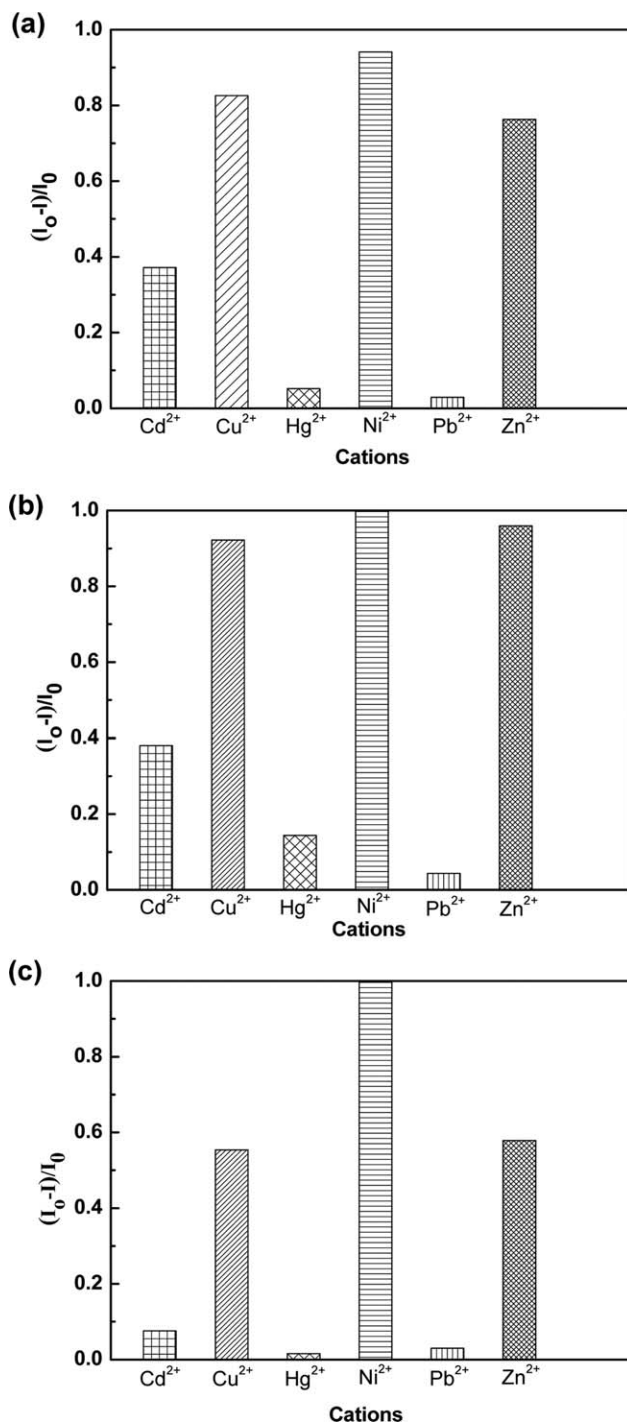


Figure 4. $(I_0 - I)/I_0$ of polymers in the presence of 0.5 equiv of a given metal ion: (a) **P1b**, (b) **P2b**, and (c) **P3**.

Table III. Stern–Volmer Constant Values of Polymers **P1b**, **P2b**, and **P3** at a Given Concentration of Metal Ions

Polymer	$K_{sv} (M^{-1})$					
	Cd^{2+}	Cu^{2+}	Hg^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
P1b	1.19×10^6	9.74×10^6	1.10×10^5	3.18×10^7	5.98×10^4	6.45×10^6
P2b	1.23×10^6	2.35×10^7	3.36×10^5	8.72×10^8	9.23×10^4	4.78×10^7
P3	1.66×10^5	2.48×10^6	3.33×10^4	6.02×10^8	6.24×10^4	2.75×10^6

All metal ions were in the form of their perchlorate salts.

polymers, **P1a**, **P1b**, **P2a**, **P2b**, and **P3**, exhibited relative low molecular weights compared to those phenylene vinylene polymers made by a Wittig condensation reaction. This was possibly due to the low solubilities of the bipyridine moiety and the resulting polymers in toluene or DMF solution; even the reaction was carried out at 110°C. It should be noted that the reaction was carried out in DMF; the obtained molecular weights of polymers were slightly higher than those carried out in toluene. In addition, when the reaction time was expanded up to 17 h, the molecular weights of the polymers did not seem to be increased. This suggests that the reaction reached saturation of the molecular weights of the polymers.

