

Design and Synthesis of Metal Ion-Recognition-Induced Conjugated Polymers: An Approach to Metal Ion Sensory Materials

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Abstract: The synthesis and metal ion responsive properties of two 2,2'-bipyridyl-phenylene-vinylene-based polymers is reported. These polymers are designed to be partially conjugated in their metal-free state and fully conjugated when exposed to metal ions so that the ion-induced conjugation enhancement can be transduced into a measurable signal. It is found that these polymers exhibit highly ionochromic effects with a wide variety of transition and main group metal ions excluding metal ions of the alkali and alkaline earth groups. For instance, both absorption and fluorescence emission bands of the polymers upon exposure to metal ions can be red-shifted up to 120 nm, depending on the metal ions present and the polymers used.

Introduction

Investigations into highly sensitive and selective molecular sensory materials have received considerable attention in recent years.¹ In particular, numerous efforts have been devoted to the design and construction of chemosensory systems that are capable of detecting metal ions in both a real-time and reversible fashion.² Among the systems reported to date, the vast majority are either crown ethers or their analogs,³ conjugated polymer-based⁴ supramolecules, or, more attractively, the combination of these two.^{5–12} The appeal of polymers containing molecular

recognition sites is that they make use of the high sensitivity of conjugated polymers (conducting polymers) to external structural perturbations and to electron density changes within the polymer backbone, when they interact with metal ions. In this context, there have been reports of sensory polymers such as azacrown or crown ether-substituted polypyrroles^{8,10} and polythiophenes,^{6,7,11} ethylene ether-substituted polythiophene and polypyrroles,^{9,12} macrocyclic ether-substituted poly(bithiophene) and poly(phenyleneethynylene)s, and calix[4]arene-based polythiophenes.^{5,13} A common feature of these sensory systems is that their functional mechanisms are based on, in most cases, ion-induced conductivity fluctuations either by lowering charge carrier mobility (electrostatic effect) or by destroying the conjugation of polymers (conformational effect). These studies have clearly demonstrated the broad scope of conjugated polymer-based, alkali metal-sensitive molecular sensory systems. On the other hand, there are few examples that show the feasibility of making conjugated polymers whose degree of conjugation is sensitive to other metal ions.^{5b,9c,11}

In this paper, we present an alternative approach to constructing new, metal ion-sensitive polymers. This approach, as illustrated in Scheme 1, is to prepare a pseudoconjugated, ligand-containing polymer that upon incorporating metal ions would undergo conformational changes, thus converting the polymer from the initial partially conjugated one to a fully or near fully conjugated entity. Such conjugation enhancement, along with the simultaneous electron density change caused by incorporating metal ions onto the backbone of polymers, in turn, should generate corresponding changes in the electronic properties of the polymers. The specific design is shown in the structures of polymer **1** and polymer **2**. Here, the oligo-phenylenevinylenes are chosen as conjugated segments that are connected covalently to 2,2'-bipyridines at their 5,5'-positions. Since the phenylenevinylene unit is designed also to be responsible for signal transduction, the different length, as in **1** and **2**, respectively, is expected to result in different responses. The

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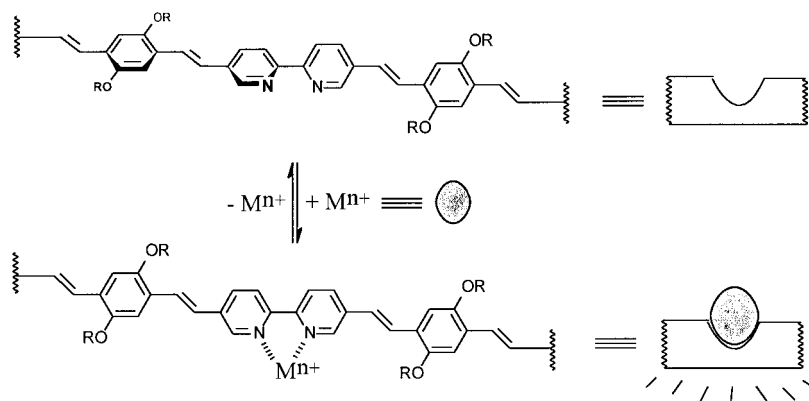
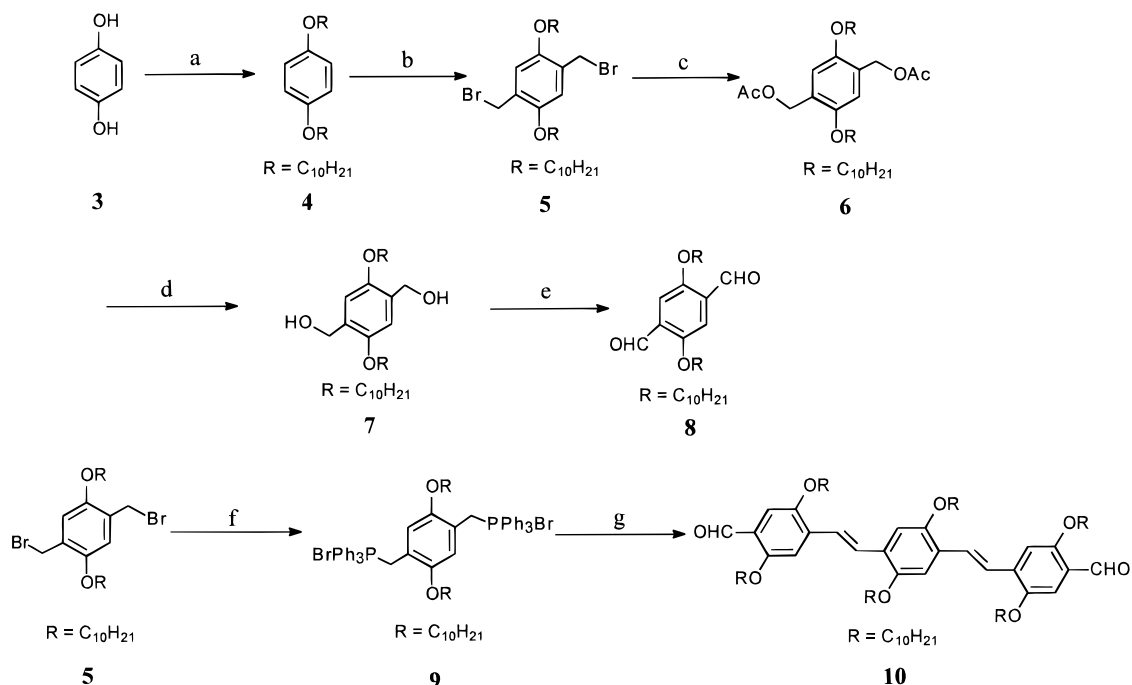
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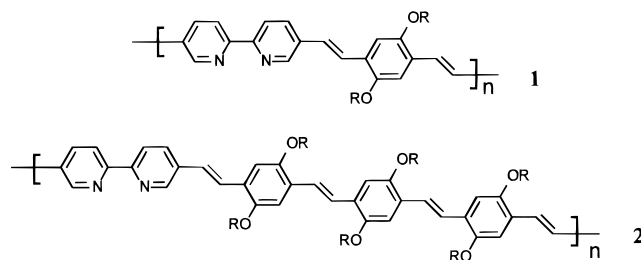
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Scheme 1. Schematic Illustration of Metal-Ion-Induced Conjugation Enhancement of the Polymer Backbone and the Corresponding Responsive Change**Scheme 2^a**

^a (a) Bromodecane, K_2CO_3 , acetonitrile, reflux, 36 h, 85%; (b) paraformaldehyde, HBr, 60 °C, 2 h, 86%; (c) KOAc, Bu_4NBr , acetonitrile, reflux, overnight, 100%; (d) $LiAlH_4$, THF, room temperature, 2 h, 99%; (e) PCC, CH_2Cl_2 , room temperature, 2 h, 87%; (f) PPh_3 , toluene, reflux, 3 h; (g) (i) **8**, $LiOEt$, CH_2Cl_2 , room temperature, 10 min; (ii) I_2 , CH_2Cl_2 , room temperature, overnight, 84%.

reason 2,2'-bipyridine was selected as a building block for these polymers is based on following considerations. It is well-known that 2,2'-bipyridine and its derivatives possess superb ability to coordinate a large number of metal ions. As such, the scope of metal ion sensors could be extended from currently well documented, crown ether-based, alkali or alkaline earth metal ion-sensitive systems to other metal ion-sensitive ensembles. More intriguingly, given the fact that there is approximately a 20° dihedral angle between two pyridine planes in a 2,2'-bipyridine when it is in its transoid-like conformation,¹⁴ such polymers are therefore not totally conjugated. When chelated with a metal ion, however, the coordination between the metal ion and bipyridine would force the twisted conformation into a planar one, making the polymers fully conjugated. In addition, incorporating 2,2'-bipyridine as a recognition unit directly into the backbone, as an integral part of a conjugated polymer, is expected to give rise to a more sensitive response upon metal ion binding. Indeed, as shall be detailed in the following

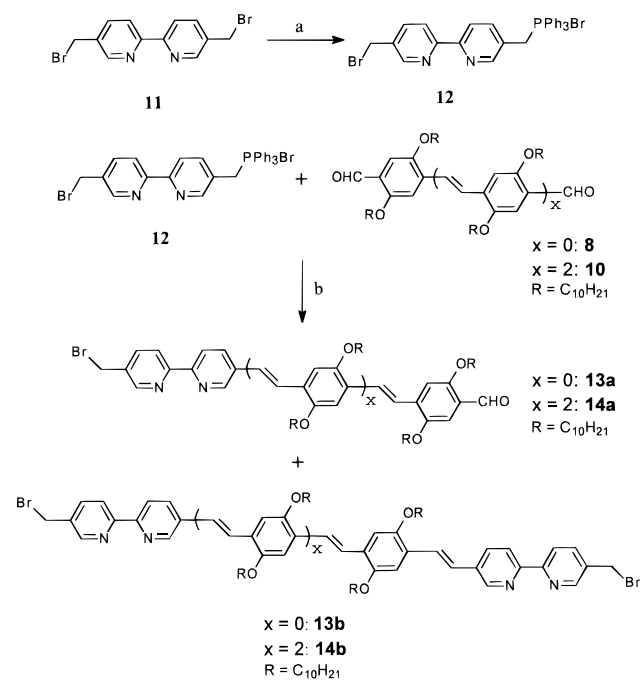
sections of this paper, it is found that such polymers are quite sensitive to a wide variety of metal ions.



