Supplementary Material (ESI) for Chemical Communications

Supplemental Materials

Insulated Conducting Polymers: Manipulating Charge Transport Using Supramolecular Complexes

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Synthetic Details

Materials. Air- and moisture-sensitive reactions and measurements were carried out in flame-dried glassware or sealed chambers using standard Schlenk-line or drybox techniques under an inert atmosphere of dry argon. $Pd(PPh_3)_4$ and *trans*-$PdCl_2(PPh_3)_2$ were obtained from Strem Chemicals. Tetrabutylammonium perchlorate and tetrabutylammonium hexalfluorophosphate were recrystallized from methanol and subsequently dried overnight under vacuum prior to use. $Cu(OTf)_2$, $Cu(CH_3CN)_4PF_6$, $LiClO_4$, $Zn(ClO_4)_2$ were obtained from Aldrich and used without further purification. Acetonitrile was obtained in Aldrich sure-seal bottles and stored over molecular sieves in an inert atmosphere of dry argon prior to use. Dichloromethane was obtained from J. T. Baker and purified through a GlassContour solvent purification system. Water used in electrochemistry experiments was purified from a Barnstead Nanopure system (18 MΩ). The synthesis of monomer **1** was described in a separate publication.[1] Monomer **2** was synthesized following procedures reported in the literature.[8]

Equipment. All reactions and manipulations were carried out under an atmosphere of inert argon or nitrogen using Schlenk techniques or in an inert-atmosphere glovebox (Innovative Technologies) unless otherwise noted. Solution 500 Mhz ^1H NMR spectra were recorded on a Varian Unity 500 spectrometer and were referenced to CD_2Cl_2 (δ = 5.32 ppm) unless otherwise noted. UV-Vis spectra were obtained in various solvents from a Cary 50 UV-Visible Spectrophotometer using a 1 cm quartz cuvette. Mass spectra were obtained on a Bruker Daltonics APEXII3 Tesla FT-ICR mass spectrometer using electrospray ionization. Fluorescence studies were conducted with a SPEC Fluorolog-2 fluorimeter (model FL112, 450 W xenon lamp). All emission and excitation spectra were corrected for the detector response and the lamp output. Quantum yields were referenced to Rhodamine 6G in ethanol ($\Phi_F = 0.95$).[2] Polymer thin films on ITO electrodes were spin cast on a EC101DT Photoresist Spinner (Headway Research, Inc.) using a spin rate of 2000 rpm from trichloroethane solutions. The time of fluorescence decay for the polymer was determined by a phase-modulation method[3] using frequencies from 10 to 200 Mhz and using Ludox-water solutions (scattering sample, $\tau = 0$ ns, right-angle geometry) as a standard. The experimental errors were typically 4-8% in phase angle and 1-3% in modulation. Electrochemical measurements were performed using a computer-controlled Autolab Model PGSTAT 20 potentialstat from Eco Chemie. The

ITO electrodes (Sheet resistance, Rs, 70 – 100 ohms) were purchased from Delta Technologies. Conductivity was measured by four-point probe techniques. XPS measurements were performed on a Kratos AXIS Ultra Imaging X-ray Photoelectron Spectrometer.

Synthesis of Poly(1). In a 10 mL flask, rotaxane **1** (50.1 mg, 0.240 mmol) was suspended in 2 mL acetonitrile. In a separate vessel, $Cu(OTf)_2$(24.0 mg, 0.664 mmol) was dissolved in 1 mL acetonitrile. The light blue Cu^{+2} solution was added dropwise to the monomer suspension. The reaction mixture turned blue initially and the monomer went into solution. The mixture was stirred at room temperature for 24 h. The reaction was quenched by adding one drop of hydrazine monohydrate. The purple solution was evaporated to dryness. The contents were dissolved in 100 mL CH_2Cl_2 and washed with 100 mL 0.01 M aqueous KCN solution. The organic layer was washed with 2x100 mL H_2O and brine then filtered. The polymer obtained was dissolved in minimal amount of $CHCl_3$ and filtered through a short celite pad into a flask of vigorously stirred methanol. After stirring for 30 minutes, the suspension was centrifuged to obtain Poly(**1**) as a red solid (43.2 mg).

