Study of Multi-dimensional Transformations with Successive Reaction in Cu(II) Coordination Polymer

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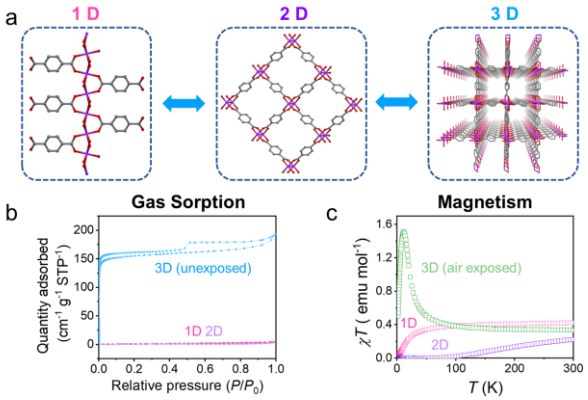
Dimensionality of atomic or molecular arrangements through chemical bonds plays a crucial role in determining the electronic properties of solids. Coordination polymers (CPs) are a promising platform for investigating dimensional transformations, because the coordination bonds (100–300 kJ mol^{-1}), which are generally weaker than covalent bonds (200–800 kJ mol^{-1}), possess thermodynamically stable but kinetically labile metal-ligand interactions. Although considerable efforts are being undertaken to develop CPs with the dimensional transformation,[1] a multi-dimensional 1D/2D/3D reversible transformation has not been accomplished.

In this study, we succeeded in realizing the 1D/2D/3D reversible transformation for the first time in CPs comprising Cu(II) ions and bidentate terephthalate (BDC^{2-}). The 2D layered coordination framework in 2D Cu-BDC[2] was reversibly transformed into 1D chains due to the dissociation of the Cu(II) paddlewheels induced by water coordination (Figure a). The kinetics of 2D to 1D successive transformation passing through an intermediate phase was investigated in situ by synchrotron XRD. The 2D-to-3D transformation was achieved by removing DMF followed by the connection of the 2D sheets (Figure a). These dimensional transformations significantly changed chemical and physical properties such as gas sorption and magnetism. Although the nitrogen gas uptake in open-framework 1D and 2D Cu-BDC was insignificant, pronounced absorption was observed for 3D Cu-BDC (Figure b). Drastic difference in magnetic behavior is consistent with their coordination structures; uniform 1D chain of Cu(II) in 1D Cu-BDC and 2D sheet based on Cu(II)-paddlewheel dimers in 2D Cu-BDC. Ferromagnetic behavior observed in air-exposed 3D Cu-BDC is mainly attributed to the 3D structure formed by the connection of 2D sheets (Figure c).



1) a) M. Edgar *et al*., *Chem. Eur. J.* **2001**, *7*, 5168. b) R. Medishetty *et al*., *Chem. Eur. J.* **2015**, *21*, 11948.

2) C. Carson *et al*., *Eur. J. Inorg. Chem.* **2009**, *2009*, 2338.