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Supporting Information

Coordination-induced reversible electrical conductivity variation in the MOF-74 analogue Fe₂(DSBDC)

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Materials

All synthesis and characterization were conducted in air-free conditions. Dry and degassed *N*,*N*-dimethylformamide (DMF), methanol (MeOH), tetrahydrofuran (THF) and dichloromethane (DCM) were obtained by degassing with a vigorous flow of Ar for 30 min and then passing the solvent through two alumina columns in a Glass Contour Solvent System. Anhydrous FeCl₂ (Strem Chemicals) was used as received. 2,5-disulfhydrylbenzene-1,4-dicarboxylic acid (H₄DSBDC),¹ Fe₂(DSBDC)(DMF)₂·x(DMF) and Fe₂(DSBDC)(DMF)₂² were prepared according to reported procedures.

Physical characterization

Infrared spectra were obtained on a Bruker Alpha FT-IR Spectrometer (contained in a N₂ filled glovebox) equipped with a diamond crystal Bruker Platinum ATR accessory. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 Thermogravimetric Analyzer at a heating rate of 2 °C/min under a nitrogen gas flow of 90 mL/min. Elemental analysis was performed by Complete Analysis Laboratories, Inc. in Parsippany, NJ.

X-ray diffraction studies

Powder X-ray diffraction (PXRD) patterns were recorded with a Bruker D8 Advance diffractometer equipped with a $\theta/2\theta$ Bragg-Brentano geometry and nickel-filtered Cu K α radiation (K α_1 = 1.5406 Å, K α_2 = 1.5444 Å, K $\alpha_1/K\alpha_2$ = 0.5). The tube voltage and current were 40 kV and 40 mA, respectively. Samples were prepared on a glass slide. The slide was put inside an airtight specimen holder ring with dome-like X-ray transparent cap. Background of PXRD patterns were corrected by Bruker Diffrac.Suite EVA software.

Gas sorption measurements

A Micromeritics ASAP 2020 Surface Area and Porosity Analyzer was used to measure nitrogen adsorption isotherms. An oven-dried sample tube equipped with a TranSealTM (Micromeritics) was evacuated and tared. $Fe_2(DSBDC)(THF)_2 \cdot x(THF)$ was transferred to the sample tube, which was then capped by a TranSealTM. The sample was heated to 170 °C, established upon by thermo-

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gravimetric analysis, and held at this temperature until the outgas rate was less than 2 mtorr/minute. The total activation time was 36 h. An N₂ adsorption isotherm was measured using a liquid nitrogen bath (77 K). The evacuated sample tube was weighed again and the sample mass was determined by subtracting the mass of the previously tared tube. Ultra high purity grade (99.999% purity) N₂ and He, oil-free valves and gas regulators were used for all free space corrections and measurements.

Two-contact probe electrical conductivity measurements

Technical details of the two-contact probe electrical conductivity measurements were introduced previously.³ A home-made apparatus, "*in situ* press", was used.⁴ Sample was added into a glass tube (inner diameter 0.21 cm, Ace Glass) in a glovebox. It was pressed into a pellet by two stainless steel rod with the same diameter, and these two rods were pressed by a clamp in a glovebox. In this way, electrical contacts between stainless steel rods and the pellet was made *in situ*, and the sample was maintained in air-free condition. The two rods were connected to electrical plugs of the glove box by alligator-equipped copper wires. The electrical plugs were further connected to a sourcemeter (Keithley model 2450) through test leads (Keithley model 8608). Current–voltage (I–V) curves were scanned at various voltage ranges according to the resistance of pellet. All I–V curves were linear, verifying Ohmic contacts between rods and the pellet was measured by a micrometer (Mitutoyo). It ranges from 70 µm to 500 µm depending on the amount of added sample.

