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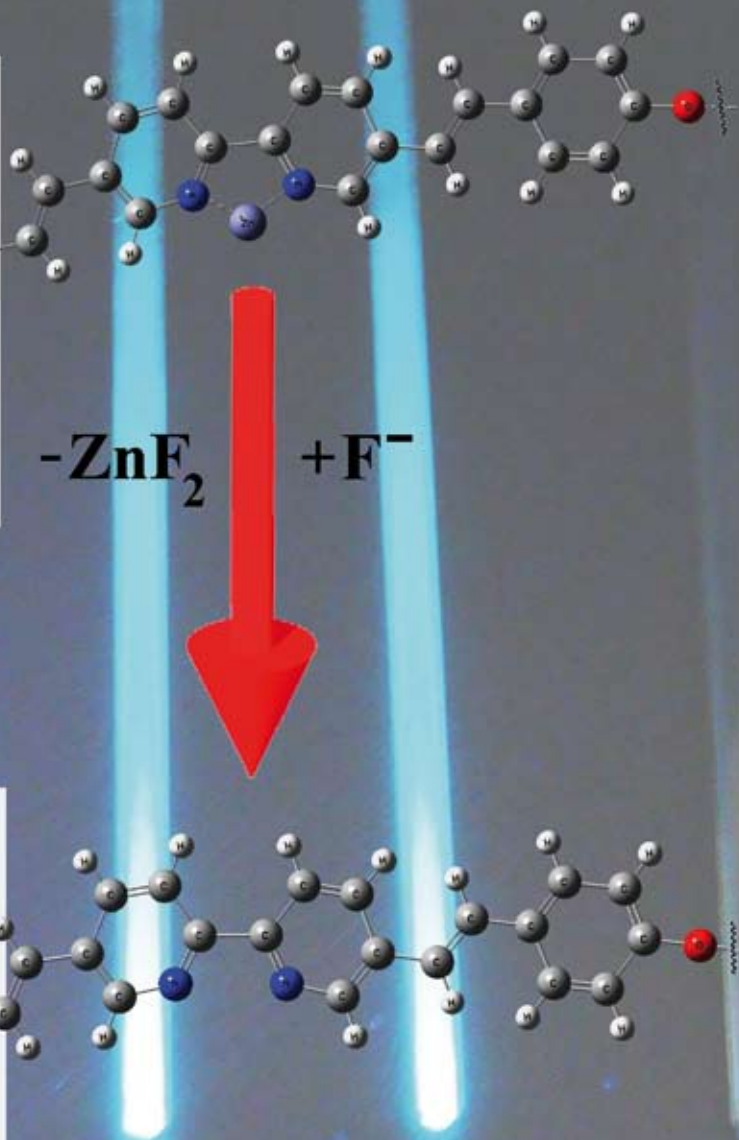
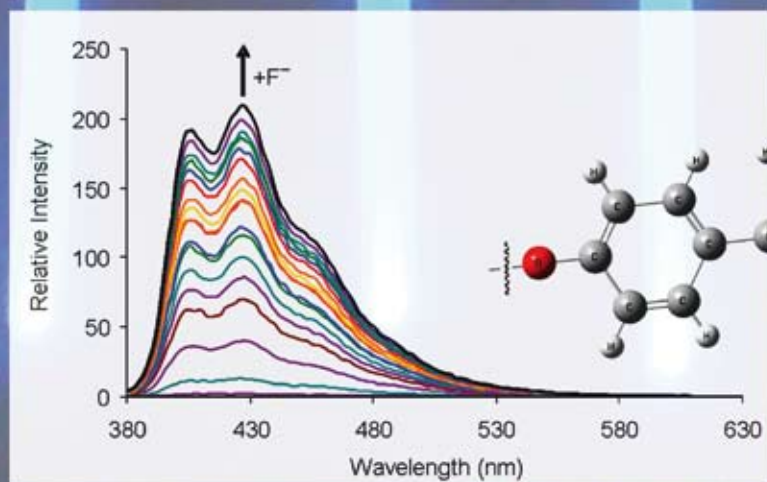
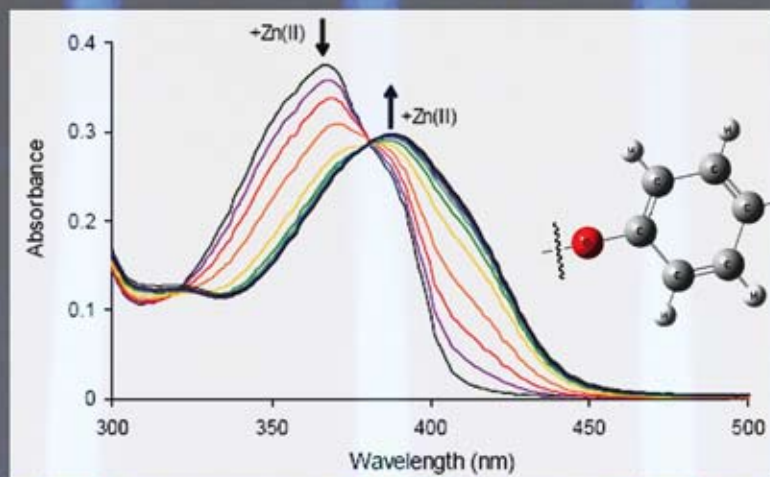
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Photoluminescence and ion sensing properties of a bipyridyl chromophore-modified semifluorinated polymer and its metallopolymer derivatives†

