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Electrochromic Polymer Films Containing Re(I) and Pt(II) Metal Centers

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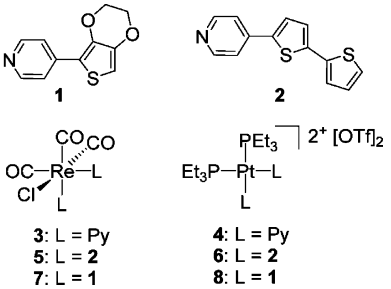
Three Re(I) complexes (**3**, **5**, and **7**) ($Re(CO)_3Cl(L)_2$) and three new Pt(II) complexes (**4**, **6**, and **8**) ($[Pt(P(Et)_3)_2(L)_2](OTf)_2$), where L = pyridine, **1** (4-Py-EDOT) or **2** (4-Py-bithiophene), were prepared and characterized. The solid-state structures of **4** and **5** were determined by X-ray crystallography. Electrochromic polymeric films of **2**, **5**, and **6** were prepared and characterized.

Polymers containing transition metals are a promising class of materials for applications in electronics, molecular sensing, and catalysis.[1−7] Inserting transition metals into polymers with π-conjugated backbones is synthetically attractive because each of the components affects the chemical, electronic, and optical properties of the overall material.[1−4] There are many examples of multidentate ligands that bind metals and integrate them into a conjugated polymer backbone.[1,2] Our laboratory has been investigating the use of hybrid pyridine/thiophene ligands (where various thiophene derivatives are attached to the 4 position of pyridine) to prepare transition-metal-containing compounds with interesting optical properties.[8] The pyridine moieties of these ligands have a high binding affinity for late transition metals with no evidence thus far of any metal−sulfur interactions with the thiophenes. These monodentate ligands are potentially of wide interest because they could be incorporated into many transition metals with at least two reactive coordination sites to prepare polymer precursors. We report the use of these hybrid ligands to prepare Re(I) and Pt(II) complexes that upon polymerization form electrochromic[9,10] materials (materials that change color upon switching of the redox states).

Chart 1



1

2

3: L = Py
5: L = **2**
7: L = **1**

4: L = Py
6: L = **2**
8: L = **1**

Re(I) complexes **3**,[11] **5**,[8] and **7**[8] were prepared by combining 1 equiv of $Re(CO)_5Cl$ and 2 equiv of pyridine, **1**,[8] or **2**[12] in a 1:1 THF/toluene mixture (Chart 1). As shown by the single-crystal X-ray structures of **3**,[13] **5**[14] (Figure 1), and **7**[8] and presumably because of the trans effect of the CO ligands, these octahedral Re(I) complexes all have the pyridine or hybrid pyridine/thiophene ligands in a cis configuration. The N−Re−N bond angle of **5** is 83.9°, which is slightly larger than the same angle in **7** (83.0°).[8] Polymers grown from **5** cannot be linear because of the cis disposition of the two hybrid pyridine/bithiophene ligands. Three new Pt(II) complexes (**4**, **6**, and **8**) were prepared by combining

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(14) Crystal data for **4**: $C_{24}H_{40}F_6N_2O_6P_2PtS_2$, fw = 887.73 g/mol, crystal size $0.10 \times 0.05 \times 0.01$ mm^3, monoclinic, space group $P2(1)/c$, $a = 19.065(2)$ Å, $b = 9.4991(8)$ Å, $c = 18.722(2)$ Å, $\beta = 102.944(1)°$, $V = 3304.45(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.784$ Mg/m^3, $\lambda = 0.710\,73$ Å, $\mu = 4.543$ mm^{-1}, $F(000) = 1760$, $T = 100(2)$ K, $R = 0.0322$, and $R_w = 0.0735$. Crystal data for **5**: $C_{21.5}H_{17}Cl_{0.5}NO_{1.50}Re_{0.5}S_2$, fw = 488.31 g/mol, crystal size $0.12 \times 0.10 \times 0.10$ mm^3, monoclinic, space group $C2/c$, $a = 16.742(5)$ Å, $b = 9.043(3)$ Å, $c = 26.653(8)$ Å, $\beta = 103.926(5)°$, $V = 3916(2)$ Å^3, $Z = 8$, $D_{calcd} = 1.656$ Mg/m^3, $\lambda = 0.710\,73$ Å, $\mu = 3.427$ mm^{-1}, $F(000) = 1944$, $T = 100(2)$ K, $R = 0.0374$, and $R_w = 0.0739$.

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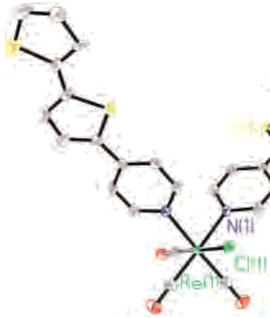

Figure 1. ORTEP diagram of **5**·$C_6H_5CH_3$ with ellipsoids drawn at 50%. The solvent molecule and H atoms are omitted for clarity.

