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Lanthanide metal-organic frameworks: synthesis and applications

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Lanthanide metal-organic frameworks (Ln-MOFs) have attracted great attention for their potential applications in gas storage and separation, catalysis, magnetism, and luminescence [1]. Based on a coordination symmetry approach, we have synthesized a series of Ln-MOFs and studied their properties.

Ln-MOFs are not very suitable for gas storage because of the high density and low stability. We have synthesized a robust microporous Tb-MOF-1 which containing 1D honeycomb-type channels. The desolvated Tb-MOF-1 shows not only excellent adsorption capabilities for N2, H2, and CO2 but also significant selective sorption of CO2 over N2 and CO2 over CH4. More importantly, due to the intrinsic property from f electron, luminescent studies of the emulsions of Tb-MOF-1 showed guest-dependent luminescent properties, which demonstrated their potentials for sensing small-molecule pollutants, such as benzene and acetone.

We further studied the mechanism of the guest-dependent luminescent properties of two isostructural Tb-MOF-2 and Gd-MOF-2 based on cubane-shaped [Ln4(μ3-OH)4]8+ clusters [2]. There are two kinds of micropores with dimensions of 3.0 × 7.0 Å2 along the b-axis and 4.5 × 5.5 Å2 along the c-axis in the cationic framework. Tb-MOF-2 exhibits an intensive green luminescence triggered by the efficient antenna effect of the ligands under UV light. Luminescent studies showed that Tb-MOF-2 could be an efficient multifunctional luminescent material for high-sensitivity sensing of small organic molecules, metal cations, and anions. Recently, we had applied a new strategy by using bimetallic Eu/Tb-MOFs as self-calibrating luminescent sensors. The enhancement and quenching from different luminescent centers in a singular material were well demonstrated due to the unusual self-calibrating mechanism based on the energy transfer from one lanthanide center to another one. Fast response and variable luminescent colors that are visible to the naked eye were also successfully achieved in this luminescent sensor. Selective luminescent detection of LPA, a biomarker for ovarian cancer that has the lowest survival rate of all gynecologic malignancies, in the presence of major components of blood plasma, was also reported.

On the other hand, lanthanide centers that are usually weakly coupled in MOFs have shown obvious advantages with respect to the study of molecular nanomagnets [3]. Based on the results concerning constraining the coordination geometries of lanthanide ions and assembly of magnetic building blocks in MOFs, we proposed two possible approaches that could be experimentally explored for the molecular magnetism in the near future: (i) chemical modification of known SMMs to serve as “complex ligands” for the construction of magnetic MOFs; (ii) doping highly magnetic anisotropic metal ions into specific axial positions in diamagnetic frameworks and varying the doping concentration. These strategies will not only bring new samples to assist an in-depth understanding of the factors governing the magnetization dynamics of molecular nanomagnets but will also produce new research interest in MOF chemistry.

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