Results and Discussion

Synthesis. The basic strategies employed for synthesizing polymers **1** and **2** are based upon Wittig-type ethylenic group formation methodology. To this end, the corresponding diphosphonium salt and dialdehyde precursors were prepared first. Scheme 2 illustrates the synthetic sequences for making dialdehydes **8** and **10**. Specifically, heating 1,4-hydroquinone **3** with 1-bromodecane in acetonitrile at reflux in the presence

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Scheme 3^a

^a (a) PPh₃, toluene, reflux, 2 h, 99.3%; (b) (i) LiOEt, CH₂Cl₂, room temperature, 3 h; (ii) TsOH, toluene, reflux, overnight, **13a**: 49.1%; **13b**: 11.3%; **14a**: 25.3%, **14b**: 34.9%.

of K₂CO₃ readily afforded 1,4-bis(decyloxy)benzene **4** in 85% yield. Subsequent bromomethylation of **4**, using a general bromomethylation procedure for aromatic compounds,¹⁵ then provided a key intermediate **5** (86% yield). The two bromomethylenes were confirmed to be at 2- and 5-positions, as opposed to 2- and 3- or 2- and 6-positions, by both ¹H-NMR and ¹³C-NMR spectra. Attempts at direct conversion of this intermediate to the dialdehyde **8** by known literature procedures were unsuccessful in our hands.^{16,17} We thus decided to use an acetylation–reduction–oxidation sequence to execute this transformation (i.e. **5** → **6** → **7** → **8**). Although this route took two more steps than a direct conversion, the synthetic efficiency turned out to be extraordinarily good. For instance, the overall yield of **8** starting from **5** in three steps was 85%. The high efficiency of transformation also ensures the ease of isolation and purification at each step. As such, the whole sequence from starting material **3** to dialdehyde **8** can be accomplished with minimal chromatographic purification. With intermediate **8**, a triphenylenevinylene dialdehyde **10** was then synthesized. It was accomplished using a double Wittig reaction of **8** with a diphosphonium salt **9** that also was made from compound **5**. Like typical Wittig-type reactions, this reaction also yielded a mixture of *trans*- and *cis*-vinylene isomers. The isomerization of the mixture to all *trans*-isomer **10** was achieved by treatment with iodine in dichloromethane at room temperature (84% overall yield).

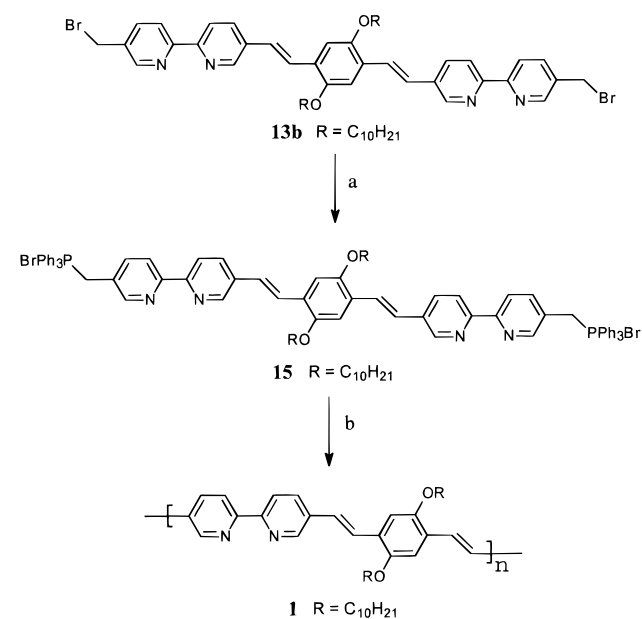
Synthesis of another building block, namely the phosphonium salts of the 2,2'-dipyridine derivatives, is shown in Scheme 3. The key precursor 5,5'-bis(bromomethyl)-2,2'-bipyridine (**11**) was prepared from β-picoline in two steps according to literature procedures.¹⁸ Further attempts at making its diphosphonium salt in refluxing toluene failed due to the poor solubility of this salt. In fact, it only afforded the monophosphonium salt (**12**)

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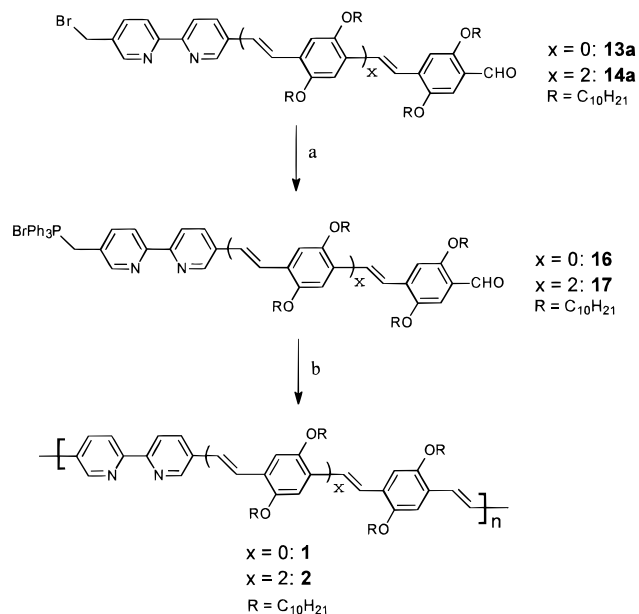
Scheme 4^a

^a (a) PPh₃, DMF, reflux, 4 h; (b) **8**, LiOEt, DMF, reflux, 2 h, **1**: 40.2%.

in the form of a white precipitate in a quantitative yield. At this point, we realized that even though the diphosphonium salt could be made by choosing other solvent systems, it might still be problematic to find an appropriate solvent for a homogenous polymerization reaction between the resultant diphosphonium salt and the dialdehyde under Wittig reaction conditions. On the other hand, if we could take advantage of the neat formation of monophosphonium salt **12**, this problem could be resolved in two ways. For example, from **12** we could synthesize a compound like **13a** or **14a** that carries a bromomethyl entity at the bipyridine end and a formyl group at the oligo-phenylenevinylene end. Further conversion of bromomethyl entity to its phosphonium salt then would enable this bifunctionalized compound to self-polymerize under Wittig reaction conditions. The merits of this type polymerization will be discussed later. Also, the monophosphonium salt **12** can be transformed to bis-(bromomethyl)bipyridine capped phenylenevinylene oligomers, such as compounds **13b** and **14b**. Their diphosphonium salt counterparts should be quite soluble owing to the presence of solubilizing groups on the phenylenevinylene moieties. In light of these considerations, we then chose to react **12** with equivalent dialdehydes **8** and **10**, respectively. As such, in the case of using aldehyde **8** compounds, **13a** and **13b** were obtained in a one-pot reaction in the yields of 49% and 11%, respectively. Likewise, compounds **14a** and **14b** were obtained when aldehyde **10** was used (25% and 35% yields, respectively). Again, these Wittig reaction products were mixtures of *trans*- and *cis*-isomers. The *cis*- to *trans*-isomerizations were achieved by heating the mixture in toluene at reflux in the presence of *p*-toluenesulfonic acid.

Syntheses of polymers **1** and **2** are highlighted in Schemes 4 and 5. Polymer **1** was prepared using two different routes. First, a soluble diphosphonium salt **15** was made from its bis-(bromomethyl) precursor **13b** in hot DMF. Copolymerization of this diphosphonium salt with a 1,4-bis(decyloxy)benzene-2,5-dialdehyde **8** under Wittig reaction conditions then gave polymer **1** (80% yield, average molecular weight $M_n = 5800$).¹⁹ The stepwise nature of this polymerization reaction dictates that

(19) The molecular weight was determined by Gel Permeation Chromatography (GPC) using polystyrene as standard. Because of the distinct difference between this rigid polymer and flexible polystyrene, data obtained here only serve as a reference.

Scheme 5^a

^a (a) Toluene, reflux, 4 h; (b) (i) LiOEt, CH₂Cl₂, room temperature, 84 h, **1**: 89.2%; (ii) LiOEt, toluene, reflux, 48 h, **2**: 92.6%.

the molecular weight of the polymer depends on the reaction time and the strict 1:1 ratio of two reactants. This latter requirement is normally hard to meet in practice, especially when the polymerization is carried out on a micro-scale. In this regard, it seems that using a building block containing both phosphonium salt and an aldehyde functional group, such as compounds **13a** and **14a**, for the polymerization may be more advantageous over using two building blocks, like compounds **13b** and **14b**. We thus selected this strategy as an alternative synthetic route for polymers **1** and **2**. The phosphonium salts **16** and **17** were made from their precursors **13a** and **14a**, respectively. Subsequent polymerization was then initiated upon addition of base (LiOEt). In this way, polymer **1** was obtained in 89% yield ($M_n = 6400$) and polymer **2** made in 92% yield ($M_n = 22000$). In spite of the limited enhancement of molecular weight, this route indeed appears to be superior to that used earlier in terms of both molecular weight and yield.

