Supporting Information for: Methyl-Rotation Dynamics in Metal-Organic Frameworks Probed with Terahertz Spectroscopy

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1. Methods

DFT Simulations

DFT calculations were performed using the CRYSTAL17 software package.(1) The M06-2X meta-global gradient approximation (meta-GGA) density functional was used for correlation and exchange (with 54% explicit Hartree-Fock exchange),(2) and the split-valence double-zeta 6-31G(d,p) basis set(3) was utilized for all calculations, based on previous success with this model.(4) The published crystallographic data(5) were used to initialize geometry optimizations, which had an energy convergence criterion of $\Delta E < 10^{-8}$ hartree. For the geometry optimizations, all parameters were allowed to fully relax (atomic positions and lattice vectors) with no constraints other than the space group symmetry of the solid. Due to the electronic structure of cobalt, spin-unrestricted calculations were performed for ZIF-67 and three electrons were initially set as unpaired in a ferromagnetic arrangement for the first five self-consistent field cycles, after which the constraint was removed. Vibrational analyses were calculated based on the optimized geometry, and the IR intensities were calculated using the Berry phase method.(6-8) A more accurate two-point numerical differentiation (program keyword NUMDERIV = 2) was used to improve the accuracy of the predicted vibrational frequencies. The energy convergence was more rigorous for the vibrational simulations, and was set to of $\Delta E < 10^{-10}$ hartree.

Experimental Spectroscopy

The experimental THz-TDS measurements were performed using a commercial Toptica TeraFlash spectrometer (Munich, Germany), and samples were prepared by mixing the samples with polytetrafluoroethylene (~4.5% w/w concentration) and pressing into 13.0 mm diameter pellets with a thickness of 2.0 mm. The low-frequency Raman measurements were performed using an Ondax (Monrovia, California, United States) THz-Raman system with a 784.7 nm centered laser excitation fiber coupled to an Andor (Belfast, United Kingdom) Shamrock 750 nm spectrograph

equipped with an Andor iDus 416 CCD. The respective pure ZIF sample was ground and placed into a 1.0 cm diameter glass capillary, with an empty capillary used for background determination.

References

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