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Hybrid Spin-Crossover Conductor Exhibiting Unusual Variable-Temperature Electrical Conductivity

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We describe the multistep synthesis of a new terthienyl-substituted QsalH ligand and an iron(3+) spin-crossover complex (**1**) containing this ligand, which electropolymerizes to produce a hybrid-conducting metallopolymer film (**poly1**). Variable-temperature magnetic susceptibility measurements demonstrate that spin-crossover is operative in the polymer film, and resistivity measurements on indium−tin oxide coated glass slides containing the polymer film exhibit intriguing temperature-dependent profiles.

A new frontier in the field of molecule-based magnetic materials is the production of *multifunctional materials*.[1] These materials feature two or more properties not naturally found associated with one another and are typically generated by combining two independently prepared molecular precursors. A prototypical example is the discovery of ferromagnetism in a molecular metal by Coronado and coworkers in 2000.[2] In this fascinating material, ferromagnetism is provided by the $[MnCr(ox)_3]$ anionic network, and electrical transport is contributed by layers of stacked bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) cations. Recently, a number of other exciting conducting materials have been reported (typically based on partially oxidized $[M(dmit)_2]^+$ cations, where M^{2+} = Ni and Pd and dmit = 4,5-dithiolato-1,3-dithiol-2-thione) containing spin-crossover complex anions, notably $Fe(Qsal)_2^+$ [Qsal is the deprotonated form of QsalH = *N*-(8-quinolyl)salicylaldimine] or other iron complexes containing different N,O-donor ligands, which undergo a thermally induced change in the spin state.[3] These materials are typically weakly conducting and exhibit spin-crossover, but the degree of interaction between these properties is weak, or no interaction is observed at all.

Our hybrid approach toward spin-crossover conductors is completely different: We focused on the preparation of conducting metallopolymers containing pendant iron spin-crossover complexes.[4] Recently, we described the variable-temperature magnetic properties of poly(terthiophene) containing a pendant cobalt−semiquinone coordination complex, in which temperature-dependent valence tautomerism was observed in the polymer film.[5] Our hybrid approach takes advantage of the inherent conducting properties and established synthetic methods available for polythiophene derivatives.[6] Also, the close spatial proximity of the spin-crossover and conducting components in these materials augurs well for a stronger interaction between the magnetic and electrical transport properties. There are very few reported hybrid materials of this type, but we do note the conductive hybrid poly(arylamino) films doped with a Mn_{12} single-molecule magnet recently reported by Bolink et al.[7] Herein we describe the synthesis and properties of a new $[Fe(Qsal)_2]^+$-based spin-crossover complex containing a terthienyl substituent **1** and the electrodeposition of a polymer film (**poly1**) from an acetonitrile solution containing **1**. We demonstrate temperature-dependent spin-crossover and intriguing variable-temperature electrical transport properties from **poly1** films.

Terthienyl-substituted QsalH ligand **6** was prepared in five steps from commercially available precursors (Scheme S1 in the Supporting Information). Complex **1** (Figure 1) was prepared by the combination of 2 equiv of **6** with $[FeCl_3]\cdot 6H_2O$, followed by metathesis with an aqueous $NaPF_6$ solution to precipitate a dark-green, analytically pure powder of **1**, which has been fully characterized (Supporting Information). Variable-temperature magnetic susceptibility measurements on powdered samples of **1** demonstrate that this complex is a spin-crossover material (Figure S2 in the Supporting Information). The spin-state switching in **1** can

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(1) Coronado, E.; Dunbar, K. R. *Inorg. Chem.* **2009**, *48*, 3293.

(2) Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Lauhkin, V. L. *Nature* **2000**, *408*, 447.