Structural Characterization of the Polymers by 1H -NMR Spectroscopy

The 1H -NMR spectrum of **P1b** is shown in Figure 1(a). The signals appearing at 7.98, 8.78, and 8.42 ppm were associated with hydrogens of the bipyridine ring. The signal of the vinylic hydrogen next to bipyridine ring appeared at 7.59 ppm. The signals for the vinylic hydrogen next to the dialkoxy substituted phenyl ring and the hydrogen of dialkoxy substituted phenyl ring were overlapped and can be observed at 7.16 ppm. The hydrogen of methylene groups attached to the oxygen appears at 4.10 ppm. The signals below 2.00 ppm (not shown here) are assigned to the octyloxy chain hydrogens. The 1H -NMR spectrum of **P2b** is shown in Figure 1(b). The δ s of all of the signals were identical compared to those of **P1b**; this indicated that **P1b** and **P2b** had the same microstructures as we expected. The 1H -NMR spectrum of **P3** is shown in Figure 1(c). Signals appeared at 8.02, 8.82, and 8.45 ppm and were associated with hydrogens of the bipyridine ring. The signal of the vinylic hydrogens next to the bipyridine ring appeared at 7.51 ppm, and the peak appearing at 7.46 ppm was associated with the hydrogens next to the edge of the dialkoxy substituted phenyl ring. The signals for the vinylic hydrogens next to the middle of the dialkoxy-substituted phenyl ring and the hydrogens of the dialkoxy substituted phenyl ring were partially overlapped and could be observed at 7.62 and 7.15 ppm. The hydrogen of methylene groups attached to the oxygen appeared at 4.10 ppm. The signals below 2.00 ppm (not shown here) were assigned to the octyloxy chain hydrogens.

Optical Properties of the Polymers

The absorption and PL spectra of polymers **P1a**, **P1b**, **P2a**, **P2b**, and **P3** were recorded in dilute THF solution. Figure 2 show that the polymers exhibited mainly one absorption peak. As expected, the absorption between 400 and 500 nm originated from the phenylene vinylene segments. For all of the polymers,

the absorption wavelength was attributed to the π - π^* transition along the polymer backbone. Polymers **P1a**, **P1b**, **P2a**, **P2b**, and **P3** exhibited absorption maxima at 447, 453, 449, 457, and 474 nm, respectively. The absorption maximum of polymer **P2a** was slightly redshifted by 2 nm compared to polymer **P1a**, and the absorption maximum of polymer **P2b** was slightly redshifted by 4 nm compared to polymer **P1b**. This was due to the extension of the conjugation length of the polymer. The absorption maximum of polymer **P3** was more redshifted compared to **P1a**, **P1b**, **P2a**, and **P2b** because of the extension of the phenylene vinylene moiety; this led to an increase in the effective conjugation length of the polymer.

The fluorescence maxima recorded for polymers **P1a**, **P1b**, **P2a**, and **P2b** were identical at 500 nm with a shoulder around 528 nm as the emission occurred from the most conjugated segment of the polymer, regardless of the chain length. The emission maximum of **P3** appeared at 539 nm; this was redshifted by 39 nm in comparison with **P1a**, **P1b**, **P2a**, and **P2b**. This was attributed to an increase in the phenylene vinylene units; this led to an increase in the conjugation of the polymer. The polymer films were prepared by the spin casting of a solution (1 mg/mL) at 600 rpm for 60 s onto glass slides. The solid-state absorption and emission maxima of all of the polymers (Table II) showed a bathochromic effect compared to those carried out in solution because of the enhanced interchain interactions in solid state. The PL quantum yields for polymers **P1a**, **P1b**, **P2a**, **P2b**, and **P3** were determined in THF solution relative to a quinine sulfate standard. The PL quantum yields of polymers **P1a**, **P1b**, **P2a**, **P2b**, and **P3** were 0.30, 0.39, 0.28, 0.27, and 0.16, respectively. The PL quantum yields for polymer **P3** were relatively low, probably because of the rotational relaxation of higher fractional phenylene vinylene moieties, which enhanced the nonradiative pathway.²³

Optical Properties of the Polymers upon the Addition of Metal Ions

The effects of the molecular recognition sites of the bipyridine-based phenylene vinylene polymers on metal sensing were investigated, as depicted in the absorption and fluorescence emission spectra of the polymers with increasing amounts of various metal ions, such as Cd^{2+} , Cu^{2+} , Hg^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} ions. The concentrations of the metal free polymers were at $1.0 \times 10^{-7} M$. The metal ions were in the form of their perchlorate salts dissolved in dilute THF solutions. Figure 3 shows the absorption spectra of polymers **P1b**, **P2b**, and **P3** upon addition of 0.5 equiv of Cd^{2+} , Cu^{2+} , Hg^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} ions. After the addition of the metal ions, in all cases the absorbance was

