Poly[*p*-(phenyleneethynylene)-*alt*-(thienyleneethynylene)] Polymers with Oligopyridine Pendant Groups: Highly Sensitive Chemosensors for Transition Metal Ions

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ABSTRACT: We report the synthesis and characterization of a series of luminescent chemosensory materials that have the conjugated polymer poly[*p*-(phenyleneethynylene)-*alt*-(thienyleneethynylene)] (PPETE) as a backbone and oligopyridine pendant sites as receptors. These polymers are soluble in common organic solvents and highly emissive. Investigations reveal that these polymers are highly sensitive to transition metal ions such as Ni^{2+}. For the terpyridine−receptor polymer ttp−PPETE, we observed ~5% initial emission quenching by Ni^{2+} concentration as low as 4×10^{-9} M. The polymers also show selectivity to different transition metal ions. The ether-linked polymer ttp−O−PPETE is also prepared which successfully demonstrates that complete conjugation is not required for emission quenching. However, the vinylene-linked ttp−PPETE was found to have a higher quenching efficiency.

Introduction

The toxicity of certain metal ions has been a constant cause of environmental concern. Thirteen heavy metal ions are listed as “priority pollutants” by the Environmental Protection Agency (EPA).[1] These metals, in different oxidation states, include chromium, manganese, cobalt, copper, zinc, molybdenum, silver, mercury, cadmium, lead, and nickel. Although a number of laboratory-based methods are available for determining the presence of trace metals/radionuclides in the environment,[2] there is an increasing need for the development of field-based sensors and remediation devices, demanding new chemosensory materials and novel, low-cost synthetic designs.

Because of their high sensitivity and ease of measurement, fluorescent sensors have received significant attention for a variety of environmental applications.[3] Conjugated polymers as fluorescent sensors are particularly attractive due to their enhanced electronic communication properties. Several groups including the seminal work by Swager et al.[4] have demonstrated that polyreceptor assemblies, electronically connected by a conjugated “molecular wire” polymer, exhibit large sensitivity enhancement over conventional molecule-based fluorescent chemosensors. The energy-transfer process can be illustrated using the state diagram shown in Figure 1. The initial excitation leads to formation of an exciton which can rapidly migrate between isoenergetic sites along the conjugated polymer backbone to a low-energy acceptor site. The result is an efficient fluorescence quenching mechanism even at very low quencher concentrations since the binding of one receptor site results in efficient quenching of several emitting units along the polymer backbone.

Lewis bases such as oligopyridyl ligands are known to coordinate a large number of transition metal ions. There are only a limited number of reports involving incorporating oligopyridyl ligands into conjugated polymers.[5−7] Wang and Wasielewski have demonstrated that when 2,2′-bipyridine was introduced into a conjugated polymer backbone, the absorption and emission profiles changed significantly upon binding different transition metals to the polymer.[5] More recently, Kimura et al. prepared PPV-based conjugated polymers with terpyridine units bound directly to the conjugated polymer framework. In the presence of transition metals, both the absorption and emission spectrum were found to shift in a quantifiable manner.[6]

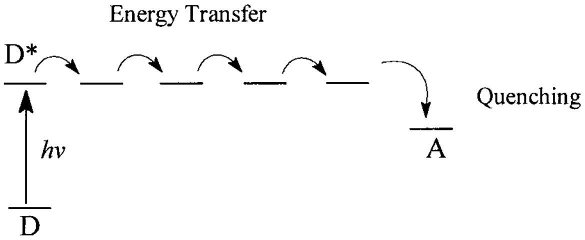

Figure 1. Illustration of energy-transfer quenching through a conjugated polymer.

Here we report the synthesis and characterization of a series of new chemosensory polymers, poly[*p*-(phenyleneethynylene)-*alt*-(thienyleneethynylene)] (PPETE) with oligopyridine pendant groups as receptors for transition metals. This new system takes advantage of the strong conjugation and luminescence properties of the polyarylene ethynylene backbone and multidentate Lewis base coordinating ability of oligopyridines to yield a highly effective transition-metal chemosensor. Given the conformational flexibility of the linking group in our PPETE systems, a fundamental question, which resulted from preliminary investigations, involved the role of pendant receptor conjugation with the backbone in the quenching mechanism. In previous literature examples, the receptor site was bound within the conjugation of the backbone.[5,6] To address this question, we have prepared two different PPETEs (ttp−PPETE and ttp−O−PPETE) with different linker groups which vary the extent of conjugation between the backbone and the receptor site (Figure 2). Fluorescence quenching experi-

