Synthesis of porous gels assembled from ruthenium-based metal-organic polyhedra

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Metal-organic polyhedra (MOPs) are supramolecular cages with an intrinsic cavity. Among various metal nodes that can be selected for MOP construction, a ruthenium paddlewheel structure is one of the fascinating metal centers because of its intriguing redox-active property, its structural integrity against redox reaction, and its applicability in catalysis. However, it remains challenging to controllably implement the ligand-exchange reaction on Ru paddlewheel complexes and synthesize Ru-based MOPs. It is necessary to assemble Ru-based MOPs into macroscopic materials for practical applications with such electrochemical properties and stability.

In this work, we demonstrate the synthesis of a series of stable cuboctahedral RuMOPs, $[Ru_2(bdc)_2]_{12}(X)_{12}$, which consist of twelve Ru_2(II,III) metal centers bridged by 24 bdc linkers (bdc = 1,3-benzenedicarboxylate derivatives, X = counter anion). The electrochemical experiments showed the stability and reversibility of Ru_2(II,III)/Ru_2(II,II) redox reaction even after the formation of RuMOPs. The redox potentials of Ru_2(II,III)/Ru_2(II,II) were not largely altered depending on the substituents of bdc ligands. Thanks to the stability of the RuMOPs and the additional coordination sites at the axial position of Ru paddlewheels, RuMOPs can be assembled with additional crosslinkers into macroscopic soft materials such as porous gels (RuGels). Time-resolved dynamic light scattering (TRDLS) revealed the assembling process of RuMOPs and the gelation time of RuGels. Furthermore, the intrinsic permanent microporosity was confirmed by nitrogen adsorption experiments on the corresponding aerogel (RuAerogels). Compared to the RuMOP itself, the RuAerogels showed almost three times higher BET surface area (230 and 620 m^2/g, respectively). These results suggest the effective formation of extrinsic microporosity between RuMOPs in the RuAerogels.