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

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Metal−organic frameworks have found many applications concerning the adsorption of small molecules,[1] but work incorporating other properties, such as electronic conduction, still lags behind. Here, we report a new microporous framework, $Cu[Ni(pdt)_2]$ (pdt^{2-} = pyrazine-2,3-dithiolate), that exhibits electronic conductivity, doping, and redox behavior. Although a number of extended coordination solids with conductivity have been reported,[2] to the best of our knowledge none have been demonstrated to display porosity at the same time. In general, porous, high-surface area materials with electronic conductivity are rare. Combining the porosity and customizability of metal−organic frameworks with electronic conductivity should open up a range of new applications for these materials. Further, in view of the well-studied redox flexibility and strong metal−ligand orbital interactions found within molecular transition metal dithiolene complexes,[3] the extension of this chemistry to metal−organic frameworks provides a promising strategy for achieving electronic conductivity.

The compound $Cu[Ni(pdt)_2]$ was synthesized using a procedure analogous to that previously described for $Cu[Cu(pdt)_2]$.[4] Reaction of $Na[Ni(pdt)_2] \cdot 2H_2O$ with CuI in acetonitrile afforded the solvated metal−organic framework as a dark red precipitate. X-ray powder diffraction data show the solid to be isostructural with $Cu[Cu(pdt)_2]$,[4] indicating the framework structure depicted in Figure 1. Here, redox-active nickel bis-dithiolate complexes are connected via square planar $Cu(pyrazine)_4$ units to form a tetragonal metal−organic framework featuring one-dimensional channels. Given the resonance forms available to the pdt^{2-} ligand, one might expect facile electron transfer within the framework, and indeed solvated $Cu[Cu(pdt)_2]$ has already been reported to have a room temperature conductivity of 1×10^{-4} S/cm.[4] We note, however, that porosity has not been explicitly demonstrated for this compound via gas adsorption measurements. Moreover, our attempts to desolvate the material led to collapse of the porous framework structure, as probed by X-ray powder diffraction (see Figure S1 in the Supporting Information).

In contrast, solvated $Cu[Ni(pdt)_2]$ can be desolvated without inducing framework collapse by heating at 120 °C under dynamic vacuum. A thermogravimetric analysis indicated a weight loss of ca. 15 wt % under such conditions (see Figure S2 in the Supporting Information). The powder X-ray diffraction pattern of the resulting solid confirmed retention of crystallinity (see Figure S1 in the Supporting Information), whereas elemental analysis showed only a slight deficit of C and S compared with the formula expected for complete desolvation. In addition, as shown in Figure 2, N_2 adsorption data collected at 77 K reveals a type I isotherm, confirming microporosity. Fits to the data afforded a BET surface area of 385 m^2/g and a Langmuir surface area of 423 m^2/g.

To the eye, $Cu[Ni(pdt)_2]$ appears to be a black powder with a slight red tinge, reminiscent of the color of the $[Ni(pdt)_2]^{2-}$ complex in solution. Diffuse reflectance spectra of $Cu[Ni(pdt)_2]$ in the UV−visible−near IR range indicate a feature implying an optical bandgap of approximately 2 eV (see Figure S3 in the Supporting Information). Consistent with this relatively large optical bandgap, the conductivity of $Cu[Ni(pdt)_2]$ is not exceptionally high, and was measured to be 1×10^{-8} S/cm at room temperature (E_a = 0.49 eV). For comparison, a one-dimensional coordination solid of nickel phenyl-1,2,4,5-tetrathiolate was previously reported to have a conductivity of 2×10^{-3} S/cm.[5]

It was anticipated that it might be possible to enhance the conductivity of $Cu[Ni(pdt)_2]$ through partial oxidation of the framework. Based on the reversible $[Ni(pdt)_2]^{2-/1-}$ couple at $E_{1/2}$ = −391 mV vs Ag/Ag^+ observed by cyclic voltammetry, I_2 was selected as an oxidant. We proceeded to treat a film of the evacuated metal−organic

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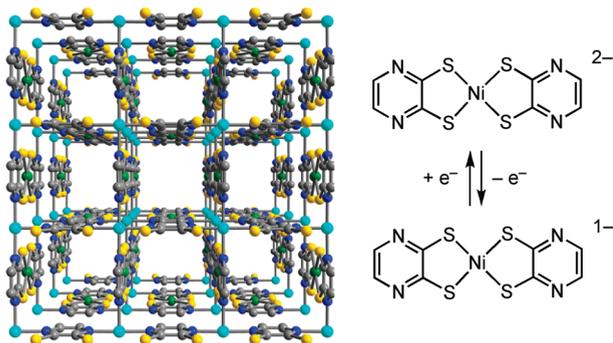
Figure 1. Left: Portion of the structure of the metal−organic framework Cu[Ni(pdt)$_2$], with light blue, green, yellow, blue, and gray spheres representing Cu, Ni, S, N, and C atoms, respectively; H atoms are omitted for clarity. Right: Redox behavior associated with the [Ni(pdt)$_2$]$^{2-}$ units within the framework.