Ion Responsive Properties. The most apparent ionochromic effects of polymers **1** and **2** are their *instant* color changes upon the addition of metal salts to the polymer solutions. The colors vary from originally fluorescent light yellow (**1**) or yellow (**2**) to pink, purple, or light blue, dependent on metal ions and polymers. Such dramatic color changes, however, were not observed with either a pure poly(phenylenevinylene)²⁰ or 5,5'-dimethyl-2,2'-bipyridyl, or a mixture of them, indicating that none of these components alone result in the observed ionochromic phenomenon. It is the target polymers that are responsible for the metal ion-induced color changes.

Further optical ion responsive properties of polymers **1** and **2** were monitored in chloroform using absorption and fluorescence emission spectroscopy. The ionochromic profiles of polymers **1** and **2** with some transition metal ions are shown in Figure 1. A more complete set of data resulted from chelation reactions between the polymers and a wide variety of metal ions is summarized in Table 1. Clearly, both polymers exhibit substantial red-shifts in absorption spectra when interacting with the respective metal ions. More interestingly, such shifting again appears to be both metal ion and polymer dependent. For

(20) Poly(phenylene vinylene) used here is made also from **5** in a one-pot reaction in THF using potassium butoxide as base. The average molecular weight of such obtained polymers is estimated as high as 3.0×10^5 by GPC.

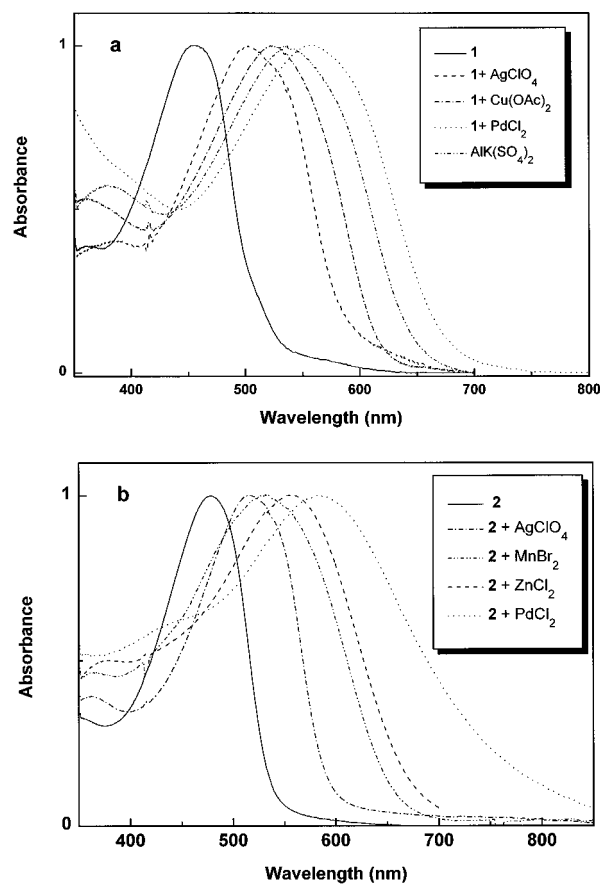


Figure 1. Absorption spectra recorded in CHCl₃ at room temperature for metal complexes of (a) polymer **1** and (b) polymer **2**. The polymer concentration is 1.0×10^{-5} M corresponding to 2,2'-bipyridyl units, and metal ion concentration is 1.0×10^{-4} M.

Table 1. Absorption and Emission Responses of Polymers **1** and **2** upon Chelating Metal Ions^a

	polymer 1		polymer 2	
	absorption (nm)	emission (nm)	absorption (nm)	emission (nm)
ion-free	455	507	478	544
Zn ²⁺	513	593	560	670
Cd ²⁺	513	627	532	652
Cu ²⁺	524	q	557	q
Ni ²⁺	513	q	532	q
Co ²⁺	519	q	532	q
Hg ²⁺	512	590	527	636
Pb ²⁺	535	468, 502 (w)	551	472, 540
Pd ²⁺	564	q	583	q
Mn ²⁺	514	q	537	q
Sn ²⁺	558	q	590	q
Fe ²⁺	529	464 (w)	551	473, 501 (m)
Ag ⁺	503	585 (w)	516	602 (w)
Cu ⁺	514	466 (w)	533	476, 503 (m)
Al ³⁺	535	590	570	674 (w)
Fe ³⁺	527	467, 492 (m)	536	480, 508 (m)
Sb ³⁺	556	472, 489 (w)	566	480, 506 (m)

^a q: quenched, w: weak, m: medium.

instance, in the case of **1** as the sensory polymer, the absorption maximum ($\Delta\lambda_{max}$) shifts from metal ion-free polymer to metal-chelated polymers range from +48 nm for Ag⁺ to +109 nm for Pd²⁺, whereas for polymer **2** the changes in absorption vary from +38 nm for Ag⁺ to +112 nm for Sn²⁺. Hence, according to these ion- or polymer-dependent responsive properties, it seems possible to detect some of these metal ions specifically (*vide infra*).

Ion-responsive properties of polymers **1** and **2** recorded by fluorescence emission spectra are also informative. Some

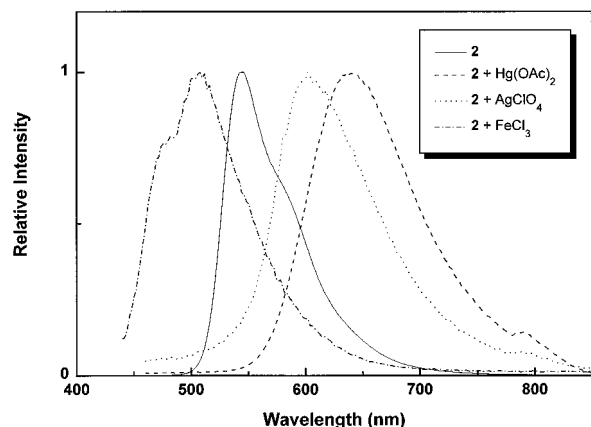


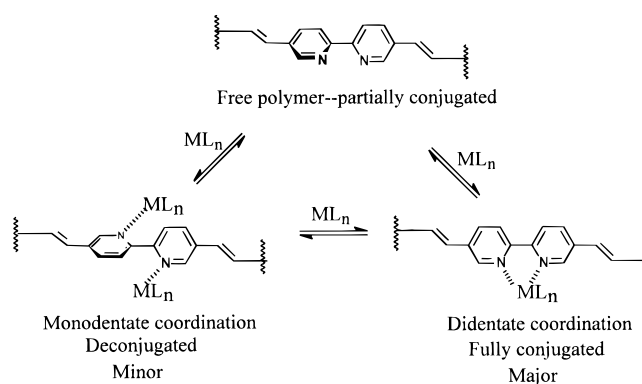
Figure 2. Fluorescence emission spectra recorded in CHCl_3 at room temperature for polymer **2** complexes with metal ions. Polymer concentration is 1.0×10^{-5} M corresponding to 2,2'-bipyridyl units, and metal ion concentration is about 1.0×10^{-4} M. Excitation wavelength is 410 nm.

representative results are illustrated in Figure 2. A complete set of data is listed also in Table 1. It is apparent that the fluorescence spectra of metal ion-containing polymers are quite different from those of the metal ion-free polymers. According to the spectroscopic effects of metal ions on polymers, the metal ions can be categorized into three groups. The first group of metal ions causes red-shifting but does not dramatically quench the fluorescence of polymers. The substantial red-shift in the fluorescence spectra for the polymers ranges from ~ 60 nm to ~ 130 nm depending on metal ion. These metal ions include Zn^{2+} , Cd^{2+} , Hg^{2+} , Ag^+ , Al^{3+} , and lanthanide ions (*vide infra*). The second group of metal ions exhibits apparent "blue shifts" in spectra when interacting with the polymers. Typical emission bands appear around 466 nm for polymer **1** and near 466 and 506 nm for polymer **2**. It was also noticed that these bands could only be seen when substantial fluorescence quenching occurred. These metal ions encompass Pb^{2+} , Fe^{2+} , Fe^{3+} , Cu^+ , Sb^{3+} , and lanthanides. The last group of metal ions are those that quench the fluorescence of polymers completely or nearly completely. These quenching metal ions include Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Sn^{2+} , and Pd^{2+} .

Control experiments using a poly(phenylenevinylene) lacking a metal recognition site in lieu of polymers **1** or **2** showed no red-shifting effects at all of both absorption and emission spectra for all metal ions tested. Thus, these findings confirm that the 2,2'-bipyridyl units are indeed essential for ion recognition in polymers **1** and **2**. Further, it was also observed that these 2,2'-bipyridyl phenylenevinylene-based polymers only respond to metal ions excluding alkali and alkaline earth metal ions. These facts are consistent with the poor coordination ability of alkali and alkaline earth metals with 2,2'-bipyridine. The observed ion-induced red-shifting of both the absorption and emission maxima of the polymers are believed to originate from two factors. One, as depicted in Scheme 1, is due to the conjugation enhancement along the polymer backbone induced by metal ion coordination to 2,2'-bipyridyl moieties. The other can be attributed to electron density variations on the main chains of the polymers, caused by introducing positively charged metal ions. Given the fact that trivalent metal ions, such as Fe^{3+} , Sb^{3+} , and Al^{3+} , do not necessarily shift λ_{max} , for instance in absorption spectra, as much as the bivalent (e.g. Fe^{2+} , Sn^{2+} , and Pd^{2+}) or monovalent (e.g. Cu^+) metal ions, it appears that the conformational change of the polymer backbone, namely from partially conjugated to fully conjugated, plays a more important role in red-shifting the spectra of the polymers.