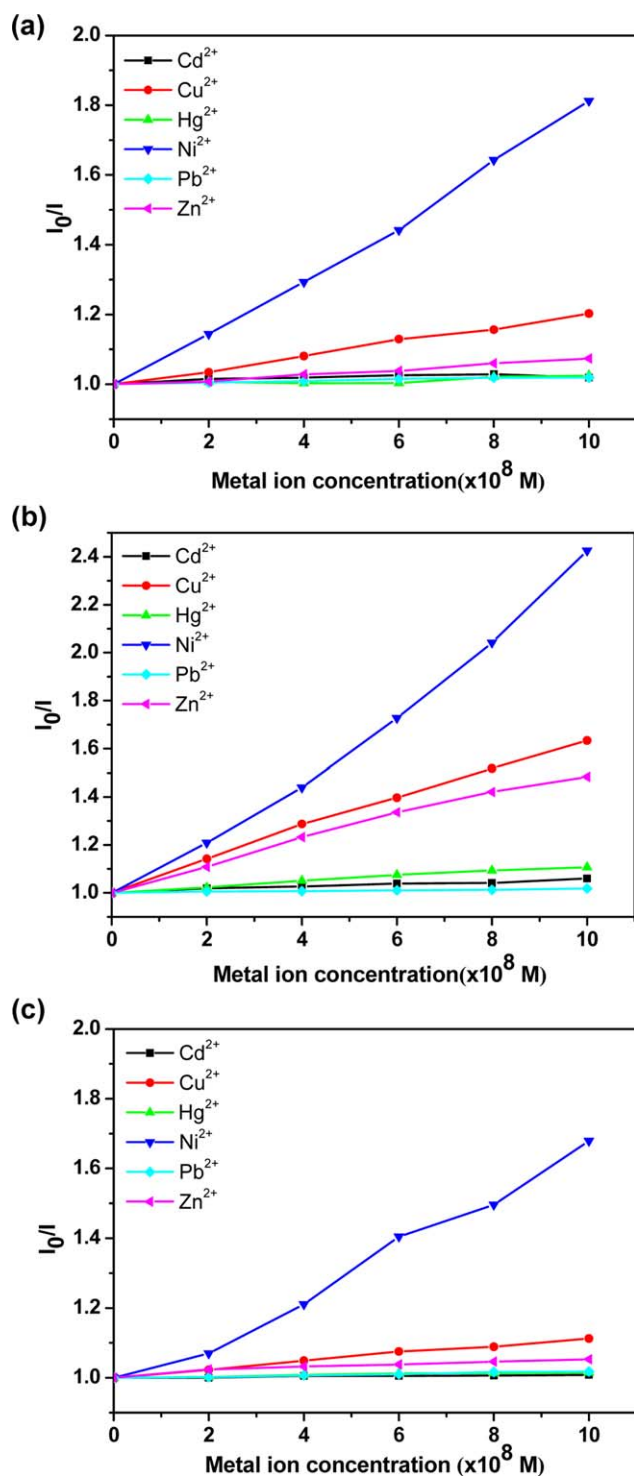


Figure 5. Stern–Volmer plots for the fluorescence quenching of (a) P1b, (b) P2b, and (c) P3 by Cd^{2+} , Cu^{2+} , Hg^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} ions in THF (polymer concentration = 1×10^{-7} M; $[\text{M}^{2+}] = 0\text{--}10 \times 10^{-8}$ M). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decreased. The absorption maximum of polymer P1b [Figure 3(a)] upon the addition of 0.5 equiv of Cu^{2+} , Ni^{2+} , and Zn^{2+} ions showed significant redshifts compared to the ion-free polymer. Upon the addition of 0.5 equiv of Cd^{2+} , Hg^{2+} , and Pb^{2+}

