CHEMISTRY OF MATERIALS

Communication

Pt-[NCN] Pincer Conducting Metallopolymers That Display Redox-Attenuated Metal−Ligand Interactions

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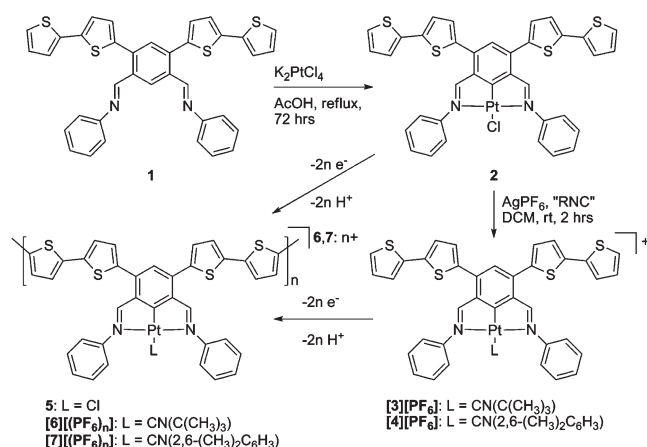
Conducting polymers are of great interest as a result of possessing both the desirable characteristics of organic polymers, such as ease of preparation and mechanical processability, and the ability to become electrically conducting upon chemical or electrochemical doping.[1] Incorporation of transition metals into these materials offers the potential for many additional applications based on complementary redox, magnetic, optical, or catalytic properties.[2]

The use of redox-active ligands has been investigated to affect the reactivity and binding properties of transition metal complexes.[3−5] A conducting polymer matrix has a large number of available oxidation states making it attractive as a redox-active ligand. The variety of oxidation states offers a means to easily tune the amount of electron density on the metal center and consequently attenuate the binding affinity of an additional ligand through an easily controlled external stimulus (i.e., applied electrochemical potential).[5,6] Therefore, carefully designed conducting metallopolymers where a metal complex has been synthetically incorporated into a conducting polymer matrix, have potential applications in small molecule storage and delivery,[3] electrochemical sensing,[7] and catalysis.[4]

Herein is reported the design, synthesis, and characterization of a novel electropolymerizable NCN pincer-type ligand (**1**), the corresponding Pt complexes (**2−4**), and the subsequent metallopolymers (**5−7**), Scheme 1. Incorporation of bithiophene into the target ligand allows for the electropolymerization of the complex. Potentiodynamic anodic polymerizations of the monomers (**2−4**)

Scheme 1. Synthesis of Pt-[NCN] Pincer Conducting Metallopolymers

form Wolf type II conducting metallopolymers[8] where the metal complexes are in electronic communication with the conducting polymer backbone but do not play a structural role. The substitution of the bithiophene units in a *meta-* arrangement should produce, upon polymerization, a conducting metallopolymer with a segmented nature. In the oxidized system, charges will localize in the oligothiophene fragments and lead to sequential withdrawal of electron density from the metal center with increasing amounts of electrochemical doping. An additional design feature is the use of a cyclometalated pincer-type ligand structure based on demonstrated chemical robustness and the presence of only one ancillary ligand, which should maximize and simplify the redox-attenuated effect reported by this ligand.
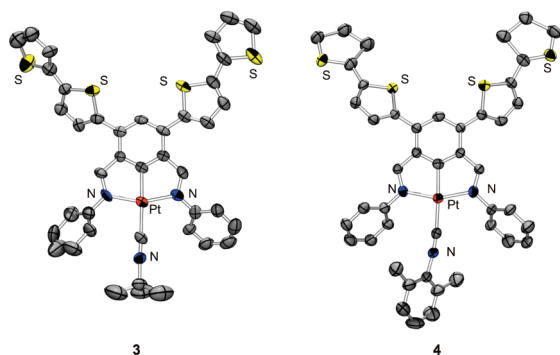
The title complexes were synthesized as outlined in Scheme 1 (see the Supporting Information for synthetic details) by modification of literature procedures. Exchange of the chloride ligand for a ligand with a vibrational spectroscopic probe was achieved by reaction of **2** with AgPF$_6$ followed by subsequent reaction with either *tert*-butyl isocyanide or 2,6-dimethylphenyl isocyanide. Crystals suitable for X-ray crystallographic structure determination were grown by slow diffusion of hexanes into a saturated solution of **3** or **4** in dichloroethane (Figure 1). In both complexes, the geometry around the platinum is slightly distorted from square planar with bond lengths and angles consistent with those previously observed for similar compounds.[9] Additionally, the coordination plane of the platinum was found to be nearly

