Reversible One- to Two- to Three-Dimensional Transformation in Cu(II) Coordination Polymer

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Abstract: A reversible transformation between 1D, 2D, and 3D is demonstrated for the first time in coordination polymers comprising Cu(II) ions and bidentate terephthalate (BDC2-). 1D uniform chains were reversibly transformed into 2D layers with the construction of Cupaddlewheels by eliminating water molecules. 2D/3D reversible transformation was achieved by removing/rebinding N.Ndimethylformamide coordinated to the paddlewheels. These dimensional transformations significantly changed chemical and physical properties such as gas sorption and magnetism. Although the uptake in open-framework 1D and 2D Cu-BDC was insignificant, pronounced absorption was observed for 3D Cu-BDC. 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 attributed to the 3D structure formed by the connection of 2D sheets.

Dimensionality of atomic or molecular arrangements through chemical bonds plays a crucial role determining the electronic properties of solids.^[1] One-dimensional (1D) arrangements promote the spin and charge fluctuations in the system,[1b,2] whereas the formation of threedimensional (3D) assemblies stabilizes long-range ordered states such as superconductivity and various types of magnetic order.^[1d,3] Two-dimensional (2D) arrangements, which represent a middle ground between 1D and 3D systems, have demonstrated a wide variety of unique electronic properties inherited from the two systems.^[1c,4] Therefore, the structure transformation among the three dimensions while retaining the components in the infinite network presents many opportunities for tailoring the aforementioned electronic properties.

Coordination polymers (CPs), which are built by coordinative self-assembly of metal ions or nodes and multidentate organic ligands, 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.^[5] It is well established that the framework structure largely depends not only on the

judicious design or choice of the components but also on the selection of synthetic conditions.^[6] In addition to the physical properties, the dimensionality of frameworks has a great potential to modify the chemical properties such as gas sorption properties,^[6a,7] which have been a long-term subject of research for practical applications such as catalysis,^[8] gas storage,^[9] and gas separation performance,^[10] in contrast to 1D and 2D CPs with open frameworks.

To date, considerable efforts are being undertaken to develop CPs with the dimensional transformation.^[11] The strategy is mainly divided into two categories, one being a chemical reaction between adjacent ligands by external stimuli and the other being a modulation of the coordination environment by the exchange or removal of solvent molecules. The formation of covalent bonds in the former strategy is fraught with drawbacks of the difficulty in back transformation. The latter strategy has afforded partial dimensional transformations (for example, 1D to 2D, 2D to 3D, or vice versa). However, to date, a multi-dimensional reversible transformation has not been accomplished.

Herein, we report the first example of the multidimensional (1D/2D/3D) reversible transformation by regulating the coordination mode in CPs composed of Cu(II) ions and bidentate terephthalate (BDC²⁻) ligands. BDC²⁻ was selected as a bridging linker because of its ability to favor a variety of coordination modes.^[12] The present system has the advantage of being very straightforward, namely, the transformation (1D/2D and $(Cu(BDC)(H_2O)_2 \cdot (H_2O),$ 2D/3D) among 1D 2D (Cu(BDC)(DMF)); DMF: N,N-dimethylformamide), and 3D (Cu(BDC)) can be reversibly achieved by a facile one-pot reaction through immersion in solution or heat treatment without the addition of secondary bidentate linkers.

2D Cu-BDC, i.e., Cu(BDC)(DMF), was prepared according to the literature (see details in the Supporting Information).^[13] The as-synthesized 2D Cu-BDC involves a layered structure with each sheet being a square grid comprising copper paddlewheels bridged by bidentate BDC linkers (Figure 1). Each copper ion lies in a CuO₅ square pyramid coordinated by four BDCs in the square base, while the apical site is occupied by an oxygen atom of DMF.



Figure 1. Schematic illustration of the 1D/2D/3D reversible dimensional transformation in Cu-BDC (gray, C; white, H; blue, N; purple, Cu; red, O). Blue areas in 3D Cu-BDC depict a Cu₂O₂ ring. In 1D Cu-BDC, guest water molecules were omitted for clarity.