ions, the absorption maximum of polymer P1b showed little change in comparison with the ion-free polymer. The plausible explanation is that the effective conjugation length could be extended with the addition of Cu^{2+} , Ni^{2+} , and Zn^{2+} ions into the polymer solution because of the strong coordination with the bidentate *N,N* site of the bipyridine moieties; this led to a decrease in the dihedral angles between two pyridine rings and an increase in the planarity of the polymers. The absorption maximum of polymer P2b [Figure 3(b)] upon the addition of 0.5 equiv of Cu^{2+} , Ni^{2+} , and Zn^{2+} ions also showed a significant redshift compared to the pristine polymer. The absorption maximum of polymer P2b upon the addition of 0.5 equiv of Cd^{2+} , Hg^{2+} , and Pb^{2+} ions showed little change. Again, this suggested that the more planar structure was observed with the addition of 0.5 equiv of Cu^{2+} , Ni^{2+} , and Zn^{2+} ions into the polymer solution. It should be noted that the absorption maximum of polymer P3 [Figure 3(c)] showed a significant redshift only with the addition of 0.5 equiv of Ni^{2+} ions to the polymer solution. This suggested that polymer P3 exhibited relatively high coordination with Ni^{2+} ions. There was no significant change in the absorption maximum of polymer P3 with the addition of 0.5 equiv of Cd^{2+} , Cu^{2+} , Hg^{2+} , Pb^{2+} , and Zn^{2+} ions to the polymer solution, except longer wavelength shoulders occurred at more than 550 nm upon the addition of Cu^{2+} and Zn^{2+} ions. This long-tail absorption for the polymer P3 chelating with Cu^{2+} and Zn^{2+} ions also quenched the fluorescence, as shown in Figure 4. In addition, the absorption and fluorescence spectra of polymer P3 upon the addition of 0.5 equiv of Cd^{2+} , Hg^{2+} , and Pb^{2+} ions did not show a significant change; this was possibly due to the weak coordination ability.

No significant changes in the emission maxima wavelength were observed for polymers P1b, P2b, and P3 in response to a series of metal ions; this indicated little formation of intramolecular charge-transfer complexes. For polymers P1b, P2b, and P3, the fluorescence quenching toward the metal ions was attributed to photoinduced electron-transfer quenching when the ions coordinated with the bidentate *N,N* site of the bipyridine moieties. The fluorescence quenching factor, $(I_0 - I)/I_0$, where I is fluorescence intensity after addition of metal ions, I_0 is the initial fluorescence intensity of polymers P1b, P2b, and P3 in the presence of 0.5 equiv of a given metal ion are shown in Figure 4. The screening of different metal ions showed that polymers P1b, P2b, and P3 were the most sensitive to Ni^{2+} ions (Figure 4) with the sensitivity in the order of Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , and Pb^{2+} for polymer P1b; Ni^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Hg^{2+} , and Pb^{2+} for polymer P2b; and Ni^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , and Hg^{2+} for polymer P3. The fluorescence quenching behavior could be attributed to many factors, including the quenching mechanisms, the nature of the metal ions, and the metal–ligand binding strength. The stronger quenching effects from the Cu^{2+} , Ni^{2+} , and Zn^{2+} ions could have been due to a combination of their strong binding with the ligand and their paramagnetic properties.²⁴

The fluorescence quenching generally includes static quenching and dynamic quenching. Each quenching behavior can be simply described by the Stern–Volmer equation. Table III shows the Stern–Volmer constants (K_{SV} 's), a quenching constant, of P1b,

P2b, and **P3**. The K_{sv} values for the addition of Ni^{2+} , Cu^{2+} , and Zn^{2+} ions were higher than those for the Cd^{2+} , Hg^{2+} , and Pb^{2+} ions in all cases. The Stern–Volmer plots (Figure 5) were found to be linear at lower concentrations; this indicated that fluorescence quenching involved a static quenching mechanism.²⁵ The results shown in Table III were consistent with the fluorescence spectrum and quenching behaviors shown in Figure 4. It should be noted that the sensitivity, selectivity, and degree of fluorescence quenching of all of the polymers chelating with metal ions were related to the ionic radius with the order Ni^{2+} (83pm) > Cu^{2+} (87pm) > Zn^{2+} (88pm) > Cd^{2+} (109pm) > Hg^{2+} (116pm) > Pb^{2+} (133pm). The possible explanation was that the increase in the ionic radius caused the decrease in the coordination ability as the ionic radius was too large for the chelation compared to the size of the semicavity of the bipyridine units; this led to the whole polymer chains being forced to be nonplanar. This was consistent with the results of the absorption spectra of polymers upon the addition of large ions, such as Cd^{2+} , Hg^{2+} , and Pb^{2+} , as there was less of a bathochromic effect compared to the polymer upon the addition of the Cu^{2+} , Ni^{2+} , and Zn^{2+} ions.