The observed blue-shifted emission bands for the second group of metal ions are certainly not caused by chelation-

Scheme 6. Possible Effects of Coordination Number on Polymer Conformation



initiated conjugation enhancement of the polymer main chain. The bands near 464–472 nm for polymer **1** and 472–480 nm for polymer **2** in fact come from metal–bipyridyl complexes within the polymers, as evidenced by corresponding control experiments of 2,2'-bipyridine with corresponding metal ions. The blue-shifted emission bands around 489–502 nm for polymer **1** and 501–540 nm for polymer **2** are believed to result from a more weakly conjugated state of the polymers. As pointed out earlier, the interplane angle between two pyridyl groups in a transoid-like bipyridine is only about 20° in solution. Therefore, they are in a nearly coplanar state. Two possible coordination interactions between bipyridyls and metal ions lead to two types of conformation changes. As depicted in Scheme 6, if the metal ions coordinate with the bipyridyl groups in a bidentate fashion, then the chelation would force the originally partially coplanar bipyridyl into a fully planar form and thus enhance the conjugation of polymer backbone. On the other hand, if the metal ions interact with bipyridyl in a monodentate way, the steric repulsion between the ligand-containing metal ions and 3,3'-protons on the adjacent pyridyl ring would force the bipyridyl into a more twisted conformation, thus degrading the conjugation of the initial polymer. We reason that it is these deconjugated segments on the polymer chain that cause the blue-shifted emission bands. There may be a three-way equilibrium among these different states of the polymers. The thermodynamic stability of each state, that most likely differs from ion to ion, determines the population of each complex. It is reasonable to believe that the bidentate coordinated, i.e. completely conjugated forms, should exist predominantly due to their thermodynamic advantage. The fact that the blue-shifted emission bands could be seen only when the major, red-shifted fluorescence from the polymers is nearly completely quenched is indicative of the minor population of these deconjugated segments. This notion is also consistent with the observation that there is no noticeable blue shift in absorption spectra for the corresponding polymer–metal complexes. The complete fluorescence quenching of polymers by the third group metal ions is most likely caused by energy or electron transfer reactions between the phenylenevinylene segments and 2,2'-bipyridine complexes.

It is conceivable that conformational changes for a polymer may not occur as readily in the solid state as in solution. From a practical viewpoint, it is interesting to see whether the metal-ion-induced responsive properties described above also hold true in the solid state. To this end, we further tested the metal ion responsive properties of polymer films. As was the case in solution experiments, a quick color change, but over a period of a few seconds, was noticed when the polymer film, spin-coated on glass, was immersed in solutions of salts. Some representative absorption spectra of films, made from polymer **2** and subsequently exposed to metal ions, are presented in

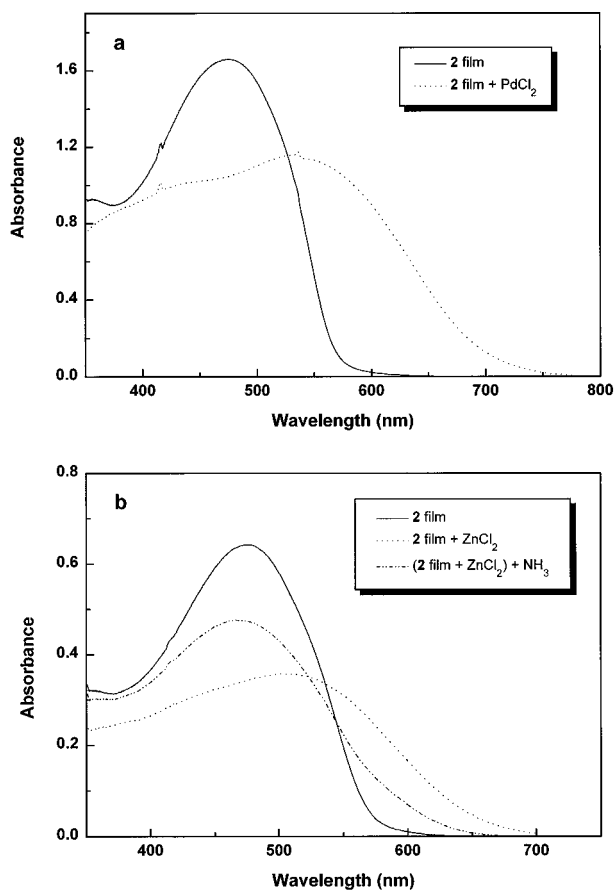


Figure 3. Absorption spectra recorded for (a) polymer **2** film before and after immersion into a PdCl_2 solution in methanol; (b) polymer **2** film before and after immersion first in a ZnCl_2 solution in methanol and then in a methanolic ammonia solution.

Figure 3. Although a significant $\Delta\lambda_{\text{max}}$ can still be seen for the polymer films before and after they were exposed to Pd^{2+} and Zn^{2+} ions, there are in fact some obvious differences in spectra of the films compared to those obtained in solution. First, the magnitudes of the wavelength shifts are smaller for polymer films. For instance, exposure of a film to Pd^{2+} resulted in a 65 nm shift, in contrast to $\Delta\lambda_{\text{max}} = 105$ nm in solution. Similarly, when Zn^{2+} was used as the ion source, a shift of 40 nm to longer wavelength was obtained for the film, as opposed to a shift of 58 nm in solution. Also, the spectra are noticeably broader for the films. Surprisingly though, such broadness extends the spectra not only to the redder but also to the bluer regions. In particular, there are two subtle shoulders that appeared at 443 and 446 nm for the films exposed to Zn^{2+} and Pd^{2+} , respectively.

These observations suggest that conformational changes indeed play a significant role in the ion responsive process of these polymers. For the metal-free polymer, the metal ion recognition unit, i.e. 2,2'-bipyridine, may take either a transoid or cisoid conformation. In solution, the rotation of two pyridyls is relatively free. It thus enables the bipyridyl to adjust its conformation and coordinate with metal ions in a bidentate form. In the solid state, however, only those bipyridyls already in cisoid conformation can undergo a bidentate coordination with metal ions, and thus a lower extent of conjugation is achieved. The rest can only form a monodentate chelation with metal ions. The equilibrium process leading to a bidentate complex, shown in Scheme 6, is no longer as feasible and therefore not favorable. As elucidated earlier, the consequence of these monodentate coordination-induced conformation changes would degrade conjugation of the polymer backbone in the initial complex. Reflected in absorption spectra, less extensive conjugation

enhancement thus results in a less distinct longer wavelength λ_{max} shift, whereas the local deconjugation of polymer backbone accounts for the blue-shifted spectral shoulders. In spite of these metal ion responsive differences between a solution and a film of polymers, it is evident that films of polymers **1** or **2** can still be considered to be quite responsive to metal ions.

One important design criterion for a practical chemosensory material is its reversibility. In other words, such a material should be able to produce a measurable signal in the presence of analytes, but also produce no signal in the absence of analytes. In light of this requirement, we explored the conditions under which metal ions bound to polymers **1** and **2** could be removed. The strategy employed here is simply to add competitive ligands, such as ammonia, into the metal ion-chelated polymer solutions, or, in the solid film case, immerse the metal ion-chelated polymer film in a dilute methanolic ammonia solution. In fact, this turns out to be quite an effective way to convert the metal ion-chelated polymers to their ion-free states. For instance, the color of polymer \cdot Zn complexes changed *instantly* from pink to the original, metal-free polymer's fluorescent yellow when a drop of methanolic ammonia solution (ca. 15 wt % concentration) was added to the polymer \cdot Zn complex solution (2 mL, 1.0×10^{-5} M). Accordingly, the absorption and fluorescence spectra also shifted back to their original wavelengths, as shown in Figure 4 for solution cases and in Figure 3b for the film. However, for the polymer \cdot Pd complex, adding ammonia to the complex solution or immersing the film in a ammonia solution did not remove the Pd from the polymer matrix. As matter of fact, removal of Pd could not be achieved until a stronger ligand, i.e. CN^- , was used (Figure 5). This observation simply reflects the difference in the stabilities of 2,2'-bipyridyl complexes with different metal ions.²¹ Nonetheless, it appears clear that the reversibility of **1** and **2** as ion sensory polymers is readily achievable if an appropriate competitive ligand is chosen. Further, the different degrees of reversibility of different competitive ligands may also open up an additional way of differentiating between metal ions.

As implicated by this finding and encouraged by the observed differences in ion response properties, we chose a palladium salt as a candidate for ion-selective detection tests using **1** and **2** as the sensory polymers. Indeed, a striking palladium ion-selective binding was observed for both polymers **1** and **2**. For example, when a solution of Pd^{2+} with other metal ions, such as Zn^{2+} (1:1 ratio for two ions, five equivalent to 2,2'-bipyridyl units), was added to the polymer **2** solution (2 mL, 1.0×10^{-5} M), only the characteristic absorption and emission spectra corresponding to the complex **2** \cdot Pd were recorded (Figure 6). Hence, such specificity in binding with the polymers, along with its special stability against ammonia, stands out as a very positive way of sensing palladium ions with the presently studied polymers.