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A difluorovinylene aromatic ether polymer (**P1**) incorporating periodic 5,5'-distyryl-2,2'-bipyridyl units as metal chelating chromophores was prepared by a transition metal-free step-growth polymerization. **P1** displays strong ionochromic and ionoluminescent effects in response to transition metals. Although significant emission quenching is observed upon exposure to most transition metal ions, bathochromically shifted emission is observed upon addition of divalent d¹⁰ ions (Zn²⁺, Cd²⁺ and Hg²⁺). A selective 10-fold increase in integrated emission intensity is observed upon addition of Zn²⁺ to **P1**. The Zn²⁺-**P1** metallopolymer acts as a ratiometric fluorescent indicator selective for fluoride anions, and the Cu²⁺-**P1** metallopolymer exhibits a striking turn-on fluorescence response (>100-fold increase in integrated intensity) selective for cyanide and fluoride anions.

Introduction

We recently detailed the utility of a facile, metal-free synthesis¹ of fluorinated aromatic vinylene ether (FAVE) polymers and subsequent extension of this protocol to incorporate periodic chromophoric subunits into FAVE backbones.² These materials are readily processed from solutions of common organic solvents to form free-standing optical films that exhibit intense, tunable photoluminescence. We have subsequently explored the ability of chromophore-modified FAVEs to serve a dual role as recognition–response units. A series of diphenylbithiophene-derived polymers, for example, produced by this protocol were tested as anion indicators. A fluoride-selective 16-fold emission enhancement was achieved over other common anions when the chromophore was enchainned by a rigid fluoropolymer.³

Encouraged by these early studies, we sought to expand the functionality of FAVE derivatives to other applications. One area of interest is in modifying the FAVE scaffold with metal chelating units. Polymer-supported metal complexes, particularly conducting metallopolymer, support a wide range of applications due to the synergistic combination of polymer processibility with the ion transport and redox properties of transition metals.^{4–8} Metal ions can also be used to control polymer morphology, providing coordinative crosslinks and templating ordered network formation or other supramolecular structures.^{4,6,9–18} Fluorinated variations of metallopolymer could maintain and augment these advantages with impressive thermal stability and resistance to atmospheric moisture typical of classical fluoropolymers. The validity of this strategy is

reflected by the improved thermal stability of a NLO-active Ru(bipyridine)₃ complex upon incorporation into a semifluorinated polyimide host.¹⁹ There have also been extensive studies on bipyridine transition metal complexes immobilized within fluoropolymer membranes, particularly Nafion, for indicators, electrode materials and fuel cell applications.^{20–33} Because most of these systems do not employ covalent attachment of the metal complexes to the polymer backbone, phase separation and boundary effects can be barriers to their utility.

Bipyridine is the most widely used ligand in coordination chemistry due to its ability to chelate a wide variety of transition and lanthanide elements,³⁴ and it has the added benefit of superior redox stability and facile synthetic modification. Consequently, bipyridyl units are privileged ligands for incorporation into metallopolymer. In the current case, chromophore-appended bipyridyl units were selected for incorporation into the FAVE scaffold to provide a convenient spectroscopic probe for metal coordination *via* absorption and photoluminescence spectroscopy. Chromophore derived 2,2'-bipyridines have well-established ionophoric responses to transition metals.^{18,35–47} Small molecule examples have been employed as fluorescent chemosensors for zinc,^{37,48} and bipyridyl-derived π -conjugated polymers and conducting metallopolymer have been used in a variety of applications, particularly as indicators.^{7,18,43,45–47,49–59} Covalent attachment of bipyridyl units to the polymer precludes phase separation and leaching of metal complexes from the polymer over time. Herein we report the preparation and characterization of a FAVE incorporating bipyridyl chromophores and application of this polymer for colorimetric and fluorescent detection of metal ions and anions.

Experimental

Materials and characterization methods

All reagents were obtained from Tetramer Technologies, LLC, Aldrich Chemical Co., TCI America, Alfa Aesar, Fisher

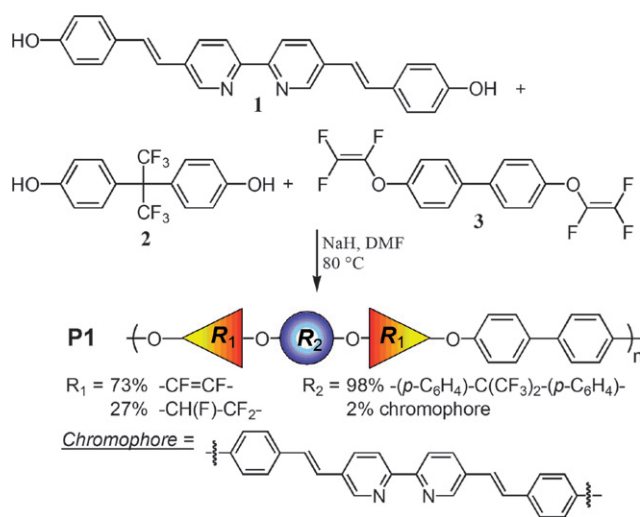
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† Electronic supplementary information (ESI) available: NMR spectra and spectra from fluorescence titrations of **P1** with metal ions. See DOI: 10.1039/b713458d