The color of the solution becomes shallow when 2D Cu-BDC is dispersed in water (Figure S1). Powder X-ray diffraction (PXRD) measurements were used to study the transformation process based on the change in the crystal structure as a function of immersion time. The PXRD pattern of the as-synthesized 2D Cu-BDC, which is closely similar to that simulated from the reported crystal structure (Figure S2),^[13] varies markedly depending on immersion time (Figure 2a). Specifically, the initial peaks assigned to 2D Cu-BDC rapidly disappear with the concurrent appearance of new peaks just after immersion for 5 min, passing through an intermediate phase. The pattern was found to be unchanged after immersion for 12 h. Le Bail profile analysis (Figure S3) reveals that the reaction product is readily assigned to 1D Cu-BDC, i.e., Cu(BDC)(H2O)2 H2O,[14] in which each copper ion is coordinated by four water molecules to afford the double aqua-bridged 1D Cu chain (Figure 1). The remaining two sites are occupied by oxygen atoms of carboxylate groups in the BDC, yielding a distorted octahedral environment around the Cu center. It is noteworthy that only one of the carboxylate groups in BDC coordinates to the Cu ions, and therefore, no chemical bonds are formed between adjacent chains (Figure 2b).^[14] Fourier transform infrared (FTIR) spectrum of 1D Cu-BDC shows disappearances of C-N (1107 and 676 cm⁻¹) and C=O (1663 cm⁻¹) vibrations of DMF, while maintaining the bands assigned to benzene ring of BDC²⁻ ligands (1386, 1154, and 1018 cm⁻¹) (Figure S4).^[15] In addition, the characteristic bands of water molecules appear in the range of 2900-3700 cm⁻¹. These spectral features are strong evidence for the successful replacement of DMF by water in 1D Cu-BDC. The antisymmetric COO⁻ stretching mode in 1D Cu-BDC was split into two distinct peaks at 1494 and 1543 cm⁻¹, which are attributed to coordinated and uncoordinated COO-, respectively,^[15a] as evidenced by the crystallographic study.



Figure 2. (a) Variation of PXRD pattern for 2D (purple) to 1D (pink) transformation by stirring in water at room temperature for different time periods. (b) Schematic illustration of the reversible transformation and different coordination modes between 1D and 2D Cu-BDC, where the coordinated DMF molecules in 2D Cu-BDC are omitted for clarity. (c) Variation of PXRD pattern for 1D (pink) to 2D (purple) transformation by stirring in DMF at 100 °C for different time periods. In (a) and (c), simulated patterns of 1D and 2D Cu-BDC are shown in black.

The back transformation from 1D to 2D Cu-BDC could be realized by stirring 1D Cu-BDC in DMF at 100 $^{\circ}$ C (Figure 2c).

The transformation from 2D to 3D Cu-BDC could be achieved by heating 2D Cu-BDC as reported previously (Figure S5).^[13] The polycrystalline powder exhibits a color change from light blue to dark blue upon heating (Figure S6). As shown in Figure 3a, the solvated 2D Cu-BDC changes its PXRD pattern to that of the desolvated 3D Cu-BDC, i.e., Cu(BDC),^[16] by heating at 250 °C for more than 2 h. We note that the drastic translation of the 2D sheets (ca. 0.5 nm) is indispensable for 2D to 3D transformation (Figure 3b). After desolvation, the open metal site at the apical position is occupied by an oxygen atom of the paddlewheel in the adjacent sheet to connect with each other. As a result, the reaction product has a 3D framework structure involving 1D square channel with the section area of ca. 0.34 nm², which is perpendicular to the 2D sheets in 2D Cu-BDC.^[16] It appears that the redshift of antisymmetric COO⁻ stretching mode from 1607 cm⁻¹ in 2D Cu-BDC to 1585 cm⁻¹ in 3D Cu-BDC (Figure S4) is consistent with the mode.^[15a] change in coordination FTIR and thermogravimetric (Figure S9) studies also affirmed the absence of DMF in 3D Cu-BDC, indicating that the 2D/3D



