Supporting Information

Crystals versus Electrochromic Films: Pathway-Dependent Coordination Networks

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EXPERIMENTAL SECTION

Materials and Methods

Solvents (AR-grade) were purchased from Bio-Lab (Jerusalem), Frutarom (Haifa, Israel), or Mallinckrodt Baker (Phillipsburg, NJ). Reagents were used without further purification. Cu(NO₃)₂·3H₂O (>98.0%) and tetrabutylammonium hexafluorophosphate (TBAPF₆) were purchased from Fluka Chemia and Sigma-Aldrich, respectively. Complex 1 was prepared according to reported procedure.[S1] Glass pressure tubes (Ace Glass, Inc., pressure tubes #15 with plunger valve, PTFE Bushing and FETFE® O-Ring, volume 50 mL) were cleaned by dipping in alkaline bath for 12 h. Subsequently, they were washed with deionized water and dried in an oven for 12 h at 130°C. Fluorine-doped tin oxide-(FTO)-coated glass substrates (2 cm × 2 cm, Rs = 10 Ω/□) were purchased from Xinyan Technology, Ltd. (Hong Kong, China). FTO-coated glass substrates were cleaned by sonication in ethanol for 10 min, dried under a stream of N₂, and subsequently cleaned for 20 min with UV and ozone in a UVOCS cleaning system (Montgomery, PA). The substrates were then rinsed with tetrahydrofuran (THF), dried under a stream of N₂, and oven-dried at 130 °C for 2 h. A Laurell automatic spin-coater, model WS-65MZ-8NPPB, was used for the formation of the SurCONs.

Formation of SolCON-A. A Wilmad® screw-cap NMR tube (⌀ = 5 mm and length = 17.8 cm) containing three layers of solvents: (i, top) a ACN solution of Cu(NO₃)₂·3H₂O (1.4 μmol, 1.0 mL), (ii, center) a layer of DCM:MeOH:ACN (0.5:0.5:1 v/v/v, 1.0 mL), and (iii, bottom) a DCM:MeOH (1:1, v/v) solution of complex 1 (0.7 μmol, 1.0 mL). The light brown product was collected after 20 days at room temperature by centrifugation and washed with ACN and ethanol.

Formation of SolCON-B. A Wilmad® screw-cap NMR tube (⌀ = 5 mm and length = 17.8 cm) containing three layers of solvents: (i, top) an ACN solution of complex 1 (0.7 μmol, 1.0 mL), (ii, center) a layer of DMF: ACN (1:1 v/v, 1.0 mL), and (iii, bottom) a DMF solution of Cu(NO₃)₂·3H₂O (1.4 μmol, 1.0 mL). The light brown product was collected after 20 days at room temperature by centrifugation and washed with ACN and ethanol.

Formation of SurCON. The SurCON was formed by using an automated spin coater equipped with three syringes containing: (i) Cu(NO₃)₂·3H₂O (4.0 mM) in ACN, (ii) complex 1 (0.6 mM) in
DCM/MeOH (1:1 v/v), and (iii) acetone for washing. The solution of Cu(NO$_3$)$_2$$\cdot$3H$_2$O was drop casted (0.7-0.8 mL) onto FTO/glass (2 cm × 2 cm), subsequently, the substrate was spun at 500 rpm (acceleration 250) for 10 s and then at 1000 rpm (acceleration 500) for 30 s. Next, a solution of complex 1 was drop casted (0.7-0.8 mL) after 80 s on the substrate, which was spun as above. Then, acetone was drop casted after 80 s and spun for 40 s at 1000 rpm (500 acceleration). The Cu(NO$_3$)$_2$/1 deposition steps is referred to as a deposition cycle. For the formation of the SurCON 18 deposition cycles were applied.

**Scanning electron microscopy (SEM) of SolCON.** Samples were prepared by placing a drop of the reaction mixture on a silicon substrate and the solvent was allowed to evaporate. SEM measurements were performed using HRSEM ULTRA-55 ZEISS and HRSEM SUPRA-55 VP ZEISS instruments at an EHT voltage of 1.5 kV. Images were collected in secondary and backscattered electron modes by using Everhart-Thornley and energy selective backscattered detectors, respectively. The SEM-energy-dispersive X-ray spectroscopy (EDS) mapping was performed by using EDS Bruker XFlash/60 mm at accelerating voltages of 4 kV and 10-12 kV. The aperture size was 30 microns. The surface of sample was coated with 5 nm-thick carbon layer.