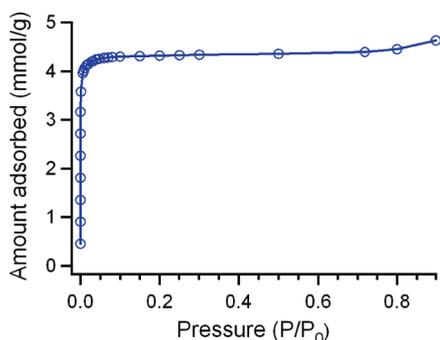**Figure 2.** Nitrogen gas adsorption isotherm for Cu[Ni(pdt)$_2$] at 77 K.

Figure 3. Conductivity of Cu[Ni(pdt)$_2$] films cast on Pt interdigitated electrodes.

framework with a stream of I$_2$ vapor at 50 °C while simultaneously recording its conductivity. As shown in Figure 3, this treatment resulted in a 10^4-fold increase in conductivity to approximately 1×10^{-4} S/cm ($E_a = 0.18$ eV). The increase in conductivity based on oxidative doping implies that the framework is a p-type semiconductor, as further supported by photocurrent experiments (see Figure S4 in the Supporting Information). After doping, the films appeared to darken slightly in color, although diffuse-reflectance UV−visible−near IR spectra revealed no large changes. Based upon electronic structure calculations performed on [Cu(pdt)$_2$]$^{1-}$,[6] which is isoelectronic with [Ni(pdt)$_2$]$^{2-}$, we expect the HOMO, and hence the valence band of the corresponding metal−organic frameworks, to have a large contribution from the S 3p orbitals of the ligand.

Exposure of the film to air for 12 h resulted in a drop in conductivity to 5×10^{-5} S/cm, suggesting that the doping can be reversed to some extent. Indeed, doping experiments carried out at 150 °C resulted in much less of an increase in conductivity, suggesting that an I$_2$ adsorption−desorption equilibrium probably determines the dopant level. It should be noted that since the sample temperature (50 or 150 °C) was higher than that of the I$_2$ reservoir (room temperature), the sublimation/deposition of I$_2$ itself should not have led to the increase in
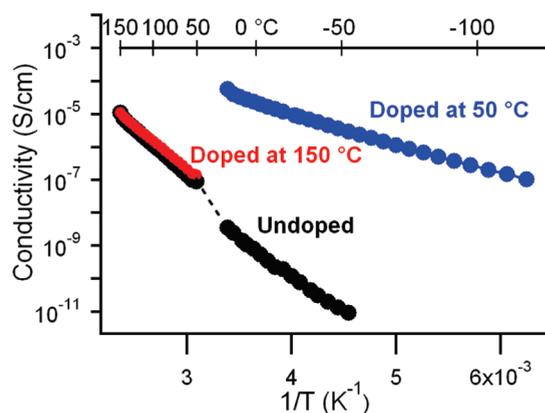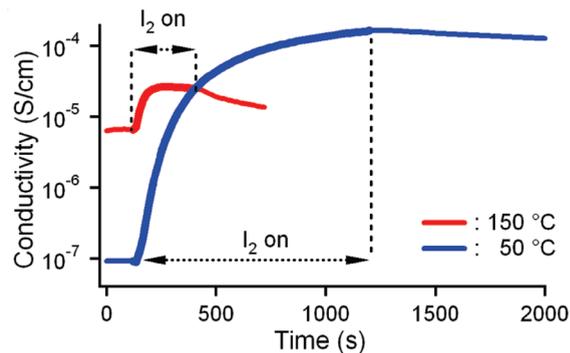
conductivity. It should further be noted that the conductivity of I$_2$ itself is not particularly high (1×10^{-9} to 1×10^{-6} S/cm, depending on the crystallographic axis).[7] We also conducted gravimetry on a 100-mg sample of Cu-[Ni(pdt)$_2$] exposed to the same I$_2$ vapor stream (23 mg/h) for 4 h, which resulted in no significant weight increase. This indicates that the amount of I$_2$ involved in the doping is very small, such that the conduction must occur primarily through the metal−organic framework rather than through I$_2$. Importantly, powder X-ray diffraction data showed no loss of crystallinity upon doping (see Figure S1 in the Supporting Information).

A recent paper reported solution-phase iodine loading of a carboxylate-based metal−organic framework.[8] Therein, an extremely high I$_2$ loading was achieved, close to complete filling of the pores, leading to an electronic conductivity of 3.4×10^{-3} to 1.7×10^{-4} S/cm. However, as the authors suggest, given the high concentration of iodine, a considerable portion of the conductivity is likely to occur through the iodine rather than through the framework. In addition, pore filling led to a loss of porosity. In contrast, Cu[Ni(pdt)$_2$] exhibits a similar conductivity via doping with a very small amount of I$_2$.