Scientific, Mallinckrodt, Baker and Adamson, or MP Biomedicals, LLC and used as received. NMR spectra were recorded on a JEOL Eclipse+ 300 or Bruker Avance 300 spectrometer and chemical shifts are reported in parts per million (δ ppm). ^1H NMR was internally referenced to tetramethylsilane (δ 0.0) or residual solvent signal, ^{13}C NMR chemical shifts were reported relative to the peak for DMSO, and ^{19}F NMR was referenced to CFCl_3 . Gel permeation chromatography (GPC) data were collected using polystyrene as a standard (Polymer Labs Easical PS-2) using a Waters 2695 Alliance System eluted sequentially through Polymer Labs PLGel 5 mm Mixed-D and Mixed-E columns at 35 °C, with absorption detection for samples in CHCl_3 .

4,4'-[(2,2'-bipyridine)-5,5'-diyl]-2,1-ethenediyl]bisphenol (1).⁶⁰ Lithium ethoxide (1 M in ethanol, 2.42 mL, 2.42 mmol) was added dropwise to a stirred solution of 5,5'-bis(bromotriphenylphosphoniummethyl)-2,2'-bipyridine⁴⁵ (1.00 g, 1.15 mmol) and 4-(*tert*-butyldimethylsiloxy)benzaldehyde⁶¹ (0.575 g, 2.42 mmol) dissolved in CH_2Cl_2 (60 mL) at room temperature. After 4 h, the reaction mixture was poured into an equal volume of H_2O . The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2×20 mL). Combined organic layers were washed with deionised water (2×50 mL), dried (MgSO_4), filtered, and concentrated under vacuum. The crude product and *p*-toluenesulfonic acid (0.100 g) were dissolved in toluene (50 mL) and the reaction mixture was heated to reflux. After 24 h, a brick red solid precipitated. The solid was collected by vacuum filtration and washed sequentially with H_2O (2×100 mL), methanol (2×100 mL), and hexanes (2×100 mL). The solid was then dried under vacuum to afford the title compound as a brick red solid (270 mg, 60%). *Note: p-toluenesulfonic acid serves a dual role, isomerising the crude mixture of (E)- and (Z)-isomers to the (E)-isomer,⁴³ and quantitatively deprotecting the hydroxyl groups to afford the title compound.* ^1H NMR (DMSO- d_6 , 300 MHz) δ 8.81 (s, 2 H, -OH), 8.42 (d, J = 7.89 Hz, 2 H), 8.27 (d, J = 7.89 Hz, 2 H), 7.46–7.39 (m, 6 H), 7.15–7.06 (m, 4 H), 6.77 (d, J = 7.89 Hz, 4 H); ^{13}C NMR (DMSO- d_6 , 76 MHz) δ 158.7, 146.8, 135.3, 132.8, 129.0, 128.6, 128.1, 126.0, 122.0, 121.0, 116.3.

P1. 5,5'-Bis(4-hydroxystyryl)-2,2'-bipyridine (0.055 g, 0.14 mmol) and 2,2-bis(4-hydroxyphenyl)hexafluoropropane⁶² (0.437 g, 1.30 mmol) dissolved in anhydrous DMF (2 mL) were added dropwise to a stirred suspension of NaH (0.070 g, 2.92 mmol) in DMF (2 mL) at room temperature, and stirred for 1 h. 4,4'-Bis(4-trifluorovinyl)oxy)biphenyl (0.500 g, 1.44 mmol) in anhydrous DMF (2 mL) was transferred into the solution *via* syringe in a single portion. The flask was then placed in a preheated oil bath at 80 °C. After 4 h at this temperature, the solution contents were precipitated into H_2O , filtered under vacuum, and washed sequentially with deionized H_2O (2×100 mL), methanol (2×100 mL), and hexanes (2×100 mL). The solid polymer was dried in a vacuum oven at 60 °C for 24 h. Additional purification was performed by dissolving the dried polymer in a minimal amount of THF and precipitated in deionized water, filtering, and washing sequentially with methanol (2×100 mL) and hexanes (2×100 mL). The solid polymer was then dried in a vacuum oven at 60 °C for an additional



Scheme 1 Synthesis and structure of **P1**. When $\text{R}_1 = -\text{CH}(\text{F})-\text{CF}_2-$, the CF_2 end is uniformly directed towards the base of the R_1 triangles. The $\text{CF}=\text{CF}$ units are present as a 45 : 55 mixture of *E*- and *Z*-configurations.

