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Elucidating Novel Reactivity of Ni $^{2+}$ in an Air Sensitive Metal Organic Framework with Variable Temperature and Low Pressure Diffuse Reflectance UV-Vis-NIR Spectroscopy

Carl K. Brozek, and Mircea Dinca
MIT, DEPARTMENT OF CHEMISTRY, 77 MASSACHUSETTS AVENUE, CAMBRIDGE, MA 02139

Figure 1. The Praying Mantis Diffuse Reflection Accessory.

Figure 2. The Praying Mantis Low Temperature Chamber.

INTRODUCTION

The popular materials known as metal organic frameworks (MOFs) are porous coordination polymers composed of organic linkers and inorganic nodes in a crystalline arrangement. These often contain transition-metal ions that absorb UV-Vis-NIR radiation whose spectra offer insight into the geometry around the absorbing ions, as well as the physicochemical properties of the atoms surrounding them. Since these two aspects govern the inherent reactivity of the ions and because these properties transform during the course of a reaction, electronic spectroscopy is a useful tool for characterizing MOFs with reactive metal nodes and observing their reactivity.

As solid-state materials, the electronic spectroscopy of MOFs depends on analyzing the diffuse reflectance of incident light scattering within their microporous crystalline lattices. The Harrick Praying Mantis^{TM} accessory is well suited for routine measurements of air-stable MOF powders, but not for monitoring the behavior of reactive metal sites in MOFs. Samples that are good candidates for reactivity studies are often air-sensitive due to the unstable nature of the metal ion. Analyzing their behavior also requires controlling *in situ* the temperature and pressure around the sample, as well as being able to dose the sample with substrates for reactivity studies. We demonstrate here that the Harrick Low Temperature Reaction Chamber accessory for the Praying Mantis^{TM} enabled spectroscopic characterization of an unusual Ni^{2+} species within a MOF and *in situ* monitoring of its reactivity with molecules under various environmental conditions.

We synthesized a novel MOF formulated as $NiZn_3O(O_2C\text{-}C_6H_4\text{-}CO_2)_3$ and referred to as Ni-MOF-5, which can be viewed as a Ni^{2+}-doped analog of the well-known material called MOF-5, where each octahedral Zn_4O cluster was replaced by $NiZn_3O$. We sought to characterize the unusual tetrahedral geometry and all-oxygen environment around Ni^{2+} using diffuse reflectance UV-Vis spectroscopy, which required maintaining the material in an inert atmosphere. We also sought to study the reactivity of this material with small molecules since Ni^{2+} in this geometry is likely to accommodate two additional molecules in its coordination sphere. Diffuse reflectance of the material as it reacts with small molecules would offer unprecedented insight into the geometrical distortions and electronic properties of Ni^{2+} in this unusual atomic environment. The Harrick Low Temperature Reaction Chamber accessory provided an inert atmosphere for measuring the diffuse reflectance of Ni-MOF-5 and supported measurements under reduced pressure and elevated temperature for monitoring the sequential loss of *N*,*N*-dimethylformamide (DMF) molecules from the Ni^{2+} site. The details of this study are reported elsewhere.[1]

EXPERIMENTAL

A commercially available UV-Vis-NIR spectrometer was used for all measurements in its double-beam mode with the Harrick Praying Mantis™ (see Figure 1) and Low Temperature Reaction Chamber equipped with SiO_2 windows (see Figure 2). All data were collected in % reflectance and later converted to the Kubelka-Munk function. $BaSO_4$ was loaded into the reaction chamber and installed into the Praying Mantis™ to establish a baseline spectrum between 2000 nm and 200 nm. This data was collected at ambient temperature and pressure and was later subtracted from all subsequent experimental traces.

