Supporting Information for

Conductivity, Doping, and Redox Chemistry of a Microporous Dithiolene-Based Metal-Organic Framework

Yoji Kobayashi, † Benjamin Jacobs, ‡ Mark D. Allendorf,* † Jeffrey R. Long* †

† Department of Chemistry, University of California, Berkeley and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720
‡ Sandia National Laboratories, Livermore, California 94551

*e-mail: mdallen@sandia.gov or jrlong@berkeley.edu

Chem. Mater.
Synthesis

Pyrazine-2,3-dithiolene

Pyrazine-2,3-dithiolene was prepared by a modified procedure of Ribas et al.\textsuperscript{1} 95 % purity pyrazine-2,3-dichloride (5.7574 g, 0.036713 mol) was dissolved in 100 mL of deoxygenated methanol. Similarly, an excess (2.6 equiv.) of 95% purity sodium hydrosulfide hydrate (21.328 g, 0.19371 mol) was dissolved in 200 mL of deoxygenated water. Both solutions were added dropwise to 300 mL of deoxygenated methanol while slowly being heated to reflux. After reflux overnight, the light yellow solution was let to cool slightly, upon which 2 aliquots of aqueous hydrochloric acid (100 mL, 1.8 M; 50 mL, 1 M) were slowly added. The resulting dark red solution (pH 7 – 8) was slowly cooled to room temperature overnight, and then further to -20 °C overnight to yield 2.3 g (43%) of product as dark red crystals, which were washed with cold methanol before collecting.

\textsuperscript{1}H NMR (\textit{d}_6-DMSO): 13.72 ppm (2H), 6.89 ppm (2H). Calculated elemental analysis (wt. %) for C\textsubscript{4}H\textsubscript{4}N\textsubscript{2}S\textsubscript{2} (144.21 g/mol): C 33.31%, H 2.80%, N 19.42%, S 44.46%; found: C 33.29%, H 2.76%, N 19.10%, S 44.60%.

\((Bu\textsubscript{4}N)\textsubscript{2}Ni(pdt)\textsubscript{2}\) and \((Bu\textsubscript{4}N)Cu(pdt)\textsubscript{2}\)

1.6 g of pyrazine-2,3-dithiol (0.011 mol) was dissolved in a solution of methanol (20 mL) containing sodium ethoxide (95 % purity, 1.6 g, 0.022 mol). To this, a methanol solution (20 mL) of anhydrous NiCl\textsubscript{2} (0.72 g, 0.0056 mol) was slowly added while stirring. After the methanol was removed \textit{in vacuo}, the solid (ca. 3.0 g) was redissolved in absolute ethanol (300 mL) and filtered to remove bulk NaCl and other insoluble residues. After removing the ethanol \textit{in vacuo}, 0.50 g (0.0012 mol, assuming a dihydrate) of this solid was dissolved/dispersed in water (10 mL). The aqueous layer was extracted portionwise with a chloroform solution (4 mL \times 5) containing a slight deficit of tetrabutylammonium bromide (0.61 g, 0.0019 mol, 0.8 equiv.)). The combined organic layers were washed twice with water, dried over Na\textsubscript{2}SO\textsubscript{4}, and evaporated to dryness.

Calculated elemental analysis (wt. %) for NiC\textsubscript{40}H\textsubscript{76}N\textsubscript{6}S\textsubscript{4} (828.02 g/mol): C 58.02%, H 9.25%, N 10.15%, S 15.49%; found: C 57.44%, H 9.24%, N 10.14%, S 15.88%.
The copper analogue was prepared in an analogous method from CuCl₂·2H₂O; however, as the complex appears to oxidize in air, the amount of tetrabutylammonium bromide was adjusted accordingly to half the amount.

\[ Na[Ni(pdt)₂]·2H₂O \text{ and } Na[Cu(pdt)₂]·2H₂O \]

The procedure as according to Ribas et al. for the preparation of Na[Cu(pdt)₂] was followed, which gave satisfactory results for the nickel complex, when using NiClO₄·6H₂O as the precursor.

