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Luminescent Properties of Water-Soluble Conjugated Metallopolymers and Their Application to Fluorescent Nitric Oxide Detection

Loi Do, Rhett C. Smith, Andrew G. Tennyson, and Stephen J. Lippard*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Water-soluble π-conjugated polymers (CPs) incorporating 5,5′-(2,2′-dipyridyl) (**CP1**) or 6,6′-(2,2′-dipyridyl) (**CP2**) units within the π-conjugated backbone were prepared as scaffolds for macromolecular metal complexation. The response of CP emission to a range of metal ions was investigated in water, 10 mM aqueous sodium dodecyl sulfate, and acetonitrile/water (95:5). Cupric ions are the most efficient quenchers of CP emission, with $K_{SV} = 1.1 \times 10^5$ and 5.2×10^4 M^{-1} in water for **CP1a** (40% bipyridyl monomer units) and **CP1b** (20% bipyridyl monomer units), respectively. Quenching is approximately twice as effective in acetonitrile/water (95:5) ($K_{SV} = 3.1 \times 10^5$ M^{-1} for **CP1a** and 1.1×10^5 M^{-1} for **CP1b**). Partial restoration of emission was observed upon exposure of Cu(II)–CP solutions to excess NO(g) in acetonitrile/water (95:5) or 10 mM SDS(aq).

Introduction

Conjugated conducting metallopolymers (CMPs) comprise one of the most exciting and underexplored classes of functional optoelectronic materials.[1−4] The unique properties of these hybrid inorganic−organic materials derive from the interaction of transition metals with the organic scaffold, with facile electron/energy transfer between distal transition metals being mediated by the π-conjugated polymer (CP) backbone. Such interactions endow CMPs with enhanced properties for a variety of applications, including electrocatalysis,[5,6] photocatalysis,[7,8] photovoltaics,[9−14] templated formation of ordered networks,[1,15−18] advanced electrode materials,[19] and conjugated coordination polymers.[20,21] CPs applied as active elements in conductivity- or fluorescence-based chemosensors[22,23] have impressive sensitivity for sensing metal ions[24−30]

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* To whom correspondence should be addressed. E-mail: lippard@mit.edu.

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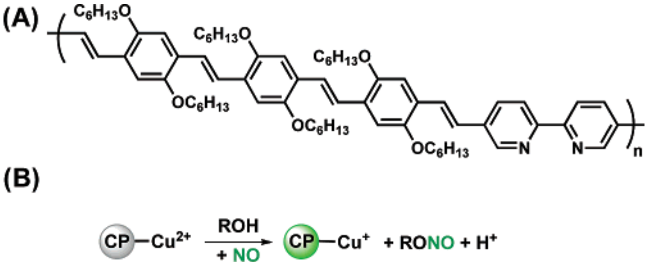
and have been adapted for the detection of improvised explosive devices (IEDs)[31−33] and metal ions. More recently, the extension of CPs to biological sensing[22,34−46] has been facilitated by the increasing number of water-soluble CPs available. CMP-based sensors are in an earlier stage of evolution, but notable resistivity-[47] and fluorescence-based[48] sensors for nitric oxide (NO) have been described.

Scheme 1. (A) Structure of a Conjugated Polymer (CP) Used To Prepare a Fluorescent NO Reporter and (B) the Proposed Turn-On Reaction of NO with CP−Cu(II) Complexes



Our laboratory has expended considerable effort to devise sensing strategies aimed at small-molecule fluorescent histological staining of neurologically important inorganic species, most notably zinc[49−59] and nitric oxide (NO).[48,60−65] NO is a challenging analyte to detect in the biological milieu because of its low concentration and short half-life in vivo.[66,67] The design of NO sensors is further complicated by the ability of other biologically relevant reactive nitrogen species (RNS) or reactive oxygen species (ROS) to produce false positive responses in certain sensing strategies.[68] Although sensors can be encapsulated within permselective polymer films[60] to exclude interfering species, only soluble dyes afford the subcellular resolution required in fluorescent microscopic imaging.[61] To approach this goal, we examined a Cu(II)−CP complex in which the CP was a bipyridyl-substituted poly(*p*-phenylenevinylene) derivative (Scheme 1A).[48] This CMP exhibits a 2.8-fold increase in integrated emission intensity upon exposure to NO(g) in dichloromethane/ethanol (4:1). NO concentrations as low as 6.3 nM were detectable. The emission enhancement is believed to result from reductive nitrosylation whereby the paramagnetic, quenching Cu(II) centers are reduced to diamagnetic, nonquenching Cu(I) by an established mechanism (Scheme 1B).[69−72] The validity of this mechanism in the copper CMP-based sensor is supported by EPR, IR, and fluorescence data. In contrast to small-molecule strategies, our CP-based approach can benefit from the enhanced sensitivity[22,23,73] of CPs to analyte-induced redox state switching, potentially impacting charge injection/charge carrier mobility along the CP backbone, in addition to redox-induced geometric reorganization of inter- and intrachain interactions. Fluorescent “turn-on” sensors derived from CPs are exceedingly scarce, especially compared to those operating via a “turn-off” mechanism.[25,29,30,48,74] The design and implementation of selective CP-based turn-on sensors for metal ions, including Hg(II)[29,30] and Fe(II),[25] is one area of particular success in this field.