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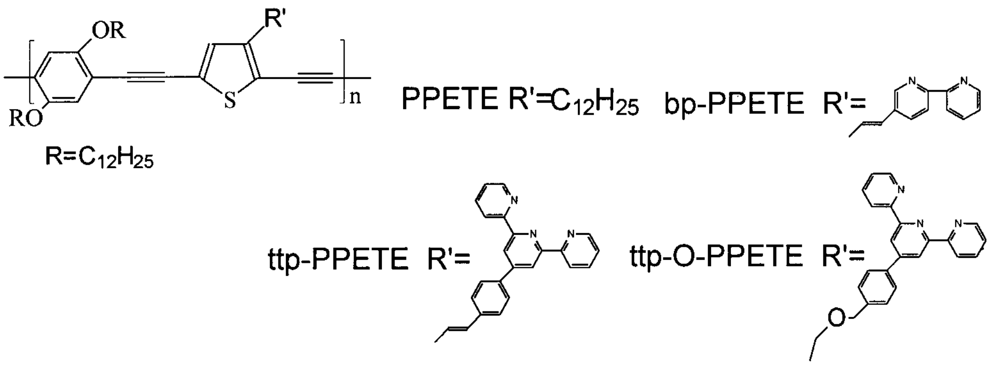
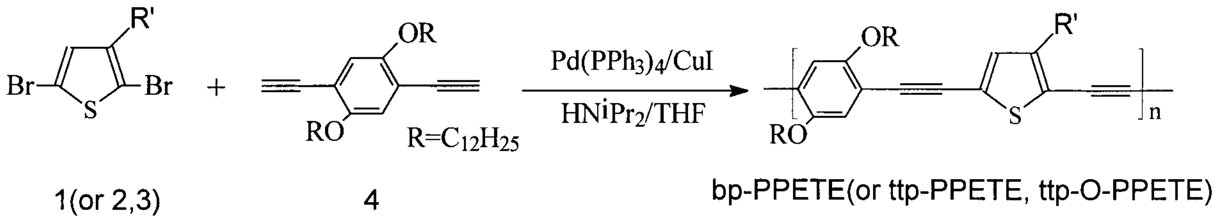


Figure 2. Structure of PPETE polymers.

Scheme 1. Synthesis of PPETE Polymers by Palladium-Catalyzed Coupling



ments enable us to determine whether complete conjugation is a requirement for efficient chemosensory activity.

Experimental Section

Materials. All materials were purchased from Aldrich and used as received unless otherwise noted. The compounds 1,4-diethynyl-2,5-diiododecyloxybenzene (**4**),[8] 5-bromomethyl-2,2′-bipyridine (**7**),[9] 4′-(4-bromomethyl-phenyl)-[2,2′:6′,2″]-terpyridine (**8**),[10] and 2,5-diiodo-3-dodecylthiophene[11] were synthesized as described previously. Satisfactory NMR characterization of all stable intermediates was observed in each case.

General Methods. NMR (^{1}H and ^{13}C) spectra were recorded on an AM-360 spectrometer. Elemental analyses were performed by QTI, Inc. Gel permeation chromatography was used to measure the molecular weight of all polymers in toluene relative to polystyrene standards. UV–vis spectra of the polymers were obtained on a Perkin-Elmer Lambda 2S spectrophotometer in tetrahydrofuran (THF) solution unless otherwise noted. Fluorescence spectra were measured on an SLM 48000s fluorimeter with variable excitation between 300 and 460 nm with 4 nm slits. Fluorescence solutions were prepared with absorption at the excitation maximum of 0.1–0.2 o.d. Quantum yields were determined relative to anthracene in ethanol with a quantum yield of 0.27 ± 0.03.[12,13] Lifetimes were measured using single-photon counting at the Regional Laser and Biotechnology Laboratory at University of Pennsylvania using a system that has been described elsewhere.[14]

Synthesis. *2,5-Dibromothiophene-3-carbaldehyde* (**5**) (Scheme 2, eq 1). To a solution of 3-thiophenecarboxaldehyde (2.5 g, 0.020 mol) in 50 mL of chloroform was added anhydrous sodium bicarbonate (4.2 g), followed by the dropwise addition of a solution of bromine (8.2 g in 50 mL of chloroform) over a period of 1 h. The reaction mixture was stirred overnight at room temperature and then filtered. The filtrate was washed with water (2 × 100 mL) and dried over $MgSO_4$. The solvent was evaporated, and the solid residue was chromatographed (silica, hexane:ethyl acetate 20:1) to give a light yellow solid **6** (yield: 75%).^{1}H NMR (360 MHz, $CDCl_3$): δ 9.78 (s, 1H, CHO), 7.33 (s, 1H). ^{13}C NMR ($CDCl_3$): 189.14, 139.33, 128.68, 124.18, 113.36. Elemental analysis: Calcd for $C_5H_2Br_2SO$: C, 22.24%; H, 0.74%. Found: C, 23.03%; H, 0.87%.