Calculated elemental analysis (wt. %) for NaNiC₈H₆N₄S₄·2H₂O (402.1066 g/mol): C 23.89%, H 2.00%, N 13.93%, S 31.89%; found: C 23.76%, H 1.95%, N 13.22%, S 32.02%.

\[ Cu[Ni(pdt)₂] \text{ and } Cu[Cu(pdt)₂] \]

The preparation of both frameworks followed a modified version of that by Takaishi et al.² and is analogous for both frameworks. In a typical preparation of Cu[Ni(pdt)₂], Na[Ni(pdt)₂] (0.60 g, 0.0015 mol) was dissolved in acetonitrile (200 mL). While this solution was stirring rapidly, CuI (0.29 g, 0.0015 mol) dissolved in acetonitrile (15 mL) was added dropwise. The resulting dark red colloid was filtered on a 0.22 µm nylon membrane filter. Scanning electron microscopy showed that Cu[Ni(pdt)₂] had formed as smooth 150-nm diameter particles, while Cu[Cu(pdt)₂] formed as rough, micron-sized particles (see Figure S5).

Calculated elemental analysis (wt. %) for Cu[Ni(pdt)₂], CuNiC₈H₆N₄S₄ after desolvation (406.63 g/mol): C 23.63%, H 0.99%, N 13.78%, S 31.54%; found: C 21.99%, H 1.02%, N 12.49%, S 27.30% The discrepancy between calculated and found results may be due to a slight decomposition of the MOF, especially on the surface; however, powder X-ray diffraction data reveal no noticeable change in structure.

Preparation of Cu[Ni(pdt)₂] electrodes

Interdigitated Pt electrodes (IDE) on glass substrates with a digit spacing of 15 µm were obtained from Abtech Scientific Co. These electrodes have a cell constant of 0.04 cm⁻¹, as defined by Sheppard et al.³-⁴ Hence, the film thickness does not adversely affect the absolute measurement of conductivity, provided that it is adequately thick. For MOF deposition, 11 mg of Cu[Ni(pdt)₂] was dispersed in 2.5 mL of acetonitrile. This suspension was placed in a tall 5 mL
vial containing the IDE. The vial was tilted in a 50 °C oil bath such that the IDE was at 45°, and left overnight to slowly evaporate. Excess portions of the films were scraped off with a soft piece of plastic before measurement. Based on gravimetry of larger substrates, we estimate the film thickness to be on the order of a few microns. For photocurrent measurements, Cu[Ni(pdt)$_2$] was deposited in a similar manner on ITO slides cut to suitable sizes.

**Measurement Details**

*Doping and Conductivity Measurements*

A N$_2$ flow-through apparatus was built from pyrex tubing and ground-glass joints. A heated tube contains the interdigitated electrode, with electrical and thermocouple feedthroughs. The atmosphere in the tube may be controlled so that it is under flowing N$_2$, flowing N$_2$/I$_2$, or vacuum. A small chamber containing granulated iodine held at room temperature provides iodine vapor (P = 0.34 torr). During the experiment, the film is heated under flowing N$_2$ at 2 °C/min to 120 °C, and then evacuated to vacuum and held for 2 hours to desolvate the sample. After 2 hrs, the sample is cooled under flowing N$_2$ to a desired temperature where the conductivity is recorded, without exposure to air. For doping experiments, the N$_2$ is directed through the iodine chamber before reaching the sample. Under these conditions, (N$_2$ = 75 mL/min, P$_{I_2}$ = 0.34 torr), the amount of iodine reaching the sample chamber is approximately 1.5 µmol/min, or 23 mg/hr. Conductivity was recorded by a 2-point measurement applying constant current and recording the potential. In separate measurements, I-V curves showed a linear response with small hysteresis, and current vs. time curves did not show significant polarization times, so we do not expect ionic conductivity or redox of the sample to be an issue.

For low-temperature measurements, the sample was desolvated (and doped) in the manner above, and then transferred to a cryostat. Mounting the sample required the film to be exposed to ambient atmosphere for 20-30 min, but the conductivity of the sample did not change by a large amount during this time. Samples were measured by the same 2-point measurement as above, while cooling at a rate of 2 °C/min under static N$_2$.