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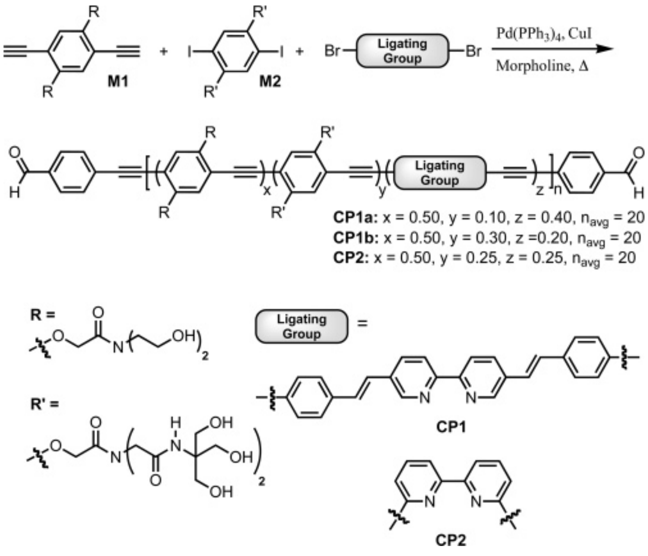
Scheme 2. Synthetic Routes to and Structures of CPs Used in the Current Study



In the current work, we investigated the interaction of water-soluble bipyridyl-appended poly(*p*-phenyleneethynylene)s (PPEs) with metal ions in organic and aqueous solution. Possible CP aggregation was probed by metal ion titrations in the presence of surfactants. Here, we report our continuing effort toward the development of turn-on fluorescent sensors for NO in aqueous solution that use CMPs as reporting elements.

Experimental Section

Materials and Methods. Polymers and monomers were prepared following reported procedures,[75,76] except for 6,6′-dibromo-2,2′-bipyridine, which was purchased from Aldrich Chemical Co. and used as received. Morpholine, used in polymerizations, was purified by passage through alumina and degassing with Ar. Dialysis of the water-soluble CPs was performed using a 1.5 mL Spin Biodialyzer (The Nest Group) equipped with cellulose membranes (MWCO = 500 Da) first with 1 mM EDTA(aq) (4 h, 16 h), followed by Millipore water (9 h, 24 h). Purification of water-soluble CPs was alternatively accomplished by using a Bio-Rad Chelex 100 resin column. The Chelex column was prepared by flushing with 1 M NaOH (2 × 3 mL), H_2O (5 × 3 mL), 1 M HCl (2 × 3 mL), and Millipore water (5 × 3 mL) prior to passing the aqueous CP solution through the column (three times each). NO gas (Matheson 99%) was purified as previously noted.[77] NMR spectra were obtained on a Varian 300 MHz spectrophotometer operating at 283 K and referenced to residual solvent signals. Reported NMR signal integrations are normalized to represent one repeat unit of the polymer as depicted in Scheme 2. Angeli's salt (AS, $Na_2N_2O_3$, an HNO donor) was purchased from Cayman Chemical Company. Water was collected from a Milli-Q Biocel (Millipore, ≥18.2 MΩ) immediately prior to use.

Polymer CP1a. Compound **M1** (31 mg, 0.070 mmol), compound **M2** (67 mg, 0.056 mmol), 5,5′-bis(4-bromostyryl)-2,2′-bipyridine (7.2 mg, 0.014 mmol), 4-bromobenzaldehyde (1.3 mg, 0.0072 mmol), $[Pd(PPh_3)_4]$ (8.1 mg, 0.0070 mmol), and CuI (1.3 mg, 0.0068 mmol) were combined with morpholine (5 mL) in a heavy-walled tube inside a glovebox. The tube was sealed with a screw cap and removed from the glovebox. The reaction mixture was stirred and heated at 100 °C for 22 h. The dark brown mixture was added to ethyl acetate to form a precipitate, which was filtered out and washed with diethyl ether. The product was then purified by passing an aqueous solution of the crude product through a Chelex 100 resin column (×3). Lyophilization of the aqueous polymer solution yielded an orange solid (32 mg, 38%). UV−vis (H_2O): λ_{max} 415 nm (ϵ = 39 000 M^{-1} cm^{-1}). Fluorescence (H_2O): λ_{em} 455 nm ($\Phi = 0.027$). M_n = 10 000 g mol^{-1}. ^1H NMR (DMSO): δ 10.1−10.3 (br, 0.09 H), 8.0−6.8 (br m, 8.4 H), 5.4−4.4 (br m, 3 H), 4.3−2.8 (br, overlaps with water in NMR solvent), 2.6−2.0 (br m, overlaps with DMSO), 2.0−1.4 (br, 1H).

