

**MS27-1-6 Highly sensitive self-healing metal-organic framework**  
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**Abstract**

Self-healing of materials is the phenomenon of restoring a damaged material to its primary properties without any external intervention. Wrinkles, cracks and other types of damage appearing on the crystals' surface have been shown to change the physicochemical properties of materials, and their propagation can lead to the eventual destruction of the material. At this point, this type of gradual degradation is almost undetectable and requires manual intervention for eventual repairs. In contrast, the self-healing materials counter degradation through the initiation of a repair mechanism that responds to the micro-damage which can be of invaluable importance for the more durable materials. It is thus important to further explore the concept of self-repair.

We have focused our scientific interest on a porous metal-organic network, [Cd(BDC)(AZPY)]<sub>n</sub> (BDC = terephthalic acid; AZPY = 4,4' - azobispyridine) exhibiting the excellent ability to self-repair its single-crystal features. When subjected to a mechanical force, as a result of tilts and conformational changes of the AZPY linkers, the crystals faces of Cd(BDC)(AZPY)]<sub>n</sub> becomes fractured and the scratches on the crystal surface start appearing. However when the pressure is released, all arose damages disappear. This process can be efficiently repeated in many compression and decompression cycles.

Appearing damages of the crystal surfaces are strongly connected to the structural changes of [Cd(BDC)(AZPY)]<sub>n</sub> under high-pressure. To compensate the mechanical stresses the crystal lattice distorts, leading to a ferroelastic phase transition from the atmospheric phase  $\alpha$  of the orthorhombic space group *Cmce* to a high pressure phase  $\beta$  of monoclinic space group *P2<sub>1</sub>/n*. The pressure induced transformation orders the -N-N- bridge of the azopyridine, which significantly reduces the lattice strain. Interestingly, depending on the guest molecules filling the voids and the type of used hydrostatic fluid, the phase transition can be observed in the range between 0.2 and 0.9 GPa.

The pleochroic [Cd(BDC)(AZPY)]<sub>n</sub> crystals exhibits several features attractive for sensor applications. They are sensitive to guest molecules, crystal environment and pressure, but they are almost unaffected by temperature. We have proven that the interplay of the framework topology with the flexibility of linkers can lead to specific types of structural transformations of MOFs.

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