A Conducting Metallopolymers featuring Valence Tautomerism

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SUPPORTING INFORMATION

CONTENTS

General experimental details S2
Preparation of 1 S3
Preparation of 2 S3
1H & 13C NMR spectra of 1 S4
EDX data for 2 and polymer film S5
Cyclic voltammogram of 1 in CH2Cl2 S5
Electropolymerization of 1 in CH2Cl2 S6
Vis-NIR spectra of poly 1 at 298 and 77 K S6
Visible spectrum of 2 at 298 and 77 K in toluene S7
µ vs. T for poly 1 and poly 2 on ITO glass. S7
References S8
GENERAL EXPERIMENTAL DETAILS

All reagents were commercially available and used as received unless otherwise stated. Deaerated and anhydrous solvents were obtained from a Puresolve PS MD-4 solvent purification system, and all air and/or moisture sensitive reactions were carried out using standard Schlenk techniques, unless otherwise stated. $^1$H/$^{13}$C-NMR spectra were recorded on a Bruker Advance 300 MHz spectrometer with a 7.05 T Ultrashield magnet using deuterated solvents. FT-IR spectra were recorded on a ThermoMattson RS-1 spectrometer as KBr discs or thin films on NaCl plates. EI and FAB mass spectra were obtained using a Kratos Concept 1S High Resolution E/B mass spectrometer. Vis-NIR spectra in solution were recorded on a Shimadzu 3600 UV-Vis-NIR spectrophotometer as solutions in ethanol at room temperature. Solution spectra at 77 K were obtained as frozen ethanol glasses in 5 mm NMR tubes immersed in a liquid N$_2$ dewar. Elemental analyses were carried out by Guelph Chemical Laboratories LTD, Guelph, ON, Canada. EDX spectra were obtained on a Pentafet EDS with Link Systems detector (beryllium windows, 20 kV energy).

Electrochemical measurements

Cyclic voltammetry (CV) experiments were performed with a Bioanalytical Systems Inc. Epsilon electrochemical workstation. 2 was dissolved in anhydrous solvent (CH$_2$Cl$_2$) and deareated by sparging with N$_2$ gas for 20 minutes. Solution concentrations were approximately $10^{-3}$ M in 2 containing 0.1 M supporting electrolyte (Bu$_4$NPF$_6$). A typical three-electrode set-up was used including a platinum working electrode (or an ITO coated glass cuvette slide), Ag wire pseudo-reference electrode, and a platinum wire auxiliary electrode. Ferrocene was used in all cases as an internal standard and was oxidized at a potential of +0.51 V in our set up; all potentials quoted are versus the ferrocene oxidation potential. The scan rate for all CV experiments was 100 mV/s.

Variable temperature magnetic susceptibility measurements

Variable temperature magnetic susceptibility measurements were recorded on a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS) with a 5.5 T magnet (temperature range 1.8 to 400 K) in an external field of 5000 Oe. 2 was carefully weighed into a gelatin capsule, which was loaded into plastic straw, and attached to the sample transport rod. Diamagnetic corrections were made using Pascal’s constants. Diamagnetic contributions from the straw and capsule were subtracted by running these free of sample.
Variable temperature Vis-NIR measurements of poly 1 and poly 2

Polymer films were grown electrochemically on ITO coated glass cuvette slides (obtained from Delta Technologies, LTD), which were cut in half prior to electropolymerization. The half slide free of polymer film was used in a background scan for the particular Vis-NIR measurement of poly 1 or poly 2. At room temperature, a background scan was recorded from 2000 to 400 nm, consisting of the film free slide held rigidly in place with a homemade film holder in an empty quartz dewar. The placement of the slide was such that the ITO coated side (determined by using an ohm meter) was always facing the light beam. Next, the slide containing the polymer film was attached to the film holder and lowered into the empty quartz dewar, and we ensured that the coated part of the slide faced the light beam. The spectrum from 2000 to 400 nm was recorded. Measurements at 77 K were identical, with the exception that the background scan consisted of the uncoated slide and dewar containing liquid nitrogen.