Data for Poly(1). ^{1}H NMR (500 Mhz, CD_2Cl_2) δ = 8.47, 8.16, 8.04, 7.94, 7.87, 7.70, 7.55, 7.26, 7.16, 7.08, 6.75, 6.67, 4.75, 4.32, 4.16, 3.94, 3.84, 1.21 ppm (all broad peaks). M_n(GPC)= 22,100 PDI≈10.

Synthesis of Poly(1, Cu). To a 1 mL CH_2Cl_2 solution of 0.01 mM Poly(**1**) was added 1 mL 0.01 mM $Cu(CH_3CN)PF_6$ in acetonitrile. The solution was stirred at room temperature for two hours then evaporated to dryness. The contents were dissolved in 5 mL CH_2Cl_2 and filtered through a pad of celite. Evaporation of the filtrate afforded Poly(**1**, Cu) as a deep red solid (19.2 mg).

Data for Poly(1, Cu). ^{1}H NMR (500 Mhz, CD_2Cl_2) δ = 8.55, 8.41, 7.96, 7.88, 7.75,7.59, 7.17, 7.11, 6.69, 6.12, 6.60, 4.67, 4.43, 4.14, 4.06, 3.88, 3.80, 3.64, 1.21 ppm (all broad peaks).

Synthesis of Poly(1, Zn). The synthesis of Poly(**1**, Zn) is analogous to that of Poly(**1**, Cu). Based on 1 mL of the 0.01 mM Poly(**1**) solution and 1 mL 0.01 mM $Zn(ClO_4)_2$ acetonitrile solution, 18.8 mg of Poly(**1**, Zn) was obtained as a red solid.

Data for Poly(1, Zn). ^{1}H NMR (500 Mhz, CD_2Cl_2) δ = 8.64, 8.10, 8.04, 7.95, 7.76, 7.48, 7.20, 7.16, 6.74, 6.70, 6.10, 4.83, 4.75, 4.39, 4.12, 3.84, 3.73, 1.23 ppm (all broad peaks).

Synthesis of Poly(1, 2). The synthesis of Poly(**1**, **2**) is analogous to that of Poly(**1**). Based on 10.1 mg **1** (0.0048 mmol) and 2.0 mg **2** (0.0048 mmol) and 9.5 mg $Cu(OTf)_2$ (0.026 mmol), we obtained 10.7 mg of Poly(**1**, **2**) as a deep red solid.

Data for Poly(1, 2). ^{1}H NMR (500 Mhz, CD_2Cl_2) δ = 8.47, 8.16, 3.03, 7.87, 7.70, 7.55, 7.27, 7.26. 7.08, 6.75, 6.66, 4.75, 4.33, 4.17, 3.94, 3.84, 1.21 ppm (all broad peaks).

Preparation of Pressed Pellets for Conductivity Measurements. Pressed pellets were prepared from chemically synthesized Poly(**1**), Poly(**1**, Cu), Poly(**1**, Zn) and Poly(**1**, **2**). Poly(**2**) for pressed pellet measurements was grown by electrochemical oxidative polymerization onto stainless steel plate electrode from a 0.1 mM solution of **2** in 0.1 M $TBAPF_6$ in DCM at a deposition current of 1 mA for 20 min. The polymer was scraped off the electrode and rinsed with copious amount of DCM. The black powder was dried under vacuum at 100°C overnight.

We prepared polymer pellets 100-200 μm thick for four-point probe conductivity measurements using a hydraulic press. The freshly prepared pellets were dried under vacuum overnight. The pellets were placed in a chamber containing iodine. A weak vacuum was pulled and the chamber was placed in an oven of 100°C for at least 2 hours to ensure complete doping. The doped polymer pellets were used immediately.