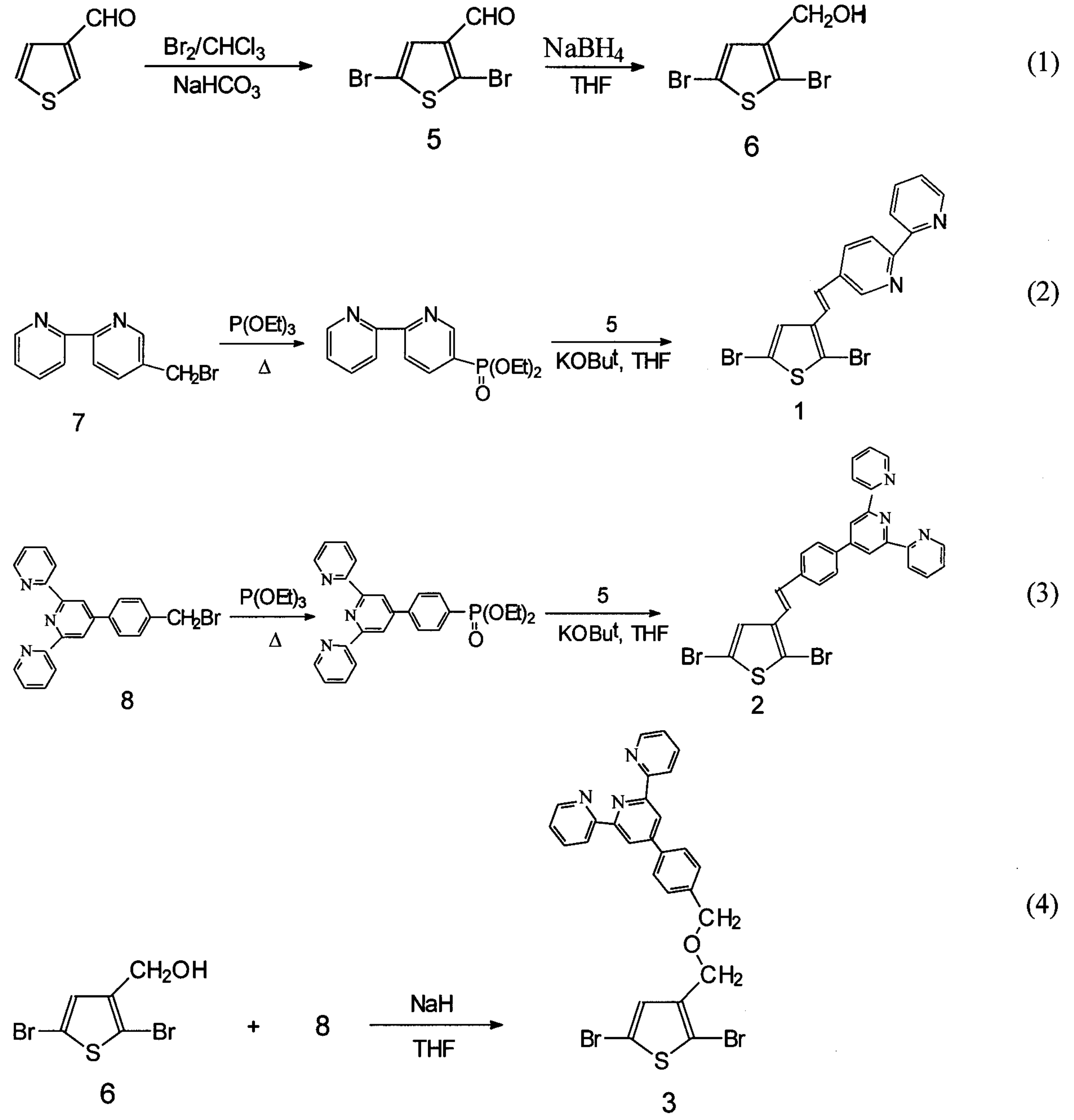
(2,5-Dibromothiophen-3-yl)methanol (**6**) (Scheme 2, eq 1). To a suspension of **5** (0.80 g, 3.0 mmol) in 85% ethanol (30 mL) was added sodium borohydride (0.34 g, 8.9 mmol). The mixture was stirred at room temperature for 1 h. The yellow suspension gradually turned light yellow in solution and was subsequently concentrated by evaporation. Ether (80 mL) was added, and the organic layer was washed with water (3 × 20 mL), dried with $MgSO_4$, and concentrated in vacuo. Chromatography of the residue (silica, hexane:ethyl acetate 6:1) yielded compound **7** as off-white crystals (0.70 g, 86%). ^{1}H NMR ($CDCl_3$): δ 1.59 (br, 1H), 4.56 (s,2H), 7.01 (s, 1H). ^{13}C NMR ($CDCl_3$): 59.26, 109.19, 111.40, 130.47, 141.43. Elemental analysis: Calcd for $C_5H_4Br_2SO$: C, 22.06%; H, 1.47%. Found: C, 22.21%; H, 1.45%.