(3) (a) Takahashi, K.; Cui, H.-B.; Okano, Y.; Kobayashi, H.; Einaga, Y.; Sato, O. *Inorg. Chem.* **2006**, *45*, 5739. (b) Faulmann, C.; Jacob, K.; Dorbes, S.; Lampert, S.; Malfant, I.; Doublet, M.-L.; Real, J. A. *Inorg. Chem.* **2007**, *46*, 8548. (c) Takahashi, K.; Cui, H.-B.; Okano, Y.; Kobayashi, H.; Mori, H.; Tajima, H.; Einaga, Y.; Sato, O. *J. Am. Chem. Soc.* **2008**, *130*, 6688.

(4) Djukic, B.; Dube, P. A.; Razavi, F.; Seda, T.; Jenkins, H. A.; Britten, J. F.; Lemaire, M. T. *Inorg. Chem.* **2009**, *48*, 699.

(5) O'Sullivan, T. J.; Djukic, B.; Dube, P. A.; Lemaire, M. T. *Chem. Commun.* **2009**, 1903.

(6) (a) Roncali, J. *Chem. Rev.* **1992**, *92*, 711. (b) Roncali, J. *Chem. Rev.* **1997**, *97*, 173. (c) Kingsborough, R. P.; Swager, T. M. *J. Am. Chem. Soc.* **1999**, *121*, 8825. (d) Wolf, M. O. *Adv. Mater.* **2001**, *13*, 545.

(7) Bolink, H. J.; Cappelli, L.; Coronado, E.; Recalde, I. *Adv. Mater.* **2006**, *18*, 920. (b) Bolink, H. J.; Coronado, E.; Forment-Aliaga, A.; Gómez-García, C. J. *Adv. Mater.* **2005**, *17*, 1018.

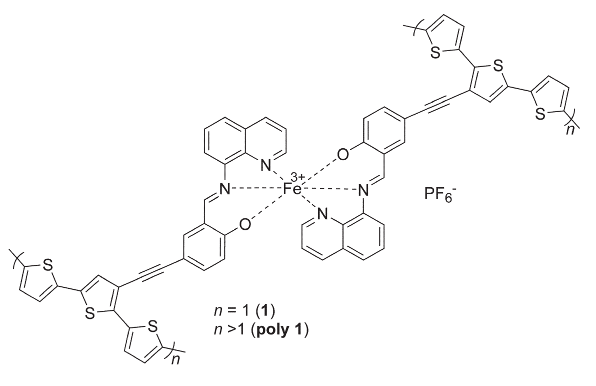

Figure 1. Molecular structures of **1** and **poly1**.

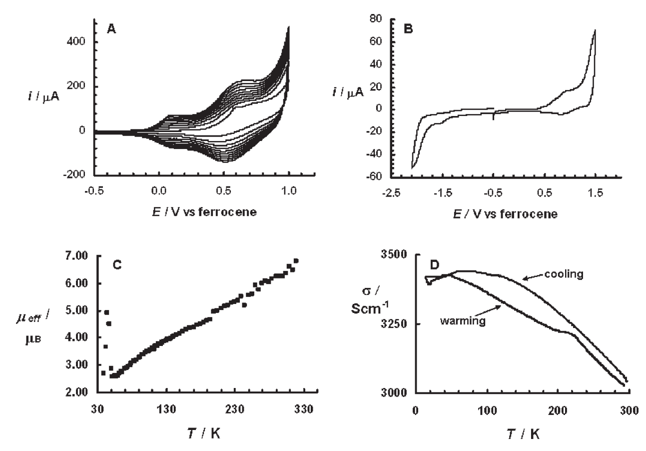

Figure 2. Electropolymerization of **1** (A) in CH$_3$CN on an ITO-coated glass slide and CV of **poly1** (B) in monomer-free CH$_3$CN (containing 0.7 M n-Bu$_4$NPF$_6$ and the potential versus a ferrocene reference). Variable-temperature magnetic properties (C) and conductivity (D) of **poly1** films on ITO-coated glass. Magnetic measurements were obtained with a SQUID magnetometer at an external field of 1.5 T, and resistivity data were obtained using the van der Pauw method, including four ohmic (gold wire) contacts applied with silver paint.