Besides the d-transition metal ions and some main group metal ions, we also tested the sensory properties of polymers **1** and **2** toward some f-transition metal ions, i.e. lanthanide salts. It is found that all lanthanide ions tested in this study also clearly demonstrate ionochromic effects (Table 2). Although these lanthanide ions themselves behave similarly in terms of both absorption and emission spectra, they can, however, be differentiated from d-transition metal ions and the main group ions in certain ways. For instance, as illustrated in Figure 7, the fluorescence spectrum of **1** \cdot Er complex shows three emission

(21) For instance, the stability constants for 2,2'-bipyridyl-zinc and -palladium complexes were found to be $\log K_1 = 5.2$ and $\log K_1 = 19.8$, respectively. Cf.: (a) McWhinnie, W. R.; Miller, J. D. In *Advances in Inorganic Radiochemistry*; Emelús, H. J., Sharpe, A. G., Eds.; Academic Press: New York and London, 1969; Vol. 12, p 141. (b) Anderegg, G.; Wanner, H. *Inorg. Chim. Acta* **1986**, *113*, 101.

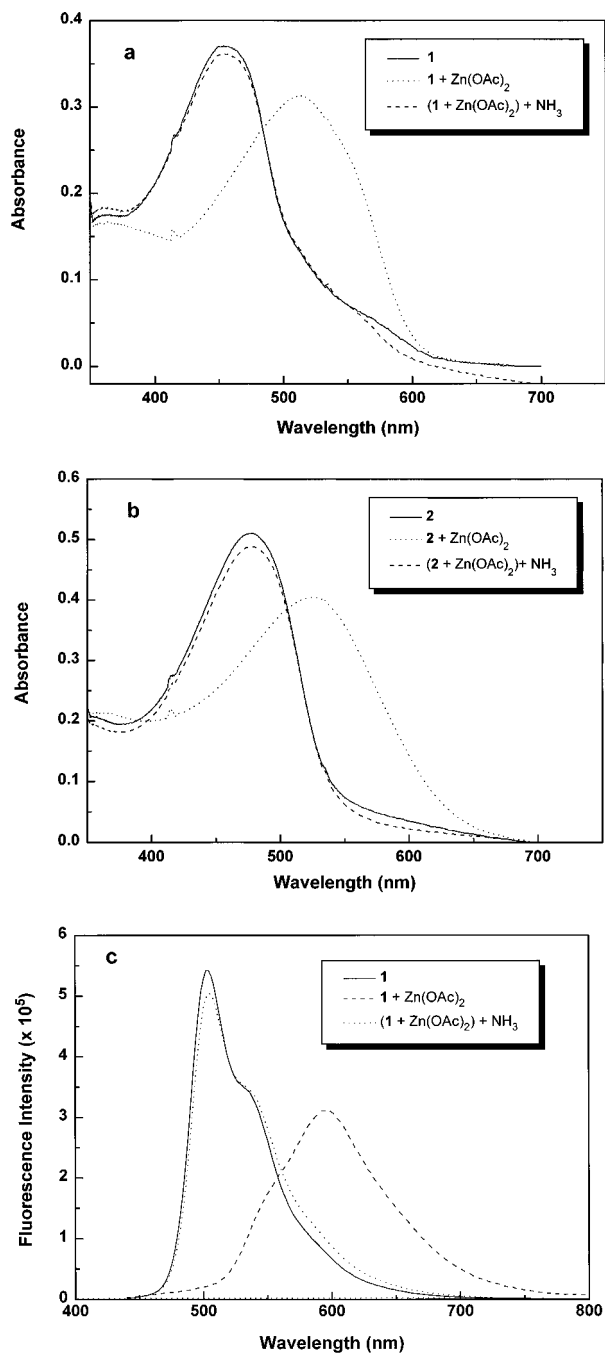


Figure 4. Absorption and fluorescence emission spectra recorded for polymers **1** and **2** and their zinc complexes in CHCl_3 at room temperature. (a) Absorption spectra for polymer **1**, its zinc complex $1 \cdot \text{Zn}$, and the complex with ammonia. (b) Absorption spectra for polymer **2**, its zinc complex $2 \cdot \text{Zn}$, and the complex with ammonia. (c) Emission spectra for polymer **1**, its zinc complex $1 \cdot \text{Zn}$, and the complex with ammonia. Polymer concentration is 1.0×10^{-5} M corresponding to 2,2'-bipyridyl units, and metal ion concentration is about 1.0×10^{-4} M. Excitation wavelength is 410 nm.

bands, at 463, 503, and 602 nm, respectively, which can be considered characteristic compared to those three groups of metal ions discussed earlier (here, Zn^{2+} , Pb^{2+} , and Cu^{2+} are representatives from each group). Perhaps, the more striking difference between these lanthanide chelated polymers and those d-transition metal ion and main group metal ion coordinated polymers is their sensitivity to methanol. Specifically, it was observed that when even a very small amount of methanol was added to the polymers with lanthanides bound, the fluorescence of the polymer complex was further quenched, and the fluorescence of free polymer was gradually restored as more

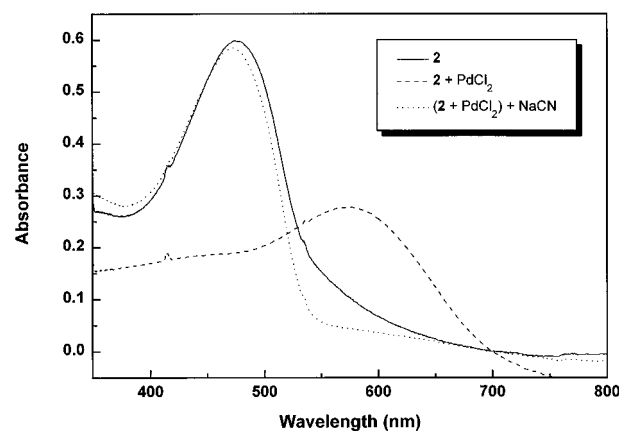


Figure 5. Absorption spectra recorded in CHCl_3 at room temperature for polymer **2** (2 mL, 1.0×10^{-5} M), its complex $2 \cdot \text{Pd}$ (PdCl_2 1.0×10^{-4} M), and the complex after addition of NaCN solution (10 μL , saturated solution in methanol).

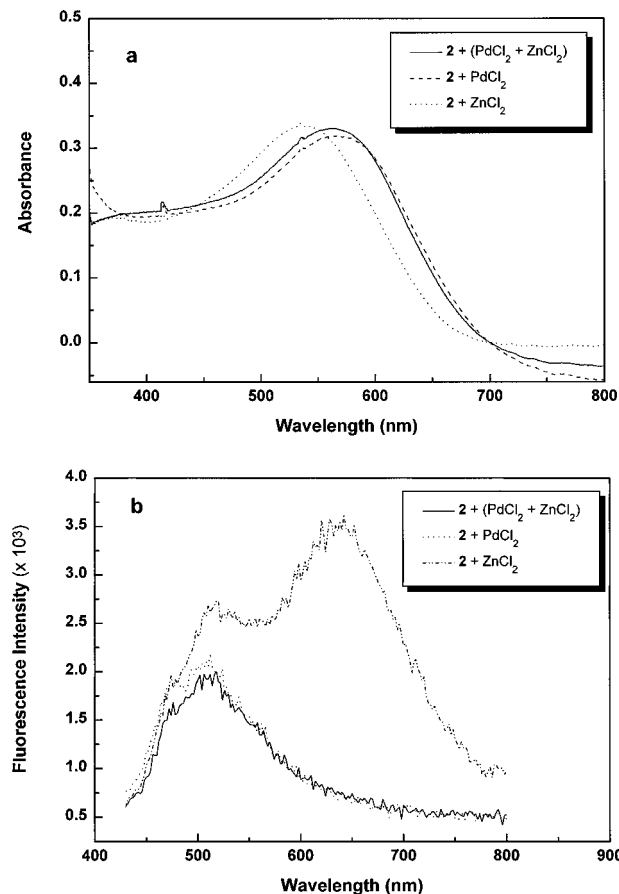


Figure 6. Optical profiles from metal ion specific binding experiments based on polymer **2**. (a) Absorption spectra recorded in CHCl_3 for polymer complexes $2 \cdot \text{Zn}$ and $2 \cdot \text{Pd}$, and a mixture of **2**, PdCl_2 , and ZnCl_2 . (b) Fluorescence emission spectra recorded in CHCl_3 for the same set of polymer complexes.

Table 2. Absorption and Emission Responses of Polymers **1** and **2** upon Chelating Lanthanide Ions

	polymer 1		polymer 2	
	absorption (nm)	emission (nm)	absorption (nm)	emission (nm)
ion-free	455	507	478	544
La^{3+}	506	469, 499, 594	516	524, 657
Ce^{3+}	497	469, 494, 573	518	522, 656
Eu^{3+}	500	466, 499, 560	526	524, 658
Er^{3+}	508	463, 503, 602	524	524, 656
Gd^{3+}	498	466, 500, 594	524	530, 655
Yb^{3+}	512	467, 502, 598	523	526, 656

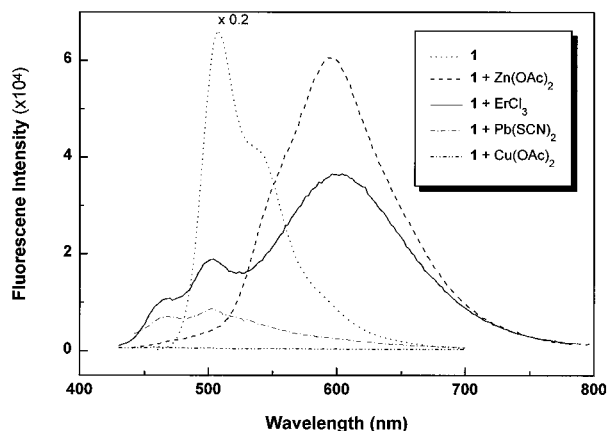


Figure 7. Fluorescence emission spectral comparison between lanthanide-polymer **1** complex and other polymer **1**-based d-transition metal and main group metal complexes. Spectra were recorded in CHCl_3 with an excitation wavelength of 410 nm.

