

Communications to the Editor

Conducting Polymetallorotaxanes: A Supramolecular Approach to Transition Metal Ion Sensors

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The integration of receptors into conducting polymer frameworks has been shown to produce efficient resistive and fluorescence responses to targeted analytes.¹ Conducting polymers that contain transition metals also present opportunities to generate a variety of new sensory functions as well as conduction by mixed valence processes.² As part of our continuing interest in sensory polymers, we have targeted conducting polymers containing metallorotaxanes.^{3,4} In this communication, we report novel conducting polymetallorotaxanes and the corresponding metal-free polyrotaxanes. We further demonstrate that these polyrotaxanes reversibly bind Cu⁺ and Zn²⁺ ions and that the threaded rotaxane structure is critical to produce the well-behaved reversible complexation.

Compound **2** (Scheme 1) was chosen to serve as the threading and polymerization element since we have recently demonstrated its utility in formation of conducting polymer–transition metal hybrid materials.² Moreover we have determined that the metal-free polymer, Poly(**2**), displays windows of conductivity in both oxidized and reduced forms.² The metallorotaxane monomers, **3** and **4**, readily assemble by combining the macrocyclic phenanthroline **1**, developed by Sauvage,⁴ **2**, and Cu⁺ or Zn²⁺ ions (1:1:1) in CH₂Cl₂ (Scheme 1). Concurrent with the assembly, we observed a red shift of the ligand-centered optical transitions. This effect is the largest for **3** (Figure 1), and the transitions associated with moiety **2** display the largest shift ($\Delta\lambda_{\text{max}} = 60$ nm). The metallorotaxanes appear to be fully associated in CDCl₃, and NMR signals⁵ for the free ligand species were not observed. An X-ray structure determination of **3** unambiguously confirms the metallorotaxane structure. As shown in Scheme 1, the Zn²⁺ ion exhibits a distorted tetrahedral structure, and **2** resides in a crescent-type conformation.⁶

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(5) **3** ¹H (CDCl₃, 250 MHz): 3.78–3.85 (broad), 6.35 (d), 7.05 (m), 7.23 (m), 7.47 (d), 7.68 (d), 8.06 (d), 8.18 (s), 8.22 (s), 8.35 (d), 8.75 (d). **4** ¹H (acetone-*d*₆, 250 MHz): 4.20–4.37 (m), 6.83 (d), 7.57 (t), 7.79 (m), 7.93 (d), 7.80 (d), 8.11 (d), 8.78 (s), 8.79 (d), 8.89 (d), 9.37 (d). NMR data for the free ligand is given in ref 4a.

(6) The crystal was obtained by slow diffusion of diethyl ether into a nitromethane solution of compound **3** at 0 °C. **3** crystallized in the triclinic space group *P*1 with *a* = 14.5800(6) Å, *b* = 14.703(1) Å, *c* = 14.172(1) Å, α = 104.830(2)°, β = 96.881(4)°, γ = 97.386(5)°. *V* = 2875.3(3) Å³, *Z* = 2, and *d*_{calcd} = 1.519 g/cm³.

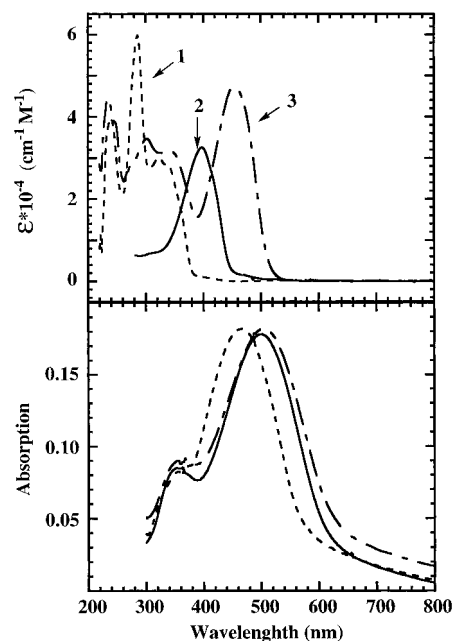


Figure 1. (top) UV–vis absorption of **1** (dashed line), **2** (solid line), and **3** (dot-dashed line) in CH₂Cl₂. (bottom) Initial Poly(**3**) film (solid line), after treatment with H₂O/ethylenediamine (3/1) (dashed line) and after dipping in 0.05 M Zn(ClO₄)₂/MeCN (dot-dashed line).