be described as gradual and without thermal hysteresis, which is typical for iron(III) spin-crossover complexes, including similar Qsal-containing derivatives.[8]

The electrochemical properties of **1** were studied by cyclic voltammetry (CV). A broad and pseudoreversible anodic wave centered at 0.60 V (vs ferrocene) is assigned to oxidation of the terthienyl substituent. Repeated scans over a potential window of −0.5 to 1.0 V resulted in the electropolymerization of complex **1**, as a transparent red film (**poly1**) deposited on a platinum button working electrode or indium−tin oxide (ITO)-coated glass slides (Figure 2A). The electrochemical properties of **poly1** were investigated by removal of the coated electrode from the solution, washing with acetonitrile, and then running the CV of the polymer in a fresh monomer-free solution (Figure 2B). The linear peak current dependence on the scan rate (Figure S1 in the Supporting Information) indicates the presence of an electroactive deposit on the working electrode.

The elemental composition of the **poly1** film was confirmed by quantitative energy-dispersive X-ray (EDX) spectroscopy. An average of 11 experiments indicate that within experimental error the Fe:S (0.25 vs 0.29 theoretical) and Fe:P (1.69 vs 1.81 theoretical) ratios are in the range expected for the purported structure. Further structural corroboration is provided by the FT-IR spectrum of the polymer film (Figure S8 in the Supporting Information). As anticipated, the FT-IR spectrum of **poly1** (KBr pellet) is very similar to the spectrum of **1** (Figure S4 in the Supporting Information). These results indicate that the desired polymeric structure was obtained from electropolymerization of **1**, without any structural alteration to the pendant iron coordination complex.

The variable-temperature magnetic properties of **poly1** films were investigated by SQUID magnetometry. Three independently prepared films of **poly1** were electrochemically generated on ITO-coated glass slides and then dried under vacuum for 24 h prior to insertion into the SQUID magnetometer. The portion of the slide containing the film was cut and weighed, and the film thickness was estimated using a Michelson interferometer (the **poly1** film thickness was estimated at 130 nm in all cases). The ITO-coated glass was loaded into a plastic straw and carefully lowered into a SQUID magnetometer. The magnetic data were acquired from 330 to 30 K at a field of 1.5 T (four direct-current scans were measured for each temperature point with a wait of 60 s for temperature stability at each point). Following the experiment, the film was removed from the glass using ethanol and gentle scrubbing with a KimWipe, and the same piece of ITO-coated glass (**poly1**-free) was loaded into the SQUID and an identical experiment was run so that the diamagnetic contribution to the susceptibility could be carefully subtracted. The paramagnetic susceptibility of the **poly1** films was calculated based on the mass of the repeat unit of the polymer, and the results, indicated as a plot of the effective magnetic moment (μ_{eff}) versus temperature, are shown in Figure 2C.

At 330 K, the magnetic moment (6.8 μ_{B}) is a little higher than the expected value for one high-spin iron(III) ion (5.9 μ_{B}). We have observed this in other metallopolymer materials with paramagnetic substituents, and the additional moment likely results from a polaronic spin contribution from the conducting polymer backbone, as well as other temperature-independent paramagnetism effects.[5] With decreasing temperature, we observed a steady decrease in the magnetic moment, indicating that a gradual spin equilibrium is operative in **poly1**. Also, the differences in the electromagnetic unit values between warming and cooling modes at each temperature point were insignificant, and no thermal hysteresis in the magnetic properties was observed. At approximately 58 K, the magnetic moment per repeat unit is about 2.6 μ_{B}, which is typical for low-spin iron(III) in other similar Qsal-containing complexes (note that this value is greater than 1.73 μ_{B}, which is the anticipated value for one unpaired electron per complex). Below 50 K, a spike in the magnetic moment is observed; the magnetic moment quickly increases to a maximum of 4.9 μ_{B} at 45 K before quickly falling back to typical low-spin values at 30 K. The likely cause for this behavior is an oxygen leak in the SQUID magnetometer; we have observed spikes of varying intensity for a number of other experiments.