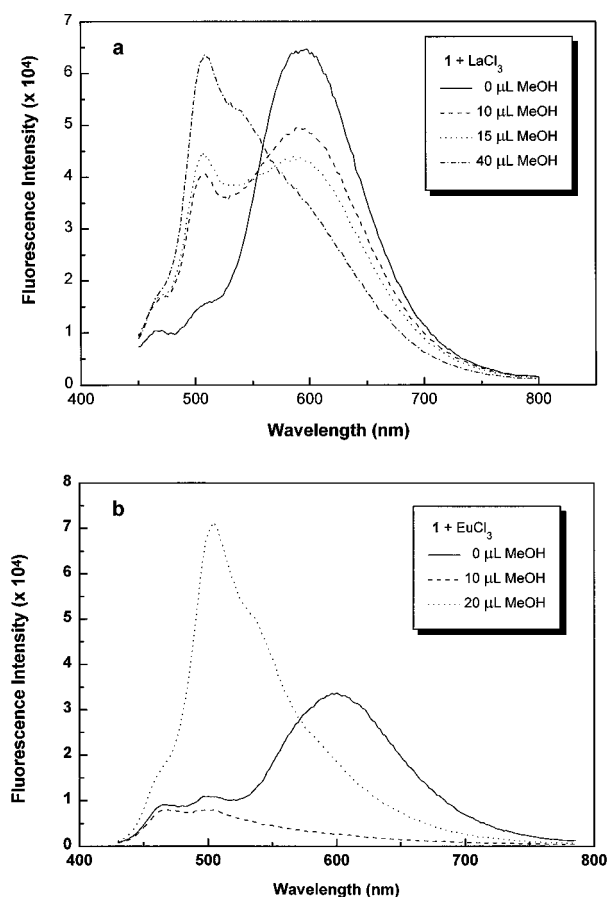


Figure 8. Fluorescence emission profiles for the methanol titration study of two different lanthanide-polymer **1** complexes. (a) Methanol titration to a **1**·La complex. (b) Methanol titration to a **1**·Eu complex. Polymer concentration is 1.0×10^{-5} M corresponding to 2,2'-bipyridyl units, and metal ion concentration is about 1.0×10^{-4} M. Excitation wavelength is 410 nm.

methanol was titrated into the solution (Figure 8a). Quite interestingly, the methanol sensitivity of the lanthanide coordinated polymers also differs from ion to ion. A comparison between polymer **1**·La complex and polymer **1**·Eu complex, for example, indicates that the latter complex is much more sensitive to methanol (Figure 8b). A similar difference was also noticed for other lanthanide-based polymer complexes.

We speculate that the observed methanol-assisted fluorescence quenching (to polymer complexes) and fluorescence restoration

(to free polymers) phenomenon may be caused by two factors. The first is that methanol might be a very good ligand for lanthanides. Binding methanol molecules to a polymer bound lanthanide, which is capable of accepting as many as eight ligands, alters the electronic properties of this metal ion. As a result, it modifies the rate of energy or electron transfer from polymer to metal ion. The second factor is that the binding between the lanthanide and 2,2'-bipyridyl is probably not strong enough to compete against methanol. Once all the coordination sites are occupied, the 2,2'-bipyridyl units are replaced by methanol, ultimately converting the polymer-metal complexes to metal-free polymers.

This unique methanol sensitivity of lanthanide-based polymers may thus furnish some useful features in terms of metal ion sensors. It provides an extremely simple and convenient means of converting the sensory polymers to their original state, offering excellent reversibility. More importantly, it may also establish the parent polymers **1** and **2** as lanthanide specific sensory materials. It does so not only because these polymers can sensitively respond to the presence of metal ions from this group, but also because their metal complexes can further signal the existence of second analytes, such as a simple methanol molecule. It is this sequential sensing capability that should enable polymers **1** and **2** to differentiate the lanthanides from other main group and transition metal ions. Furthermore, the differences in methanol sensitivity among the lanthanide-based polymers also yield a way to distinguish between the lanthanides themselves.

Concluding Remarks. We have designed and synthesized two bipyridyl-phenylenevinylene-based polymers (**1** and **2**) for metal ion sensor studies. These polymers are found to be highly ionochromic to a wide variety of transition metal ions and main group metal ions excluding the alkali and alkaline earth metal ions. The sensitivity of these polymers arises from ion-recognition-induced conjugation enhancement and electronic density changes on the polymer backbones. The observed ionochromic responses are, to a certain degree, ion dependent. The dependence of the response may be associated with metal ion size, coordinating ability with 2,2'-bipyridyl, redox properties, etc. The most striking finding perhaps is the specific sensing of palladium ion by both polymers. Reversibility of these polymers as ionosensitive materials is excellent. The conversion of metal ion chelated polymers to their original state, i.e. metal free polymers, can be readily achieved by treating them with various competitive ligands, such as ammonia or cyanide depending on metal-polymer complexes. The sensory responses of polymers **1** and **2** toward lanthanides are basically distinguishable from d-transition and main group metal ions in both absorption and emission spectra. More importantly, the resultant polymer-metal complexes demonstrate unique high sensitivity to such analytes as methanol, which permits further differentiation from d-transition and main group metal ions. This finding thus serves to implicate another potential application of polymers **1** and **2** as sequential and multiple purpose sensory materials. It appears especially true when considering the fact that after the first sensory event, namely binding the transition metal ions to the polymer, the resultant polymer-metal complex could still bind various kinds of ligands. Binding the second type of ligand to the polymer-metal complex in turn would change the electronic structure of the complex, which would enable the polymer to produce a second, new signal. In summary, the study presented herein has demonstrated a new approach to sensitive, selective, and highly reversible metal ion responsive polymers.

Experimental Section

General Information. Proton and carbon nuclear magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded on General Electric GE-300 or Bruker 500 NMR spectrometers using tetramethylsilane (TMS) as internal standard. Laser desorption mass spectra were obtained with a Kratos MALDI III spectrometer. UV/visible spectra were obtained using a Shimadzu UV-160 spectrophotometer. Fluorescence spectra were recorded using a Photon Technology International fluorimeter. Absorption and fluorescence emission measurements of polymeric sample solutions were carried out in chloroform with a concentration of 1.0×10^{-5} M relative to repeating units in a polymer. THF used for reactions was prepared by distillation from LiAlH_4 and stored over dry molecular sieves. Solvents DMF and toluene were dried over dry molecular sieves for at least 2 days. All other solvents and reagents were of reagent grade quality and used as received. Molecular weights of polymers were determined by using a Beckman 110B solvent delivery module system, Phenomex Phenogel columns with 500 Å and 1000 Å pore size, and a Waters variable wavelength detector, at a flow rate of 1.0 mL/min. All molecular weights were measured against polystyrene standards in THF. Thin layer chromatography (TLC) was performed on commercially prepared silica gel plates purchased from Whatman International, Inc. Column chromatography was performed using Merck silica gel 60.

Synthesis. 1,4-Bis(decyloxy)benzene (4). A suspension of 1,4-hydroquinone **3** (27.5 g, 250 mmol), 1-bromodecane (155 mL, 750 mmol), and K_2CO_3 (104.0 g, 750 mmol) in acetonitrile (500 mL) was heated at reflux for two days before being poured into water (600 mL). The precipitates were first collected by filtration and then dissolved in a minimum of hot hexane. Subsequently, the resulting hot solution was poured into methanol (600 mL) to precipitate the product. The precipitates were filtered off and dissolved in hot hexane (200 mL) again. Reprecipitation of resulting solution in methanol then gave 83.0 g pure product **4** as a white solid after filtered and dried under vacuum (85%). ^1H NMR (CDCl_3) δ (ppm) 0.88 (t, $J = 6.86$ Hz, 6H, CH_3), 1.27 (m, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.45 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.78 (quintet, 4H, $J = 8.14$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 3.85 (t, $J = 6.40$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 6.82 (s, 4H, aromatic). Mass spectrum m/e calcd for $\text{C}_{26}\text{H}_{46}\text{O}_2$: 390.6, found 390.6.

2,5-Bis(bromomethyl)-1,4-bis(decyloxy)benzene (5). To a suspension of **3** (5.9 g, 15.1 mmol) and paraformaldehyde (0.93 g, 31.0 mmol) in acetic acid (50 mL) was added HBr (6.0 mL, 31 wt % in acetic acid) all at once. This mixture was then heated to 60–70 °C with stirring for 2 h. As the reaction proceeded, the suspension changed to clear solution first and then became a thick suspension again. After cooling to room temperature, this suspension was poured into water (300 mL). The precipitates were filtered and dissolved in hot chloroform. Reprecipitation of resulting solution in methanol then gave **5** (7.5 g, 86.1% yield) as a white, loose solid after being filtered and dried under vacuum. ^1H NMR (CDCl_3) δ (ppm) 0.88 (t, $J = 6.42$ Hz, 6H, CH_3), 1.28 (m, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.49 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.81 (quintet, 4H, $J = 6.43$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 3.98 (t, $J = 6.42$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 4.52 (s, 4H, CH_2Br), 6.85 (s, 2H, aromatic). ^{13}C NMR (CDCl_3) δ (ppm) 14.1 ($\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 22.7 ($\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{CH}_3$), 26.1 ($\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{CH}_3$), 28.7 (CH_2Br), 29.3–29.5 ($\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{CH}_3$), 31.9 ($\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{CH}_3$), 69.0 ($\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{CH}_3$), 114.6 (C3,C6), 127.5 (C1,C4), 150.6 (C2,C5). Mass spectrum m/e calcd for $\text{C}_{28}\text{H}_{48}\text{BrO}_2$: 576.7, found 576.2.