24 h to afford the polymer as a pale yellow fibrous solid (0.580 g, 58%). ^1H NMR (DMSO- d_6 , 300 MHz) δ 8.40–8.35 (m), 8.20–8.15 (m), 7.80–7.60 (m), 7.50–7.27 (m), 6.84 (broad dt, J = 58.4 Hz, CHFCF_2); ^{19}F NMR (DMSO- d_6 , 283 MHz) δ -63.3 [s, $\text{C}(\text{CF}_3)_2$], -85.2 (AB pattern, J_{ab} = 144.8 Hz, CHFCF_2), -120.8 and 122.5 [d, J = 39.6 Hz, (*Z*)- $\text{CF}=\text{CF}$], -127.2 and -129.2 [d, J = 108.6 Hz, (*E*)- $\text{CF}=\text{CF}$], -141.2 (d, J = 59.2 Hz, CHFCF_2). GPC in CHCl_3 relative to polystyrene gave a monomodal distribution of $M_n = 22\,800$ ($M_w/M_n = 2.8$). DSC analysis on the second heating at $10^\circ\text{C min}^{-1}$ to 200 °C gave $T_g = 92^\circ\text{C}$ and TGA ($10^\circ\text{C min}^{-1}$) gave T_d (at 10 wt% loss) = 420 °C in nitrogen and 426 °C in air. Anal. calcd for $\text{C}_{30.98}\text{H}_{17.44}\text{N}_{0.04}\text{O}_{4.128}$ (using the monomer ratios reported in Scheme 1): C, 55.66; H, 2.63; N, 0.08. Found: C, 55.36; H, 2.96; N, 0.24.

General spectroscopic methods

Photoluminescence (PL) spectra were acquired on a Varian Cary Eclipse fluorescence spectrophotometer. Absorption spectra were recorded on a Varian Cary 50 Bio absorption spectrophotometer. Samples for all absorbance and PL spectra used tetrahydrofuran (THF) as solvent in Spectrosil quartz cuvettes having a path length of 1 cm. Initial solutions for PL analysis were filtered through 0.2 μm PTFE syringe filters prior to analysis. The THF solvent for all optical measurements was purified and made anhydrous/anaerobic by passage through alumina columns under a N_2 atmosphere employing an MBraun solvent purification system. Photoluminescence quantum yields were measured relative to quinine bisulfate ($\Phi = 0.564$) in 0.1 N aqueous sulfuric acid.⁶³ Polymer concentrations are reported as moles of bipyridyl monomer unit per L. Metal salts used for ion screening were $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$, $\text{Cu}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$, $\text{Zn}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$, $\text{Cd}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$, $\text{K}(\text{PF}_6)$, $\text{Na}(\text{PF}_6)$, $\text{Mg}(\text{SO}_4)$, CaCl_2 , $\text{Eu}(\text{NO}_3)_3$, $[\text{Cu}(\text{NCMe})_4][\text{BF}_4]$, $\text{Hg}(\text{O}_2\text{CCF}_3)_2$, and $\text{Fe}(\text{OTf})_2$. **CAUTION: perchlorate salts are potentially explosive and should only be handled in small quantities by trained personnel who are familiar with their hazards.**

Metal ion selectivity of P1. A 3.0 mL aliquot of 3×10^{-5} M **P1** was added to a cuvette. 4.5×10^{-4} L of 2.0×10^{-2} M metal (20 equiv.) was added to the polymer solution. Absorbance changes were observed for transitional metals. The experiment was repeated and followed by PL spectroscopy using 3.0×10^{-7} M **P1** and a 5.0×10^{-7} L aliquot of the metal ion solution.

Absorption titration of polymer with metal ions. A 3.0 mL aliquot of the 3×10^{-5} M polymer in THF solution was added to a cuvette. Aliquots (2.25×10^{-6} L) of 2.0×10^{-3} M metal ion solution were added to the polymer solution and changes were followed by collecting an absorption spectrum after each addition.

PL titration of polymer with metal ions. Same as for absorption titration, but using 3.0×10^{-6} M **P1**, and followed by photoluminescence with $\lambda_{\text{ex}} = 370$ or 420 nm.

Displacement test of anions to metal in M^{2+} -P1 complexes ($M^{2+} = \text{Zn}^{2+}$ or Cu^{2+}). A 3.0 mL aliquot of the 3.0×10^{-6} M **P1** was added to a cuvette, followed by 4.5×10^{-6} L of 2.0×10^{-3} M $\text{Zn}(\text{ClO}_4)_2$ or $\text{Cu}(\text{ClO}_4)_2$ and collection of an initial emission spectrum. A 0.45×10^{-6} L aliquot of 2.0×10^{-2} M anion solution (F^- , Cl^- , Br^- , I^- , HSO_4^- , PO_4^{3-} , or $^- \text{O}_2\text{CCH}_3$, as tetrabutylammonium salts) was then added to the cell and another emission spectrum collected.

Fluorescence titration of M^{2+} -P1 ($M = \text{Zn}^{2+}$ or Cu^{2+}) with anions. A 3.0 mL aliquot of 1.5×10^{-6} M **P1** in THF was added to a quartz cell. 2.25×10^{-6} L (1 equiv.) of 2.0×10^{-3} M $\text{Zn}(\text{ClO}_4)_2$ or $\text{Cu}(\text{ClO}_4)_2$ solution was added to the cuvette to make M^{2+} -P1. Both Zn^{2+} -P1 and Cu^{2+} -P1 complexes were titrated by addition of 11×10^{-6} L (0.5 equiv.) aliquots of 2.0×10^{-4} M tetrabutylammonium fluoride. The titration was followed by PL spectroscopy up to addition of ten equiv. of anion. The Cu^{2+} -P1 complex was titrated with tetrabutylammonium cyanide solution in identical fashion. The excitation wavelength was 370 nm for these titrations.

