Coordination Polymers

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Control of Interpenetration for Tuning Structural Flexibility Influences Sorption Properties**

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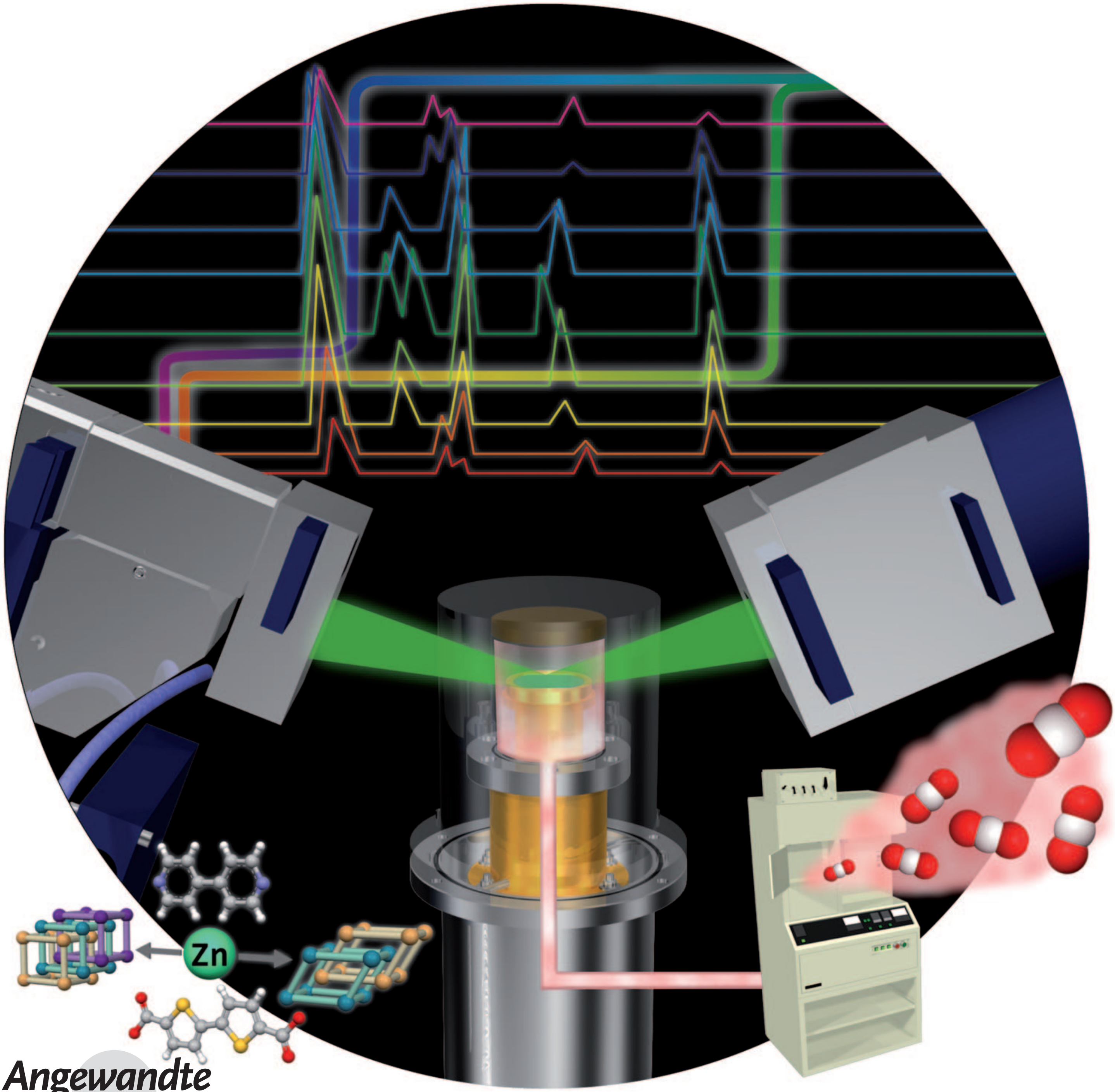
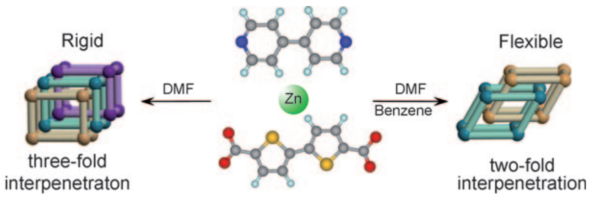