**UV/Vis Spectroscopy of SurCON.** A Cary 100 spectrophotometer was used to record UV/Vis absorbance spectra using Cary Win UV-Scan application program, version 3.00 (182) by Varian (200-800 nm). The transmittance was measured using the Cary Win UV-Kinetics application program, version 3.00 (182) by Varian. Bare substrates were used to compensate for the background absorption.

**Transmission Electron Microscopy.** Samples of SurCON on FTO/glass were prepared by sectioning in a Helios Focused Ion Beam Microscope (Thermo Fisher Scientific Microscopy Solutions, TFS, Hillsborough, USA). The sample was first coated with a 300-nm-thick layer of carbon, followed by coating a 350-400 nm-thick layer of platinum using electron-beam-assisted deposition. This process was followed by anion-beam-assisted deposition of a 200-250-nm-thick layer of platinum. The platinum coating protects the SurCON from ion-beam damage. A TFS Tecnai F20 Twin (200 kV, FEG) instrument was used to collect energy dispersive X-ray spectrum images (EDS) on an EDAX Phoenix Si(Li) detector. High-angle annular dark field images were collected on a Fischione Model 3000 detector. For the analysis of SolCON, a suspension (10 µL)
of as-synthesized crystals was dispersed on lacey carbon support on molybdenum grids for TEM analysis. Nanobeam electron diffraction (NBED) data were obtained in a double aberration-corrected TFS Themis-Z microscope, equipped with a high-brightness FEG at an acceleration voltage of 200 kV. For the 4D-STEM recording, the sample was kept at liquid N\textsubscript{2} temperature in a Gatan 914 cryo-holder (Gatan Inc., Pleasanton/CA, USA) to avoid radiation damage to the crystals. The EMPAD (electron microscope pixel array detector) allowed rapid data collection of the entire unsaturated diffraction pattern with a pixel dwell time of 1 \( \mu s \) for each pattern. An electron probe with a convergence angle of 0.2 mrad was adjusted in STEM microprobe mode and further defocussed by typically 5-10 \( \mu m \) to reduce probe size and electron flux. A primary beam current of less than 4 pA was used. Typically, diffraction patterns were acquired over a raster of 128 \( \times \) 128 pixels. The total exposure in the 4D-STEM experiments was approximately 1 e/Å\textsuperscript{2}.

**X-ray Photoelectron Spectroscopy (XPS) of SurCON.** FTO/glass (1.0 cm \( \times \) 1.0 cm) was used for XPS measurements using a Kratos AXIS ULTRA system, having a monochromatic Al K\( \alpha \) X-ray source (\( h\nu = 1486.6 \text{ eV} \)) at 75 W and detection pass energies ranging between 20 and 80 eV. Curve-fitting analysis was based on Shirley or linear background subtraction and the application of Gaussian-Lorentzian line shapes.

**Electrochemical characterization of SurCON.** The electrochemical measurements were carried out using a CHI660A or CHI760E electrochemical workstation. The modified FTO/glass served as the working electrode, Ag/Ag\textsuperscript{+} was used as the reference electrode, and a Pt wire as the counter electrode. Tetrabutylammonium hexafluorophosphate (TBAPF\textsubscript{6}), in ACN (0.1 M) was used as the supporting electrolyte.
X-ray crystallography. A single crystal of SolCON-B suitable for X-ray diffraction was coated with Paratone oil (Hampton Research, CA, USA), mounted on a MiTeGen loop and flash frozen in liquid nitrogen. Diffraction data were recorded on Rigaku Synergy system equipped with a Dectris Pilatus 300K Cd-Te detector. Data were measured with MoKα radiation at 100(2) K. The data were collected and processed with Rigaku OD CrysAlisPro 1.171.40.60a (2019). The structure was determined by direct methods using SHELXT-2018 with SHELXL-2013 and SHELXL-2016/4.[52-54] The crystal data have been deposited with the CSD (Table S1).