Absorption titration of Zn^{2+} -P1 with F^- . As described for fluorescence titration, but using 2.0×10^{-5} M Zn^{2+} -P1 and 1.5×10^{-6} L (0.5 equiv.) of 2.0×10^{-2} M tetrabutylammonium fluoride and following titration by absorption spectroscopy.

Fluorescence titration of CN^- with Cu^{2+} -P1 in THF from 0.5 equiv. to 10 equiv. A 3.0 mL aliquot of the 1.5×10^{-6} M **P1** in THF solution was added to a cuvette. A 2.25×10^{-6} L (1 equiv.) aliquot of 2.0×10^{-3} M $\text{Cu}(\text{ClO}_4)_2$ solution was added to the cuvette to generate Cu^{2+} -P1. 11×10^{-6} L (0.5 equiv.) of the 2.0×10^{-4} M CN^- in THF solution was added to the Cu^{2+} -P1 solution after each scan ($\lambda_{\text{ex}} = 370$ nm) until a total of ten equiv. CN^- had been added.

Results and discussion

Polymer **P1** was readily prepared in 58% isolated yield by step-growth condensation of 5,5'-bis(4-hydroxystyryl)-2,2'-bipyridyl and commercially-available 2,2'-bis(4-hydroxyphenyl)hexafluoropropane (6F bisphenol-A) and 4,4'-bis(trifluorovinyl)oxy)biphenyl⁶²

(Scheme 1). GPC analysis showed a monomodal distribution and moderate molecular weight ($M_n = 22\,800$, $M_w/M_n = 2.8$). Proton and ^{19}F NMR spectral analyses indicate 73% -FC=CF- and 27% -CH(F)-CF₂- linkers (**R**₁, Scheme 1) and 2% bipyridine monomer composition. Pale yellow **P1** is intensely photoluminescent in the solid state or solution under UV irradiation ($\lambda_{\text{em}} = 426$ nm, with a quantum yield (Φ) of 0.49(0.06) (average of seven independent determinations) with $\lambda_{\text{ex}} = 370$ nm in THF) and is soluble in common organic solvents such as chloroform, dichloromethane, THF, and DMSO. Although this work focuses on the behavior of **P1** in solution, it is worth noting that **P1** can be spun or drop cast to form high quality, free-standing transparent films that retain the high luminescence of the initially precipitated sample. One of the main attractive features of fluoropolymers is their high thermal stability. The thermal robustness of **P1** was confirmed by DSC analysis ($T_g = 92$ °C) and TGA, with $T_d = 420$ °C (at 10 wt% loss) in nitrogen and 426 °C in air. Even without protection under an inert nitrogen environment, these values are well above the operation temperature of thin film devices and are markedly higher than common fluorine-free organic polymers in air.

The response of **P1** to an excess (20 equiv.) of metal ions in solution was examined by absorption spectroscopy (Fig. 1a). Metal-free **P1** exhibits λ_{max} at 368 nm, and the absorption

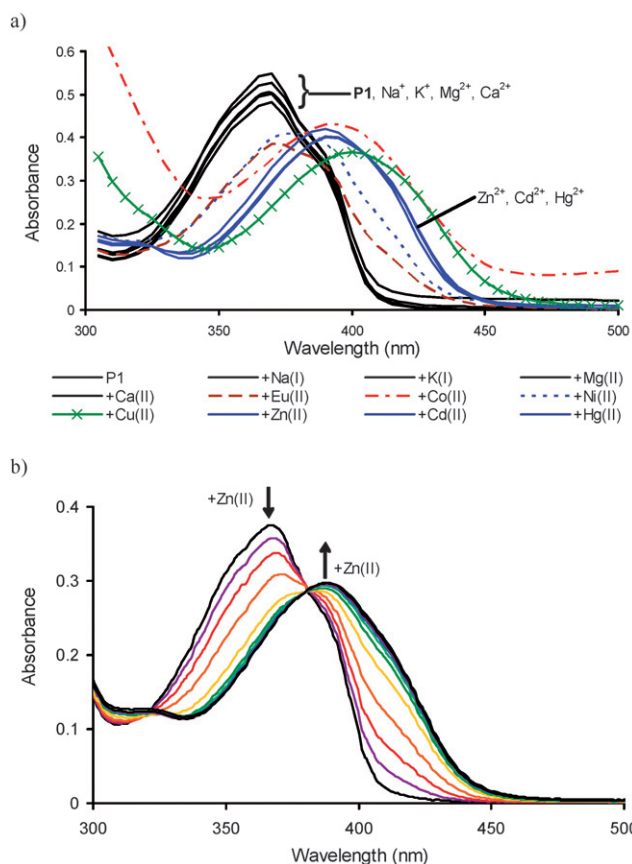


Fig. 1 (a) Absorption spectra for **P1** alone (initial concentration of 3.0×10^{-5} M) and in the presence of 20 equiv. of the indicated metal ions in THF. (b) Progressive changes in the absorption spectrum of **P1** (initial concentration of 3.0×10^{-5} M) as $\text{Zn}(\text{ClO}_4)_2$ is added (as 2.25×10^{-6} L aliquots of 2.0×10^{-3} M solution) in THF. Spectra are corrected to account for the dilution factor.