5-2[(2,5-Dibromo-thiophen-3-yl)-vinyl]-2,2′-bipyridine (**1**) (Scheme 2, eq 2). A mixture of 5-bromomethyl-2,2′-bipyridine (0.12 g, 0.5 mmol) and triethyl phosphite (2 g) was heated slowly to 120 °C for 1 h. Excess triethyl phosphite was removed from the reaction mixture by vacuum distillation to give a faint yellow oil. The residue was dissolved in THF; **5** (0.14 g, 0.5 mmol) was added. When dissolution was complete, KOBu^t (0.55 mL, 1 M in THF) was added. The mixture was stirred at room temperature for 2 h. The product mixture was poured into ethanol. The solid was filtered and subsequently recrystallized from THF and ethanol to give an off-white solid (yield 76%). ^{1}H NMR (360 MHz, $CDCl_3$): 8.72 (m, 2H), 8.43 (d, 2H), 7.97 (dd, 1H), 7.83 (t, 1H), 7.32 (m, 1H), 7.24 (s, 1H), 7.01 (dd, 2H, *trans*-vinyl-H). Elemental analysis: Calcd for $C_{16}H_{10}Br_2N_2S$: C, 45.50%; H, 2.37%; O, 6.64%. Found: C, 46.11%; H, 2.55%; O, 6.58%.

4′-{4-[2-(2,5-Dibromothiophen-3-yl)-vinyl]phenyl}-2,2′:6′,2″-terpyridine (**2**) was synthesized from 4′-(4-bromomethylphenyl)-2,2′:6′,2″-terpyridine by the same method described for **1** above (Scheme 2, eq 3), producing a yellow solid **2** (yield 80%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 8.75 (s, 2H), 8.73 (d, 2H), 8.67 (d, 2H), 7.92 (d, 2H), 7.86 (td, 2H), 7.62 (d, 2H), 7.35 (td, 2H), 7.24 (s, 1H, 4-pyrrole-H), 7.02 (dd, 2H, *trans*-vinyl-H). Elemental analysis: Calcd for $C_{27}H_{17}Br_2N_3S$: C, 56.35%; H, 2.96%; N, 7.30%. Found: C, 55.19%; H, 2.81%; N, 7.07%.

4′-[4-(2,5-Dibromothiophen-3-yl-methoxymethyl)phenyl]-2,2′:6′,2″-terpyridine (**3**) (Scheme 2, eq 4). NaH (98 mg, 2.45 mmol) was added to a solution of (2,5-dibromothiophen-3-yl)methanol (**6**) (0.67 g, 2.45 mmol) in THF (30 mL). After initial gas evolution ceased, **8** (2.0 g, 3.48 mmol) was added. The reaction mixture was refluxed for 5 h under nitrogen, cooled to room temperature, and diluted with ether (100 mL). The organic layer was washed with water (3 × 30 mL), dried over $MgSO_4$, and concentrated in vacuo. Chromatography of the residue (silica, hexane:ethyl acetate 10:1) yielded **3** as a white crystal (1.3 g, 60%). ^{1}H NMR ($CDCl_3$): δ 8.75 (s, 2H), 8.73 (d, 2H),

Scheme 2. Synthesis Sequence for the 2,5-Dibromothiophene Units (1−3)



8.67 (d, 2H), 7.92 (d, 2H), 7.89 (td, 2H), 7.48 (d, 2H), 7.37 (td, 2H), 7.02 (s, 1H), 4.60 (s, 2H) 4.46 (s,2H). ^{13}C NMR ($CDCl_3$): 156.17, 155.87, 149.93, 149.06, 139.11, 138.71, 137.95, 136.95, 130.91, 129.63, 128.30, 127.76, 127.43, 123.85, 121.41, 118.86, 71.94, 65.94. Elemental analysis: Calcd for $C_{27}H_{19}OBr_2N_3S$: C, 54.64%; H, 3.20%; N, 7.08%. Found: C, 56.57%; H, 3.29%; N, 7.53%.

bp−PPETE. Diisopropylamine (2 mL) was added to a mixture of compound **1** (0.50 g, 0.82 mmol), 1,4-diethyl-2,5-dihexadecyloxybenzene (**4)** (0.48 g, 0.82 mmol), $Pd(PPh_3)_4$ (50 mg, 0.043 mmol), and CuI (40 mg, 0.21 mmol) in 10 mL of THF under an argon atmosphere. The mixture was refluxed for 24 h, and then chloroform (20 mL) was added. The organic phase was washed twice with dilute $NaHCO_3$ solution. The organic phase was collected and dried over $MgSO_4$. After the solvent was removed under reduced pressure the residue was washed with hot acetone, hot water, and hot MeOH to afford a yellow solid (yield 88%). Elemental analysis: Calcd for $C_{50}H_{62}O_2N_2S$: C, 79.58%; H, 8.22%; N, 3.71%. Found: C, 75.66%; H, 8.16%; N. 3.25%.

ttp−PPETE. This material was prepared by reaction of compounds **2** and **4** using a procedure identical to bp-PPETE (yield 80%).[15] Elemental analysis: Calcd for $C_{61}H_{67}O_2N_3S$: C, 76.90%; H, 7.40%; N, 4.64%. Found: C, 74.25%; H, 7.50%; N, 4.46%.

ttp−O−PPETE. This material was prepared by reaction of compounds **3** and **4** using a procedure identical to bp−PPETE (yield 78%). Elemental analysis: Calcd for $C_{61}H_{71}O_3N_3S$: C, 79.14%; H, 7.68%; N, 4.54%. Found: C, 74.36%; H, 7.70%; N, 3.71%.

