Supporting Information

Switchable Electrical Conductivity in a Three-Dimensional Metal–Organic Framework via Reversible Ligand $n$-Doping

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Materials and Methods

General. All manipulations were carried out under an inert atmosphere of nitrogen or argon unless otherwise noted. Anhydrous solvents were obtained by filtration through drying columns on an mBraun system, except for N,N-dimethylformamide which was purchased from Sigma-Aldrich (anhydrous, 99.8%) and sparged with argon prior to use. Bulk powders and thin films of the MOF ZnNDI were synthesized according to the literature procedures. Tetra-n-butylammonium fluoride (TBAF; 1.0 M in THF) was purchased from Sigma-Aldrich.

Spectroscopy. UV-vis spectra were measured on a Varian Cary 5000 spectrophotometer, with MOF thin films on glass slides placed in DMF solutions in quartz cuvettes. EPR spectra were measured on a Bruker EMX spectrometer.

Powder X-ray Diffraction. PXRD data were recorded on a PANalytical XPert3 diffractometer with a Cu Kα X-ray source and PIXcel 1d detector, in a Bragg-Brentano geometry.

Scanning Electron Microscopy. ZnNDI powders were spread on a conductive carbon tape and then coated by a Au-Pd (1:1 mixture) layer by Cressington 108 sputter coater for 20 seconds (few nanometers of conductive Au/Pd layer). SEM imaging was performed using a Zeiss Sigma VP operating at 15 kV. To better understand the topological structure of the samples, secondary electron (SE) detector was used with positive 300 volts applied to its Faraday cage to enhance the signal-to-noise ratio. The working distance was kept around 5.2 mm and remained consistent through the imaging of particles at different locations.

Experimental Procedures

Details of Fluoride Soaking Procedure

In a nitrogen-filled glovebox, three 25 mg portions of ZnNDI were dispensed into separate 20 mL vials, then 7 mL DMF was added to each along with a magnetic stir bar. To vial A was added 200 µmol of TBAF (200 µL of a 1.0 M TBAF solution in THF), to vial B was added 50 µmol TBAF, and to vial C was added 25 µmol TBAF. The vials were capped and the suspensions were stirred gently (200 rpm) at room temperature. After 24 hours, each suspension was filtered and the recovered black solids were washed with fresh DMF followed by Et₂O, then dried under vacuum. Samples A-C prepared in this manner were stored under nitrogen as dry powders prior to further measurement.

Electrical Conductivity Measurements

Conductivity measurements were performed under a dry N₂ atmosphere at 302 K in an MBRAUN MB-200B glovebox using a home-made two-contact probe pressed pellet setup. Dried bulk powder samples of MOF were loaded into dry glass tubes and pressed between two stainless steel rods, which also served as current collectors. The cell was then moved inside a hydraulic press, which was hand-tightened fast. Linear I-V curves were then obtained using a Keithley 2450 sourcemeter connected to the cell with test leads. The applied voltage was varied depending on the resistance of the pellet, but
was generally within −1 to +1 V, except for the least conductive samples where voltage limits were raised to ±5-10 V. Following the initial measurement, the cell was allowed to stand for 15 minutes, and retightened by hand. I-V curves were then recollected, and this process was repeated several times until the change in resistance between measurements was minimal. Pellet thicknesses were obtained with a Mitutoyo micrometer after the electrical measurements, using the arithmetic mean of five measurements for each pellet. To test the as-synthesized material, a Keithley 6517B high resistance electrometer was used, and voltages up to ±50 V were applied without any measurable current response above background noise level.

**EPR Data Collection and Analysis**

Samples were prepared in a nitrogen-filled glove box by mixing powdered eicosane with the MOF sample to be measured in known w/w mixtures. Powdered samples were put into precision-bore 4 mm OD quartz EPR tubes, and sample height was measured in order to determine total sample volume. Samples were large enough to fill the entire resonator for all measurements. All measurements were performed at room temperature.