Polymer Molecular Weight Determination

To determine the molecular weight of the polymers, we modified the HPLC settings to mimic the capabilities of a GPC instrument. The guard column of the HPLC was removed as it trapped the rotaxanated polymer. The polymer sample was eluted with THF with 0.5% triethylamine to suppress protonation. A calibration was performed using PEO standards, and the polymer's elugram was compared to the calibration curve to determine the molecular weight.

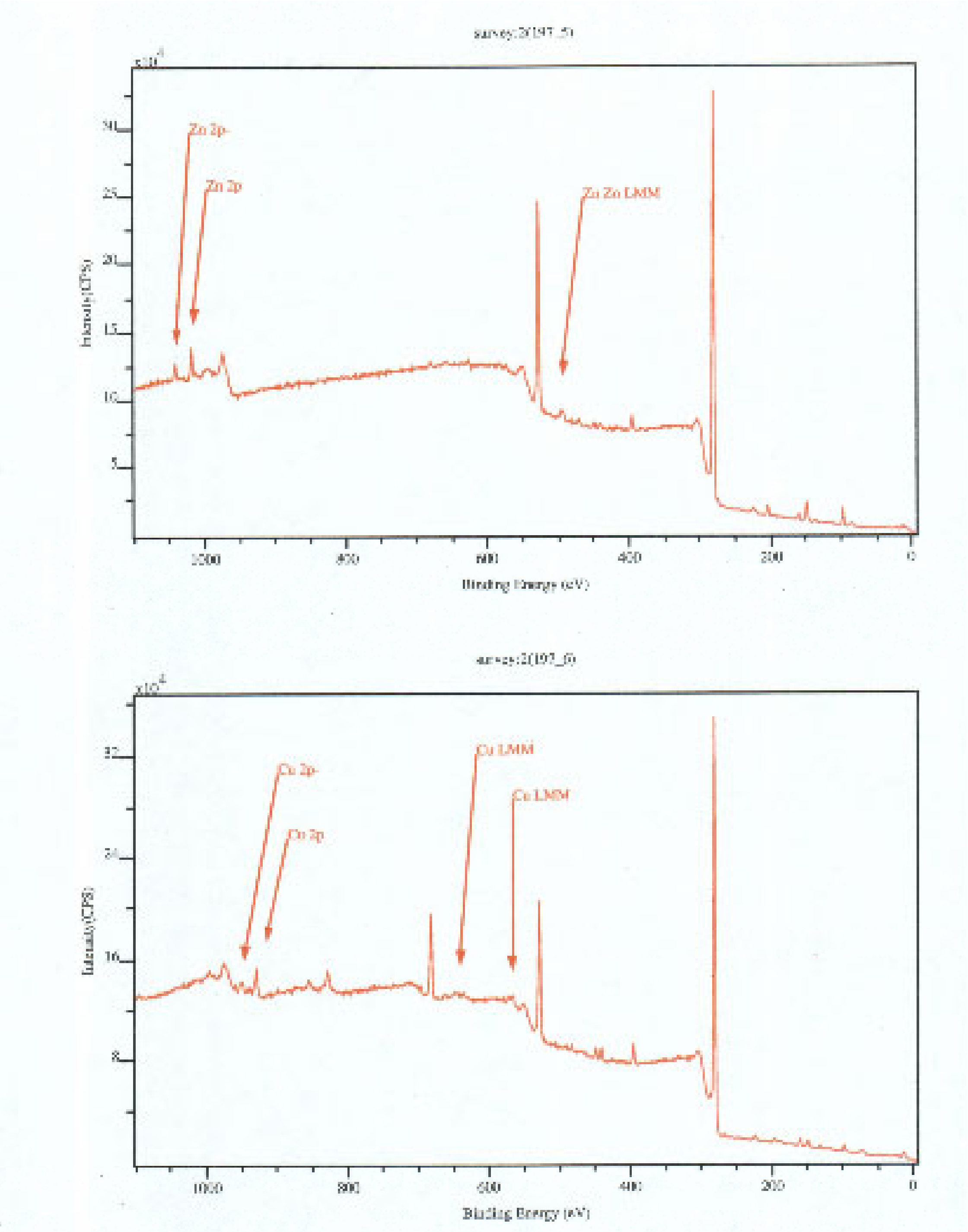

Figure S1. X-ray photoelectron spectra of Poly(**1**, Zn) (top) and Poly(**1**, Cu) (bottom) thin films on ITO electrodes.