Figure 3. (a) Variation of PXRD pattern for 2D (purple) to 3D (blue) transformation by heating at 250 °C under vacuum for different time periods. (b) Schematic illustration of the reversible transformation (purple octahedron: paddlewheel Cu dimer, gray quadrangular prism: BDC ligand, blue cylinder: intersheet Cu–O bonds) and different coordination modes between 2D and 3D Cu-BDC. (c) Variation of PXRD pattern for 3D (blue) to 2D (purple) transformation by stirring in DMF at 120 °C for different time periods. In (a) and (c), simulated patterns of 2D and 3D Cu-BDC are shown in black.



Figure 4. (a) N_2 gas sorption isotherms of 1D Cu-BDC (pink), 2D Cu-BDC (purple), and 3D Cu-BDC (blue) at 77 K and (b) pore width distribution of 3D Cu-BDC (inset: 1D square channel in 3D Cu-BDC). In (a), profiles of 1D and 2D Cu-BDC are strongly overlapped.

dimensional transformation occurs by the removal of coordinated DMF. We found that the dispersion of 3D Cu-BDC in DMF with stirring at 120 °C promoted the reconstruction of 2D Cu-BDC by the coordination of DMF to isolate the 2D sheets. As the reaction time increased, the gradual disappearance of peaks of 3D Cu-BDC and the concurrent appearance of peaks of 2D Cu-BDC were observed in PXRD patterns (Figure 3c). The reconstruction of 2D Cu-BDC was almost complete in 6 h.

The nitrogen adsorption-desorption measurements were conducted to evaluate the porous properties of 1D, 2D, and 3D Cu-BDC. Although there is little uptake in 1D and 2D Cu-BDC with open-framework structures, pronounced absorption was observed for 3D Cu-BDC (Figure 4a). A sharp uptake at $P/P_0 < 0.1$ indicates the presence of micropores, where the Brunauer-Emmett-Teller (BET) surface area was estimated to be approximately 550 m² g⁻¹. The average pore size was estimated to be 0.7 nm using the micropore analysis method (Figure 4b), which is comparable to that expected from the crystal structure (0.78 nm; inset of Figure 4b).^[16] Thus, it is apparent that the present dimensional transformation, especially between 2D and 3D Cu-BDC, can control the gas sorption properties depending on the coordination environment.

Furthermore, the dimensional transformation has the potential to control the magnetic properties, because the species and dimensionality of frameworks have a great effect on magnetic interactions between the open-shell transition metal ions.^[17] Temperature dependences of magnetic susceptibility (χ) of 1D, 2D, and 3D Cu-BDC under 10 kOe are displayed in Figures 5a–c, respectively.

