Poster Presentation

MS066.P09

DABCO-based lattice framework for reversible chromic behaviors

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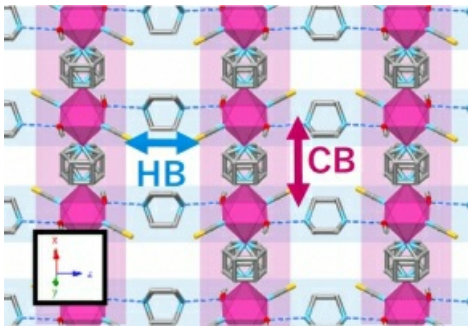
Single-crystal-to-single-crystal (SCSC) transformation is of the interesting phenomena that were observed for molecular crystals[1]. Drastic change of its structure, color and solid state properties are occurred. The SCSC process are achieved with breaking and forming a new bond through dynamic motion of components in the lattice. Since its transformation passes without loss in crystallinity, sophisticated lattice design is required to realize robust but flexible molecular framework[2].

Here, we focused on 1,4-diazabicyclo[2.2.2]octane (DABCO) for the frame component. Because the molecule is well-known that exhibit molecular rotation and flexible conformational change even in the crystalline state. In addition large molecular sizes are also interesting to make free space in lattice. By an exploration of the new single crystalline materials with DABCO, we successfully achieved crystallization of DABCO-based network in which hydrogen bond (HB) chains and coordination bond (CB) chains are 'knitted' together, yielding pinkish single crystals of [Co(DABCO)(NCS)2(MeOH)]DABCO (1). A Co center employs 6-hold octahedral coordination environment with two of DABCO, N-coordinated isothiocyanate and MeOH for coordination ligands. A DABCO molecule coordinated to Co ions so as to form a one-dimensional coordination chain. And there was crystallographically another DABCO molecule that bridged the coordination chains through hydrogen bond with proton of MeOH, constructing two-dimensional framework structure (Figure. 1). It was interesting that the pinkish crystals of 1 showed drastic color change to blue around at 90℃ (named to 1' of blue crystal). The blue state by 1' was stable even when it was backed to room temperature. Details on the chromic behavior were studied by TG, GC-MS and temperature dependent powder XRD measurements and it was cleared that transformation from 1 to 1' was accounted for by desorption process of MeOH molecules at crystalline state. Further exploration revealed that crystals 1' were active for interacting with varieties of solvent molecules such as alcohol of CnH2n+1OH, where reactivity was depending of n.

In summary, we revealed that crystal 1 exhibit interesting chromic behavior due to desorption and adsorption of guest solvent molecules. These results will be emphasized if one considers DABCO taking into robust framework. Plasticity expected by DABCO will be harmonized with flexibility of molecular based framework structure, and those structural states will be more highlighted for developing SCSC transformation or related phenomena.

[1] Z. Liu et al., Dalton Trans, 2012, 41, 6827-6832.
[2] S. Rodriguez-Jimenez et al., Angew. Chem. Int., 2016, 55, 1-6.



Keywords: Single-crystal-to-single-crystal transformation, host-guest, chromism