

Local structure of CPO-27-Ni Metallorganic Framework upon dehydration and coordination of NO

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CPO-27-Ni: Electrostatic potential map.

Internal surfaces of CPO-27-Ni are characterized in large extent by a positive surface with the exception of the O_{OHs} and the O_{Cu} closeness as documented by the electrostatic potential map depicted in Figure S1. The electrostatic potential map has been obtained on periodic single-point calculations done at the BLYP/DN level (GGA functional) with the DMol³ program (as embedded in Materials Studio 4.0, Accelrys Inc.)^{1, 2} on the unit cell of CPO-27-Ni as obtained in literature from XRD refinement of its structure.³

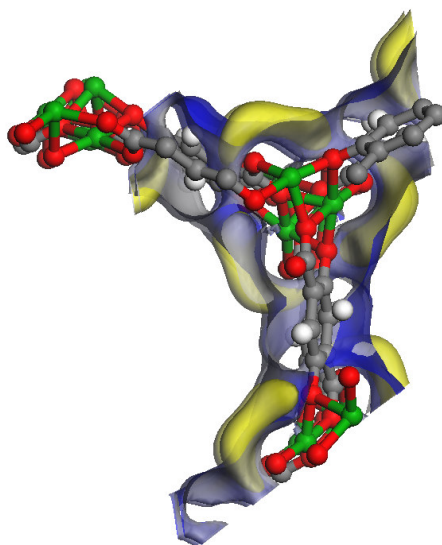


Figure S1. Portion of the tridimensional structure of CPO-27-Ni, representing the Ni^{2+} first coordination sphere and the electrostatic potential map: isosurfaces at -0.015 and +0.015 a.u. (atomic units) are reported in yellow and blue, respectively. View orthogonal to the honeycomb channel

Electronic spectroscopies: Photoluminescence.

Comparison between the photoluminescence of CPO-27-Ni and the H₄dhtp linker. The linker is significantly more fluorescent than the MOF. The absence of a double emission peak for the linker excited at 350 nm implies that the emission peak observed for CPO-27-Ni at 565 nm can be assigned to a charge transfer from the ligand to the metal (LMCT).

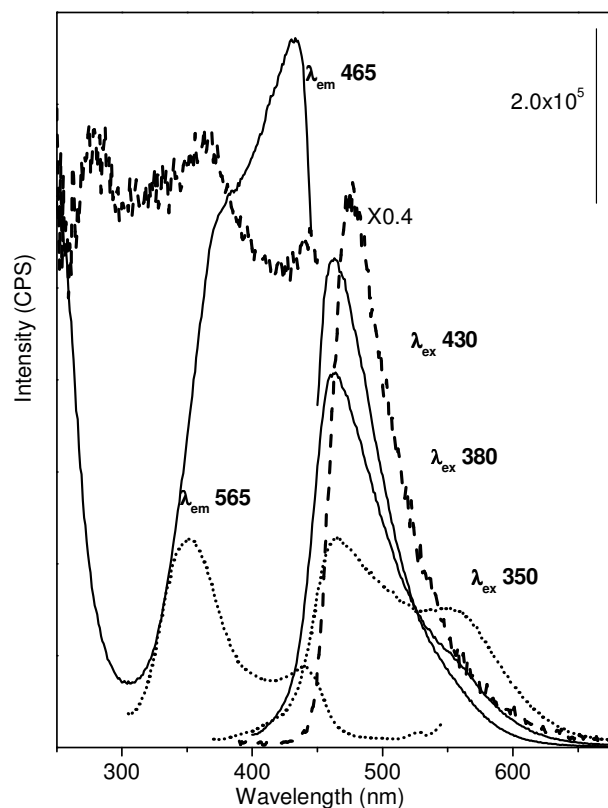


Figure S2. Comparison between photoluminescence spectra of as synthesized CPO-27-Ni and H₄dhtp ligand (dashed line). Solid and dotted curves are used to identify corresponding excitation and emission spectra of CPO-27-Ni.