2,5-Bis(acetylmethyl)-1,4-bis(decyloxy)benzene (6). A solution of **4** (6.0 g, 10.4 mmol), potassium acetate (3.1 g, 31.3 mmol), and tetra-*n*-butylammonium bromide (0.5 g) in a mixture of acetonitrile (100 mL) and chloroform (50 mL) was heated at reflux overnight. The resulting mixture was poured in water (200 mL) and extracted with chloroform (3×100 mL). The extracts were combined and washed with water (2×100 mL). Solvent from the resultant organic solution was removed on a rotary evaporator after drying over anhydrous sodium sulfate. This furnished product **6** (5.6 g, 100% yield). ^1H NMR (CDCl_3) δ (ppm) 0.88 (t, $J = 6.85$ Hz, 6H, CH_3), 1.27 (m, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.44 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.76 (quintet, 4H, $J = 6.83$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 3.94 (t, $J = 6.43$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 5.14 (s, 4H, CH_2OAc), 6.88 (s, 2H, aromatic). Mass spectrum m/e calcd for $\text{C}_{32}\text{H}_{54}\text{O}_6$: 534.8, found 534.9.

2,5-Bis(hydroxymethyl)-1,4-bis(decyloxy)benzene (7). To a suspension of LiAlH_4 (0.9 g, 22.4 mmol) in dry THF was added a solution of **6** (3.0 g, 5.6 mmol) in dry THF (100 mL) dropwise. The mixture was stirred at room temperature for 2 h. The excess of LiAlH_4 was quenched by addition of ethyl acetate at 0 °C. The resulting suspension was poured into water and followed by extraction with chloroform (3×75 mL). The extracts were combined and washed with water (2×100 mL). Removal of solvent under reduced pressure on a rotary evaporator furnished a white solid. It weighed 2.5 g (99.1% yield) after drying under vacuum. ^1H NMR ($\text{CDCl}_3 + \text{CD}_3\text{OD}$) δ (ppm) 0.89 (t, $J = 6.30$ Hz, 6H, CH_3), 1.28 (m, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.44 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.78 (quintet, 4H, $J = 6.30$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 3.97 (t, $J = 6.31$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 4.67 (s, 4H, CH_2OH), 6.92 (s, 2H, aromatic).

2,5-Bis(decyloxy)benzene-1,4-dialdehyde (8). A suspension of **7** (2.4 g, 5.3 mmol) and pyridinium chlorochromate (PCC) (4.6 g, 21.3 mmol) in methylene chloride (200 mL) was stirred at room temperature for 2 h. The reaction mixture was then directly transferred onto the top of a short silica gel column. The highly fluorescent product **8** was then washed off the column with chloroform. Thus, compound **8** was obtained in 85.8% (2.03 g). ^1H NMR (CDCl_3) δ (ppm) 0.88 (t, $J = 6.90$ Hz, 6H, CH_3), 1.28 (m, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.45 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.84 (quintet, 4H, $J = 6.61$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 4.08 (t, $J = 6.60$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 7.43 (s, 2H, aromatic), 10.52 (s, 2H, CHO). ^{13}C NMR δ (ppm) 14.1 ($\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 22.6 ($\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{CH}_3$), 26.0 ($\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{CH}_3$), 29.0–29.5 ($\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{CH}_3$), 31.8 ($\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{CH}_3$), 69.2 ($\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{CH}_3$), 111.5 (C3,C6), 129.2 (C1,C4), 155.2 (C2,C5), 189.4 (CHO). Mass spectrum m/e calcd for $\text{C}_{28}\text{H}_{48}\text{O}_4$ ($\text{M}^+ + 2\text{H}$): 448.7, found 448.4.

2,5-Bis(decyloxy)-1,4-bis(2,5-didecoxy-4-formyl)phenylenevinylenebenzene (10). A suspension of **5** (0.576 g, 1.0 mmol) and triphenylphosphine (0.550 g, 2.1 mmol) in toluene was heated at reflux for 3 h. The solvent was then removed from the resulting clear solution under reduced pressure. The resulting residue, along with dialdehyde **8** (0.893 g, 2.0 mmol), was dissolved in methylene chloride (50 mL). To this solution was added lithium ethoxide solution (2.5 mL, 1.0 M in ethanol) dropwise via a syringe at room temperature. The base should be introduced at such a rate that the transient red-purple color produced upon the addition of base should not persist. The resulting solution was allowed to stir for 10 min more after the completion of base addition. This solution was then poured into a dilute aqueous HCl. The organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. The residues, after removal of solvents, contained both *E*- and *Z*-isomers. A solution of this isomer mixture and iodine (500 mg) in methylene chloride (50 mL) was stirred at room temperature overnight. The dark brown solution was then diluted with methylene chloride and washed consecutively with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution (1.0 M, 2×75 mL) and water. After concentration on a rotary evaporator, this solution was loaded onto a silica gel column and eluted with a mixture of hexane and chloroform (1:1 v/v). This afforded 1.07 g of compound **10** as a yellow fluorescent solid. Yield 83.9%. ^1H NMR (CDCl_3) δ (ppm) 0.85–0.89 (m, 18H, CH_3), 1.25–1.40 (m, 72H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.47–1.57 (m, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.83–1.90 (m, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_3$), 4.02–4.12 (m, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 7.15 (s, 2H, central phenyl-*H*), 7.20 (s, 2H, aromatic H3,H3'), 7.33 (s, 2H, aromatic H2,H2'), 7.49 (d, $J = 16.56$ Hz, vinyl-*H*), 7.58 (d, 2H $J = 16.53$ Hz, vinyl-*H*), 10.45 (s, 2H, CHO). Mass spectrum m/e calcd for $\text{C}_{84}\text{H}_{140}\text{O}_8$ ($\text{M}^+ + 2\text{H}$): 1278.0, found 1278.0.

[[5-(Bromomethyl)-2,2'-bipyridin-5-yl]methyl]phosphonium Bromide (12). A mixture of 5,5'-bis(bromomethyl)-2,2'-bipyridine **12**¹⁸ (0.34 g, 1.0 mmol) and triphenylphosphine (0.52 g, 2.0 mmol) in toluene (25 mL) was heated at reflux for 2 h. The white precipitate was filtered off while the suspension was still hot. The collected solid was washed with toluene and subsequently dried under vacuum. This afforded the monophosphonium salt (**12**) as a white solid (0.60 g, 99.3% yield). ^1H NMR (CDCl_3) δ (ppm) 4.51 (s, 2H, CH_2Br), 5.90 (d, $J = 17$ Hz, 2H, CH_2PPh_3 and pyridyl H4 and H4'), 7.60–7.89 (m, 15H, phenyl-*H*), 8.01 (d, $J = 8.13$ Hz, 2H, pyridyl H3), 8.15 (d, $J = 8.14$ Hz, 2H, pyridyl H3'), 8.32 (s, H, pyridyl H6), 8.55 (s, 1H, pyridyl H6').

2,5-Bis(decyloxy)-4-[[5'-(bromomethyl)-2,2'-bipyridin-5-yl]vinyl]benzaldehyde (13a) and 2,5-Bis(decyloxy)-1,4-bis[[5'-(bromomethyl)-2,2'-bipyridin-5-yl]vinyl]benzene (13b). To a solution of compounds **12** (0.60 g, 1.0 mmol) and **8** (0.45 g, 1.0 mmol) in methylene chloride (30 mL) was added lithium ethoxide (1.0 mL, 1.0 M solution in THF) dropwise via a syringe at room temperature. The resulting solution was allowed to stir at room temperature for 3 h before being poured into water. The organic phase was separated and washed with water. Solvent was then taken off under reduced pressure. The residue, dissolved in small amount of chloroform, was loaded onto the top of a silica gel column. Elution with 0–0.25% MeOH in CHCl₃ thus gave rise to product **13a** as a yellow solid (0.34 g, 49.1% yield) and product **13b** as a brown solid (0.11 g, 11.3% yield), respectively. Further *Z*- to *E*-isomerizations were achieved by heating solution of the respective compound in toluene in the presence of TsOH overnight. For **13a**: ¹H NMR (CDCl₃) δ (ppm) 0.89 (m, 6H, CH₃), 1.26 (m, 12H, OCH₂CH₂CH₂(CH₂)₆CH₃), 1.51 (m, 4H, OCH₂CH₂CH₂(CH₂)₆CH₃), 1.87 (quintet, 4H, *J*' = 6.42 Hz, *J*'' = 6.43 Hz, OCH₂CH₂CH₂(CH₂)₆CH₃), 4.06 (t, *J* = 6.43 Hz, 2H, OCH₂CH₂CH₂(CH₂)₆CH₃), 4.13 (t, *J* = 6.43 Hz, 2H, OCH₂CH₂CH₂(CH₂)₆CH₃), 4.55 (s, 2H, CH₂Br), 7.20 (s, 1H, phenyl-*H*), 7.33 (d, *J* = 15.85 Hz, vinyl-*H*), 7.35 (s, 1H, phenyl-*H*), 7.58 (d, *J* = 16.71 Hz, vinyl-*H*), 7.88 (dd, *J*' = 8.47 Hz, *J*'' = 2.14 Hz, 1H, pyridyl H₄), 8.04 (dd, *J*' = 8.57 Hz, *J*'' = 2.14 Hz, 1H, pyridyl H₄'), 8.45 (dd, *J*' = 8.04 Hz, *J*'' = 2.57 Hz, 2H, pyridyl H₃ and H₃'), 8.71 (s, 1H, pyridyl H₆), 8.82 (s, 1H, pyridyl H₆'), 10.47 (s, 1H, CHO). Mass spectrum *m/e* calcd for C₄₀H₅₅BrN₂O₃: 691.8, found 691.7. For **13b**: ¹H NMR (CDCl₃) δ (ppm) 0.87 (m, 6H, CH₃), 1.01–1.85 (m, 32H, OCH₂(CH₂)₈CH₃), 4.00 (t, *J* = 5.57 Hz, 4H, OCH₂(CH₂)₈CH₃), 4.55 (s, 4H, CH₂Br), 7.16 (s, 2H, phenyl-*H*), 7.24 (d, *J* = 16.77 Hz, vinyl-*H*), 7.66 (d, 2H, *J* = 16.27 Hz, vinyl-*H*), 7.87 (d, 2H, *J* = 7.71 Hz, pyridyl H₄ and H₄''), 7.88 (d, *J* = 7.38 Hz, pyridyl H₄' and H₄'''), 8.43 (d, *J* = 8.57 Hz, pyridyl H₃, H₃', H₃'', and H₃'''), 8.69 (s, 2H, pyridyl H₆ and H₆''), 8.80 (s, 2H, pyridyl H₆' and H₆'''). Mass spectrum *m/e* calcd for C₅₂H₆₂Br₂N₄O₂: 934.9, found 934.4.

