

MS37-O5 A Series of Highly Stable
Isoreticular Lanthanide Metal-Organic
Frameworks with Tunable Luminescence
Properties Solved by Rotation Electron
Diffraction and X-ray Diffraction

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Systematic design and control of pore size, shape and functionality in metal-organic frameworks (MOFs), without changing the underlying topology, has attracted large attention.[1] The isoreticular synthesis of MOFs has been mostly achieved with metal clusters and organic linkers of various sizes. In fewer cases, isoreticular MOFs built from inorganic chains have been synthesized, mainly by combining transition metals with ditopic or tetratopic linkers. Here we present a new series of porous isoreticular lanthanide-based MOFs (LnMOFs) (denoted SUMOF-7I, -7II, -7III and -7IV; Ln = La, Ce, Pr, Nd, Sm, Eu and Gd) synthesized by combining Ln-carboxylate inorganic chains and tritopic organic linkers of variable sizes [2].

The structure of SUMOF-7I was solved by single crystal X-ray diffraction (SXRD). The crystals of other SUMOFs were too small to be studied by SXRD. Therefore, we applied the rotation electron diffraction (RED) method, which has shown to be very powerful for structure solution of unknown inorganic crystals [3]. The structures of SUMOF-7II and -7III were solved by combining RED with powder X-ray diffraction (PXRD). The SUMOF-7s display 1D pseudo-hexagonal channels with the pore diameter gradually enlarged from 8.4 Å to 23.9 Å, as a result of increasing sizes of the organic linkers (Fig. 1). SUMOF-7I, -7II and -7III show extraordinary thermal stability and remarkable tolerance towards hot water, organic solvents, and aqueous media with pH values ranging from 2 to 11. *In-situ* SXRD study shows that the water molecules coordinated to lanthanide ions in SUMOF-7I could be removed by heating, and re-coordinated to lanthanide ions when the activated crystal was exposed to air for one day. The luminescent properties of these materials can be tuned by doping with different ratios of lanthanide ions as well as by incorporating guest dye molecules in the pores. The combination of tunable pore apertures, accessible metal sites, high thermal and chemical stability, and tunable luminescence properties, makes the SUMOF-7 series a very promising platform for applications in optical sensing, heterogeneous catalysis, and photocatalysis.

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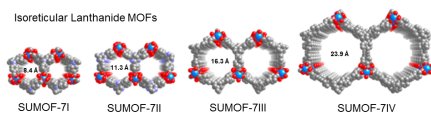


Figure 1. Crystal structures of SUMOF-7I to -IV. The free diameter of the pore aperture is given, taking into account the van der Waals radii of the atoms.

Keywords: metal-organic framework, isoreticular MOFs, structure determination, electron diffraction, in-situ XRD, luminescence property