

# Tunable Properties from Structural Reversibility: Responsive Metal-Organic Frameworks

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Literature Seminar

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Metal Organic Frameworks (MOFs) are defined as an ordered array of repeating units consisting of metals and organic linkers that span either in two or three dimensions<sup>1</sup>. Interesting properties of many MOFs arise from the fact that they are porous, giving them capability to store other molecules via adsorption mechanism or host-guest chemistry<sup>2,3</sup>. This capability of storage has led to applications in gas storage and separation processes<sup>4</sup>.

Since the discovery of MOFs, major improvement has been made in the systematic design and gas storage capacity of MOFs<sup>5,6</sup>. In addition, a significant effort has also been focused on the structural flexibility that is associated with a group of MOFs<sup>7,8</sup>. In fact, many unique properties such as gated and selective adsorption are associated with this structural flexibility<sup>9,10</sup>. Those properties might be used to explore new application of MOFs as stimuli responsive materials with switchable properties<sup>8</sup>. Responsive materials with switchable properties are particularly interesting because their functionality can be activated on-demand. This seminar will highlight some works related to the development of MOFs as a responsive material with switchable properties.

In the first work, Yaghi and co-workers<sup>11</sup> reported a structurally non-interpenetrated MOF-123 that could reversibly transform into an interpenetrated MOF-246 upon ligand removal or addition (Figure 1). This transformation is exquisite, as previously known MOFs could only have reversible degree of interpenetration. Isothermal adsorption and Powder X-Ray Diffraction (PXRD) studies show intermediate structures in the transition going from MOF-123 to MOF-246, and this gradual structural transformation is also associated with changes in gas adsorption profiles, until finally MOF-246 shows no adsorption capability due to complete interpenetration. This structurally reversible MOF-123 is an exhibition of reversibility in porosity and ultimately adsorption properties.

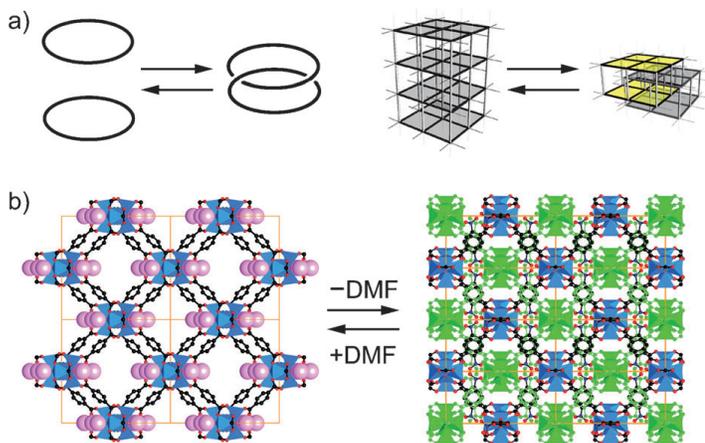


Figure 1: a) The idea of interpenetration (left) and the three-dimensional picture (right). b) Reversible process from MOF-123 (left) to MOF-246 (right). Interpenetrated network is shown in green.

The second work was reported by Kitagawa and co-workers<sup>12</sup>; they introduced a system where structural transformation can be triggered by exposure to UV light (Figure 2). Their approach is to introduce trans-azo-benzene molecule as a guest molecule inside  $[\text{Zn}_2(\text{terephthalic acid})_2(\text{triethylenediamine})]$  MOF. Inclusion of the azo-benzene forced the MOF to adopt an orthorhombic structure and the composite does not have nitrogen gas adsorption capacity. However, UV irradiation of the azobenzene inside the MOF will induce isomerization of the guest from trans-azobenzene to cis-azobenzene. The cis-azobenzene would force the MOF to adopt a tetragonal structure, and the composite showed improvement in the gas adsorption capacity. The tetragonal structure can be reverted back to the orthorhombic structure by heating the system. This system is showing an example of switchable gas adsorption capacity in MOFs by using UV trigger.

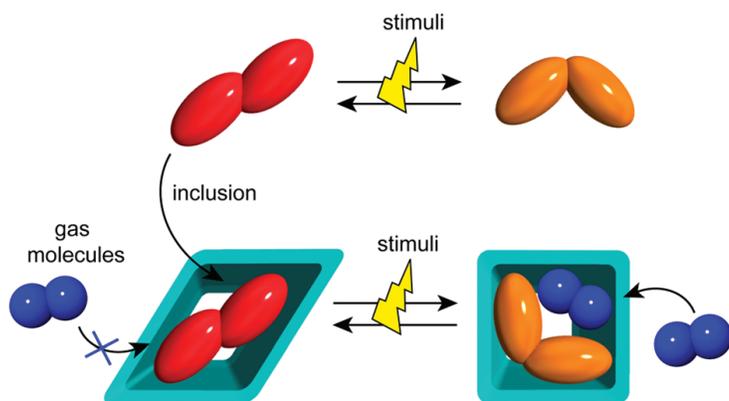


Figure 2: Illustration of tunable adsorption capacity that is induced by structural conformation of the guest molecules. The red and orange objects are the different isomers of the guest molecules.

In the previous work, the conformation of azo-benzene triggers the structural transformation of the MOF, which is correlated to the gas adsorption capacity. However, one could think the reversed process might also be possible. Kitagawa and co-workers<sup>13</sup> introduced a composite system by using  $[\text{Zn}_2(\text{terephthalic acid})_2(\text{triethylenediamine})]$  as the MOF and distyryl benzene (DSB) as the guest (Figure 3). DSB is a dye molecule known to have fluorescence property that is dependent on its structural conformation, where a planar structure is known to have a higher quantum yield for the excitation-emission process. Introduction of gas molecules into the composite will force the MOF' structure from orthorhombic to tetragonal as well as planarization of the DSB. The planarization will produce higher quantum yield in the excitation-emission process, shown by higher emission intensity. This process is a showcase of controlled fluorescent switching by gas adsorption. Coupled with the fact that this composite is selective toward certain gases, these properties are useful for the development of gas sensors.

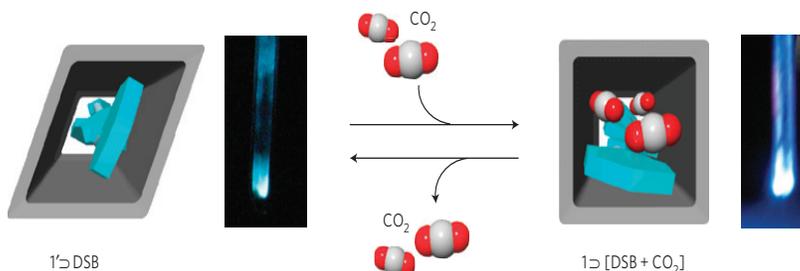


Figure 3: Illustration of reversible fluorescent response from  $[\text{MOF} + \text{DSB}]$  composite. This process is induced by  $\text{CO}_2$  gas inclusion.

In conclusion, MOFs are a versatile area of research owing to its unique porous and flexible structure. These properties have been exploited not only to develop MOFs for gas storage, but also stimuli responsive MOFs with switchable properties. Significant progress has been accomplished over the years and more research will continue in this promising area in order to produce MOFs whose properties can be activated on-demand.

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