Poster

Crystallographic insights into diverse water stability mechanisms of Zn-MOFs

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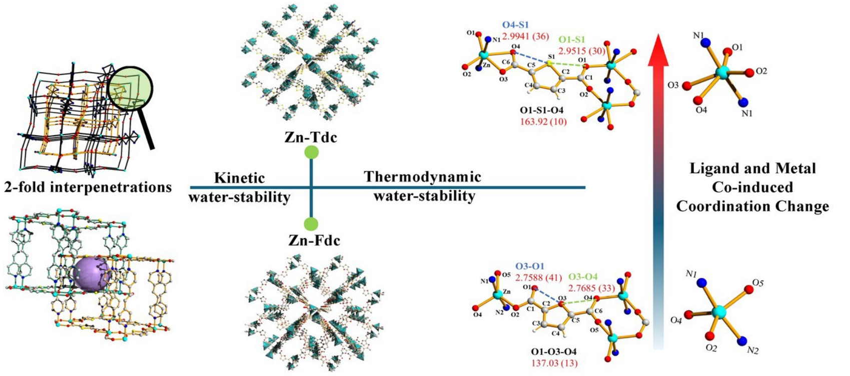
Zinc, known for its non-toxicity and exceptional biocompatibility, with various coordination geometries, is an ideal metal for constructing Metal-Organic Frameworks (MOFs). MOF-5 is a highly representative Zn MOF, which is distinguished by its high specific surface area and thermal stability. However, the application of MOF-5 is significantly limited as it undergoes irreversible degradation within hours under air with high relative humidity. To address the challenge of enhancing water stability in MOFs, two major strategies could be employed: (1) forming metal carboxylate frameworks consisting of high-valence metal ions or building metal azolate frameworks with nitrogen-donor ligands to establish thermodynamic water-stable MOFs; (2) functionalizing MOFs either by hydrophobic pore surfaces or with blocked metal ions to achieve kinetic water-stable MOFs [1]. Water-stable Zn MOFs are typically formed solely by nitrogen-donor ligands; even when carboxylate ligands are present, it necessitates shielding the metal- oxygen bonds with additional functional groups. These strategies significantly reduce the structural diversity, and inevitably mask a substantial portion of the metal node activity. Thus, the preparation of water-stable Zn MOFs with carboxylate ligands while keeping metal active sites exposed, presents a challenge within MOF chemistry.

Due to its excellent biocompatibility, Zn^{2+} plays a crucial role in over 300 metalloenzymes, interestingly, Zn^{2+} enhances the stability of these proteins and nucleic acids in aqueous solution [2]. The design of stable Zn MOFs could draw inspiration from this aspect. Research has discovered that six coordination is the most stable form of Zn^{2+} in water.[3] Based on this insight, we introduced a layer- pillared structure, where layers are coordinated by carboxylic acid (2,5-Furandicarboxylic acid (Fdc), 2,5-Thiophenedicarboxylic acid (Tdc)), and the interlayers are pillared by nitrogen-donor ligands (1,2-Bis(4-pyridinyl)ethene). Utilizing mixed solvothermal strategies, we obtained two new crystal structures, Zn-Fdc and Zn-Tdc. As depicted in Scheme 1, we discovered that both MOFs demonstrate outstanding kinetic water stability, retaining their crystallinity and structural integrity. In terms of topology, both MOFs exhibit a 2-fold interpenetration feature, which transforms the originally one-dimensional channel into a semi-enclosed three- dimensional pore, significantly reducing water diffusion speed, and enhancing their water stability. However, Zn-Tdc exhibits better thermodynamic stability over Zn-Fdc, which can be attributed to the differences in coordination model between the two MOFs. This difference, as analysed through crystallography of the MOFs, is jointly effected by ligands and metal: the variance in the interaction forces between thiophene and furan with the carboxylic acid functional groups within the molecules leads to differences in their geometric, which in turn affects the relative positions of the carboxylic acids to the metal; meanwhile, the zinc metal tends to form a more stable hexacoordinate mode, thereby applying distinct attraction or repulsion forces to the ligands.



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Ligand & Metal Co-Induced Metal Coordination Changes

Scheme 1. Schematic representation illustrating the kinetic and thermodynamic stability between Zn-Tdc and Zn-Fdc.

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