Polymer CP1b. Compound **M1** (31 mg, 0.070 mmol), compound **M2** (50 mg, 0.045 mmol), 5,5′-bis(4-bromostyryl)-2,2′-bipyridine (12 mg, 0.022 mmol), 4-bromobenzaldehyde (1.3 mg, 0.0072 mmol), $[Pd(PPh_3)_4]$ (8.1 mg, 0.0070 mmol), and CuI (1.3 mg, 0.0068 mmol) were combined with morpholine (5 mL) in a heavy-walled tube inside a glovebox. The tube was sealed with a screw cap and removed from the glovebox. The reaction mixture was heated at 50 °C for 48 h. The orange mixture was added to ethyl acetate to give a precipitate. Isolation of the precipitate and washing with ethyl ether gave an orange solid (77 mg, 99%). The crude solid was dissolved in a 1.0 mL portion of 1 mM aqueous EDTA and dialyzed against 1 mM EDTA(aq) (4 h, 16 h) and water (9 h, 24 h). The aqueous polymer solution was lyophilized to give the final product. UV−vis (H_2O): λ_{max} 415 nm (ϵ = 33 000 M^{-1} cm^{-1}). Fluorescence (H_2O): λ_{em} 455 nm ($\Phi = 0.020$). M_n = 12 000 g mol^{-1}. ^1H NMR (DMSO): δ 10.1−10.3 (br, 0.09 H), 8.0−6.8 (br m, 5.2 H), 5.4−4.4 (br m, 7 H), 4.3−2.8 (br, overlaps with water in NMR solvent), 2.6−2.0 (br m, overlaps with DMSO), 2.0−1.4 (br, 2 H).

Polymer CP2. Compound **M1** (31 mg, 0.070 mmol), compound **M2** (50 mg, 0.045 mmol), 6,6′-dibromo-2,2′-dipyridyl (14 mg, 0.045 mmol), 4-bromobenzaldehyde (1.3 mg, 0.0071 mmol), $[Pd(PPh_3)_4]$ (8.2 mg, 0.0071 mmol), and CuI (1.3 mg, 0.0071 mmol) were combined with morpholine (5 mL) in a heavy-walled tube inside a glovebox. The tube was sealed with a screw cap and removed from the glovebox. The reaction mixture was stirred and heated at 70 °C for 24 h. The orange mixture was added to ethyl acetate to give a precipitate. Isolation of the precipitate and washing with diethyl ether gave an orange solid. The orange solid was purified by dissolving it in 3 mL of Millipore water and passing it through a Chelex column, followed by lyophilization to afford the final product (18 mg, 24%). UV−vis (H_2O): λ_{max} 381 nm (ϵ = 14 000 M^{-1} cm^{-1}). Fluorescence (H_2O): λ_{em} 455 nm ($\Phi = 0.0047$). M_n = 8900 g mol^{-1}. ^1H NMR (DMSO): δ 10−9.5 (br 0.08 H), 8.5−6.5 (br m, 3 H), 6.0−4.4 (br, 4 H), 4.4−3.0 (br, overlaps with water in NMR solvent), 2.8−2.2 (br m, overlaps with DMSO), 2.0−1.4 (br, 2 H).

General Spectroscopic Methods. Absorption spectra were recorded on a Cary 1E spectrophotometer. Fluorescence spectra were acquired on a Photon Technology International Quanta Master 4L fluorimeter. All NO reactions and measurements conformed to the standards and practices previously reported by our laboratory.[48,60−65] Circulating water baths were used to maintain all samples at 25 ± 1 °C. Samples for fluorescence had a path length of 1 cm in Spectrosil quartz cuvettes, with an optical density of <0.06 and volumes of 3 mL. Slit widths, excitation wavelengths, and integration times were kept constant for all experiments involving a given CP. Quantum yields (Φ) were determined by averaging the results

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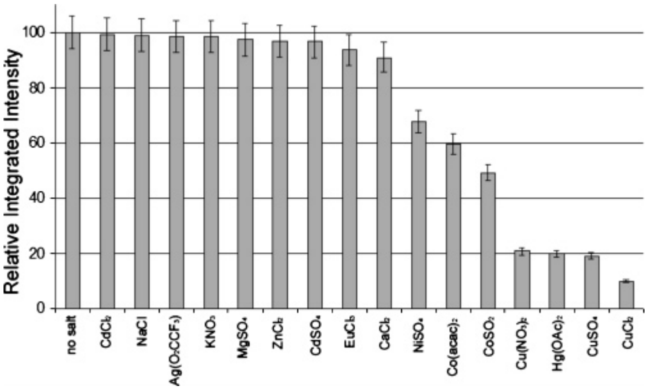

Figure 1. Relative metal-induced quenching of **CP1b** integrated emission in water. The concentration of **CP1b** was 2.07 μM, and 10 equiv of metal ion were added in each case. Individual fluorescence spectra are provided in Figure S1 of the Supporting Information.

of three values from samples with an optical density of <0.04 in Spectrosil quartz cuvettes with a path length of 1 cm. Values were referenced to NIST-issued quinine bisulfate (in 0.105 M perchloric acid in Millipore water, $\Phi = 0.546$). All experiments were performed in triplicate.

Metal Ion Selectivity. A 3.0 mL aliquot of a 2.07 μM **CP1b** solution in H_2O was added to each of 17 PMMA cuvettes. Metal-free fluorescence spectra were acquired for the samples, and then 10 equiv of each metal salt were added by the addition of a 10 μL aliquot of a 6.21 mM stock solution of metal salt to each cuvette. The salts used were $CdCl_2$, NaCl, $Ag(O_2CCF_3)$, KNO_3, $MgSO_4$, $ZnCl_2$, $CdSO_4$, $EuCl_3$, $CaCl_2$, $NiSO_4$, $Co(acac)_2$, $CoSO_4$, $Hg(OAc)_2$, $CuSO_4$, $Cu(NO_3)_2$, and $CuCl_2$. Fluorescence spectra were then recorded within 1 min of the addition and again after about 10 min. No differences between the 1 and 10 min spectra were observed. The relative quenching efficiency of each metal ion is summarized in Figure 1, and individual fluorescence spectra are provided in Figure S1 of the Supporting Information.

