

Kinetic assembly of coordination networks creates flexible and functional materials

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Interactive pores in porous coordination networks play a key role in trapping unstable species, chemical transformation, and so on [1-3]. We reported porous coordination networks prepared by kinetic assembly which can be used to produce interactive pores. The interactive pore can be used for I₂ chemisorption and chemical transformation of small sulfur allotropes, from S₂ to bent-S₃ via cyclo-S₃. We performed selective formation of porous coordination networks kinetically/thermodynamically from CuI cluster and rigid T_d symmetry ligand, 4-TPPM (tetra-4-(4-pyridyl)phenylmethane), by changing cooling ratio of the hot DMSO solution of the mixture. Because the interactive pore is the key component to create functionality, it is required to extend the availability of interactive pores. Such interactive pores can be modified by changing metal source (clusters) and ligand coordination geometry. Here we report the kinetic assembly of porous coordination using Cu-Halide clusters and several pyridine-type ligands (Figure 1) to generate several interactive pore sites; we report new kinetic network formation using 4-TPPM and CuX cluster and the dynamic structural change of the kinetic network to produce highly luminescence coordination networks and flexible network formation using 3-TPPM and CuI cluster to show dual interactive sites showing iodide interactive pore sites and Cu pseudo-open metal sites.

When we performed kinetic/thermodynamic assembly using [Cu₄Br₄(PPh₃)₄] and 4-TPPM, we obtained coordination network composed of Cu₂Br₂ dimer and 4-TPPM as kinetic network and that composed of CuBr helical chain and 4-TPPM as thermodynamic network. When we heat the kinetic network at 573 K, it turned to luminescent crystalline powder. Both single crystal analysis and Rietveld refinement of PXRD indicates the transformation to the network composed of Cu⁺ connectors and 4-TPPM linkers with CuBr₂⁻ guests. The high quantum yield was obtained for this network (13%). We clarified that the electronic transitions in this network include TSCT in addition to the typical metal–ligand charge transfer (MLCT) observed in conventional Cu complexes. The atomic coordinates of the molecules determined from X-ray structure analysis enabled a clear understanding of the nature of the TSCT transitions.

When we performed kinetic/thermodynamic assembly using [Cu₄I₄(PPh₃)₄] and 3-TPPM, we obtained coordination network composed of Cu₂I₂ dimer and 3-TPPM as kinetic network and that composed of CuI helical chain and 3-TPPM as thermodynamic network. Using 3-TPPM, rotation motion of pyridine ring was restricted. Interestingly the thermodynamic network, CuI helical network shows I₂ chemisorption to make chemical bond with iodide in the interactive pore and Cu in the network so that Cu act as pseudo-open metal sites.

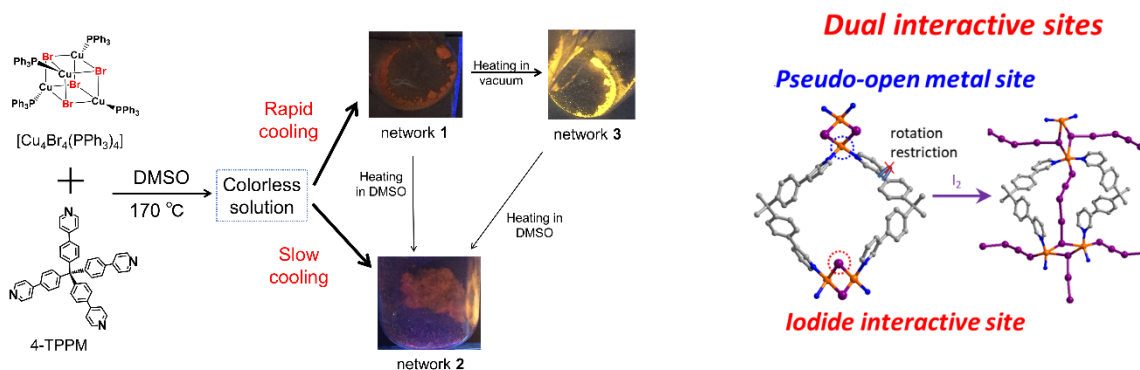


Figure 1. Kinetic assembly using CuBr cluster and 4-TPPM (left) and I₂ chemisorption to helical network with CuI and 3-TPPM.

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[3] Ohtsu, H. & Kawano, M. (2017) *Chem. Commun.* **53**, 8818.

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