Interaction with NO: IR data

NO dosed on a CPO-27-Ni pellet gives rise to a very strong band centered at 1840 cm^{-1} (due to the formation of $\nu(\text{NO})$ of $\text{Ni}(\text{II})\cdots\text{NO}$ adduct) that easily becomes so intense to go out of scale. Part a) of Figure S3 reports the set of spectra obtained till to reach the equilibrium pressure of 1 mbar. Part b) of Figure S3 reports the set of spectra collected along a prolonged outgassing in dynamic vacuo. The last spectrum has been obtained after 30 minutes of pumping. It is clear that NO is not completely reversible at room temperature.

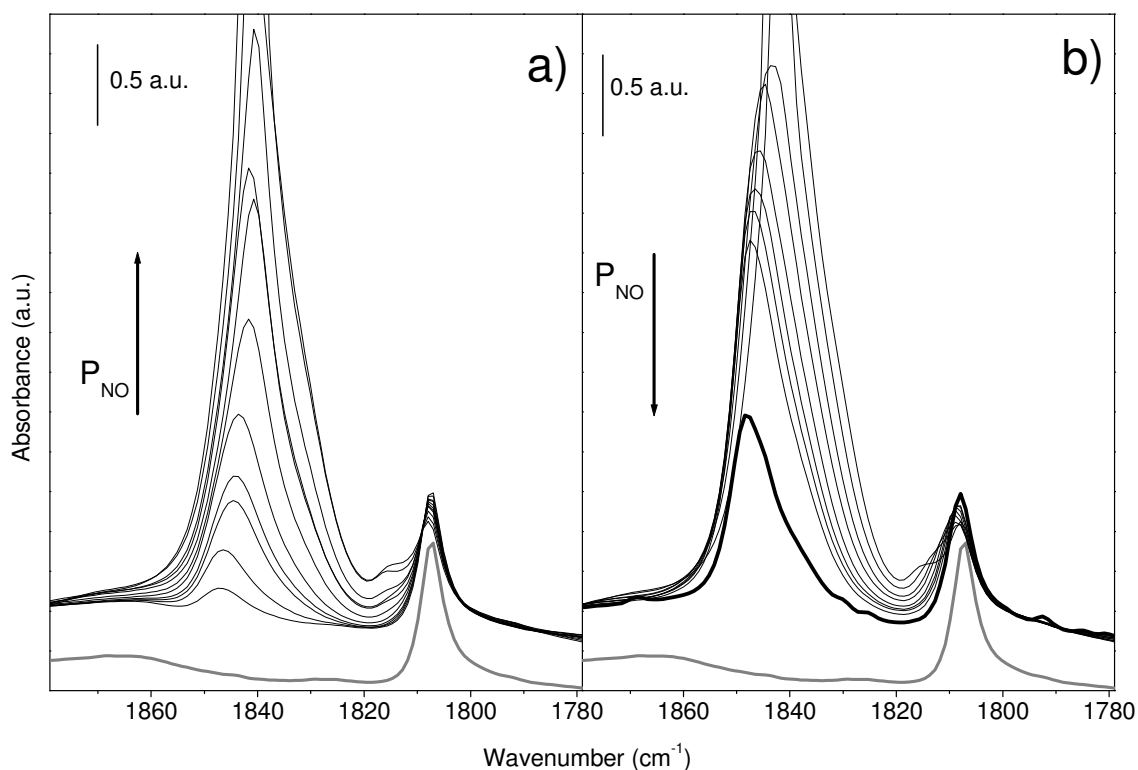


Figure S3. Part a): FTIR spectra of increasing NO equilibrium pressures (P_{NO}) dosed at RT on CPO-27-Ni (equilibrium $p_{\text{max}} = 0.001\text{ Torr}$). Part b): spectra obtained upon successive progressive outgassing.

The bold black spectrum refers to a prolonged outgassing at RT down to 10^{-3} Torr. In both frames the bold gray curve, vertically translated for clarity, reports the spectrum collected before NO dosage, showing the framework mode at 1807 cm^{-1} .

References

1. *Materials Studio Modeling 4.0*, Accelrys Software Inc.: San Diego, CA, 2005.
2. Delley, B., *J. Chem. Phys.* **1990**, 92, 508-517.
3. Dietzel, P. D. C.; Panella, B.; Hirscher, M.; Blom, R.; Fjellvag, H., *Chem. Commun.* **2006**, 959-961.