Model PPETE. This material was prepared by reaction of 2,5-diiodo-3-dodecylthiophene and **4** using a procedure identical to bp−PPETE (yield 85%). Elemental analysis: Calcd for $C_{50}H_{78}O_2S$: C, 80.86%; H, 10.51%. Found: C, 79.19%; H, 10.43%.

Results and Discussion

Synthesis. Following the seminal work of Heck and others,[16] the palladium-catalyzed cross-coupling reaction has become a powerful tool in preparing a wide range of PAE type conjugated polymers with functional or multifunctional groups.[17] To synthesize the PPETE

Scheme 3. Synthesis of Model Polymer PPETE

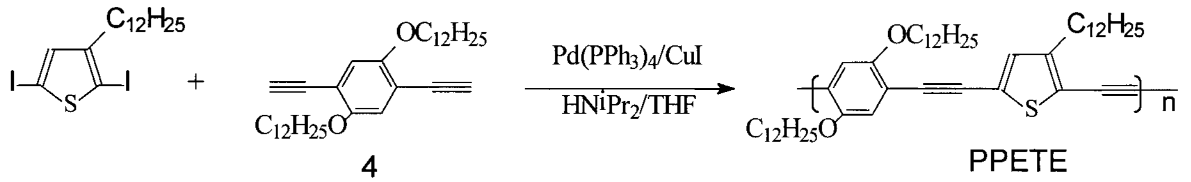


Table 1. Molecular Weights and Polydispersities of PPETE Polymers Determined by GPC Relative to Polystyrene Standards in THF Solution at Room Temperature

polymers	PPETE	bp−PPETE	ttp−PPETE	ttp−O−PPETE
M_n	3.2×10^5	1.8×10^4	1.7×10^5	1.9×10^5
polydispersity (M_w/M_n)	2.8	2.5	1.4	1.5

polymers using this reaction (Scheme 1), the corresponding precursors 1,4-diethynyl-2,5-didodecyloxybenzene (**4**) and 2,5-dibromo-thiophene substituted with different binding sites (**1**−**3**) were first synthesized. 1,4-Diethynyl-2,5-didodecyloxybenzene (**4**) was synthesized from 1,4-hydroquinone in four steps as described previously.[8]

The synthetic sequence for the 2,5-dibromo-thiophene units (**1**−**3**) is outlined in Scheme 2. The compound 2,5-dibromothiophene-3-carbaldehyde (**5**) was readily synthesized from the bromination reaction of 3-thiophenecarboxaldehyde with Br_2 in the presence of $NaHCO_3$ (Scheme 2, eq 1). Initial attempts to synthesize 2,5-diiodo-3-thiophenecarboxaldehyde with I_2 (catalyzed by HgO or $Hg(OAc)_2$) according to literature methods were not successful. This is likely due to the presence of the aldehyde group in the reactant thiophene monomer. Bipyridine phosphite or terpyridine phosphite was prepared by reacting 5-bromomethyl-2,2′-bipyridine (**7**) or 4′-(*p*-bromomethylphenyl)-2,2′:6′2″-terpyridine (**8**) with triethyl phosphite and subsequently treated in situ with 2,5-dibromo-3-thiophenecarboxaldehyde (**5**) under Horner−Wittig−Emmons conditions.[18] This gives the polymer precursors **1** and **2** with a yield of 76% and 80%, respectively (Scheme 2, eqs 2 and 3).

The precursor compound (2,5-dibromothiophen-3-yl)-methanol (**6**) can be easily prepared by reduction of 2,5-dibromo-3-thiophenecarboxaldehyde (**5**) using sodium borohydride (yield 86%) (Scheme 2, eq 1). Thus, the ether-linked monomer **3** was obtained by adding the bromide **8** to a suspension of the sodium salt of alcohol **6**, which was generated from the reaction of **6** with sodium hydride (Scheme 2, eq 4).