Table S1. Crystal data and structure refinement of SolCON-B.

| Characteristic                           | Value                                      |
|-----------------------------------------|--------------------------------------------|
| Formula                                 | C_{288}H_{216}Cu_{12}N_{60}O_{48}           |
| CCDC                                    | 2095187                                    |
| Formula weight                          | 6047.68 (g/mol)                            |
| Temperature                             | 100 K                                      |
| Wavelength                              | 0.71073 Å                                  |
| Crystal system                          | Monoclinic                                 |
| Space group                             | C2/m                                       |
| Unit cell dimensions                    | a = 25.9724(9) Å, α = 90°                  |
|                                         | b = 20.8477(10) Å, β = 93.339°             |
|                                         | c = 20.9552(8) Å, γ = 90°                 |
| Volume                                  | 11327.2(8) Å³                              |
| Z                                        | 1                                          |
| Density (calc)                          | 0.887 mg/m³                                |
| Absorption coefficient                  | 0.603 mm⁻¹                                 |
| F (000)                                 | 3096                                       |
| Crystal size                            | 0.120 mm × 0.120 mm × 0.080 mm             |
| Theta range                             | 1.59° to 30.23°                            |
| Index range                             | -36≤h≤29, -27≤k≤29, -28≤l≤29               |
| Reflections collected                   | 73402                                      |
| R_{int}                                 | 0.1245                                     |
| Completeness (%)                        | 99.8                                       |
| Data/restraints/parameter               | 14847/0/468                                |
| Goodness-of-fit on F²                   | 0.943                                      |
Final $R [I>2\sigma(I)]$ $R_1=0.0871$, $wR_2=0.2262$  
$R$ (all data) $R_1=0.1321$, $wR_2=0.2403$  
Largest diff peak and hole 2.559 e\text{-Å}^{-3} and -0.569 e\text{-Å}^{-3}$
Figure S1. (Top) Experimental nanobeam electron diffraction (NBED) pattern of SolCON-A overlayed with data shown at the top. (Bottom) Simulated electron diffraction (ED) from the single-crystal data of SolCON-B. Circles exemplifies matching diffractions.
**Figure S2.** Spectroelectrochemical (SEC) performance of the SurCON on FTO/glass (2 cm × 2 cm) in a 0.1 M TBAPF$_6$/ACN electrolyte solution using Pt wire and Ag wire, as counter and reference electrodes, respectively. (A) EDS-SEM images. (B) SEC using double potential steps: 0.4-1.8 V ($\lambda_{\text{max}} = 596$ nm). (C) Cyclic voltammograms (CVs) with scan rates of 0.05-0.9 V/s. (D) Exponential and linear correlations between the peak currents ($I$) and scan rates ($\nu$) (left), and $I$ and $\nu^{1/2}$ (right) respectively, during oxidation (top) and reduction (bottom) ($R^2 > 0.99$ for all fits). (E) SEC measurements using double potential steps: 0.4 V to 1.8 V at different switching times (F). Dependence of the contrast ratio ($\Delta T$) on the switching time.
Figure S3. The surface and electrochemical characterization of SurCON before and after immersion in a 4.0 mM solution of Cu(NO$_3$)$_2$·3H$_2$O in ACN for 3 days. (A) UV/Vis absorption spectra, (B) Cyclic voltammograms (CVs) recorded at a scan rate of 100 mV/s, (C) Photographs of the colored and bleached states using an electrolyte solution of 0.1 M TBAPF$_6$ in ACN. Reduced state (Fe$^{2+}$, 0.4 V) and oxidized state (Fe$^{3+}$, 1.8 V).
Figure S4. A NMR tube containing three layers of solvents with complex 1 and PdCl₂(PhCN)₂ was kept for more than 20 days at room temperature: (top) a THF solution of PdCl₂(PhCN)₂ (1.4 μmol, 1.0 mL), (center) a layer of DCM:MeOH:THF (0.5:0.5:1 v/v, 1.0 mL), and (bottom) a DCM/MeOH (1:1, v/v) solution of complex 1 (0.7 μmol, 1.0 mL). Chart 1: (A) Reaction of PdCl₂(PhCN)₂ and iron complex 1, and proposed structure of the formed network. For a related study, see reference [S5]. Chart 2: (A) Scanning electron microscopy (SEM) image. (B) SEM and EDS-SEM images (C) X-ray photoelectron spectroscopy (XPS) spectra. The ratio of Pd/Fe is ~3.9 and N/Fe is ~12.1.

References
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