According to Ohm's law, plots of current density versus electric field strength were used to calculate electrical conductivity,

$$\sigma = \frac{J}{E}, J = \frac{I}{A}, E = \frac{V}{t}$$

where σ is electrical conductivity, J is current density, E is electric field strength, I is current, V is voltage, A is area of the pellet, and t is thickness of the pellet. The advantage of J–E curves versus I–V curves is that J–E curves normalize the thickness and area of pellets so that they clearly show different electrical conductivity values of different materials.

Because electrical conductivity values in the various forms of $Fe_2(DSBDC)$ are very different, we plot J–E curves in log scale (Fig. 5),

$$lg(J) = lg(\sigma) + lg(E)$$

Therefore, in log scale, the slope of each J–E curve is 1, and the intercept on the y-axis is $lg(\sigma)$.

Fe₂(DSBDC)(DMF)₂·x(DMF)

Fe₂(DSBDC)(DMF)₂·x(DMF) was synthesized according a reported procedure.² Anhydrous FeCl₂ (330 mg, 2.60 mmol), H₄DSBDC (120 mg, 0.52 mmol), and dry and degassed DMF (20 mL) were added into a 100 mL Schlenk flask. The resulting clear yellow (a little bit orange) solution was heated at 140 °C for 18 h under nitrogen to afford dark red-purple crystals (< 200 μ m). The flask was transferred into a glovebox, and reaction mixture was transferred into a vial. The product was soaked in 10 mL of dry and degassed DMF for 12 h, and the solvent was refreshed twice. The product was dried under vacuum at 24 °C for 0.5 h, resulting in dark red-purple solid. Elemental analysis calcd. for Fe₂(C₈H₂O₄S₂)(C₃H₇NO)₃ C, 36.64; H, 4.16; N, 7.54; S, 11.51. Found: C, 36.58; H, 4.07; N, 7.39; S, 11.38. IR (Diamond-ART, cm⁻¹): 2926 (w, br), 1654 (s), 1533 (s), 1437 (m), 1360 (s), 1305 (m), 1233 (m), 1146 (w), 1088 (m), 923 (w), 842 (m), 794 (w), 675 (w), 631 (w), 563 (w).

Fe₂(DSBDC)(DMF)₂

Fe₂(DSBDC)(DMF)₂·*x*(DMF) was soaked in 15 mL of dry and degassed DCM for three times for 12 h, and the solvent was refreshed twice. The product was dried in vacuo at 100 °C for 2 h to afford a dark red-purple solid. Elemental analysis calcd. for Fe₂(C₈H₂O₄S₂)(C₃H₇NO)₂ C, 34.73; H, 3.33; N, 5.79; S, 13.25. Found: C, 34.62; H, 3.18; N, 5.69; S, 13.29. IR (Diamond-ART, cm⁻¹): 2924 (w, br), 1654 (s), 1535 (s), 1437 (w), 1363 (s), 1305 (w), 1233 (w), 1148 (w), 1087 (w), 923 (w), 842 (w), 791 (w), 677 (w), 635 (w), 561 (w), 526 (w).

DMF-soaked Fe₂(DSBDC)(DMF)₂

Fe₂(DSBDC)(DMF)₂ was soaked in 10 mL of dry and degassed DMF for 12 h. The product was dried under vacuum at 24 °C for 0.5 h to afford dark red-purple solid.

Fe₂(DSBDC)(MeOH)₂·x(MeOH)

Fe₂(DSBDC)(DMF)₂·*x*(DMF) was soaked in 15 mL of dry and degassed MeOH, and the solvent was refreshed twice. The product was kept wet in MeOH to prevent decomposition. IR (Diamond-ATR, cm⁻¹): 3547 (w), 3313 (s, br), 2940 (w), 2832 (w), 1657 (w), 1530 (s), 1446 (w), 1363 (s), 1307 (w), 1241 (w), 1154 (w), 1086 (w), 1008 (w), 920 (w), 843 (w), 791 (w), 633 (w), 564 (w), 529 (w).