CONCLUSIONS

Alternating copolymers incorporating bipyridine and phenylene vinylene were successfully prepared by a Wittig condensation reaction. The polymers exhibited relatively low molecular weights compared to those phenylene vinylene polymers made by the Wittig condensation reaction because of the low solubility of the bipyridine moiety and the resulting polymers. The photophysical properties of the copolymers were significantly affected by the phenylene vinylene units. The conjugated polymers performed their intended role as turn-off fluorescent chemosensors for Cd^{2+} , Cu^{2+} , Hg^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} ions. The absorption maxima of the polymers upon the addition of 0.5 equiv of Cu^{2+} , Ni^{2+} , and Zn^{2+} ions showed significant redshifts compared to the ion-free polymers because of the increase in the planarity on the polymer backbone. The results indicate that the polymers showed a higher sensitivity in sensing the Cu^{2+} , Ni^{2+} , and Zn^{2+} ions than in sensing Cd^{2+} , Hg^{2+} , and Pb^{2+} ions. Such polymers can provide a crucial template for the synthesis and design of highly sensitive chemosensory materials.

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REFERENCES

1. Cheng, X.; Li, S.; Jia, H.; Zhong, A.; Zhong, C.; Feng, J.; Qin, J.; Li, Z. *Chem. Eur. J.* **2012**, *18*, 1691.

2. Masanta, G.; Lim, C. S.; Kim, H. J.; Han, J. H.; Kim, H. M.; Cho, B. R. *J. Am. Chem. Soc.* **2011**, *133*, 5698.
3. Aragay, G.; Pons, J.; Merkoci, A. *Chem. Rev.* **2011**, *111*, 3433.
4. Yu, C.-Y.; Shih, T.-Y. *Synth. Met.* **2014**, *191*, 12.
5. McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.
6. Valeur, B.; Leray, I. *Coord. Chem. Rev.* **2000**, *205*, 3.
7. Wu, J.; Liu, W.; Ge, J.; Zhang, H.; Wang, P. *Chem. Soc. Rev.* **2011**, *40*, 3483.
8. Wu, X.; Xu, B.; Tong, H.; Wang, L. *Macromolecules* **2011**, *44*, 4241.
9. Fan, L.-J.; Zhang, Y.; Murphy, C. B.; Angell, S. E.; Parker, M. F. L.; Flynn, B. R.; Jones, W. E. *Coord. Chem. Rev.* **2009**, *253*, 410.
10. Jeong, Y.; Yoon, J. *Inorg. Chim. Acta* **2012**, *381*, 2.
11. Martinez-Manez, R.; Sancenon, F. *Chem. Rev.* **2003**, *103*, 4419.
12. Ji, X.; Yao, Y.; Li, J.; Yan, X.; Huang, F. *J. Am. Chem. Soc.* **2013**, *135*, 74.
13. Siebert, R.; Tian, Y.; Camacho, R.; Winter, A.; Wild, A.; Krieg, A.; Schubert, U. S.; Popp, J.; Scheblykin, I. G.; Dietzek, B. *J. Mater. Chem.* **2012**, *22*, 16041.
14. Bao, Y.; Wang, H.; Li, Q.; Liu, B.; Li, Q.; Bai, W.; Jin, B.; Bai, R. *Macromolecules* **2012**, *45*, 3394.
15. Liu, Y.; Zhang, S.; Miao, Q.; Zheng, L.; Zong, L.; Cheng, Y. *Macromolecules* **2007**, *40*, 4839.
16. Jurcic, M.; Peveler, W. J.; Savory, C. N.; Scanlon, D. O.; Kenyon, A. J.; Parkin, I. P. *J. Mater. Chem. A* **2015**, *3*, 6351.
17. Miao, Q.; Wu, Z.; Hai, Z.; Tao, C.; Yuan, Q.; Gong, Y.; Guan, Y.; Jiang, J.; Liang, G. *Nanoscale* **2015**, *7*, 2797.
18. Luo, H.-Y.; Jiang, J.-H.; Zhang, X.-B.; Li, C.-Y.; Shen, G.-L.; Yu, R.-Q. *Talanta* **2007**, *72*, 575.
19. Wang, B.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1997**, *119*, 12.
20. Sharma, A.; Sharma, N.; Kumar, R.; Shard, A.; Sinha, A. K. *Chem. Commun.* **2010**, *46*, 3283.
21. Banjoko, V.; Xu, Y.; Mintz, E.; Pang, Y. *Polymer* **2009**, *50*, 2001.
22. Wu, T.-Y.; Chen, Y. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 1272.
23. Motloung, S. V.; Dejene, F. B.; Swart, H. C.; Ntwaeaborwa, O. M. *J. Sol–Gel Sci. Technol.* **2014**, *70*, 422.
24. Szaciłowski, K.; Macyk, W.; Drzewiecka-Matuszek, A.; Brindell, M.; Stochel, G. *Chem. Rev.* **2005**, *105*, 2647.
25. Bhalla, V.; Arora, H.; Singh, H.; Kumar, M. *Dalton Trans.* **2013**, *42*, 969.