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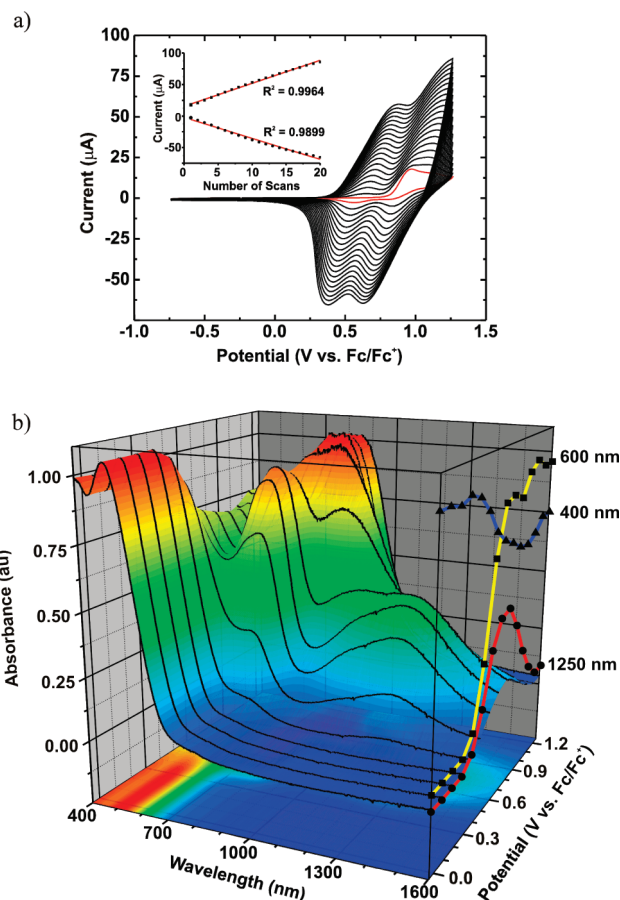*Chem. Mater., Vol. 22, No. 8, 2010* 2415

Figure 1. View of **3** and **4** showing the labeling of selected atoms. Displacement ellipsoids are scaled to the 50% probability level. Hydrogen atoms, counterions, and solvent molecules have been omitted for clarity.

coplanar with the cyclometalated phenyl portion of the pincer ligand, with torsion angles of 8° and 3° for complexes **3** and **4**, respectively.
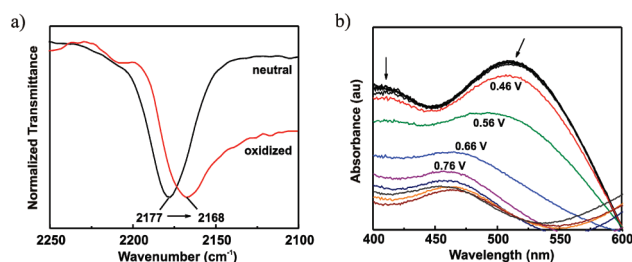
UV−visible spectroscopic characterization of **1** revealed a single absorption at 366 nm due to the $\pi-\pi^*$ UV−vis transition of the bithiophene group. The absorption was found to blue shift approximately 25 nm in complexes **2−4** as a result of platinum complexation. In addition, the complexes display a LMCT absorption at approximately 450 nm, consistent with other platinum-pincer complexes in which the cyclometalated phenyl ring of the pincer ligand is nearly coplanar with the platinum coordination plane.[10] Upon polymerization, an expected red-shift of the $\pi-\pi^*$ transition of the bithiophene system to near 400 nm was observed because of the extended aromatic system formed between the monomer units. The energy of this transition is consistent with that of quarter-thiophene[11] and confirms the electronically segmented nature of the conducting metallopolymers.

Electropolymerization of **2**, **3**, and **4** was performed (see the Supporting Information). Upon substitution of the chloride with isocyanide, both complexes (**3** and **4**) show a monomer oxidation at 0.9 V, polymer oxidations at 0.8 V and > 1.2 V, and polymer reductions at 0.4 and 0.6 V (Figure 2a). The observed electropolymerization is similar to that reported for 1,3-bis(2,2′-bithiophen-5-yl)benzene.[12] To investigate the electronic perturbation of the conducting metallopolymers as a function of electrochemical doping, spectroelectrochemistry of **6** and **7** was performed; the results for **7** are shown in Figures 2 and 3.