The polymerizations in all cases were performed under Heck coupling conditions.[16] Substituted dibromothiophene was reacted with diethynylbenzene in THF catalyzed by 5 mol % $Pd(PPh_3)_4$ and 5 mol % CuI (Scheme 1). For comparison purposes, the model polymer PPETE was synthesized from 2,5-diiodo-3-dodecylthiophene and **4** using the same conditions (Scheme 3). This polymer has the same backbone as the other PPETE polymers but has long alkyl chains in place of the receptor connected to the backbone. IR and NMR spectra of the polymers indicated that the polymerization was complete as evidenced by the disappearance of the acetylenic groups. Further, the formation of the ethynyl link was confirmed by the presence of 2184 cm^{-1} stretch (for ttp−PPETE) in the FTIR. Each of the polymers was notably fluorescent and very soluble in common organic solvents such as THF, chloroform, and toluene.

The number-average molecular weight (M_n) and polydispersity of these polymers were determined by GPC relative to polystyrene standards. The results of the polycondensations are summarized in Table 1. Given the rigidity of the PPETE polymers, the M_n might be overestimated by a factor of 2−3 since the standard polystyrene is a flexible coil polymer[19] while the PPETE polymer was expected to be more rigid.

Photophysical Properties. Absorption and emission spectra were collected for all polymer systems in THF solution. The photophysical data are summarized in Table 2. For the model polymer PPETE, only one peak is observed in the absorption spectrum ($\lambda_{max} = 448$ nm). This can be assigned to the $\pi-\pi^*$ transition of the conjugated polymer backbone. All of the receptor-substituted polymers have two absorption bands. The lower energy bands (λ_{max} = 444−462 nm) can be assigned to $\pi-\pi^*$ transitions on the conjugated polymer backbone. The higher energy bands (around 300 nm) can be assigned to a $\pi-\pi^*$ and n−π^* transitions in the pendant bipyridyl or terpyridyl group by comparison to the absorption spectra of the monomer (**1**−**3**). From the absorption data shown (Figure 3a), it is clear that both the lower energy bands of the bp−PPETE and ttp−PPETE are red-shifted and broadened relative to that of the model polymer PPETE. This can be rationalized on the basis of the increased conjugation of the polymer backbone since the pendant groups were connected to the backbone by conjugated double bonds. On the other hand, the lower energy peak in absorption of ttp−O−PPETE shows no red shift compared to the model PPETE polymer. This is consistent with a lack of conjugation with the pendant group of the polymer backbone.

The polyarylene ethynylene class of polymers is known to be highly emissive with quantum yields of 0.7 and higher.[19] All of the polymers prepared here were found to be highly emissive with quantum yields of 0.38−0.54 (Table 2). A representative emission spectrum is shown in Figure 3b. The emission spectra of bp−PPETE, ttp−PPETE, and ttp−O−PPETE were nearly identical. This is consistent with limited perturbation of the lowest energy $\pi-\pi^*$ state of the polymer by the receptor. All three polymers were broadened relative to that of the model polymer PPETE. The emissions of bp−PPETE and ttp−PPETE polymers also showed a red shift while the ttp−O−PPETE has no red shift comparing to the model PPETE polymer. This result agrees with the trend in absorption spectra.

The emission lifetimes measured by single photon counting were found to be less than 1 ns. This is consistent with the $\pi-\pi^*$ nature of the excited states. Emission decays could not be satisfactorily fit as single-exponential, unimolecular process. In each case, lifetimes were best fit by a biexponential decay model (eq 1). Multiexponential emission decays have been observed previously for this class of PAE polymers.[19]

$$y(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \qquad (1)$$

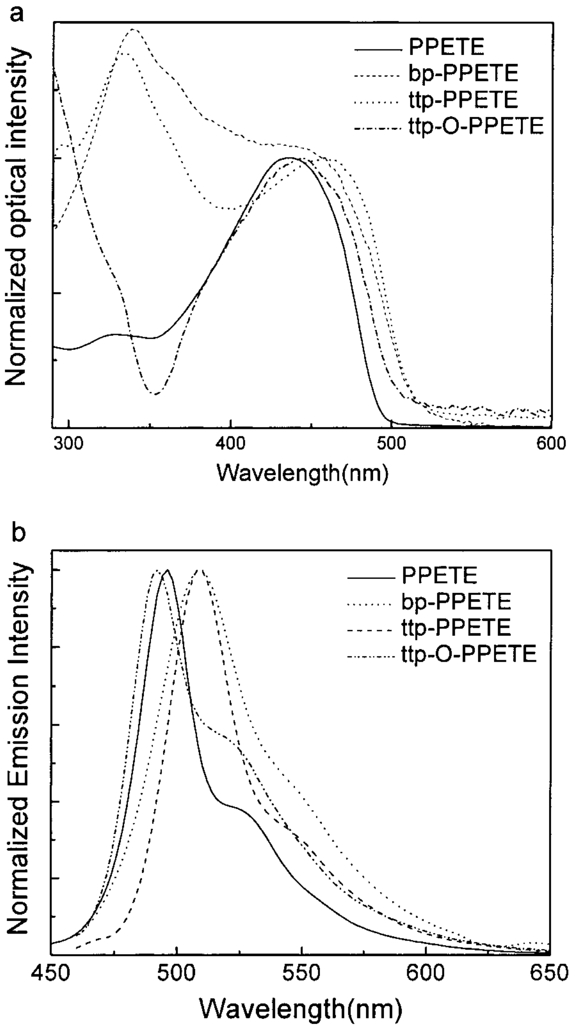


Figure 3. Absorption (a) and emission (b) spectra of the PPETE polymers in THF solution.