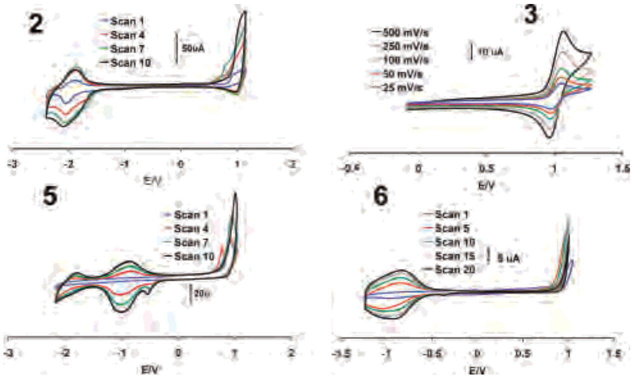

Figure 2. Cyclic voltammetry for compounds **2**, **3**, **5**, and **6** in acetonitrile with 0.1 M Bu_4NPF_6 as the supporting electrolyte. All potentials are shown referenced to the Fc/Fc$^+$ redox couple.

1 equiv of $Pt(PEt_3)_2(OTf)_2$[15] with 2 equiv of either pyridine, **1**, or **2** in CH_2Cl_2. Removal of the solvent followed by recrystallization from CH_2Cl_2/toluene led to isolation of analytically pure compounds in 69−79% yields. All three compounds were characterized by ^1H and ^{13}C NMR along with elemental analysis, and all data were consistent with their proposed structures. Although derivatives of compound **4**, specifically where other atoms or groups are attached to the pyridine, are common in the literature, especially in the field of supramolecular chemistry,[16−19] we were surprised not to find **4** itself reported in the literature. A thermal ellipsoid diagram shows the details of the cation of **4** in Figure S1 in the Supporting Information (SI), which is a slightly distorted square-planar structure with the pair of phosphine ligands and the pair of pyridine ligands situated cis to one another. The N−Pt−N angle exhibits compression (83.73°, similar to the N−Re−N angle of **5**), the P−Pt−P angle is elongated (95.11°), and the two P−Pt−N angles are close to 90° (91.33° and 89.98°).

All of the cyclic voltammetry experiments for this study were conducted under inert atmosphere conditions in acetonitrile with 0.1 M Bu_4NPF_6 as the supporting electrolyte. Full experimental details and tabulated data can be found in the SI. All redox values are reported versus the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple. First, we examined complexes **3** and **4** to investigate any redox activity resulting from the metal center bound to two pyridine ligands. Pyridine itself shows no redox chemistry in the window of interest. Compound **3** exhibited only one reversible wave at 1.01 V (Figure 2, top right) with a scan rate dependence consistent with species in solution (see the SI) and two irreversible waves near the edges of the solvent window ($ip_a = 1.8$ V and $ip_c = -2.8$ V, in the SI). Neutral Re derivatives like $ReCl(CO)_3L$, where L is 2,2′-bipy or phen, exhibit an irreversible oxidation wave attributed to expulsion of the chloride ligand and replacement with an equivalent of CH_3CN[20,21] in the general potential range where **3** shows a reversible wave. By using pyridine derivatives instead of 2,2′-bipy or phen derivatives as a scaffold for thiophenes, the result may be polymers with increased stability under oxidative conditions. Compound **4** exhibits a single irreversible reduction wave at $ip_c = -1.8$ V (Figure S2 in the SI) and a scan-rate-dependent irreversible oxidative wave at $ip_a = 1.4$ V. To avoid interference from this electrochemically irreversible redox chemistry, complexes **5**−**8** were examined in the window between the irreversible redox waves.

Under oxidative conditions, **1** and **2** undergo electrochemically induced coupling resulting in dimers or other oligomers. Ligand **1** has only a single site available for oxidative coupling, due to the blocking ethylenedioxy group, but a small percentage of compound **2** could undergo both α and *β* couplings resulting in dimers with a variety of structures. Compound **1** exhibited an irreversible oxidative wave at $ip_a = 1.0$ V (Figure S3 in the SI). Scanning to 1.300 V resulted in the growth of a film, as demonstrated by the increase in the current passed with each scan in the region of ∼−0.50 to −1.50 V. The film growth stopped after ∼20 scans, and the film demonstrated a quasi-reversible peak associated with dimer formation. Removal of the electrode and electrochemistry in a solution of the supporting electrolyte without the monomer present show that the dimer electrochemistry has $E_{1/2} = -0.89$ V (Figure S4 in the SI). The films of the dimers of compound **1** were easily washed off of the electrode.

Cyclic voltammetry of **2** over a window of +1.0 to −2.2 V resulted in the growth of a much more robust film that had a reversible wave with $E_{1/2} = -0.95$ V and a pseudo reversible wave with $ip_c = -1.8$ V (Figure 2, top left). Similar systems have seen reductive waves associated with radical anion and dianion formation in the range of −1 to −2.2 depending on the length of the thiophene bridge and capping moieties.[22−25] The scan rate dependence of the redox

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process at −0.95 V is consistent with a surface-bound species (see the SI). Films of oligomers of **2** passed ∼5 times more current than films of **1** and were much more stable to handling and washing. This may be attributable to the much lower solubility in acetonitrile of **2** compared to **1**.