Fe₂(DSBDC)(THF)₂·x(THF)

Fe₂(DSBDC)(MeOH)₂·*x*(MeOH) was soaked in 15 mL of dry and degassed THF, and the solvent was refreshed twice. The product was dried under vacuum at 24 °C for 0.5 h and was collected in a N₂-filled glovebox as dark red solid. IR (Diamond-ATR, cm⁻¹): 2967 (w), 2832 (w), 1655 (w), 1535 (s), 1440 (w), 1360 (s), 1304 (w), 1233 (w), 1149 (w), 1086 (w), 1042 (w), 921 (w), 883 (w), 842 (w) 792 (w), 635 (w), 561 (w), 529 (w).

Activated Fe₂(DSBDC)

Fe₂(DSBDC)(THF)₂·x(THF) was activated upon heating under dynamic vacuum (< 10 μ mHg) at 170 °C for 36 h to yield 38.3 mg (0.11 mmol, 22% calculated based on the amount of H₄DSBDC used in the synthesis of Fe₂(DSBDC)(DMF)₂·xDMF) of dark red powder. Elemental analysis calcd. for Fe₂(C₈H₂O₄S₂) C, 28.43; H, 0.60; S, 18.98. Found: C, 28.53; H, 0.66; S, 18.79. IR (Diamond-ART, cm⁻¹): 1652 (w), 1528 (s), 1372 (s), 1308 (m), 1237 (w), 1155 (w), 1087 (w), 1030 (w), 923 (w), 845 (w), 792 (w), 641 (w), 571 (w), 550 (w).

DMF-soaked Fe₂(DSBDC)

The activated Fe₂(DSBDC) was soaked in 10 mL of dry and degassed DMF for 12 h. The product was dried under vacuum at 24 °C for 0.5 h to afford dark red-purple solid.

DCM-soaked Fe₂(DSBDC)

The activated Fe₂(DSBDC) was soaked in 10 mL of dry and degassed DCM for 12 h. The product was dried under vacuum at 24 °C for 0.5 h to afford dark red solid. IR (Diamond-ART, cm⁻¹): 1651 (w), 1529 (s), 1371 (s), 1305 (m), 1234 (w), 1153 (w), 1086 (w), 1027 (w), 921 (w), 845 (w), 790 (w), 731 (w), 641 (w), 573 (w), 551 (w).

Computation details

Beginning with the experimentally determined crystal structure of $Fe_2(DSBDC)(DMF)_2 \cdot x(DMF)$, DMF molecules were manually deleted, and the framework was geometrically optimized using PBEsol, ⁵ a 500 eV cutoff and a 2 x 2 x 2 k-grid, as implemented in VASP, ⁶ a commercial solid-state software package. Higher-level electronic structure calculations were then used to recover an accurate band gap (HSE06), ⁷ with a 500 eV cutoff and Gamma only sampling of the first Brillouin zone. The electron energies were aligned to the vacuum level using a method detailed previously.⁸ The electron energies of DMF were computed in Gaussian09 using HSE06/6-311+G*.



Fig. S1. TGA profile of $Fe_2(DSBDC)(DMF)_2 \cdot x(DMF)$ obtained at a heating rate of 2 °C/min under a constant stream of N_2 .



Fig. S2. Desolvation-induced amorphization of $Fe_2(DSBDC)$. Activating $Fe_2(DSBDC)(DMF)_2 \cdot x(DMF)$ under vacuum at 200 °C for 2 days and evacuating $Fe_2(DSBDC)(MeOH)_2 \cdot x(DMF)$ under vacuum at 24 °C for 2 h both result in almost amorphous product.



Fig. S3. TGA profile of Fe₂(DSBDC)(THF)₂·x(THF) obtained at a heating rate of 0.5 °C/min under a constant stream of N₂.



Fig. S4. Linear BET plot of the activated $Fe_2(DSBDC)$. The portion of the N_2 adsorption isotherm (red) shown in this figure was converted to a linear BET plot (blue) that was used to calculate the BET surface area of the activated $Fe_2(DSBDC)$. The resulting fit reveals a surface area of 624 m²/g with a correlation coefficient of 0.9998003 and a C constant of -8372.





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