The χ value of 1D Cu-BDC was estimated to be 1.40 × 10⁻³ emu mol⁻¹ at 300 K, which is consistent with that expected from a paramagnetic S = 1/2 spin of Cu(II) ions. Upon cooling, it exhibits a gradual increase followed by a broad maximum at approximately 10 K owing to the antiferromagnetic (AF) fluctuations (Figure 5a).^[18] The χ value can be well fitted by an S = 1/2 Heisenberg AF linear chain model^[19] with g = 2.12 and $J/k_{\rm B} = -10.4$ K ($k_{\rm B}$: Boltzmann constant). For 2D Cu-BDC, the χ value can be represented by the combination of a singlet-triplet model of AF coupled spin pairs^[13,20] with g = 2.09 and $J/k_B = -226$ K and 0.66% of Curie tail (Figure 5b). We note that these magnetic behaviors are consistent with their coordination structures, namely, the uniform 1D chain of Cu(II) ions in 1D Cu-BDC and the 2D sheet based on paddlewheel-type Cu(II) dimers in 2D Cu-BDC. The unexposed 3D Cu-BDC sample follows the singlet-triplet model^[20] with q = 2.10 and $J/k_{\rm B}$ = -224 K (Figure 5c), similar to 2D Cu-BDC. The lack of inter-dimer interactions is attributed to the orientation of the doubly occupied d_{z2} orbital towards the oxygen atom in an adjacent sheet (see Figure 3b). As shown in Figure 5c, exposure to air significantly affects the magnetic behavior. Whereas the room-temperature χ value (1.17 × 10⁻³ emu mol⁻¹) is comparable to that of 1D Cu-BDC, the temperature dependence follows the Curie-Weiss law with Weiss temperature θ = +17.5 K (Figure S10), indicating the ferromagnetic interactions. The magnetization curve at 2 K exhibits a pronounced sigmoidal curve with a saturation magnetization of ca. 2500 emu Oe mol⁻¹ at 10 kOe, which becomes almost invariant after exposure to air for 6 days (Figure S11). The magnetization value apparently exceeds that expected from the Brillouin function for S = 1/2 at 2 K, although the saturation magnetization value is lower than that for S = 1/2 ferromagnet (5585 emu Oe mol⁻¹). According to the equation, $k_{\rm B}\theta = 2zJS(S+1)/3$, where z is the number of nearest neighbor spin sites (we assumed z = 6), the J value of air-exposed 3D Cu-BDC was estimated to be +5.83 K.

To unveil the ferromagnetic interactions observed in airexposed 3D Cu-BDC, time-dependent FTIR spectra were measured while exposed to air. As shown in Figure S12, the peaks at 771, 929, 1279, 1698, and 2500-3200 cm⁻¹ which can be assigned to the uncoordinated H₂BDC,^[21] become significant with increasing exposure time. Additionally, the sharp peak assignable to O-H group attached to Cu(II) ions^[22] was observed at 3570 cm⁻¹ in airexposed 3D Cu-BDC. These spectral changes indicate the partial removal of BDC from the copper ion, which is possibly due to the hydrolysis of 3D Cu-BDC as schematically represented in Figure S13. Reduced crystallinity as indicated by PXRD pattern (Figure S14) and reduced pore space as indicated by N₂ sorption isotherm (Figure S15) confirmed the degradation of framework structure.

These experimental results strongly suggest that this structural degradation reduces the intra-dimer antiferromagnetic interactions along the superexchange pathways through singly occupied $d_{x_{2-y_2}}$ orbitals of Cu(II) ions and 2p orbitals of oxygen atoms in bridging BDC ligands. It is apparent that the liberated spins play a crucial role in the Curie-Weiss paramagnetic behavior with inter-



Figure 5. Temperature dependence of magnetic susceptibility (χ : open squares) of (a) 1D Cu-BDC, (b) 2D Cu-BDC, and (c) unexposed (blue) and airexposed (green) 3D Cu-BDC under 10 kOe. Calculated magnetic susceptibilities based on the Bonner-Fisher model^[19] in (a) and Bleaney-Bowers model^[20] in (b) and (c) are shown in black solid lines. (d) Magnetization curve of unexposed (blue) and air-exposed (green) 3D Cu-BDC at 2 K. A black dotted line shows the ideal Brillouin function for S = 1/2.

dimer ferromagnetic interactions, although the actual coordination environment around Cu(II) ions remains unclear at present. Of particular importance is that the 3D structure formed by the connection of 2D sheets is responsible for the observed ferromagnetic behavior.

In summary, we proposed a facile one-pot synthetic strategy to realize 1D/2D/3D reversible transformation in CPs for the first time. The dimensional transformations, which were successfully achieved by exchanging or removing/rebinding solvent molecules coordinated to Cu(II) ions, are accompanied by a pronounced change in gas sorption and magnetic properties. The present study enables us to develop new multidimensional architectures to implement the rational control of properties related to dimensionalities.

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Reversible multi-dimensional transformation of a coordination polymer composed of Cu(II) ions and terephthalate ligands was achieved for the first time by controlling the coordination environment. The dimensional transformation led to the significant changes in chemical and physical properties specific to coordination polymers, such as gas sorption and magnetism.