*Photocurrent Measurements*

Cu[Ni(pdt)$_2$/ITO electrodes were prepared as mentioned above. n-Si was cleaned in a buffered oxide etch solution (NH$_4$F/HF) immediately before use. The electrolyte was a 1:10
MeOH/H₂O solution containing 0.1M KCl, aerated prior to use. Light from a focused 1000W Xe lamp was filtered through 10 cm of water and 5 mm of pyrex, and chopped at 0.5 Hz during measurements. A Ag/AgCl reference electrode was used, and the potential was scanned at 25 mV/s.
Supplemental Data

X-ray diffraction

Figure S1. Powder X-ray diffraction patterns of Cu[Cu(pdt)$_2$] and Cu[Ni(pdt)$_2$].

Powder X-ray diffraction shows that Cu[Cu(pdt)$_2$] and Cu[Ni(pdt)$_2$] can be described as having the same unit cell, $P4_2/mmc$ (S. G. no. 131), with a very similar $a$ parameter (6.8222(4) Å vs. 6.82870(30) Å, respectively) and slightly shorter $c$ parameter for the Cu-Ni framework (16.5165(16) Å vs. 16.2176(12) Å, respectively). Changing the metal in the dithiolene complex would be expected to affect the $c$ parameter more than the $a$ parameter.

It is also evident that while Cu[Cu(pdt)$_2$] collapses under desolvating conditions, Cu[Ni(pdt)$_2$] remains structurally stable. The structure of Cu[Ni(pdt)$_2$] is also preserved after exposure to I$_2$ vapor.
Thermal Gravimetry Analysis (TGA)

TGA of Cu[Ni(pdt)$_2$] (below, Fig. S2) shows a weight loss of 15 % complete below 120 °C. IR spectra indicate the possibility of water and acetonitrile in the pores, implying possible compositions of Cu[Ni(pdt)$_2$]-3.8H$_2$O or Cu[Ni(pdt)$_2$]-1.7MeCN.

![Thermogravimetric analysis of as-synthesized Cu[Ni(pdt)$_2$]](image)

**Figure S2.** Thermogravimetric analysis of as-synthesized Cu[Ni(pdt)$_2$]

Diffuse-reflectance UV-vis-NIR Spectra

As shown below, Cu[Ni(pdt)$_2$] exhibits a larger optical bandgap (2.0 eV) than Cu[Cu(pdt)$_2$]. The spectral features remain largely unchanged upon doping with iodine.

![Diffuse-reflectance UV-vis-NIR spectra.](image)

**Figure S3.** Diffuse-reflectance UV-vis-NIR spectra.
Photocurrent Experiments

Photocurrent measurements of Cu[Ni(pdt)₂] deposited on ITO were recorded, and compared with results from a n-doped Si(111) sample. Chopping the light enhances the difference between the dark and light current; a large photocurrent is indicated by a large sawtooth shape. The MOF electrode’s photocurrent (Fig. S4a) increases towards more negative potentials, implying that the material is a photocathode, or in other words, a p-type semiconductor.⁵⁻⁷ If the MOF were n-type, as in the n-Si sample, a photocurrent should be observed at positive potentials, which is what we observe in Fig. S4b. Since no external redox couple has been added, the redox of water/air is thought to be contributing to the photocurrent.

Figure S4. Photocurrent measurements of Cu[Ni(pdt)₂] deposited on ITO (a), and of n-Si (b).
**Particle Size and Morphology of Cu[Ni(pdt)] and Cu[Cu(pdt)]**

Preparing the MOFs via rapid stirring of reagents results in particles of different sizes. Cu[Cu(pdt)] forms large (5 µm) rough disks/spheres, whereas Cu[Ni(pdt)] forms small (150 nm) particles, the latter of which form a stable colloid in acetonitrile.

![Scanning electron microscopy images of (a) Cu[Cu(pdt)] and (b) Cu[Ni(pdt)]](image_url)

**Figure S5.** Scanning electron microscopy images of (a) Cu[Cu(pdt)] and (b) Cu[Ni(pdt)]

**References**