Neat Ni-MOF-5 was loaded into the reaction chamber under an inert atmosphere of a N_2-filled glovebox. This sample had previously been soaked in a bath of DMF to achieve a DMF-adduct of Ni-MOF-5. The reaction chamber was attached to the Praying Mantis™ and

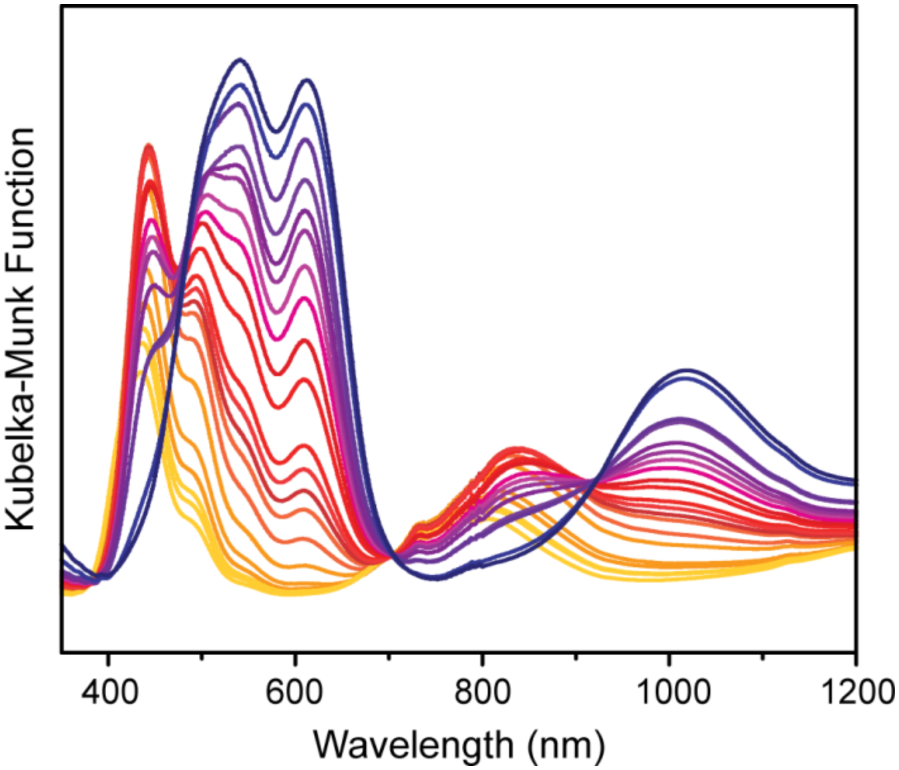

Figure 3. Diffuse reflectance spectra of a DMF-adduct of Ni-MOF-5 collected *in situ* while heating the sample under reduced pressure. The initial trace is shown in yellow and progresses through orange, red, and terminates in blue.

connected to circulating water through the ports. To regulate the temperature of the sample, the reaction chamber was connected to the Harrick Automatic Temperature Controller™ through a K-type thermocouple.

A spectrum of this sample was collected under ambient conditions followed by another collection after introducing dynamic vacuum through the valve, which is connected directly to the sample holder. We elevated the temperature in 10 °C increments to 200 °C, collecting spectra once the temperature stabilized after each step. When the sample enclosure reached 200 °C, we collected spectra every 3 minutes until the data appeared qualitatively to stop evolving.

RESULTS AND DISCUSSION

The resulting set of spectra is shown in Figure 3 in Kubelka-Munk units without normalization. The initial trace taken under dynamic vacuum at room temperature is shown in yellow. Subsequent data progress from yellow to orange to red and terminate in blue.

The evolution of the data suggested the Ni^{2+} site in the DMF-adduct transformed under vacuum and elevated temperature. The final blue trace matched the expected absorption profile of tetrahedral Ni^{2+} while the earlier spectra corresponded six and five-coordinate Ni^{2+}. Since DMF is likely to bind to the vacant coordination sites of Ni^{2+} in Ni-MOF-5, the additional atoms around Ni^{2+} are likely from pendant DMF molecules. The tight isosbestic point near 700 nm suggested the Ni^{2+} underwent a clean transformation from six to five to four coordinate geometry due to subsequent loss of two DMF molecules at each metal site.

CONCLUSION

These data offer unprecedented insight into the transformation of a reactive metal site in a MOF. The Harrick Low Temperature Reaction Chamber enabled collecting diffuse reflectance spectra in situ for the DMF adduct of Ni-MOF-5 as Ni^{2+} lost DMF molecules subsequently from its coordination sphere. The final trace captures Ni^{2+} in an unusual pseudo-tetrahedral environment that would be impossible to analyze without an inert atmosphere. Hence, the Harrick accessory facilitated a study that establishes MOFs as a new platform for reactivity studies and coordination chemistry of inorganic species that are difficult to achieve as molecules.

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[1] Brozek, C. K.; Dincă, M. *Chemical Science* **2012**, *3*, 2110-2113.