

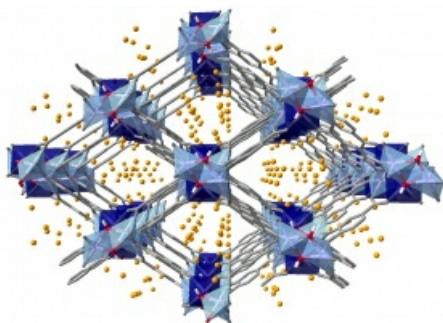
*Binding guest molecules to frameworks: pressure-induced chemisorption in breathing MOFs*Arianna Lanza¹, Luzia Germann², Martin Fisch³, Nicola Casati⁴, Piero Macchi⁵¹Italian Institute Of Technology, Pisa, Italy, ²Max-Planck Institute for Solid State Research, Stuttgart, Germany, ³University of Bern, Bern, Switzerland, ⁴Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland, ⁵Department of Chemistry and Biochemistry, University of Bern, Bern, Switzerland
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MOFs with stereochemically accessible unsaturated metal centres could in principle allow chemisorption of small molecules on the metal sites. This characteristic, together with framework flexibility, are desirable features for the design of promising catalysts, selective sieves or absorbents. Moreover, by varying metal centres, their oxidation state, organic linkers, guest molecules, stereochemical features etc., the potential and complexity of MOFs can be tuned towards to the desired properties. Efforts to rationalize the synthesis of frameworks with specific features would therefore benefit from comparative studies involving systematic variations of their structure, which can be induced by external stimuli (temperature, pressure) as well as by chemical modifications. In this work, we investigated the role of controlled structural modifications on the physico-chemical properties of a family of isostructural MOFs.

A flexible and porous MOF, based on CoII connectors and benzotriazolide-5-carboxylato linkers, was found to selectively react with guest molecules trapped in the channels during the sample preparation or after an exchange process. Upon compression or cooling, the system underwent a reversible, non-oxidative nucleophilic addition of the guest molecules to the metal ions. Depending on the guests, stepwise increase in the metal coordination up to its saturation could be achieved.

Isorecticular MOFs were obtained by replacing the CoII nodes with other divalent transition metals and adjusting the synthetic conditions. The obtained MOF series shows in principle the same kind of reactivity but with different sensitivity to guest exchange, temperature variations and pressure-induced breathing.

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