

The Effect of Molecular Guest Binding on the $d-d$ Transitions of Ni^{2+} of CPO-27-Ni: a Combined UV-Vis, Resonant Valence to Core XES and Theoretical Study

Carlo Lamberti,^{1,2,*} Erik Gallo,³ Evgeny Gorelov,⁴ Alexander A. Guda,² Aram L. Bugaev,² Francesca Bonino,³ Elisa Borfecchia,³ Gabriele Ricchiardi,³ Diego Gianolio,⁵ Sachin Chavan⁶

¹ Department of Physics, CrisDi and INSTM Reference Center, University of Turin, Via P. Giuria 7, I-10125 Torino, Italy.

² International research Center “Smart Materials”, Southern Federal University, Zorge Street 5, 344090 Rostov-on-Don, Russia

³ Department of Chemistry, NIS and INSTM Reference Center, University of Turin, Via Quarello 15, I-10135 Torino, Italy.

⁴ European XFEL GmbH Holzkoppel 4, 22869 Schenefeld, Germany.

⁵ Diamond Light Source Ltd, Harwell Science and Innovation Campus, OX11 0DE, Didcot, United Kingdom

⁶ Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315, Oslo, Norway
carlo.lamberti@unito.it

Due to their remarkable ability to tune framework porosity, topology as well as framework compositions have made Metal Organic Frameworks (MOFs) represent a new emerging class of materials with high potentialities in the fields of gas storage, gas separation and purification, gas sensors, and catalysis [Butova, et al., *Russ. Chem. Rev.* **2016**, 85, 280]. The full understanding of the structural and electronic properties of molecular adducts formed on metal sites insides MOFs cavities is a crucial prerequisite in order to perform a rational design of MOFs structures for targeted application in the mentioned fields.

We used Ni K-edge resonant valence to core X-ray emission spectroscopy (RVtC-XES, also referred to as direct RIXS, collected at ESRF ID26 beamline), an element-selective bulk-sensitive synchrotron-based technique, to investigate the electronic structure of CPO-27-Ni metal-organic framework (MOF) [Bonino, et al., *Chem. Mater.* **2008**, 20, 4957] upon molecular adsorption of significant molecular probes: H_2O , CO , H_2S and NO .

We compare RVtC-XES with UV-Vis spectroscopy, and we show that the element-selectivity of RVtC-XES is of strategic significance to observe the full set of $d-d$ excitations in Ni^{2+} which are partially overshadowed by the low-energy $\pi-\pi^*$ transitions of the Ni-ligands in standard diffuse reflectance UV-Vis experiments. Our combined RVtC-XES/UV-Vis approach provides access to the whole set of $d-d$ excitations allowing us a complete discussion of the changes undergone by the electronic configuration of the Ni^{2+} -sites hosted within the MOF upon molecular adsorption. The experimental data have been interpreted by multiplet ligand-field theory calculations based on Wannier orbitals [Gallo et. al., *Inorg. Chem.* **2017**, 56, 14408].

This study represents a step further in understanding the ability of the CPO-27-Ni MOFs in molecular sorption and separation applications. This work was supported the Mega-grant of the Russian Federation Government to support scientific research at Southern Federal University, No. 14.Y26.31.0001. A.A.G. acknowledges the grant of the President of Russia for young scientists no. MK-7300.2016.2. We are indebted with Pieter Glatzel (ESRF) and with Silvia Bordiga (University of Turin) for in depth discussion on RVtC-XES and UV-Vis spectra respectively.