Porous coordination polymers (PCPs),[1–8] which are obtained by assembling metal ions and bridging ligands, have been developed to provide a nanometer-sized coordination space that is potentially applicable in gas storage,[9–19] heterogeneous catalysis,[20–23] and separation.[24–29] The synthesis of PCPs has been particularly profitable in terms of designability, because in principle we can systematically construct structures and tune the sorption properties of these PCPs. Interpenetration in PCPs[30] has been considered an undesirable feature because of a decrease in the available void space. However, recent reports demonstrated that some interpenetrated PCP frameworks showed a high gas-uptake capability that was attributed to an increase in internal surface area.[31] Moreover, structural transformations in response to a critical amount or specific characteristics of guest molecules provide excellent case studies for the investigation of structural dynamism in PCPs.[32,33] Dynamic effects can arise either locally from flexible ligands and/or flexibility of the coordination geometry of the metal ions,[34–37] or from the global cooperative movement of the framework on a periodic scale, such as the sliding of interpenetrated networks during guest accommodation for example.[38–40] These dynamic effects can occur simultaneously and contribute to one another. Usually, the thermal stability of flexible structures is less than that of rigid structures in a single network; however, this problem can be overcome by the use of interpenetration. Therefore, control over the interpenetration degree in PCPs is of the utmost importance.[41–43] Recent reports have shown a variety of interpenetrations in three-dimensional (3D) jungle-gym-like structure composed of dinuclear $M_2(COO)_4$ paddle wheel units ($M = Co, Ni, Cu, Zn, Cd, Mn$) with carboxylate- and pyridyl-based organic building blocks.[44,45] The dinuclear paddle wheel units connected with carboxylate-based organic building blocks afford two-dimensional (2D) layer structures. The 2D layers are pillared by pyridyl-based organic building blocks at the axial positions of paddle wheel units, resulting in forming the 3D jungle-gym analogue structure with a primitive cubic (**pcu**)[46] net topology (hereafter denoted JAST framework). Furthermore, recent synthetic reports have shown that the control of interpenetration can be achieved by liquid-phase epitaxial growth,[47] use of template molecules in synthetic solution,[48–50] rational design of ligands,[51] or by changing the concentration of reagents.[52] Herein, we show a new method for tuning structural flexibility and sorption behavior by controlling the degree of interpenetration of 3D JAST-type PCPs, and even those that are composed of the same chemical components (Scheme 1).



Scheme 1. Control of degree of interpenetration and structural flexibility in a coordination polymer using the solvent molecule as a template. C gray, N blue, O red, S yellow, H light blue.

A mixture of two types of single crystals was obtained from the reaction of $Zn(NO_3)_2{\cdot}6\,H_2O$, 2,2′-bithiophene-5,5′-dicarboxylic acid (btdc), and 4,4′-bipyridine (bpy) under solvothermal synthesis. As a result of single-crystal X-ray diffraction analyses,[56] it was shown that one had a three-fold interpenetrated JAST framework $\{[Zn_2(btdc)_2(bpy)]{\cdot}x\,S\}_n$ (**1**$\cdot x$S) (S = solvent), while the other crystal of $\{[Zn_2(btdc)_2(bpy)]{\cdot}y\,S\}_n$ (**2**$\cdot y$S) possessed a two-fold interpenetrated JAST framework (Figure 1; Supporting Information, Table S1). We suspected that lowered homogeneity of the reaction solution resulted in the formation of the two types of crystals. Therefore, to obtain a pure compound, the bulk synthesis was carried out with vigorous stirring to keep the reaction solution homogeneous. Consequently, the pure crystalline powder of three-fold dense phase of **1**$\cdot x$S was obtained, which was confirmed by X-ray powder diffraction (XRPD) patterns (Supporting Information, Figure S1).

On the other hand, it is surprising that pure crystalline powder of **2**$\cdot y$S was obtained when the mixed solvent of benzene and DMF (1:1) was used (Supporting Information, Figure S2). The larger size of benzene molecules in the solvent medium acts as a template during the assembly process and prohibits the denser packing of frameworks, giving rise to the two-fold interpenetrated structure of **2**$\cdot y$S. Various other additional solvent molecules, such as toluene, cyclohexane, naphthalene, and mesitylene, were tested to control the degree of interpenetration. As a result, the same two-fold interpenetrated compound was obtained when

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Supporting information for this article, including synthetic methods and of physical measurements, is available on the WWW under http://dx.doi.org/10.1002/anie.201002259.