3´-(5-ethynyl-2,2´-bipyridine)-2,2´:5´,2´-terthiophene (1). 5-ethynyl-2,2´-bipyridine 1 (0.681 g, 3.78 mmol) and 3´-bromo-2,2´:5´,2´-terthiophene 2 (0.825 g, 2.52 mmol) were dissolved in deareated and anhydrous N,N-diisopropylamine (65 mL). PdCl$_2$(PPh$_3$)$_2$ (0.053 g, 3 mol %) and CuI (0.014 g, 3 mol %) were added to the reaction mixture, which was refluxed for 60 h. The reaction mixture was concentrated and passed through a pad of celite. The filtrate was then extracted into CHCl$_3$ (3 × 60 mL), washed with brine, dried over magnesium sulfate, filtered, and concentrated to dryness. The crude product was flash chromatographed over neutral alumina using 10:1 hexanes:EtOAc as eluent to yield 0.637 g (59%) of a brilliant yellow solid. Mp: 143-145°C. $^1$H-NMR (300 MHz, CDCl$_3$) = $\delta$ 8.90 (d, 1H, $J= 3$ Hz), 8.72 (dd, 1H, $J= 9$, 3 Hz), 7.98 (dd, 1H, $J= 9$, 3 Hz), 7.85 (td, 1H, $J= 9$, 3 Hz), 7.52 (dd, 1H, $J= 6$, 3 Hz), 7.34 (m, 5H), 7.10 (dd, 1H, $J= 9$, 3 Hz), 7.06 (dd, 1H, $J= 9$, 3 Hz) ppm. $^{13}$C-NMR (CDCl$_3$) = $\delta$ 155.4, 154.9, 151.4, 149.3, 139.2, 139.0, 137.0, 136.0, 135.5, 134.4, 128.0, 127.3, 126.7, 126.1, 125.8, 125.2, 124.3, 124.0, 121.3, 120.4, 120.2, 117.1, 91.2, 89.3 ppm. MS (EI+): $m/z$ 426 (M$^+$, 100%). FT-IR (KBr) = 3425 (s, br), 3061 (w), 2922 (m), 2853 (w), 2201 (w), 1637 (w), 1588 (m), 1541 (w), 1452 (s), 1432 (m), 1364 (w), 1228 (w), 1089 (w), 1022 (w), 859 (w), 805 (m), 792 (m), 742 (m), 684 (s), 649 (w), 458 (w) cm$^{-1}$. Anal. Calcd for C$_{24}$H$_{14}$N$_2$S$_3$: C: 67.58, H: 3.31, N: 6.57 %. Found: C, 67.91; H, 3.55; N, 6.22 %.

bis-(3,5-di-tert-butyl-1,2-semiquinone)(1)cobalt(II) (2). To a solution of Co$_4$(DDBSQ)$_8$ (0.175 g, 0.088 mmol) in anhydrous and deaerated toluene (15 mL) was added solid 1 (0.150 g, 0.469 mmol), and the mixture was stirred overnight under N$_2$ at room temperature. The solution was concentrated by half, and cooled in ice-water. The very dark green precipitate was isolated by vacuum filtration, washed with cold toluene, and dried to afford 0.160 g (43%) of 6. MS (FAB+): $m/z$ 926 [M$^+$, 100%], 911 [(M − CH$_3$)$_4$]$,^+$, 100%. FT-IR (KBr) = 3445 (m, br), 3061 (w), 2952 (s), 2902 (m), 2862 (m), 2202 (m), 1577 (m), 1490 (s), 1467 (s), 1355 (m), 1281 (w), 1243 (s), 1157 (w), 1093 (w), 1028 (w), 983 (m), 903 (w), 844 (w), 826 (w), 694 (m), 494 (w) cm$^{-1}$. Anal. Calcd for C$_{24}$H$_{14}$N$_2$S$_3$Co = C: 67.44, H: 5.88, N: 3.03, S: 10.39. Found: C, 67.14; H, 5.64; N, 3.00; S, 10.15%.
$^1$H NMR spectrum of 1 (CDCl$_3$)

$^{13}$C NMR spectrum of 1 (CDCl$_3$)
EDX data for 2

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EDX data for poly 2

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The “apparent concentration” is calculated directly from the intensity of the characteristic X-ray peak before corrections for atomic number, absorbance, and fluorescence (ZAF).

Cyclic voltammogram of 1 in CH₂Cl₂
Electropolymerization of 1 in CH$_2$Cl$_2$.

Vis-NIR spectra of poly 1 at 298 and 77 K.
Visible spectrum of 2 at 298 and 77 K in toluene.

$\mu$ vs. T for poly 1 (♦) and poly 2 (■) on ITO glass.
References


2 O’Sullivan, T.J.; Djukic, B.; Dube, P.A.; Lemaire, M.T. *unpublished results*.