Optical Response of CP1a. Titration of CP1a with $CuSO_4$ in H_2O. (See Figure S2 in Supporting Information.) A 3.0 mL aliquot of a 2.07 μM **CP1a** solution in H_2O was added to a quartz cell with an optical path length of 1 cm. Small aliquots (1.8−18 μL) of a 3.45 mM $CuSO_4$ solution in H_2O were added to the fluorescence sample, where 1.8 μL represents 1.0 equiv of Cu(II)/mol of bipyridyl unit in the polymer backbone. A total of 36 μL of the $CuSO_4$ solution were added. Progressive reduction in fluorescence was observed upon addition of Cu(II). The integrated fluorescence intensity was quenched by 1.6-fold upon addition of 20 equiv of Cu(II).

Response of CP1a−Cu(II) Complex to Excess NO in H_2O. A 3.0 mL aliquot of a 2.07 μM **CP1a** solution in H_2O was added to a quartz cell with an optical path length of 1 cm. A 36 μL aliquot of a 3.45 mM $CuSO_4$ solution in H_2O was added to form the **CP1a**−Cu(II) complex. The quartz cell was sealed with a gastight screw cap equipped with a septum. A 250 μL aliquot of NO(g) (82 equiv/Cu(II) ion) was added using a gastight syringe through the cell septum, and the solution was shaken. A 1.5-fold quenching was observed from the integrated fluorescence of the **CP1a**−Cu(II) complex spectra within 1 min of addition.

Titration of CP1a with $CuSO_4$ in CH_3CN/H_2O (95:5). (See Figure S3 in Supporting Information.) A 3 mL aliquot of a 2.07 μM **CP1a** solution in CH_3CN/H_2O (95:5) was added to a quartz cell with an optical path length of 1 cm. Small aliquots (20 × 18 μL) of a 34.5 μM $CuSO_4$ solution in H_2O were added to the fluorescence sample, where 18 μL represents 0.1 equiv of Cu(II)/mol of bipyridyl unit in the polymer backbone. Additional aliquots (13 × 1.8 μL) of a 34.5 μM $CuSO_4$ solution in H_2O were then added to the fluorescence sample, where 1.8 μL represents 1.0 equiv of Cu(II)/mol of bipyridyl unit in the polymer backbone. Progressive reduction in fluorescence was observed upon addition of Cu(II). A total of 20 equiv of Cu(II) was added to the polymer sample, leading to a 7.1-fold decrease in integrated fluorescence.

Response of CP1a−Cu(II) Complex to Excess NO in MeCN/H_2O (95:5). A 3.0 mL aliquot of a 2.07 μM **CP1a** solution in acetonitrile/water (95:5) was placed in a quartz cell with an optical path length of 1 cm. A 36 μL aliquot of a 3.45 mM $CuSO_4$ solution in H_2O was added to form the **CP1a**−Cu(II) complex. The quartz cell was sealed with a gastight screw cap equipped with a septum. A 250 μL aliquot of NO(g) (82 equiv/Cu(II) ion) was added using a gastight syringe through the cell septum, and the solution was shaken. A 3.2-fold turn-on was observed within 1 min of addition.

Response of CP1a−Cu(II) Complex to Nitroxyl in CH_3CN/H_2O (95:5). Under an atmosphere of dry nitrogen, a 2.07 μM solution of **CP1a** was prepared in CH_3CN/H_2O (95:5). A 3.0 mL aliquot of the solution was added to a quartz cuvette. Ten equivalents of $CuSO_4$ were added to form **CP1a**−Cu(II), and a basal fluorescence spectrum was acquired. A 30 μL aliquot (10 μM, 50 equiv, in 1 M KOH) of AS and 60 μL of pH 7.4 HEPES, to induce decomposition to HNO, were subsequently added. The stock solution of Angeli's Salt was prepared at pH 11 and kept frozen until just prior to use. The fluorescent response of the sample was measured within 1 min of addition, and little if any change was noted over a period of 1 h.

Optical Response of CP1b. Titration of CP1b with $CuSO_4$ in H_2O. (See Figure S4 in Supporting Information.) A 3.0 mL aliquot of a 2.07 μM **CP1b** solution in H_2O was added to a quartz cell with an optical path length of 1 cm. Small aliquots (1.8−18 μL) of a 3.45 mM $CuSO_4$ solution in H_2O were added to the fluorescence sample, where 1.8 μL represents 1.0 equiv of Cu(II)/mol of bipyridyl unit in the polymer backbone. A total of 36 μL of $CuSO_4$ solution was added. The integrated fluorescence intensity was quenched by 13-fold upon addition of 10 equiv of Cu(II).