Compounds **5** and **6** form polymers under oxidative conditions because they each contain 2 equiv of ligand **2**. For compound **5**, the first scan exhibits an oxidative peak at ip_a of ∼0.9 V whose position steadily becomes more positive with increasing scans. The oxidations of **2** and **3** overlap, and we propose that the small reductive wave seen with **5** is from reduction of a similar species observed in **3** but that much of that oxidized species was removed by an electrochemical step, namely, electron transfer to the attached bithiophene, which then undergoes a chemical coupling step. Upon scanning in the reverse direction, a relatively sharp reversible wave is observed at $E_{1/2} = -1.91$ V. The sharpness of this wave is usually indicative of a molecular-based redox couple (as opposed to a broader polymer-based wave). Although we did not observe a reversible redox wave at this potential with **3**, many similar compounds do exhibit a reversible peak in this range.[20,21] With an increase in the number of scans, this wave at $E_{1/2} = -1.91$ V broadens, which is indicative of the overlap of a polymer-based and ligand-based redox couple. The polymer film redox couple grows with an increase in the number of scans, and the resulting film is stable to rinsing. The $E_{1/2}$ value of poly-**5** is ∼0.96 V more difficult to reduce compared to **2**. Complex **6** exhibits a much simpler cyclic voltammogram, consistent with the simplicity of the electrochemistry of the model complex **4**. Upon scanning in the oxidative direction, there is an irreversible peak just above 1.0 V and growth of a redox couple centered at $E_{1/2} = -0.93$ V associated with poly-**6**. We were unable to grow any films of transition metals bound to **1** (using **7** and **8**).

Figure 3 shows films of **2**, **5**, and **6** grown on indium−tin oxide (ITO)-coated glass plates. The films were made by holding the ITO plate at oxidizing potentials in solutions of the monomer for 2 min. After growing of the films, the plates were pulled out of the monomer solutions, rinsed with clean acetonitrile, and replaced in monomer-free acetonitrile/supporting electrolyte solutions. Films of **2** and **6** behaved similarly, demonstrating electrochromic behavior by switching between a reddish magenta color at low potentials (−0.9 and −1.1 V, respectively, in parts a and c of Figure 3) and a blackish-purple color when held at −0.1 V (parts b and d of Figure 3). This further demonstrates the lack of participation of the Pt(II) metal center in the behavior of the film. Much more striking is the polyelectrochromism associated with films of **5** (Figure 3e−g). A solution of compound **5** as a monomer in acetonitrile exhibits a yellow/orange color, similar to when poly-**5** is held at a potential of −0.1 V. Upon reduction of the polymer, the film takes on a distinct green color when held at −2.0 V, and upon exposure of the film to a voltage of 1.0 V, the polymer film takes on a purple color. UV−vis spectra of these films can be found in the SI. The similar behavior observed between **2** and **6** gives us confidence that their electrochromic behavior is not metal-based, where films of **5** show what is likely cooperative behavior between the polymer and the Re(I) metal centers.

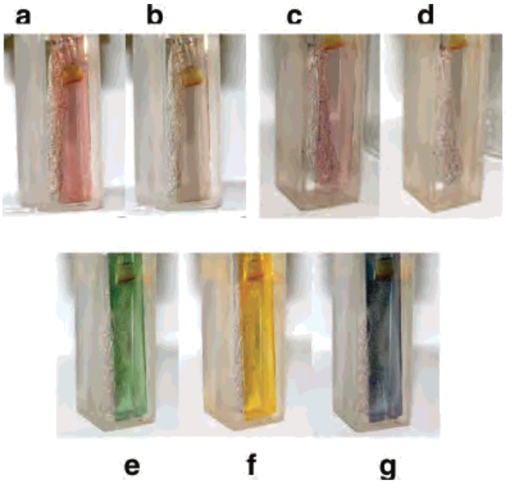

Figure 3. Photographs of films of **2**, **5**, and **6** grown on ITO plates and held at various potentials. Plates a and b are films of **2** held at −0.9 and −0.1 V (vs Fc/Fc$^+$), respectively. Plates c and d are films of **6** held at −1.1 and −0.1 V, respectively. Plates e−g are films of **5** held at −2.0, −0.1, and 1.0 V, respectively.

We have shown that compound **2** can be bound to late transition metals and used to prepare polymer films with the transition metal held directly in the conjugated backbone of the conducting polymer. The polymer films exhibit metal-dependent behavior. For **6**, the electrochemistry of the Pt(II)-containing polymer looks very similar to that the free ligand **2**, where Re(I)-containing **5** produces a polymer film with very different electrochemical properties. We are in the process of exploring the conductivity of these films and removing the chloride ligand from **5** to explore the use of those complexes as molecular sensors. We believe that **2** is especially useful in that it can be applied to potentially any late transition metal with at least two open coordination sites to prepare a polymer precursor.

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Supporting Information Available: X-ray crystallographic file (CIF) for **4** and **5** and additional experimental, structural, and electrochemical details. The material is available free of charge via the Internet at http://pubs.acs.org.

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