A 2D Field-Power experiment was used to create a power curve for Sample A (Figure S1), which was used to determine a non-saturating microwave power. A microwave power of 0.2996 mW was chosen for all quantitation scans, well within the linear regime of the power curve.

Extrapolation of the linewidth vs. power curve to zero-power shows a minimum linewidth of 7.383 G, largely due to inhomogenous broadening (b = 1.47).

An eicosane blank showed no background, and all samples had a Q value of 4800 in the resonator. Scans were 236 G wide, providing ample baseline for accurate integration. Single integration was performed on each spectrum before baseline correction to provide better correction before double integration for quantitative values. A modulation amplitude of 0.40 G at 100 kHz was also used for all spectra. Spin quantitation of the samples was performed by double integration of the spectrum, and calculation of absolute spins according the equation:

\[
  n_S = \frac{c}{f(B_1, B_m)} \times \{G_R \times C_t \times n\} \times \left\{\sqrt{P} \times B_m \times Q \times n_B \times S \times (S + 1)\right\}
\]

Where \(c\) is the point sample calibration factor (provided by resonator manufacturer); \(B_1\) is the microwave magnetic field; \(B_m\) is the modulation amplitude; \(f(B_1, B_m)\) is the spatial distribution of \(B_1\) and \(B_m\) (also provided by resonator manufacturer); \(G_R\) is the receiver gain, \(C_t\) is the conversion time; \(n\) is the number of scans; \(P\) is microwave power; \(Q\) is the quality factor of the resonator; \(n_B\) is the Boltzmann temperature correction; \(S\) is electronic spin; and \(n_S\) is the absolute number of spins.

Using the calculated spins/mm\(^3\), the sample w/w, and the sample volume and mass, the total number of spins/mg MOF were calculated. The extent of ligand reduction was then calculated based on the general formula \([(TBA)_x(ZnNDI)]\), in which one charge-balancing TBA\(^+\) cation is required for each NDI ligand in the MOF that has been reduced to its radical anion form.
DFT Calculations

All structures were optimized with PBEsol\textsuperscript{4} as implemented in VASP\textsuperscript{5–7} using the PAW plane wave method\textsuperscript{8} and a 500 eV planewave cutoff basis set. A Γ centered 1x1x1 k-grid was converged to ionic and electronic criteria of 0.005 eV and $1\times10^{-6}$ eV, respectively. The HSEsol06\textsuperscript{9} (PBEsol+25% HF) level of theory was used to recover more accurate band-gap energies using the same convergence criteria. Band structures were constructed using the structure from our optimization, sampling at explicit k-points along the high symmetry path. Electron energies were aligned to the vacuum using a previously reported method\textsuperscript{10}. Reduction was modeled by addition of electrons to the system. These data were used to demonstrate the radical locality, rather than their energetics.

Supplemental Data Figures

![Microwave power curve measured for sample A.](Figure S1)
Figure S2. Isotropic EPR spectra of doped samples A–C.

Figure S3. Singly integrated EPR spectra of doped samples A–C.
Figure S4. Time-lapsed UV-vis spectra of a ZnNDI thin film exposed to fluoride (60 nM TBAF in DMF), showing a fast initial reduction followed by gradual continued reduction over the course of several hours.

Figure S5. (left) Time-lapsed UV-vis spectra (3 hours) after removal of a ZnNDI thin film from a TBAF/DMF solution, in a sealed cuvette under N₂. (right) Time-lapsed spectra (10 min) after opening the cuvette to air.

Figure S6. UV-vis spectrum of a ZnNDI thin film after reduction followed by soaking in aerated DMF, displaying an identical spectrum to the as-synthesized neutral material.
Figure S7. SEM images at different magnification levels for as-synthesized ZnNDI.
Figure S8. SEM images at different magnification levels for reduced MOF ZnNDI-A.
**Figure S9.** Visual plots of (a) conduction band orbitals for neutral, as-synthesized ZnNDI, and (b) spin density for ZnNDI after reduction.
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