Titration of CP1b with $CuSO_4$ in CH_3CN/H_2O (95:5). (See Figure S5 in Supporting Information.) A 0.30 mL aliquot of a 30 μM **CP1b** solution in H_2O was combined with 2.70 mL of CH_3CN in a quartz cell with an optical path length of 1 cm. Small aliquots (10 × 2.6 μL) of a 3.45 μM $CuSO_4$ solution in H_2O were added to the fluorescence sample, where 2.6 μL represents 1.0 equiv of Cu(II)/mol of bipyridyl unit in the polymer backbone. Progressive reduction in fluorescence was observed upon addition of Cu(II). A total of 10 equiv of Cu(II) was added to the polymer sample, giving an integrated fluorescence quenching of 4.0-fold.

Optical Response of CP2. Titration of CP2 with $CuSO_4$ in H_2O. (See Figure S6 in Supporting Information.) A 3.0 mL aliquot of a 14 μM **CP2** solution in H_2O was added to a PMMA cuvette with an optical path length of 1 cm. Small aliquots (1.2 μL) of a 3.45 mM $CuSO_4$ solution in H_2O were added to the polymer sample, where 1.2 μL represents 0.1 equiv of Cu(II)/mol of bipyridyl unit in the polymer backbone. Progressive reduction in fluorescence was observed upon addition of Cu(II). A total of 6 equiv of Cu(II) (72 μL) was added, quenching the integrated emission by 2.8-fold.

Response of CP2−Cu(II) Complex to Excess NO in H_2O. A 3.0 mL aliquot of a 14 μM **CP2** solution in H_2O was added to a quartz cell with an optical path length of 1 cm. A 72 μL aliquot of a 3.45 mM $CuSO_4$ solution in H_2O was added to form the **CP2**−Cu(II) complex. The quartz cell was sealed with a gastight screw cap equipped with a septum. The fluorescence sample was saturated with nitrogen and purged under vacuum three times. A 250 μL aliquot of NO(g) (41 equiv/Cu(II) ion) was added using a gastight syringe through the cell septum, and the solution was shaken. A 10% quenching of integrated emission was observed within 1 min of addition.

Titration of CP2 with $CuSO_4$ in CH_3CN/H_2O (95:5). (See Figure S7 in Supporting Information.) A 3.0 mL aliquot of a 14 μM **CP2** solution in CH_3CN/H_2O (95:5) was added to a quartz cuvette with an optical path length of 1 cm. Small aliquots (1.2 μL) of a 3.45 mM $CuSO_4$ solution in H_2O were added to the polymer sample, where 1.2 μL represents 0.1 equiv of Cu(II)/mol of bipyridyl unit in the polymer backbone. Progressive reduction in fluorescence was observed upon addition of Cu(II). A total of 7 equiv of Cu(II) (84 μL) was added, giving an integrated fluorescence quenching of 11-fold.

Response of CP2−Cu(II) Complex to Excess NO in CH_3CN/H_2O (95:5). A 3.0 mL aliquot of a 14 μM **CP2** solution in CH_3CN/H_2O (95:5) was added to a quartz cell with an optical path length of 1 cm. An 84 μL aliquot of a 3.45 mM $CuSO_4$ solution in H_2O was added to form the **CP2**−Cu(II) complex. The quartz cell was sealed with a gastight screw cap equipped with a septum. The fluorescence sample was saturated with nitrogen and purged under vacuum three times. A 250 μL aliquot of NO(g) (35 equiv per Cu(II) ion) was added using a gastight syringe through the cell septum, and the solution was shaken. A 3.5-fold increase in integrated emission was evident within 1 min of addition.

Titration of CP2 with $CuSO_4$ in 10 mM SDS(aq). A 3.0 mL aliquot of a 14 μM **CP2** solution in 10 mM SDS(aq) was added to a PMMA cuvette with an optical path length of 1 cm. Small aliquots (1.2 μL) of a 3.45 mM $CuSO_4$ solution in H_2O were added to the polymer sample, where 1.2 μL represents 0.1 equiv of Cu(II)/mol of bipyridyl unit in the polymer backbone. Progressive reduction in fluorescence was observed upon addition of Cu(II). A total of 70 equiv of Cu(II) (840 μL) was added, giving an integrated fluorescence quenching of 4.2-fold.

Response of CP2−Cu(II) Complex to Excess NO in 10 mM SDS(aq). A 3.0 mL aliquot of a 14 μM **CP2** solution in 10 mM SDS(aq) was added to a quartz cell with an optical path length of 1 cm. An 0.84 mL aliquot of a 3.45 mM $CuSO_4$ solution in H_2O was added to form the **CP2**−Cu(II) complex. The quartz cell was sealed with a gastight screw cap equipped with a septum. The fluorescence sample was saturated with nitrogen and purged under vacuum three times. A 250 μL aliquot of NO(g) (3.5 equiv/Cu(II) ion) was added using a gastight syringe through the cell septum, and the solution was shaken. A 30% increase in integrated fluorescence was observed within 1 min.