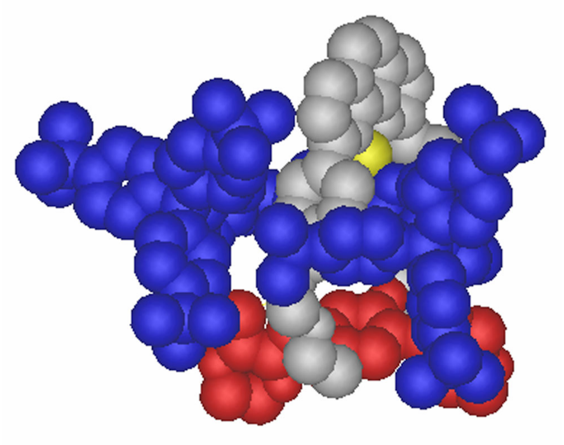

Figure S2. Computer modeling of monomer **1** using PM3 geometry optimization.

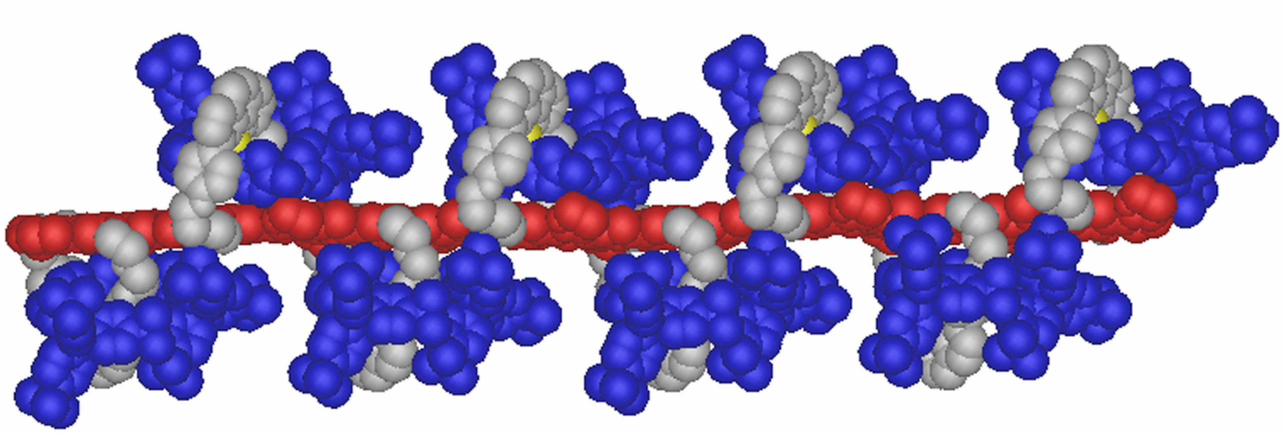

Figure S3. Molecular mechanics computer modeling of an octamer of Poly(**1**, Cu) using the above rotaxane as a fixed building block

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(1) Kwan, P.; Swager, T. M. *J. Am. Chem. Soc.* **2005**, *127*, 5902-5909.

(2) Du, H; Fuh, R. A.; Li, J.; Corkan, A.; Lindsey, J. S. *Photochem. Photobiol.* **1998**, *68*, 141-2.

(3) (a) Hieftje, G. M.; Vogellstein, E. E. In *Modern Fluorescence Spectroscopy*; Wehry, E. L. Ed.; Plenum Press: New York, 1981. (b) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1986.