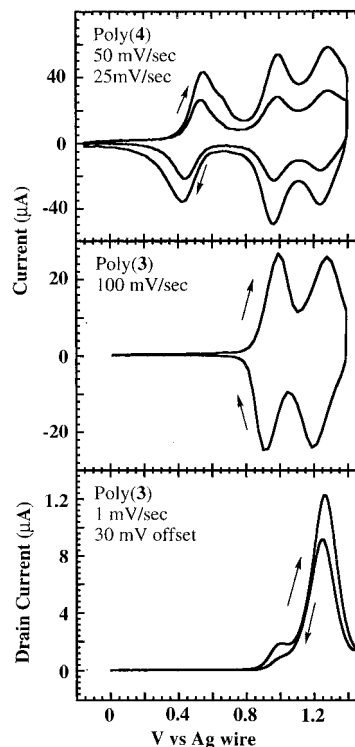
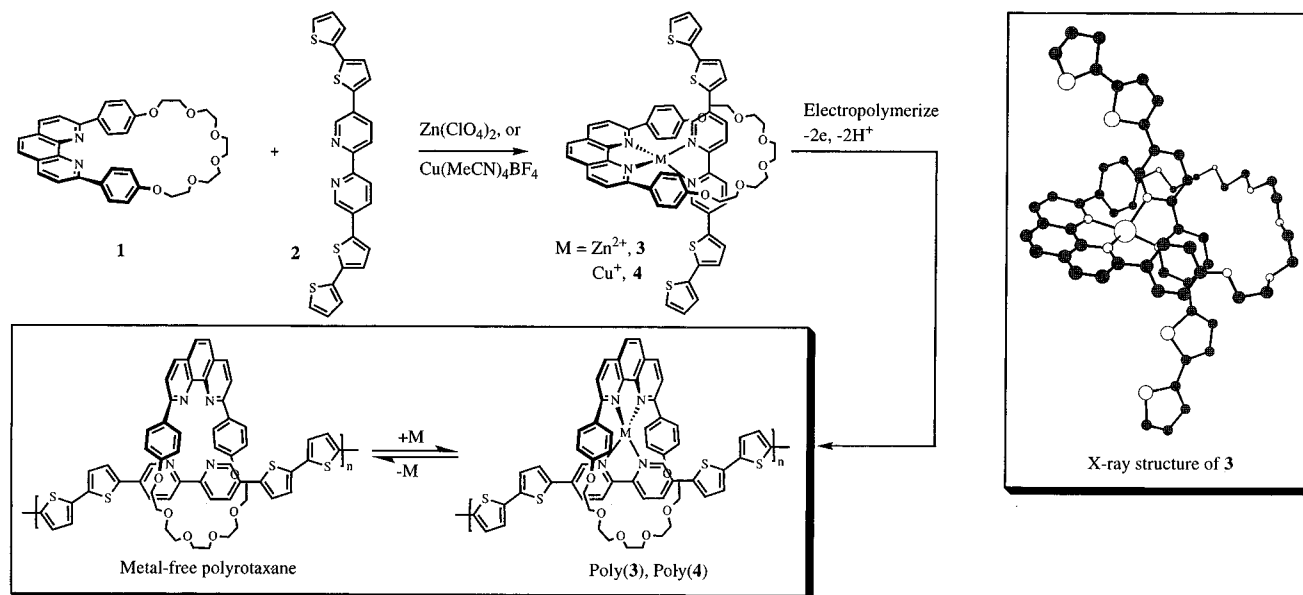


Figure 2. (top and middle) Cyclic voltammetry of Poly(**4**) and Poly(**3**) in CH₂Cl₂/0.1 M [(*t*-Bu)₄N]PF₆ on interdigitated microelectrodes with 5 μm spacing in N₂ atmosphere. (bottom) Conducting (drain) current vs electrochemical potential of Poly(**3**) (same device and medium as for the CV shown in the middle). Note that the drain current is directly proportional to the conductivity. *E*_{1/2}(ferrocene) = 0.40 V vs Ag wire.