Results and Discussion

Design of Conjugated Metallopolymers. The goal of this study was to prepare water-soluble analogues of our previous CP-based NO sensor (Scheme 1A). Water-soluble CPs interact with biological materials to varying degrees depending on the identity of their solubilizing side chains. “Nonspecific interactions”[78] with biological species or CP aggregation, whether by interchain or intrachain interactions, can have deleterious effects on the emission efficiency of CPs in aqueous solution. Such factors compelled us to employ nonionic water-soluble CPs incorporating polyol side chains of the type first reported by others.[75,76] These polymers are especially attractive scaffolds for biological sensing applications because the emission of these polymers will be less dependent on ionic strength or pH than similar CPs with ionic side chains. Dendrimers featuring a polyol-substituted periphery efficiently permeate cell membranes for drug delivery, suggesting that polyol-encapsulated CPs may exhibit similar penetrating or localizing behavior with cell surfaces.

Many metal-ligating units have been explored for chelating transition metals to CPs. A stronger interaction between the transition metal and the CP π-system will perturb CP emission more upon metal ion binding or redox changes and thus afford the most responsive sensor. Not surprisingly, ligating groups incorporated directly into the conjugated main chain facilitate stronger interactions than do side chain binding groups. Other considerations when selecting a metal-binding group are the overlap of the metal and CP redox potentials and metal binding affinity.[2] Numerous CMPs with bipyridyl ligating groups feature strong interaction between metal ions and CPs. The optical responses of several bipyridyl-modified CMPs and the nature of geometric and charge density response to metal binding have been well-characterized.[2,16,24,79−86] We have taken advantage of the sensitivity of a bipyridyl-substituted poly(*p*-phenylenevinylene) (PPV) derivative to develop an efficient sensor for NO.[48] Concentrations as low as 6.3 nM NO can be detected in organic solvent upon reductive nitrosylation of Cu(II) bound to the CP. This early success led to our initial selection of bipyridyl functionalities as the metal-ligating module of CMP sensors (Scheme 2) applied to aqueous detection of NO. The bipyridyl substituents in **CP1** were selected to mimic those used previously in our highly sensitive NO sensor (Scheme 1A). Attachments at the 3,3′-positions of the 2,2′-bipyridyl group provide an alternative substitution pattern, and the requisite monomer is commercially available.

Syntheses. Scheme 2 illustrates the syntheses of CPs used in the current study via modification of a literature procedure.[75,76] Palladium-catalyzed Sonogashira-type coupling of diethynylaryls and diiodoaryls with various fractions of metal-ligating monomers facilitated rapid assembly of ligand-modified CPs. A small fraction of 4-bromobenzaldehyde was added as an end cap to limit the degree of polymerization (*n*, Scheme 2) to twenty monomer units (as defined in Scheme 2). The number average molecular weights (M_n) of purified polymers were somewhat higher than the statistically anticipated value ($n = 23$, 22, and 25 for **CP1a**, **CP1b**, and

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Table 1. Key Physical Parameters for **CP1** and **CP2**

	CP1a	**CP1b**	**CP2**
$\lambda_{\pi-\pi^*}$ (nm)[a]	415	415	381
ϵ (M^{-1} cm^{-1})[a]	39 000	33 000	14 000
λ_{em} (nm)[a]	455	455	455
Φ (%)[b]	2.7	2.0	0.47
K_{SV} (M^{-1}), H_2O[c]	1.1×10^5	5.2×10^4	9.2×10^4 [e]
K_{SV} (M^{-1}), MeCN/H_2O[c,d]	3.1×10^5	1.1×10^5	5.0×10^4

[a] In water. [b] Average of three measurements. [c] For quenching with Cu(II). [d] In acetonitrile/water (95:5). [e] In 10 mM SDS(aq).

CP2, respectively), presumably because of the removal of some lower molecular weight fractions by precipitation from ethyl acetate and rinsing with ethyl ether in the course of purification. Because Cu(I) can bind to bipyridyl-substituted PPEs,[16,87−89] additional precautions were taken to remove traces of this ion used in the course of preparation. If ligand-modified CPs are insoluble in water, transition metals can be removed by washing an organic solution of the CP with EDTA(aq).[16] For water-soluble CPs, this method is not viable. We have employed two alternatives that are generally applicable for removing trace metal ions from water-soluble CPs. The first method involves dialysis, using a low molecular weight cutoff membrane (500 Da), of aqueous CP against 1 mM EDTA(aq) (exchanging dialysate at 4 and 16 h) to remove metals, followed by pure water (exchanging dialysate at 9 and 24 h) to remove residual EDTA. This method removes metal ions very effectively, but is very slow, and only milligram quantities of CP can be purified at a time. A second, more rapid method is to pass aqueous CP through a column of Chelex 100, a metal-chelating resin. We found that three sequential elutions of the CP yielded a material with emission properties identical to those of materials purified by dialysis. This second procedure allows more rapid purification of CPs and on a larger scale.

Spectroscopic Properties and Response to Metal Ions. UV−vis and fluorescence experiments using the purified CPs were conducted in water and acetonitrile/water (95:5) to examine possible solvatochromic effects. Visually, **CP1** and **CP2** are bright orange solids, both with fluorescence emission centered at ~455 nm in water. Table 1 summarizes some key spectroscopic parameters of the polymers. The first stage of our NO sensing strategy is to find a suitable quencher of the CP emission that could undergo redox reactivity with NO. Consequently, we screened a number of transition metal ions that could produce this desired response, as well as other metal ions found in biology (Figure 1).