Table 1 Dissociation constants and photoluminescent quenching characteristics of **P1** with selected transition metal ions in THF. Data are normalized so that $I/I_0 = 1$ for **P1**. I and I_0 represent integrated emission intensity before and after addition of metal ions, respectively. Details are provided in the Experimental Section, and photoluminescence spectra for individual quenching experiments are provided in the ESI

| Ion | $K_d/\mu\text{M}$ | I/I_0 | I/I_0 | $\lambda_{\text{max}}/\text{nm}$ |
|------------------|-------------------|--|--|----------------------------------|
| | | ($\lambda_{\text{ex}} = 370 \text{ nm}$) | ($\lambda_{\text{ex}} = 420 \text{ nm}$) | |
| Co^{2+} | 6.6 | 0.02 | 0.24 | 394 |
| Cu^{2+} | 33 | 0.01 | 0.22 | 400 |
| Zn^{2+} | 0.58 | 0.20 | 9.3 | 390 |
| Cd^{2+} | 9.5 | 0.52 | 1.1 | 390 |
| Hg^{2+} | 24 | 0.35 | 3.7 | 390 |

spectrum is not significantly impacted by alkali or alkali earth metals (Na^+ , K^+ , Mg^{2+} , or Ca^{2+}). Transition and lanthanide ions, however, induced a notable bathochromic shift of up to 32 nm in λ_{max} , the largest shift being observed for Cu^{2+} ($\lambda_{\text{max}} = 400 \text{ nm}$). The observation of this type of ionochromic behavior, well known for small molecule bipyridine derivatives,^{37,48} suggests that bipyridyl units in **P1** exhibit chelation-induced electronic and geometric perturbations similar to those of polymer-free analogues. To determine whether incorporation into the FAVE polymer had altered the *affinity* of bipyridine units for metal ions, we determined the dissociation constant (K_d , Table 1) of the **P1**- Zn^{2+} complex from a spectroscopic titration (Fig. 1b; K_d was derived using a modification of the Benesi–Hildebrand method⁶⁴). The K_d determined for **P1** ($5.8 \times 10^{-7} \text{ M}$) is within an order of magnitude of that for unmodified 2,2'-bipyridine under identical conditions ($4.6 \times 10^{-6} \text{ M}$), indicating that **P1** binds slightly more strongly to Zn^{2+} than does 2,2'-bipyridine and further confirming that incorporation into the polymer does not compromise ligating ability. The somewhat higher affinity of metals for **P1** *versus* 2,2'-bipyridine is anticipated because of the electron-releasing *p*-aryloxystyryl substituents^{65–67} at the 5 and 5' positions of bipyridyl units in the polymer. Although bipyridine-substituted polymers sometimes become insoluble upon metallation due to the formation of coordination crosslinking,^{18,45} there is no evidence of precipitation upon metallation of **P1**, presumably due to the low percentage of bipyridyl units and favorable solubility of the fluoropolymer backbone.

The impact of excess (20 equiv.) metal ions on **P1** photoluminescence was investigated. Two excitation wavelengths were selected for this study: one near λ_{max} for metal-free **P1** (370 nm) and another near λ_{max} of bathochromically shifted transition metal-**P1** complexes (420 nm). Metal-free **P1** has little absorbance at the later wavelength, so only emission from the M^{n+} -**P1** complex will be observed. The relative integrated emission intensities (380–730 when $\lambda_{\text{ex}} = 370 \text{ nm}$ or 430–830 nm when $\lambda_{\text{ex}} = 420$) of **P1** with selected metal ions upon excitation at both wavelengths are provided in Table 1. Interestingly, an *increase* in integrated emission intensity, accompanied by a 44 nm bathochromic shift of λ_{em} to 468 nm, was observed only upon addition of divalent d^{10} metal ions with excitation at 420 nm, with Zn^{2+} ions initiating a significantly greater (10-fold increase) enhancement than any other ions. Complexes of d^{10} ions have a filled d-shell and are often emissive, though their analogues with partially filled d-shells often are not.

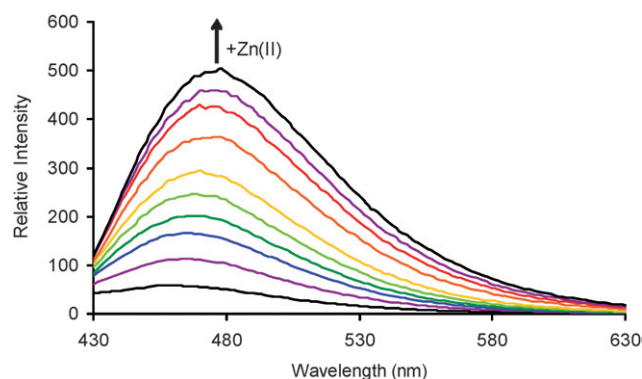


Fig. 2 Progressive changes in the fluorescence spectrum of **P1** (initial concentration of $1.5 \times 10^{-6} \text{ M}$) as a total of 1 equiv. $\text{Zn}(\text{ClO}_4)_2$ is added ($\lambda_{\text{ex}} = 420 \text{ nm}$ in THF). The lowest intensity spectrum is for **P1** alone.