Chemosensor Quenching Response. The addition of a Lewis base receptor to the conjugated polymer backbone provides the opportunity to observe modulated fluorescence and absorption response characteristics in the presence of Lewis acids such as toxic transition metals. The emission of the polymers was monitored in THF using steady-state fluorescence spectroscopy. The emission intensity of polymer ttp–PPETE as a function of concentration of Ni^{2+} in THF is shown in Figure 4. We observed 5% emission quenching at Ni^{2+} concentrations as low as 4×10^{-9} M[20] (not shown in this figure). The emission intensity decreases to about 60% of the initial intensity at concentrations as low as 2.0×10^{-7} M. In these experiments, the terpyridyl receptor concentration was held fixed at 3.08×10^{-6} M. Control experiments using the model polymer PPETE show no emission quenching in the presence of any of the transition-metal ions in THF solution. This suggests that the emission quenching response we observed involves the interaction of the transition metal quenchers with the bipyridyl or terpyridyl receptors.

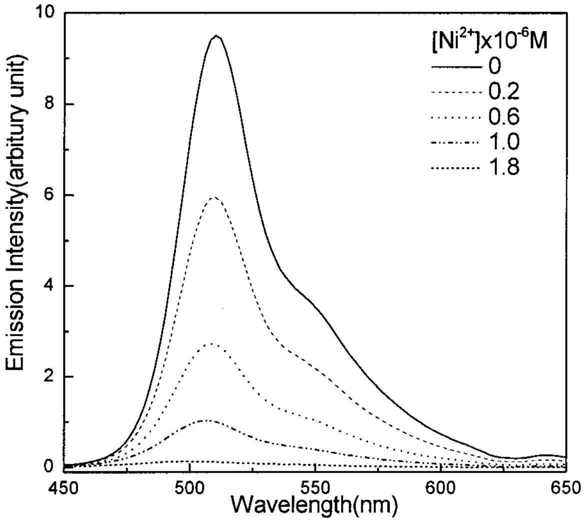


Figure 4. Emission spectra recorded in THF at room temperature for Ni^{2+} complexes with ttp–PPETE. The polymer concentration is 3.08×10^{-6} M corresponding to receptor unit.

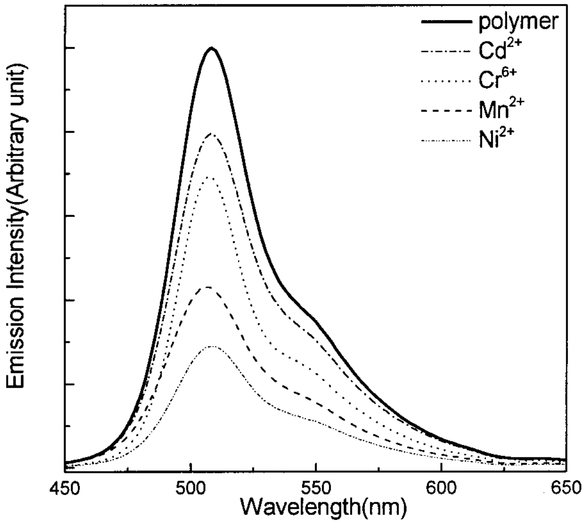


Figure 5. Emission quenching of ttp–PPETE polymer by different transition metal ions. The polymer concentrations are held fixed at 3.08×10^{-6} M corresponding to receptor unit. Transition metal ions are 1.54×10^{-6} M.

The polymer ttp–PPETE also shows sensitivity to several other transition-metal ions such as Cr^{6+}, Co^{2+}, Cu^{2+}, and Mn^{2+}. Because of the varying chelating ability of terpyridine with different transition metals, this polymer shows some selectivity toward the different transition metals (Figure 5). In these experiments, both the ttp–PAE polymer and transition-metal quencher concentration were held fixed at 3.0×10^{-6} and 1.5×10^{-7} M, respectively. The polymer was quenched to 29.0% of its initial intensity in the presence of Ni^{2+} under these conditions, while 79.6% of the intensity

Table 2. Photophysical Properties of PPETE Polymers in THF Solution at Room Temperature

			lifetime (component)		
	absorbance (λ_{max}, nm)	emission (λ_{max}, nm)	τ_1(ns) (A_1)	τ_2 (ns) (A_2)	quantum yield
model PPETE	448	496	0.547 (0.854)	0.081 (0.146)	0.54
bp–PPETE	344, 462	508	0.582 (0.758)	0.122 (0.242)	0.38
ttp–PPETE	338, 454	508	0.567 (0.617)	0.208 (0.383)	0.40
ttp–O–PPETE	276, 444	488	0.599 (0.586)	0.233 (0.414)	0.45