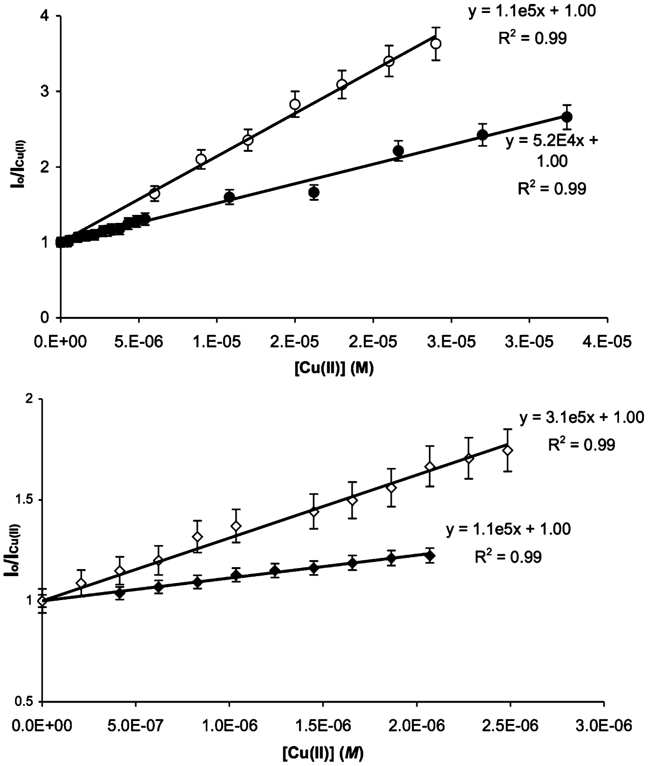

Figure 2. Stern−Volmer plots for the titration of **CP1b** with CuSO4 (top) in water (solid circles) or acetonitrile/water (95:5) and **CP1a** (bottom) in water (solid diamonds) and acetonitrile/water (95:5) (unfilled circles). The concentration of CP was 2.07 μM in all cases. The equations and R^2 values for the linear fits (black lines) are provided to the right of each set of data points.

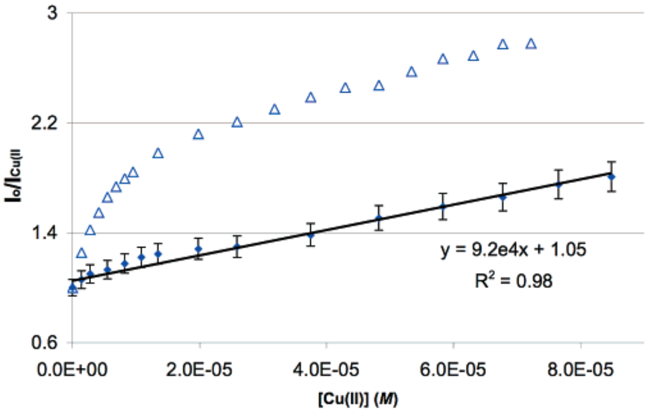

Figure 3. Stern−Volmer plots for the titration of **CP2** (14 μM) with $CuSO_4$ in water (triangles) and in 10 mM SDS(aq) (diamonds with error bars and linear fit). The equation and R^2 value for the linear fit are provided in the bottom right of the graph.

CMP emissive properties and metal ion-induced quenching efficiency may depend on the counteranion of the transition metal salt used to metalate the CP.[27,89] For example, the use of different counteranions was offered as an explanation for discrepancies in the observed Cu(II)-induced quenching of emission from a bipyridyl-containing polyfluorene.[89] Near total quenching was accomplished with $CuCl_2$, but $CuSO_4$ caused only slight quenching in that system. Counterion effects could influence the dynamic range, sensitivity, and kinetics of NO detection by a Cu(II)-bound CMP. To rule out such influences in our system, the emission response of **CP1b** to $CuCl_2$, $CuSO_4$, and $Cu(NO_3)_2$ was investigated. Only slightly more quenching was observed with $CuCl_2$ (90%) versus $Cu(NO_3)_2$ (79%) or $CuSO_4$ (81%) (experimental error ±6%), and $CuSO_4$ was used in further titrations (Figures 2 and 3).

Our approach to NO detection by reductive nitrosylation has focused on Cu(II)−fluorophore complexes. We therefore studied the interaction of **CP1** and **CP2** with Cu(II) in more

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detail. Stern−Volmer plots for the titrations of **CP1** in water and in acetonitrile/water (95:5) are shown in Figure 2, and the derived Stern−Volmer constants (K_{SV}) are listed in Table 1. The Stern−Volmer plots ($I_o/I_{Cu(II)}$ vs [Cu(II)], Figure 2) are linear for **CP1**, in agreement with previous observations that PPEs are quenched by a static binding mechanism.[27,73] **CP1a** and **CP1b** differ only in the relative fraction of bipyridyl units in the main chain (40% versus 20%, respectively), so K_{SV} should be approximately twice as high for **CP1a**. This trend was observed in both water and acetonitrile/water (95:5). Quenching is approximately twice as efficient in acetonitrile/water (95:5) versus water for both polymers.