Compounds 14a and 14b. To a solution of compounds **12** (0.237 g, 0.39 mmol) and **10** (0.500 g, 0.39 mmol) in methylene chloride (50 mL) was added lithium ethoxide (0.4 mL, 1.0 M solution in THF) dropwise via a syringe at room temperature. The resulting solution was allowed to stir at room temperature for 24 h before being poured into methanol. The orange precipitate was filtered off by suction. The solid was dissolved in small amount of chloroform and loaded onto the top of a silica gel column. Elution with 0–0.25% MeOH in CHCl₃ thus gave rise to product **14a** as a brown solid (0.15 g, 25.3% yield) and product **14b** as a dark brown solid (0.24 g, 34.9% yield), respectively. Further *Z*- to *E*-isomerizations were achieved by heating solutions of the respective compounds in toluene in the presence of TsOH overnight. For **14a**: ¹H NMR (CDCl₃) δ (ppm) 0.87 (m, 18H, OCH₂CH₂CH₂(CH₂)₆CH₃), 1.26 (m, 72H, OCH₂CH₂CH₂(CH₂)₆CH₃), 1.54 (m, 12H, OCH₂CH₂CH₂(CH₂)₆CH₃), 1.88 (m, 12H, OCH₂CH₂CH₂(CH₂)₆CH₃), 4.07 (m, 12H, OCH₂CH₂CH₂(CH₂)₆CH₃), 4.55 (s, 2H, CH₂Br), 7.15 (s, 2H, phenyl H₃' and H₆''), 7.18 (d, *J* = 14.5 Hz, 2H, vinyl-*H*), 7.21 (d, *J* = 14.77 Hz, 2H, vinyl-*H*), 7.33 (s, 1H, phenyl H₆), 7.52 (s, 3H, phenyl H₃, H₃', and H₆'), 7.62 (d, *J* = 16.52 Hz, vinyl-*H*), 7.64 (d, *J* = 16.49 Hz, vinyl-*H*), 7.87 (d, *J* = 8.23 Hz, 1H, pyridyl H₄), 8.00 (d, *J* = 8.35 Hz, 1H, pyridyl H₄'), 8.42 (d, *J* = 8.24 Hz, 1H, pyridyl H₃), 8.43 (d, *J* = 8.16 Hz, 1H, pyridyl H₃'), 8.70 (s, 1H, pyridyl H₆), 8.80 (s, 1H, pyridyl H₆'), 10.45 (s, 1H, CHO). Mass spectrum *m/e* calcd for C₉₆H₁₄₇N₂O₇ (M⁺ – Br): 1441.2, found 1441.5. For **14b**: ¹H NMR (CDCl₃) δ (ppm) 0.87 (m, 18H, OCH₂CH₂CH₂(CH₂)₆CH₃), 1.26 (m, 72H, OCH₂CH₂CH₂(CH₂)₆CH₃), 1.55 (m, 12H, OCH₂CH₂CH₂(CH₂)₆CH₃), 1.88 (m, 12H, OCH₂CH₂CH₂(CH₂)₆CH₃), 4.08 (m, 12H, OCH₂CH₂CH₂(CH₂)₆CH₃), 4.55 (s, 4H, CH₂Br), 7.15–7.22 (m, 6H, phenyl H₃, H₆, H₆', H₆'' and vinyl-*H*), 7.26 (m, 2H, vinyl-*H*), 7.52 (m, 4H, phenyl H₃', H₃'', vinyl-*H*), 7.61 (d, *J* = 16.48 Hz, 2H, vinyl-*H*), 7.87 (d, *J* = 8.20 Hz, 2H, pyridyl H₄ and H₄'), 8.00 (d, *J* = 6.59 Hz, 2H, pyridyl H₄' and H₄'''), 8.41 (m, 1H, pyridyl H₃, H₃', H₃'', and H₃'''), 8.69 (s, 2H, pyridyl H₆, H₆'), 8.80

(s, 2H, pyridyl H₆' and H₆'''). Mass spectrum *m/e* calcd for C₁₀₈H₁₅₆N₄O₆ (M⁺ – 2Br): 1606.5, found 1606.3.

Polymer 1. Route A: A suspension of **13b** (0.108 g, 0.115 mmol) and triphenylphosphine (0.100 g, 0.380 mmol) in DMF (25 mL) was heated at reflux for 4 h before letting it cool. To this clear solution was added lithium ethoxide (230 μL, 1.0 M in THF) all at once. Subsequent addition of compound **8** to this deep red solution did not result in a homogenous solution. However, compound **8** (0.051 g, 0.115 mmol) started to dissolve and the red color began to fade gradually when heating the mixture near 100 °C. Soon after the clear solution was obtained, a yellow-brown solid precipitated out. Heating was continued for 2 h, and then the reaction mixture was allowed to cool down to room temperature. The solid was collected by suction filtration and dried under vacuum (55 mg, 40.2%). Extraction with a micro-Soxhlet extractor using ethyl acetate as the solvent for 24 h (until the extract was colorless) then afforded polymer **1** with an average molecular weight of 5800 based on polystyrene standard by GPC.

Polymer 1. Route B: A solution of **13a** (0.34 g, 0.49 mmol) and triphenylphosphine (0.144 g, 0.55 mmol) in toluene (20 mL) was heated at reflux for 4 h. The solvent was then removed on a rotary evaporator under reduced pressure. To a solution of the resulting residue in methylene chloride was added lithium ethoxide via a syringe dropwise. The reaction mixture was allowed to stir at room temperature for 48 h before being poured into methanol (500 mL). The precipitates were filtered by suction and subsequently dissolved in CHCl₃ and washed with water. Removal of solvent under reduced pressure afforded polymer **1** as a dark brown solid (0.26 g, 89.2% yield). Further extraction of the obtained polymer with a micro-Soxhlet extractor using ethyl acetate as the solvent until the extract was colorless gave a polymer with *M_n* = 6400 by GPC. ¹H NMR (CDCl₃) δ (ppm) 0.89 (br, OCH₂CH₂CH₂(CH₂)₆CH₃), 1.28 (br, OCH₂CH₂CH₂(CH₂)₆CH₃), 1.58 (br, OCH₂CH₂CH₂(CH₂)₆CH₃), 1.92 (br, OCH₂CH₂CH₂(CH₂)₆CH₃), 4.11 (br, OCH₂CH₂CH₂(CH₂)₆CH₃), 7.17 (br, phenyl-*H*), 7.49–7.70 (m, vinyl-*H*), 7.98 (br, pyridyl H₄), 8.44 (br, pyridyl H₃), 8.80 (br, pyridyl H₆).

Polymer 2. A solution of compound **14a** (0.15 g, 98.6 μmol) and triphenylphosphine (50 mg, 190 μmol) in toluene (20 mL) was heated at reflux for 4 h. After being cooling to room temperature, lithium ethoxide (100 μL, 1.0 M in THF) was added to this solution dropwise. The resulting solution was heated at reflux for an additional 48 h. The product was precipitated out from methanol and collected by filtration. This furnished polymer **2** as a dark brown solid (0.13 g, 92.6% yield). Further extraction of the obtained polymer with a micro-Soxhlet extractor using ethyl acetate as the solvent until the extract was colorless gave a polymer with *M_n* = 22000 by GPC. ¹H NMR (CDCl₃) δ (ppm) 0.87 (br, OCH₂CH₂CH₂(CH₂)₆CH₃), 1.28 (br, OCH₂CH₂CH₂(CH₂)₆CH₃), 1.56 (br, OCH₂CH₂CH₂(CH₂)₆CH₃), 1.90 (br, OCH₂CH₂CH₂(CH₂)₆CH₃), 4.09 (br, OCH₂CH₂CH₂(CH₂)₆CH₃), 7.15 (br, phenyl-*H*), 7.46–7.75 (m, vinyl-*H*), 8.00 (br, pyridyl H₄), 8.42 (br, pyridyl H₃), 8.80 (br, pyridyl H₆).

Polymer–Metal Complex Formation. Polymer–metal complex solutions used for optical measurements in general were prepared from a polymer solution (2 mL, 1.0 × 10^{−5} M in chloroform) and a metal salt solution (0.1–0.2 mL, 1.0 × 10^{−3} M in methanol) at room temperature. The polymer–lanthanide complexes were prepared the same way as other transition and main group metal-based polymer complexes except the solvents were evaporated off after mixing polymer and metal ion together so that they were methanol-free once redissolved in chloroform. Polymeric films were made by spin-coating solutions of the polymers on glass plates.

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