Three-Dimensional van der Waals Frameworks Assembled from Octahedral Metal-Organic Polyhedra

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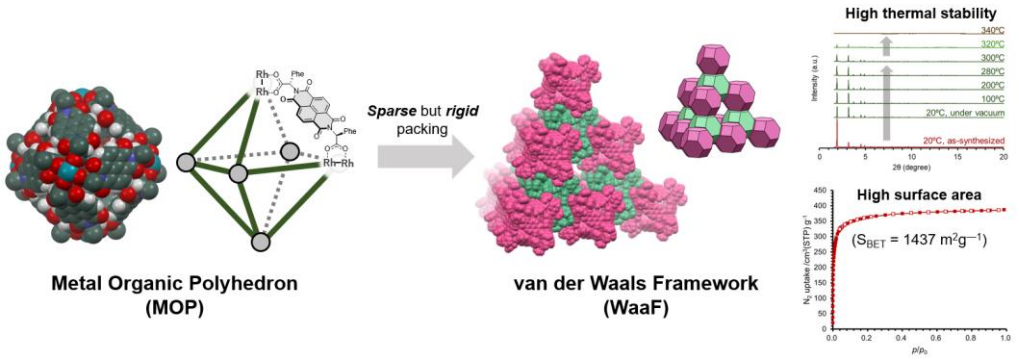
Highly directional, strong intermolecular interactions are believed to be essential to synthesize porous framework materials. For instance, coordination, covalent, and hydrogen bonds are used to assemble molecular components to form MOFs, COFs, and HOFs, respectively. On the contrary, van der Waals (vdW) interaction, one of the most ubiquitous intermolecular interactions, is known as a non-directional, weak interaction. Due to the less controllable nature, vdW interaction has been barely used to construct porous frameworks.

In this study, we demonstrate that vdW interaction drives the assembly of a porous framework from supramolecular building blocks, so-called metal-organic polyhedra (MOPs), a group of cage-shaped metal complexes with high structural modularity.[1] We synthesized a novel octahedral MOP from Rh(II) ions and naphthelenediimide (NDI) derivatives. X-ray diffraction experiments revealed that twelve NDI moieties as edges are connected by six Rh_2 paddlewheel vertices, leading to the formation of triangle faces with large NDI moieties. The face-to-face vdW interactions between MOPs generate diamond-like packing structure of MOPs in a crystalline phase, with a huge void space in the network (~36%, calculated from the X-ray structure). This porous framework built with vdW interactions, named as van der Waals framework (WaaF), showed outstanding porosity (BET surface area: 1437 m^2g^{-1}) and high thermal stability (crystallinity retained up to 320 ºC) even after the removal of guest molecules. This work highlights an overlooked potential of less directional/weak vdW interactions toward the design of porous framework materials.



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