Poster

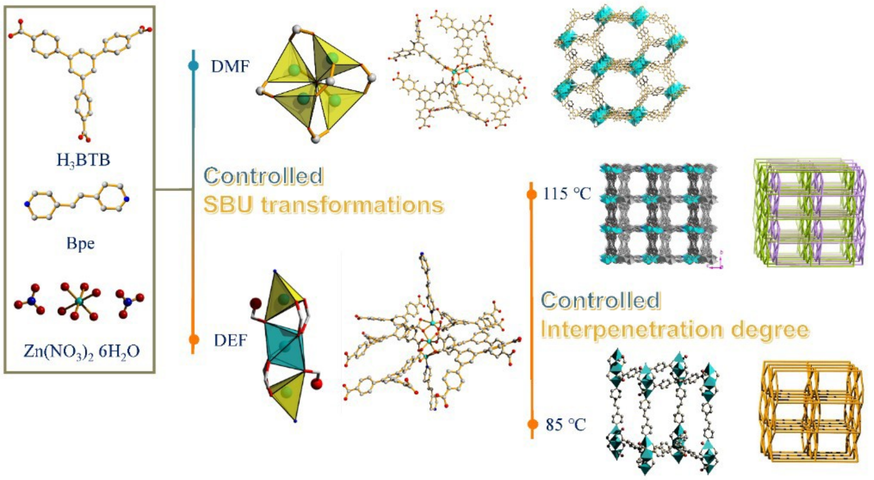
Control of structure and interpenetration degree transformations in Zn-MOFs

Chongting REN[1], Xu JIA[1], Luc VAN MEERVELT[1]

Biochemistry, Molecular and Structural Biology, Department of Chemistry, KU Leuven, Belgium

chongting.ren@kuleuven.be

Metal-Organic Frameworks (MOFs), constructed by periodic arranged inorganic nodes and bridging organic ligands, have become one of the largest fields of chemistry for over twenty-eight years. The applications of MOF chemistry reach into numerous areas including climate, environment, energy, water, and health. However, all the excellent properties of MOFs fundamentally rely on their structures. Thus, the exploration of existing structures and the design of novel frameworks is significant research within the domain of MOF molecular chemistry [1]. Building chemically distinct and framework isomeric MOFs constitute two pathways toward structural innovation. Employing different metal nodes and organic ligands is a traditional strategy for creating chemically distinct MOFs, which typically embody characteristics of their individual components as well as novel attributes of porous crystalline materials. The construction of framework isomeric MOFs consists of interpenetrated, conformational and orientation isomers, which, while utilizing the same ligand and metal species, exhibit distinct network structures [2]. Through these two construction approaches, tens of thousands of MOFs have been fabricated. Nevertheless, works that unify and apply both approaches within a single system are relatively limited.



Scheme 1. The impact of different solvent types and temperature control on the interpenetration of Zn-MOFs.

We used Zinc as the metal node, and 1,3,5-Tris(4-carboxyphenyl)benzene (**H_3BTB**) and 1,2-Bis(4-pyridinyl)ethene (**Bpe**) as ligands to synthesize a series of MOFs. By employing different solvents, we were able to control the structure of the second building unit (**SBU**) in the MOFs. Specifically, dimethylformamide (DMF) encouraged the formation of a $Zn_4(O)O_{12}$ cluster that can solely coordinate with carboxylates, leading to the *dia* topology in **Zn-BTB**. In contrast, diethylformamide (DEF) induced the formation of a **$Zn_3O_{10}N_2$** cluster that coordinates with both ligands, giving rise to pillar-layered structures. Furthermore, when employing DEF, the control over synthesis temperature allowed for the regulation of the interpenetration. At lower reaction temperatures, non- interpenetrated **NI-Zn-bpe** was obtained, while at higher temperatures, 2-fold interpenetrated **I-Zn-bpe** was formed. The structures of **Zn-BTB** and **NI-Zn-bpe** in this work were obtained by single crystal X-ray diffraction (XRD), while **I-Zn-bpe** is confirmed by powder XRD. The crystal structure of **NI-Zn-bpe** suggests superior theoretical porous properties. Due to its largely electronically conjugated system and multiple hydrogen-bond acceptors, **NI-Zn-bpe** could potentially be applied as crystalline host material for small molecules.

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[2] Makal, T. A., Yakovenko, A. A., Zhou, H.-C., (2011) J. Phys. Chem. Lett. 2, 1682.