

Size-Dependent Optical Gap Shifts in Dynamic MOF Nanocrystals Achieved Through Elevated Temperatures

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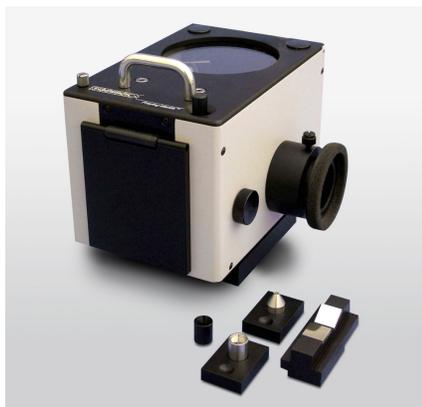


Figure 1. [The Praying Mantis™ Diffuse Reflection Accessory.](#)



Figure 1. [The Praying Mantis™ Low Temperature Chamber.](#)

INTRODUCTION

Prior work from our lab has shown that the metal–linker bonds of metal–organic frameworks (MOFs) exist in a dynamic equilibrium between tightly and loosely bound states.^{1–3} We therefore anticipate MOF optical behavior that can be tuned by altering the equilibrium of metal–linker tight and loose bond configurations via external stimuli. Particle size offers another important parameter for controlling optical properties without altering the atomic composition of a material. Here, we demonstrate that the optical gaps of common MOFs decrease by hundreds of millielectronvolts at temperatures far below MOF decomposition, in stark contrast to the behavior of conventional semiconductors. These results illustrate the utility of harnessing labile metal–ligand bonds—the basic building block of inorganic structure–function relations—in achieving unprecedented size- and stimuli-dependent properties. This study employs the Harrick Low Temperature Reaction Chamber accessory for the Praying Mantis to facilitate spectroscopic characterization of the size-dependent optical properties of MOF MIL-125.

To understand the impact of particle size and dynamic bonding on the optical properties of MOFs, we targeted $\text{Ti}_8\text{O}_8(\text{OH})_4(\text{terephthalate})_6$ (MIL-125) due to its frequent use as a sensitizer for photoredox reactivity and because seminal reports of MOF optical properties were first demonstrated with it and related derivatives, such as $\text{Ti}_8\text{O}_8(\text{OH})_4(2\text{-amino-terephthalate})_6$ (MIL-125-NH₂).

Three batches of MIL-125 nanoparticles were prepared with particle sizes controlled by varying the equivalents of benzoic acid, as a modulator, relative to the amount of $\text{Ti}(\text{O}i\text{Bu})_4$ precursor. After synthesis, the samples were washed thoroughly with fresh *N,N*-dimethylformamide (DMF) and methanol and then dried. To probe the impact of thermal energy on the optical absorption of MIL-125 nanoMOFs, variable-temperature diffuse-reflectance UV–vis spectra were collected on powder samples of each of the three sizes using the Harrick Reaction Chamber. The materials were kept under dynamic vacuum and analyzed between 163 and 523 K.

EXPERIMENTAL

A UV-Vis-NIR spectrometer in double beam mode with the Harrick Low Temperature Reaction Chamber (CHC-CHC-4) and Praying Mantis accessory

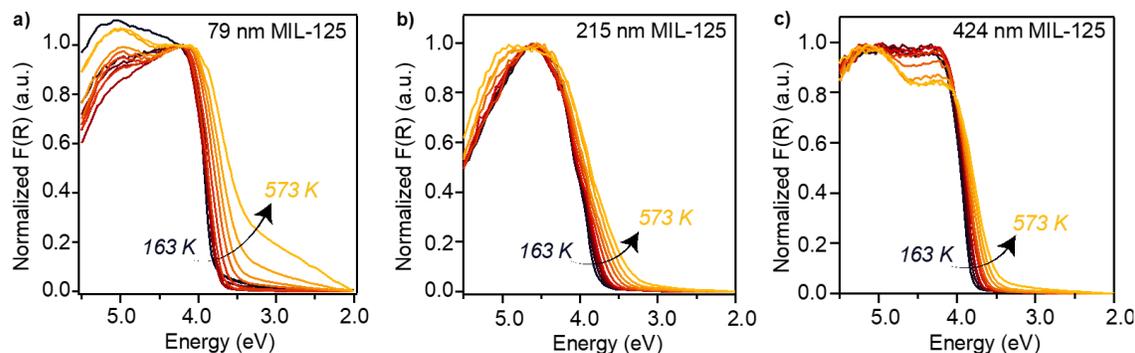


Figure 3. Variable-temperature diffuse reflectance UV-vis spectra of MIL-125 nanoparticles with diameters (a) 79, (b) 215, and (c) 24 nm.

(DRP) were used to collect the measurements under dynamic vacuum. Data were collected in %reflectance and converted to the Kubelka-Munk function. To take a baseline, BaSO_4 was added into the reaction chamber and a spectrum was collected at ambient temperature. Then, various sizes of MIL-125 particles were loaded into the chamber and a temperature controller (ATK-024-3) was attached to the Reaction Chamber with a K-type thermocouple. Furthermore, circulating water was connected to regulate the temperature of the sample.

The samples were evacuated at room temperature and cooled to 163K. Spectra were then taken in 25K increments between 163 and 29K and 50K increments between 298 and 573K.

RESULTS AND DISCUSSION

Qualitatively, all three samples exhibit dramatic changes to their absorption profiles with several distinct features: (1) higher temperatures induce the formation of low-energy absorption tails, (2) higher temperatures cause the low-energy peak maxima to red-shift, and (3) higher temperatures cause an inversion of the relative intensities of high-energy charge-transfer bands. Variable temperature absorption spectra of TiO_2 were collected to investigate the accuracy of these shifts.

While drastic changes in absorption tailing often indicate defect creation, these features are reversible across a wide temperature range in the 79 nm MIL-125 particles. Compared to the retention of electronic symmetry in thermal shifts of conventional semiconductors, thermal shifts in MOFs involve more severe geometric distortions. While all sizes show temperature-dependent absorption profiles, smaller particles

exhibit far greater sensitivity to temperature.

CONCLUSION

This experimental study shows that the optical gaps of MOFs MIL-125 decrease at elevated temperatures to a far greater degree than conventional semiconductors and that this effect becomes magnified for smaller nanoparticle sizes. On the basis of fitting the temperature-dependent optical gaps to a model based on vibronic coupling, these results suggest that MOF metal-linker bonding becomes more dynamic and flexible with smaller particle sizes, allowing control over optical behavior difficult to achieve with other classes of molecules and materials.

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