The characteristic ν_{CN} of the isocyanide ligand was utilized as a means to probe the amount of electron density at the platinum metal center of the conducting metallopolymer. Due to the absence of π-back-bonding with the isocyanide ligand, in both the monomer (**4**) as well as the conducting metallopolymer (**7**), the ν_{CN} of the bound isocyanide ligand occurs at 2177 cm^{-1}, 60 cm^{-1} higher than that of the free isocyanide. Upon oxidation of the polymer

Figure 2. Polymerization of **4** and spectroelectrochemistry of **7**. (a) Electropolymerization of **4** in 0.1 M TBAPF$_6$ in DCM at 0.1 V/s. Initial scan shown in red. Inset: Current versus number of scans. (b) UV−vis−NIR spectroelectrochemistry of **7**. Side: Trace of absorbancce versus potential at given wavelengths.
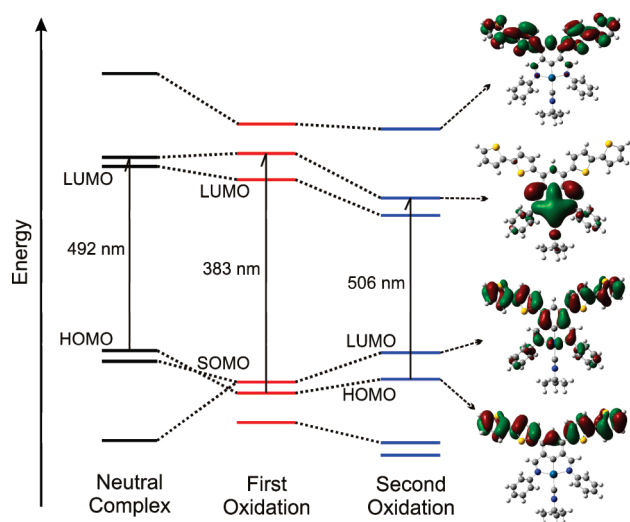

Figure 3. Spectroelectrochemistry of **7**. (a) IR spectrum of ν_{CN} region of **7** at 0 V and after oxidation to 1.27 V vs Fc/Fc$^+$. (b) Expansion of UV−visible spectroelectrochemistry in the LMCT region.

film to 1.27 V vs Fc/Fc$^+$, the ν_{CN} was observed to lower to 2168 cm^{-1} (Figure 3a). This lowering in frequency of the ν_{CN} toward that of free isocyanide indicates a weakening of the Pt−C σ-bond and demonstrates that the withdrawal of electrons from the conducting polymer backbone is a viable means of attenuating the binding of ancillary ligands on the metal center in this system. Upon return of the polymer film to 0 V, the ν_{CN} returned to 2177 cm^{-1}, demonstrating a reversibility of the redox-attenuated effect.

To further monitor the effects of electrochemical doping of the conducting polymer backbone on the platinum metal center, UV−vis−NIR spectroelectrochemical investigations of **5−7** were performed. We demonstrate

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Figure 4. Walsh correlation diagram of calculated molecular orbitals of neutral complex, first oxidation, and second oxidation of complex **3**.

here for the first time that through changes in the LMCT absorption it is possible to directly examine the changes in electron density at the metal center. The low energy transitions (800–1400 nm) observed during oxidation (Figure 2b) are consistent with the formation of polaron and bipolaron states within the conjugated polymer backbone.[13,14] However, unlike the broad low-energy transitions typically observed in oxidized polythiophene,[14] these low-energy transitions are more discrete, as would be expected because of the inability of the quinoidal form of the oxidized thiophene fragment to extend through the aromatic system of the pincer ligand. It would then be expected that as the electrons are removed from the π-system of the conducting polymer backbone, less electron density would be available for donation to the metal resulting in an increase in the energy of the LMCT band. The increase in energy of the LMCT absorption is consistent with observed changes in the energy levels of the

molecular orbitals associated with this transition when variable-oxidation state DFT calculations were performed for **3**, **3$^+$**, and **3^{2+}** (Figure 4). These calculations predict that the energy of the LMCT absorption will reach a maximum with the first oxidation of the conducting polymer backbone and will be lowered in energy with the second oxidation. In practice, the observed changes in the LMCT are consistent with the DFT calculations and a blue shift of the LMCT absorption is observed (Figure 3b), which reaches a maximum near 0.8 V, coinciding with the first oxidation potential of the thiophene backbone. At higher potentials, the LMCT band begins to lower in energy although full investigation of the second oxidation of the conducting polymer backbone is not available within the electrochemical window of the solvent. Upon subsequent reduction of the polymer film, the peaks observed in the UV−vis−NIR spectrum return to the positions identical to those of the neutral polymer film.

We report a conducting metallopolymer based on an electropolymerizable NCN pincer ligand. This system clearly displays redox attenuated metal−ligand interactions as monitored by IR (ν_{CN}) and, for the first time, UV−vis (LMCT) spectroelectrochemistry. The later result is particularly significant as it demonstrates that electron density at metal centers in conducting metallopolymers can be directly monitored without the incorporation of a reporter ligand. This realization has utility in the applications of conducting metallopolymers in redox-mediated catalysis and sensors.

Supporting Information Available: Synthetic details, electrochemistry, calculations (PDF); X-ray CIF files of **3** and **4**. This material is available free of charge via the Internet http://pubs.acs.org.

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