Because of the nonlinearity of the Stern−Volmer plot for **CP2** emission quenching by Cu(II) in water (Figure 3), an accurate K_{SV} could not be calculated using the simple static binding model. The lower solubility of **CP2** in water versus **CP1** was noted during the preparation of stock solutions, suggesting that aggregation may contribute to this divergent behavior. This observation was further explored by titrating an aqueous solution of **CP2** with Cu(II) in the presence of a surfactant (10 mM sodium dodecyl sulfate, SDS) known to disrupt CP aggregation in aqueous solution.[90] The titration curve was much more linear in the presence of SDS, but at the expense of quenching efficiency ($K_{SV} = 9.2 \times 10^4$ M^{-1}, Figure 3). The overall low affinity of Cu(II) to the CPs in aqueous solution compared to measurements in organic solution is probably the result of competitive binding of Cu(II) with amide/polyol side chains.

NO Detection by Cu(II)−CP Complexes. Given the efficient quenching of CP emission by Cu(II) and its ability to be reduced by NO(g), we examined the emission response of cupric CMPs to NO in water and in acetonitrile/water (95:5). Surprisingly, the addition of NO(g) to **CP1a**−Cu(II) in H_2O lead to 50% *quenching* of emission. In this case, NO presumably acts as a collisional quencher, similar to the well-known fluorescence quenching ability of O_2. The addition of NO to **CP1a**−Cu(II) in acetonitrile/water (95:5) gave a more desirable 3.2-fold fluorescence turn-on (Figure 4), approximately the same relative turn-on observed for the Cu(II) complex of the PPV derivative shown in Scheme 1. Reductive nitrosylation produces protons (Scheme 1), which quench the emission of metal-free bipyridyl-substituted CPs. Exposure of premetalated Cu(II)−**CP1** to 4 μM HCl(aq) affords no change in emission intensity. Thus protons are not responsible for the observed emission fluctuations. We have been unable to conduct these experiments in buffer because of CMP insolubility or poor quenching efficiency by Cu(II).

Notably, emission is not changed upon the addition of Angeli's salt, a nitroxyl (HNO) donor (Figure 4; see Experimental section for details), to **CP1a**−Cu(II). This finding represents an advance in selectivity because HNO produced a turn on of emission from the previous CP−Cu(II) NO sensor.[48]

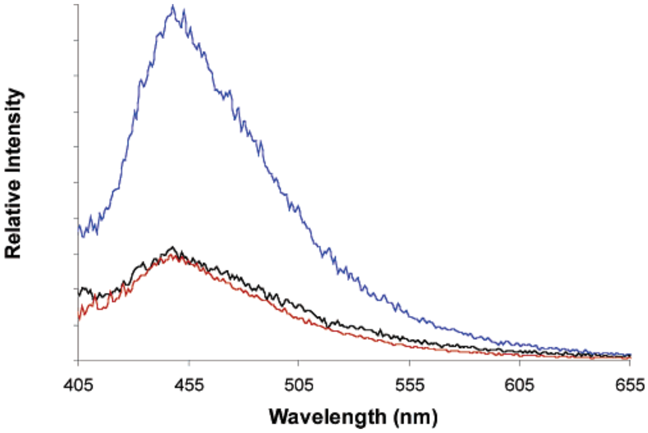

Figure 4. Fluorescence spectra for **CP1a**−Cu(II) (black trace), **CP1a**−Cu(II) with 50 equiv Angeli's salt (red trace), and **CP1a**−Cu(II) with NO(g) (blue trace). **CP1a** concentration was 2.07 μM in acetonitrile/water (95:5). Details are provided in the Experimental Section.

The **CP2**−Cu(II) complex responded similarly to the **CP1a**−Cu(II) complex upon reaction with excess NO(g), with a 30% fluorescence turn-off observed in H_2O and a 3.2-fold fluorescence turn-on in acetonitrile/water. In the presence of 10 mM SDS(aq), excess NO(g) produced a modest 1.3-fold fluorescence turn-on. This experiment demonstrates the importance of inter- and intrachain influences on CMP analyte response and should be considered in all water-soluble CP work.[78] The modest response of **CP1** and **CP2** to NO is not surprising given the observed potential for metal-binding competition with polyol side chains.

Summary

Water-soluble conjugated polymers were prepared, and their photophysical properties and fluorescence response to metal ions were characterized in three solvent systems. Of the metal ions samples, Cu(II), Co(II), and Hg(II) most efficiently quench CP emission. The quenching of **CP1** with Cu(II) appears to take place by a static quenching mechanism and is roughly twice as efficient in acetonitrile/water (95:5) as in pure water. In contrast, **CP2** emission is quenched by a different mechanism, possibly because of aggregation in aqueous solution. In the presence of surfactant, the quenching of **CP2** emission by Cu(II) does support a static quenching mechanism. Modest emission turn-on of up to 3.2-fold is observed upon reaction of Cu(II)−CP complexes with NO(g). This turn-on response is selective for NO versus HNO, a noted improvement over our previous CP-based NO sensor. The modest turn-on and Cu(II) quenching efficiency are most likely consequences of the competitive binding between Cu(II) and CP side chains or water. Although NO detection in water was not accomplished in the absence of surfactant, this study, employing water-soluble CMPs, represents an important step toward that goal. Future efforts will focus on improving the metal binding affinity through the incorporation of alternative ligating units and water-solubilizing side chains.

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Supporting Information Available: Individual fluorescence spectra for metal ion selectivity and titrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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