

Poster Presentation

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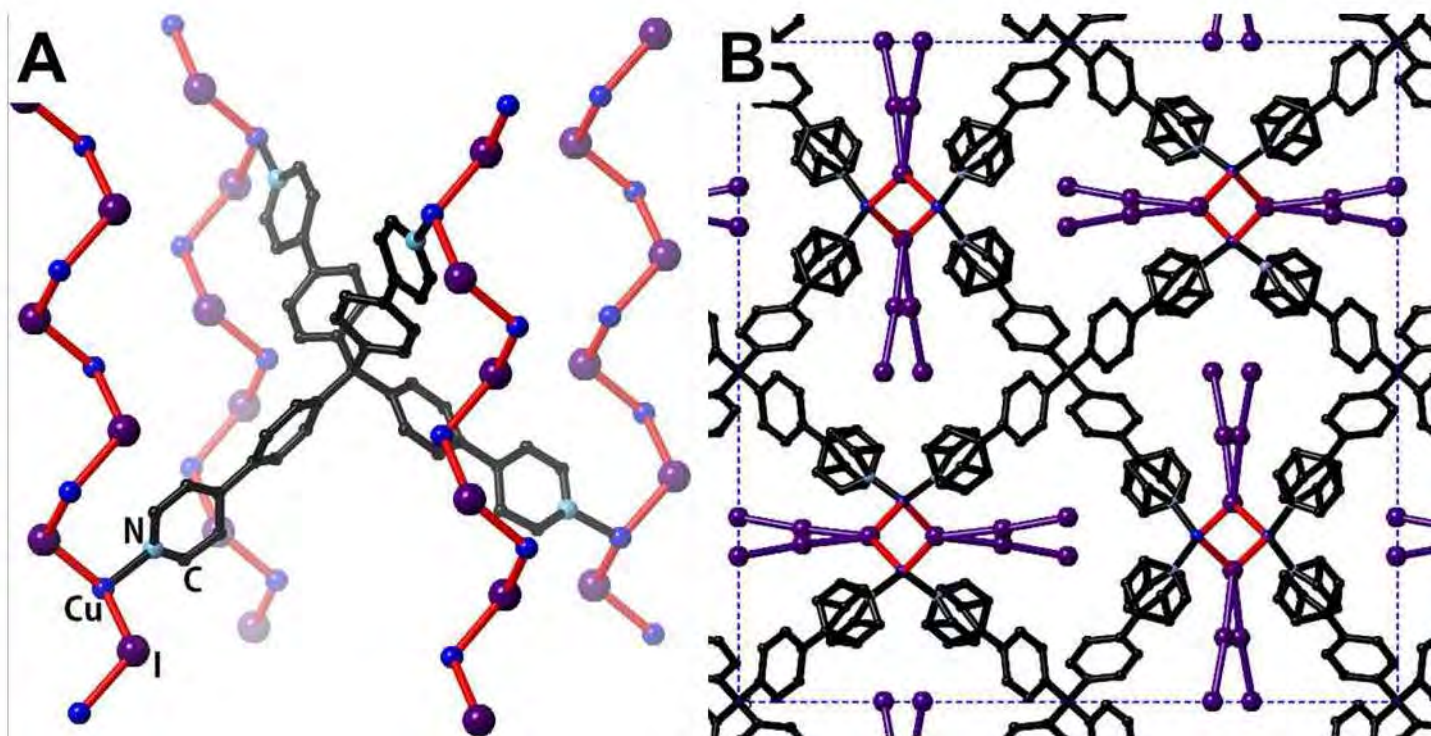
Kinetic Assembly of a Thermally Stable Porous Coordination Network

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The advantage of porous coordination network synthesis is designability by changing metal sources and ligands.[1] Therefore, not only many commercially available ligands but also newly synthesized ones were used for networking. On the other hand, most of metal sources are common reagents or stable metal moieties because they can be more predictable as a metal connector. So far, there is no report focusing on usage of labile metal sources for selective network formation. One of the promising methods to produce unique networks with such labile metal sources is kinetic control[2] because labile metal sources produce various species in solution. In this talk, we will introduce selective syntheses of thermally stable porous coordination networks using a labile Cu₄I₄ cubane cluster [Cu₄I₄(PPh₃)₄] (1) and a rigid tetradentate T_d-symmetry ligand tetra-(4-(4-pyridyl)phenyl)methane (2) by kinetic and thermodynamic control.[3] On heating the mixture of 1 and 2 in DMSO at 453 K, a homogenous colorless solution was obtained. Rapid cooling (~20 Kmin⁻¹) of the solution produced yellow needle crystals, {[CuI₂(2)]•solvent}_n (3a) that shows novel CuI helical chain unit, in 99% yield (Fig. A). On the other hand, slow cooling (~3 Kmin⁻¹) produced orange block crystals, {[Cu₂I₂(2)]•solvent}_n (3b) that shows rhombic Cu₂I₂ dimer unit, in 95% yield. Both the network crystals can keep the crystallinity up to 673 K under N₂ atmosphere. In kinetic product 3a, due to the unique structure, iodides of the CuI chains facing to 1D channel, the network crystal shows chemisorption of I₂ by making a covalent bond with an iodide of part of the CuI chains to form an I₃⁻ group (Fig. B). On the other hand, in thermodynamic product 3b, Cu₂I₂ dimer units are hindered by bridging ligand 2. That is why network crystal 3b shows only physisorption of I₂, even though network has 1D channel similar to 3a.

[1] Yumi Yakiyama, Akira Ueda, Yasushi Morita et al., *Chem. Commun.* 2012, 48, 10651-10653., [2] M. Kawano, T. Haneda, D. Hashizume et al., *Angew. Chem. Int. Ed.* 2008, 47, 1269-1271., [3] H. Kitagawa, H. Ohtsu, M. Kawano, *Angew. Chem. Int. Ed.* 2013, 52, 12395-12399.



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