The variable-temperature resistivity of electrodeposited films of **poly1** on ITO-coated glass was investigated using the van der Pauw method.[9] Four ohmic contacts (gold wires)

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[8] (a) Oshio, H.; Kitazaki, K.; Mishiro, J.; Kato, N.; Maeda, Y.; Takashima, Y. *J. Chem. Soc., Dalton Trans.* **1987**, 1341. (b) Hayami, S.; Gu, Z.-z.; Yoshiki, H.; Fujishima, A.; Sato, O. *J. Am. Chem. Soc.* **2001**, *123*, 11644. (c) Dickinson, R. C.; Baker, W. A., Jr.; Collins, R. L. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1531.

[9] van der Pauw, L. J. *Philips Res. Rep.* **1958**, *13*, 1.

were carefully applied to the film with silver paint. Figure 2D is a plot of the reciprocal of resistivity (conductivity) of the **poly1** film coated on ITO glass versus temperature. In all experiments, the conductivity of the **poly1** film and the ITO-coated glass is significantly higher than the conductivity of the bare ITO-coated substrate (after careful removal of the **poly1** film using an ethanol-soaked KimWipe and gentle scrubbing; Figure S3 in the Supporting Information), indicating a substantially conductive **poly1** film. We estimate the conductivity of the **poly1** film to be on the same order of magnitude as other poly(terthiophene) materials (approximately 10–100 $S \cdot cm^{-1}$), after subtraction of the substrate contribution.[6] Although the circuit gains a considerable amount of conductivity from the ITO substrate, the film is significantly more conductive than other reported spin-crossover conductors. Another intriguing aspect of the conductivity profiles is the unusual and dramatic differences observed between cooling and warming measurements. We speculate that this conductivity difference may result from structural changes that originate at the pendant coordination complex, resulting from spin-crossover [typically the differences in the Fe–N coordinate bond lengths between the high- and low-spin isomers are on the order of 0.15 Å for iron(3+) spin-crossover complexes containing a N_4O_2 donor set].[10] The effect of this structural change is transmitted to the poly(terthiophene) chain, resulting in the observed hysteretic conductivity profile. To rule out the possibility that the observed conductivity changes in **poly1** are the result of temperature-dependent morphological changes to the polymer structure, which are independent of the structural changes imparted by spin-crossover, an identical variable-temperature resistivity experiment was performed on a metal-free polymer generated from ligand **6** (**poly2**), as well as an analogous manganese(2+) complex containing ligand **6**, which was electropolymerized on ITO (**poly3**). Indeed, the cooling and warming resistivity data acquired from **poly2** or **poly3** films (Figure S3 in the Supporting Information) are nearly identical. Why we do not observe a similar thermal hysteresis in the magnetic properties of **poly1** films is peculiar. We are currently investigating the variable temperature magnetic and electrical transport properties of other metallopolymer films on ITO substrates to help shed more light on the properties of the **poly1** system.

We have reported the synthesis and variable-temperature magnetic and electrical transport properties of a hybrid spin-crossover conducting metallopolymer, which exhibits intriguing variable-temperature conductivity profiles. We continue to investigate the unusual properties exhibited by the present system and are actively pursuing the synthesis of other metallopolymers.

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Supporting Information Available: Synthetic details for all new compounds and complexes, FT-IR spectra of **1** and **poly1**, EDX data from **1** and **poly1**, ESI mass spectrum of **1**, variable-temperature magnetic susceptibility data for **1**, and variable-temperature resistivity measurements of **poly1**, **poly2**, and **poly3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Nihei, M.; Shiga, T.; Maeda, Y.; Oshio, H. *Coord. Chem. Rev.* **2007**, *251*, 2606.