The redox properties of dithiolene complexes in solution are well-documented. The redox behavior usually has a substantial contribution from both the metal and the ligand, depending on the precise nature of the two

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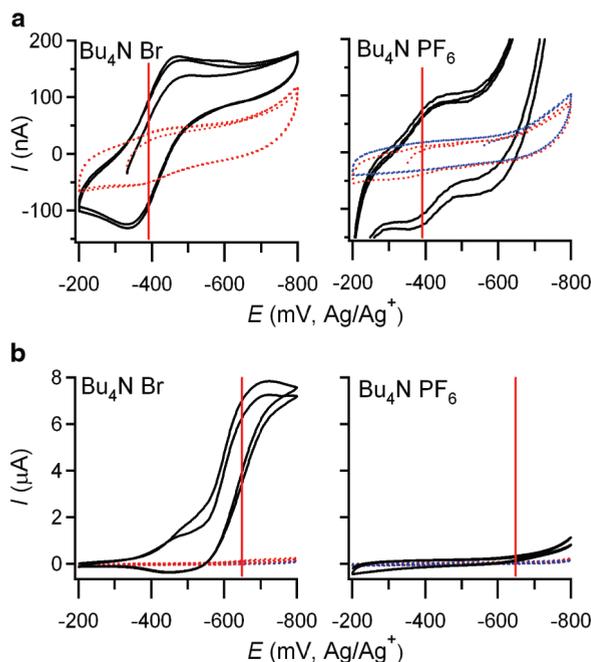
Figure 4. Cyclic voltammograms of Cu[Ni(pdt)$_2$] (a) and Cu[Cu(pdt)$_2$] (b) cast on a Pt disk electrode, in different supporting electrolytes (TBABr and TBAPF$_6$, in MeCN, 0.1 M). Recorded at 10 mV/s. The dotted blue line indicates the bare Pt disk electrode before MOF deposition, whereas the red dotted line indicates the Pt electrode after polishing off the deposited MOF. The red vertical line indicates $E_{1/2}$ for the dithiolene complex in solution.

species.[3,9] The redox couple for the tetra-*n*-butylammonium salt of [Cu(pdt)$_2$]$^{2-/1-}$ in acetonitrile was observed at $E_{1/2} = -648$ mV vs Ag/Ag$^+$ by cyclic voltammetry, close to literature values reported vs Ag/AgCl.[6] For [Ni(pdt)$_2$]$^{2-/1-}$, the redox couple was observed at $E_{1/2} = 391$ mV vs Ag/Ag$^+$. Casting suspensions of Cu[Cu(pdt)$_2$] (2−3 μm particles) and Cu[Ni(pdt)$_2$] (150 nm particles) onto Pt disk electrodes resulted in the redox responses shown in Figure 4. The observed peaks are in the same vicinity of the molecular complexes in solution, as indicated by the red vertical lines. The peaks are absent when the Pt disk is bare (red dotted lines), appear after deposition of the framework, and disappear when the framework is removed by polishing (blue dotted lines). Thus, the redox couple is indeed from the solid metal−organic framework, rather than from soluble impurities. The separation between oxidation and reduction peaks implies that diffusion of the charge-balancing or electroactive species is rate-limiting. Typically, for electrochemically grown hexacyanoferrate films, diffusion is not a factor, and hence the peaks are not separated.[10] However, peak separation has been observed in cyclic voltammograms of hexacyanoferrate particles deposited on graphite electrodes, which is a closer analogue of our metal−organic framework-deposited electrodes.[11]

Comparing different supporting electrolytes, sharp redox peaks for both frameworks are observed only when small anions such as bromide are used. For example, in Figure 4a, for Cu[Ni(pdt)$_2$], when the anion of the supporting electrolyte is large, such as hexafluorophosphate, the redox peak is not as clearly defined compared to when the anion is bromide. We attribute this to the pore size effect of the framework, because redox changes in the solid film ideally requires charge-balancing counteranions to diffuse into the pores of the structure. In Figure 4b, the difference is even more extreme, and the faradaic current for Bu$_4$NBr is much larger than for Bu$_4$NPF$_6$. This is because the Cu[Cu(pdt)$_2$] particles are larger (2−3 μm vs 150 nm, see Figure S5 in the Supporting Information), and bulk diffusion through the pores becomes more important. Additionally, the current observed for Cu[Cu(pdt)$_2$] is much larger than for Cu[Ni(pdt)$_2$], because the inherently higher conductivity permits more of the aggregated particles to be electrically addressed.

The foregoing results demonstrate several key steps toward expanding the applications of metal−organic frameworks to include electronic devices. First, bandgap tuning in a framework was shown to be feasible by changing the metal coordinated to the dithiolate linker from copper to nickel. Second, the ability to dope the optical bandgap of the porous material was demonstrated. It was further established that the frameworks are p-type semiconductors. In addition, we have shown that dithiolene-based metal−organic frameworks of this type can sustain permanent porosity, thereby creating a potentially versatile platform for generating hybrid, ordered nanoscale electronics. Given the wide range of molecular dithiolene complex chemistry known, these properties suggest that these and related metal−organic frameworks may find applications as new electronic and photoactive microporous materials.

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