Complexes of the heavier divalent d^{10} ions, Cd^{2+} and Hg^{2+} , also tend to exhibit lowered emission relative to their Zn^{2+} analogues due to the “heavy ion effect”.⁶⁸ The uniquely emissive nature of Zn^{2+} complexes has been exploited in the design of emission turn-on chemosensors for Zn^{2+} , including recently reported small molecules comprising chromophore-modified bipyridine derivatives.^{37,48} Fluorescent titrations of **P1** with selected transition metals were undertaken and dissociation constants were determined from these data (Table 1). Fluorescence spectra for the titration of **P1** with Zn^{2+} are provided in Fig. 2 and spectra for the other ions in Table 1 are provided in the ESI. The 10-fold increase in integrated emission exhibited by **P1** is in the range of commercially-available⁶⁹ fluorescent indicators for Zn^{2+} ,^{70–74} suggesting that, although **P1** is not water soluble, this system may be practically applicable in other contexts.

Many chromophore-modified macromolecular ligand scaffolds have been studied for metal ion detection; however, in some cases the emission response of fluorescent metallopolymer has shown a dependence on counteranions.^{40,46,75} A recent theoretical study notes that the extent of interaction between anion and metal dictates the magnitude of the observed ionochromic response in chromophore-derived bipyridyls.³⁶ If counteranion effects are significant, the resultant optical perturbations could be utilized for anion detection. In light of these well known anion effects, it is surprising that metallopolymer have not been more aggressively investigated as anion indicators. We therefore explored counteranion effects on the ionochromic response of **P1** by adding exogenous anions (as tetrabutylammonium salts) to **P1** premetallated with $\text{Zn}(\text{ClO}_4)_2$ or $\text{Cu}(\text{ClO}_4)_2$. Noncoordinating perchlorate anions were selected for initial metallation to maximize the potential for strong interaction between the metal and added anions. We initially screened eight common anions (F^- , Cl^- , Br^- , I^- , CN^- , HSO_4^- , PO_4^{3-} and $-\text{O}_2\text{CCH}_3$, all added as tetrabutylammonium salts) by monitoring addition of excess anion (up to 10 equiv.) by absorption and fluorescence spectroscopy. Only F^- and CN^- produced notable changes. This is perhaps not surprising in light of the well known use of CN^- as a masking agent in complexometric analysis, and the generally diminished solubility of metal fluorides.^{76–79} Most complexometric studies have been carried out in aqueous solution; however, recent studies related to the current work have been reported in both aqueous and organic solutions. For example,

displacement of quenching Cu^{2+} ions from a fluorogenic ligand in aqueous buffer has been applied in a ratiometric metal ion sensing strategy,⁸⁰ and a variety of indicator displacement assays for anions rely on fluorogenic or colorimetric changes resulting from displacement of fluoro/chromophores from metal ions in a variety of solvent systems.^{81–84}

Of the anions screened, the Zn^{2+} -**P1** complex only responded to fluoride. Both absorption and emission spectra returned to those observed for metal-free **P1** as up to 10 equiv. of F^- were added (Fig. 3a,b). The marked shift in λ_{max} and λ_{em} in response to F^- makes the Zn^{2+} -**P1** complex an ideal candidate for use as a ratiometric indicator. Ratiometric fluorescence indicators are