Solutions of **3** or **4** (0.42 mM) readily electrochemically polymerize to deposit polymetallorotaxane, Poly(**3**) or Poly(**4**),

Scheme 1



films on electrodes cycled from 0–1.4 V vs Ag wire in $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [(t\text{-Bu})_4\text{N}]\text{PF}_6$. Polymerization on interdigitated microelectrodes allows for *in situ* conductivity measurements as a function of electrochemical potential.⁷ As shown in Figure 2, the $\text{Cu}^{1+/2+}$ redox couple at 0.48 V vs Ag wire is easily discernible from that of the polymer backbone by comparison of Poly(3) to Poly(4). Determination of the current as a function of scan rate confirms that all of the electrochemically active groups are surface confined. The $\text{Cu}^{1+/2+}$ couple is less reversible than the polymer-centered processes, and this kinetic sluggishness is more apparent at high scan rate with an additional shoulder at 0.67 V. The cyclic voltammograms of Poly(3) and Poly(4) both display two well-defined redox waves centered at 0.96 and 1.23 V vs Ag wire (Figure 2). This profile differs from Poly(2) which displays two unresolved waves.^{2,8} We propose that the sharpening of the analogous redox peaks in Poly(3) and Poly(4) is the result of localization of the redox processes. Consistent with this localization, the conductivity profile (drain current) of Poly(3) shows behavior characteristic of a redox conduction with the maxima at the half-wave potential.⁹ This behavior is different from Poly(2) which exhibits only one peak in its conductivity profile.^{2,8} Poly(4) displays a conductivity profile very similar to Poly(3), and as a result of slow electrochemical kinetics, no redox conductivity is observed for the $\text{Cu}^{1+/2+}$ couple.

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(8) We have previously reported the electrochemistry of Poly(2) in $\text{MeCN}/0.1 \text{ M } [(t\text{-Bu})_4\text{N}]\text{PF}_6$ solutions with Ag/Ag^+ as reference electrode. We found qualitatively similar behavior in CH_2Cl_2 .

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Critical to potential sensory properties of conducting polyrotaxanes is the reversibility of metal ion binding. Zn^{2+} binding was readily probed by UV–vis spectroscopy (Figure 1). As synthesized on ITO glass, Poly(3) is red ($\lambda_{\text{max}} = 501 \text{ nm}$). The metal-free polyrotaxane is produced by rinsing the Poly(3) with a $\text{H}_2\text{O}/\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (3/1) solution, and the film changes to yellow ($\lambda_{\text{max}} = 467 \text{ nm}$). Retreatment of Zn^{2+} ions produces Poly(3) and shifts the absorbance back to the initial state. These results are consistent with the shifts described earlier for the formation of 3 (Figure 1, top). Similar investigations with Poly(2) show some sample and solvent dependence. Poly(2) exhibits no UV–vis shift in $\text{Zn}^{2+}/\text{MeCN}$ solution but gave 12 nm red shifts when immersed in CH_2Cl_2 with or without Zn^{2+} ions for a day. Polyrotaxane binding of Cu^+ and Cu^{2+} ions is also reversible and under further investigation.

In conclusion, we have synthesized the first conducting polymetallorotaxanes by electrochemical polymerization of metallorotaxanes. These supramolecular systems reversibly bind zinc and copper ions and exhibit conductivity profiles characteristic of localized redox conductors. We plan to expand our investigations of conducting polyrotaxanes to systems containing different donor atoms and binding sites for the detection of a variety of metal ions.

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