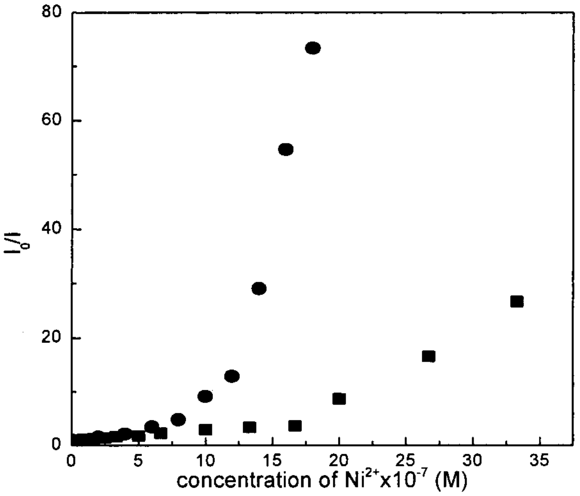


Figure 6. Stern–Volmer plots of ttp–PPETE (circle) and bp–PPETE (square) emission quenched by Ni^{2+} in THF at room temperature. The polymer concentrations are both 3.08×10^{-6} M corresponding to receptor unit.

remained when Cd^{2+} was used as the quencher. No quenching was observed in the presence of common cations such as Na^+ or Ca^{2+}. The polymer was also not responsive to Pb^{2+} and Hg^{2+}.

The bp–PPETE and ttp–PPETE polymers are quenched to varying degrees by the different transition metals tested. Figure 6 shows a Stern–Volmer quenching analysis of bp–PPETE and ttp–PPETE polymer emission quenched by [Ni^{2+}]. In these experiments, the concentrations of these two polymers were 3.08×10^{-6} M in receptor sites. The ttp–PPETE was more sensitive to Ni^{2+} ion, where a Ni^{2+} concentration of 1.0×10^{-6} M quenched ttp–PPETE to 10.9% of its original emission intensity, while only to 38.2% for emission intensity of bp–PPETE. This is consistent with the tridentate nature of the terpyridyl pendant, while the bipyridyl group is bidentate. It is interesting to note the nonlinear nature of the Stern–Volmer plot in Figure 6. Dynamic quenching processes would be expected to give a straight line with a *Y*-intercept of 1. Preliminary data in our lab show that there is no change in the lifetime as a function of metal concentration,[21] suggesting that in this case the mechanism of the quenching process involves complexation rather than collisional deactivation. Nonlinear behavior for polymer-based fluorescence quenching has been observed previously[22] and is the basis of continuing analysis in our lab.[23]

To understand whether the conjugation between the receptors and the polymer backbone was necessary to ensure enhanced sensory behavior, we designed the ether-linked polymer ttp–O–PPETE. This polymer has the same receptor and backbone as ttp–PPETE. The key difference between these two polymers was that in the ttp–O–PPETE polymer the receptors were not in conjugation with the PPETE backbone. The relative quenching efficiency between these two polymers was examined at a polymer concentration of 3.08×10^{-6} M in THF solution. The total emission response for each polymer in the presence of Ni^{2+} was determined. The emission from the ttp–O–PPETE polymer remains sensitive to Ni^{2+} ions. However, the ttp–PPETE was found to be 2.6-fold more efficient than ttp–O–PPETE. For example, when the Ni^{2+} concentration was 1.0×10^{-6} M, 14.4% of the original emission intensity from ttp–PPETE remained, compared to 37.9% for the emission intensity with ttp–O–PPETE. Thus, the conjugation of the receptors to the polymer backbone clearly enhances the electronic communication and the sensitivity of polymer chemosensory behavior. However, we conclude that the conjugation of receptors to the polymer backbone is not required for the fluorescence response. The successful demonstration of quenching in the absence of conjugation to the receptors provides more design flexibility in the synthesis of new conjugated polymer chemosensors.

Conclusion

We have successfully designed and synthesized a series of conjugated PPETE polymers with different oligopyridyl receptors using a palladium-catalyzed coupling reaction. Each of the polymers is notably fluorescent and very soluble in common organic solvents, making them suitable for application to large-scale spin-coating production. These polymers show significant sensitivity to transition-metal ions due to the enhanced electronic communication properties of the conjugated polymers. Further, our result shows that complete conjugation of the pendant receptors to the polymer backbone is not required for enhanced emission quenching. However, the fully conjugated, vinylene-linked, ttp–PPETE was found to have the highest overall quenching efficiency.

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Supporting Information Available: ^{1}H NMR spectra of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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