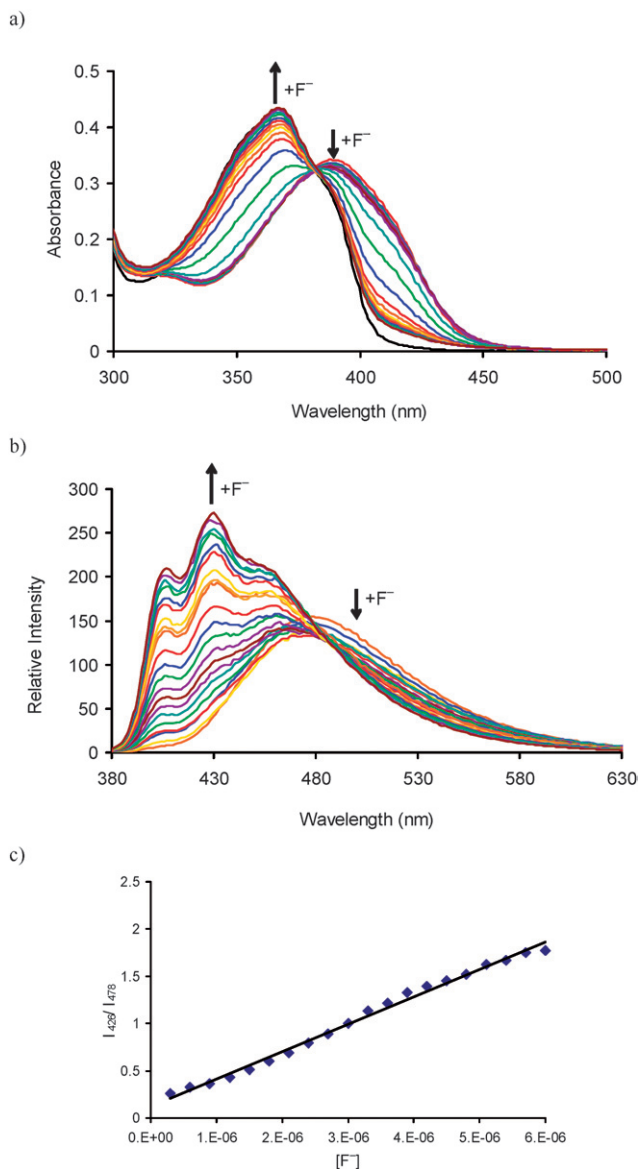


Fig. 3 Changes in absorption (a, initial Zn^{2+} -**P1** concentration of 2.0×10^{-5} M; spectra are corrected to account for the dilution factor) and fluorescence ($\lambda_{\text{ex}} = 370$ nm, initial Zn^{2+} -**P1** concentration of 1.5×10^{-6} M); (b) spectra of the Zn^{2+} -**P1** complex as tetrabutylammonium fluoride (TBAF) concentration is varied from 0 to 3×10^{-5} M, and calibration curve for determining $[\text{F}^-]$ from the ratio of intensity (I) at 426 nm to that at 478 nm (c). All spectra were measured in THF.

among the best for accurate quantification of analyte concentration.^{85–89} In the current example, $[\text{F}^-]$ can be determined using the calibration curve (Fig. 3c) obtained by plotting the ratio of emission intensities at 426 nm and 478 nm *versus* $[\text{F}^-]$. The calibration curve maintains linearity within the micromolar concentration range and suggests an estimated lower detection limit of 6.0×10^{-7} M (11 ppb).

Another anion detection strategy we explored was to displace a strongly quenching metal ion from the fluorescent polymer with the aim of restoring emission. For this purpose we selected the Cu^{2+} -**P1** complex because Cu^{2+} is the most efficient emission quencher with $\lambda_{\text{ex}} = 370$ nm. Remarkable emission enhancement was observed upon addition of 30 μM fluoride (≥ 100 -fold, Fig. 4a) or cyanide (≥ 100 -fold, Fig. 4b) to the metallopolymer, while none of the other anions screened elicited a notable response.

Facile methods for colorimetric and fluorescence-based detection of fluoride and cyanide have been aggressively pursued recently due to their biological/toxicological activity.^{90–105} These anions are produced upon hydrolysis of G agents, a subclass of organophosphorus nerve agents comprising three of the seven globally stockpiled chemical warfare agents. Hydrolysis of Sarin and Soman produce fluoride, and Tabun hydrolysis yields cyanide.¹⁰⁶ The high selectivity of Cu^{2+} -**P1** for these specific hydrolysis products could be harnessed to provide facile G agent detection. A related strategy involving metal ion decoordination

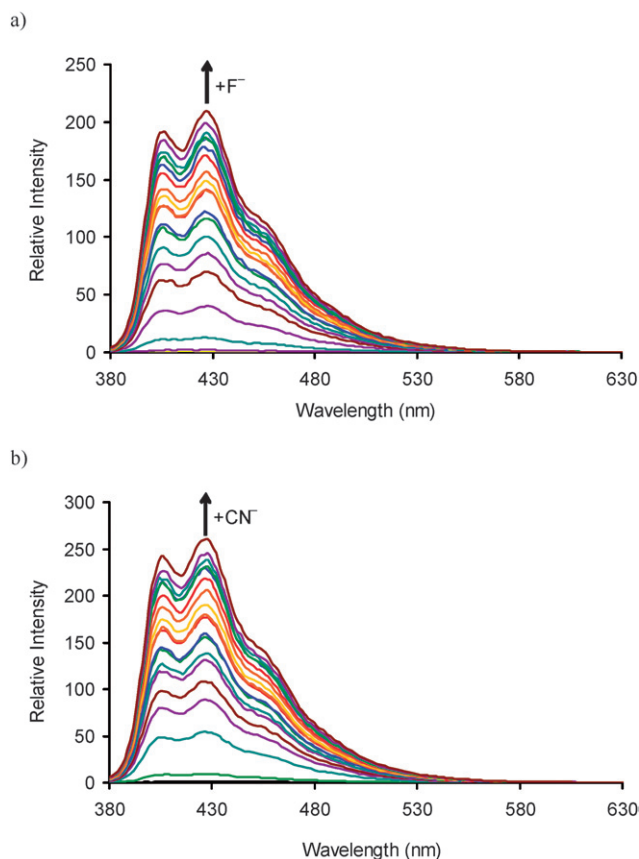


Fig. 4 Changes in the fluorescence spectrum of Cu^{2+} -**P1** complex as up to 3×10^{-5} M TBAF (a) or TBACN (b) are added ($\lambda_{\text{ex}} = 370$ nm) in THF.

from nitrogen donor ligands has recently shown promise for emission turn-on detection of nerve agent simulants.¹⁰⁷

Conclusions

We have extended a facile metal-free protocol for the preparation of FAVE polymers to prepare a 2,2'-bipyridyl chromophore-modified variation (**P1**) that serves as an effective macromolecular metal ligating scaffold. **P1** exhibits a strong ionochromic response to metal ions, including a highly selective 10-fold turn-on fluorescence response to Zn^{2+} ions. The Zn^{2+} -**P1** metallopolymer is an effective ratiometric fluorescent indicator for fluoride, while the Cu^{2+} -**P1** metallopolymer affords a highly-responsive turn-on fluorescence response to fluoride or cyanide. Extension of the synthetic route used herein to prepare additional metal chelating FAVEs, as well as application of **P1** derivatives in thin film and handheld devices are currently underway.

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