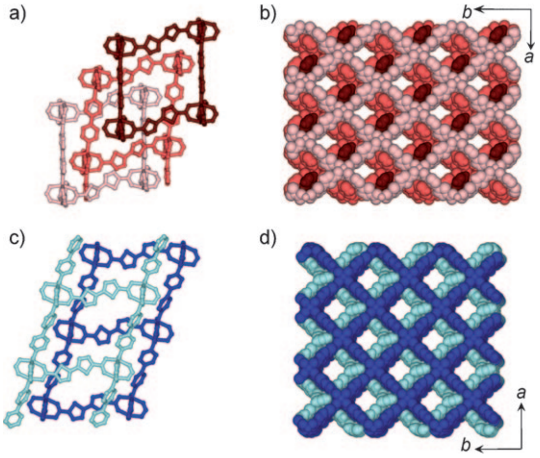

Figure 1. Crystal structures of **1** (a,b) and **2** (c,d). a,c) Three-fold and two-fold interpenetrating modes, respectively, shown as stick models. Hydrogen atoms are omitted for the clarity. b,d) Channel views with space-filling models along the *c* axis.

toluene or cyclohexane was used as a template; however, further large molecules (naphthalene or mesitylene) did not work as templates. Neither three-, two-fold interpenetrated, nor non-interpenetrated structures were obtained in the solution of DMF/naphthalene or DMF/mesitylene (Supporting Information, Table S2).

The crystal data show that the compositions of both JAST frameworks are the same. The net topology of **1** and **2** are primitive cubic (**pcu**)[46] with differences in the interpenetrating behavior. Compound **1** consists of three-fold interpenetration generated by a translation along the *c* axis (vector norm: 9.38 Å), while compound **2** exhibits a two-fold interpenetration with the single nets related by an inversion center, thus belonging to different classes of interpenetration: class I a for **1** and class II a for **2**.[42,43] In the structure of **1**, both pyridyl rings of each bipyridine interact with the thiophene rings through π–π stacking (distance 3.4 Å; Supporting Information, Figure S3). When we focus on one cubic unit constructed from four bpy and eight btdc ligands, the eight pyridiyl and eight thiophene rings interact with thiophene and pyridyl rings of the other networks, respectively, and therefore one cubic unit interacts with the other network at 16 positions by π–π interactions, resulting in the rigid structure of **1**. On the other hand, no significant π–π interactions can be found in the structure of **2**. Only relatively short contacts between two hydrogen atoms of bpy and carboxylic oxygen atoms (2.9 Å), and a hydrogen atom of thiophene ring and a carboxylic oxygen atom (2.5 Å) are observed, resulting in a rather flexible structure of **2** compared to **1** (Supporting Information, Figure S4). The results of thermogravimetric analysis (TGA) showed that compound **2** was stable up to 270 °C, which is 60 °C lower than that of **1** (Supporting Information, Figure S5). Based on the crystallographic data and the van der Waals radii of the atoms, compound **1** and **2** provide square channels with dimensions of 3.8×3.8 Å^2 and 6.3×6.3 Å^2, respectively, when viewed along the *c* axis (Figure 1; Supporting Information, Figures S6,S7).

To explore the permanent porosity and structural dynamics of both compounds, the CO_2 sorption properties on **1** and **2** at 195 K were investigated using coincident XRPD/adsorption measurement equipment. We found that both compounds showed completely contrasting sorption behaviors. The sorption isotherm of **1** shows that the saturated amount of CO_2 adsorbed is about 55 cm^3(STP) g^{-1}, which corresponds to one CO_2 molecule per unit formula (Figure 2 a). Although the intensity and position of 110 and 020 in the XRPD patterns are slightly changed depending on the adsorption of guest molecules, the other peaks are almost unchanged (Figure 2 b). The cell parameters for the patterns at B, C, and D were calculated by Le Bail analysis (Supporting Information, Table S3). It is noteworthy that the main structure of three-fold interpenetrated compound **1** is maintained even when CO_2 guest molecules are accommodated in its pores, indicating that compound **1** has a rigid framework.

On the other hand, because of the lower degree of interpenetration and the absence of specific interactions between the two interpenetrated frameworks, **2** is expected to possess the dynamic features involving framework transformations (sliding motions and/or shrinkage/expansion). The desolvated structure of **2** (dried **2**) was determined (Supporting Information, Table S1, Figure S8).[56] It is noteworthy that the 2D sheets constructed from zinc paddle wheel units and dicarboxylates are considerably strained from a square to a rhomboidal grid shape, which is indicative of flexible nature

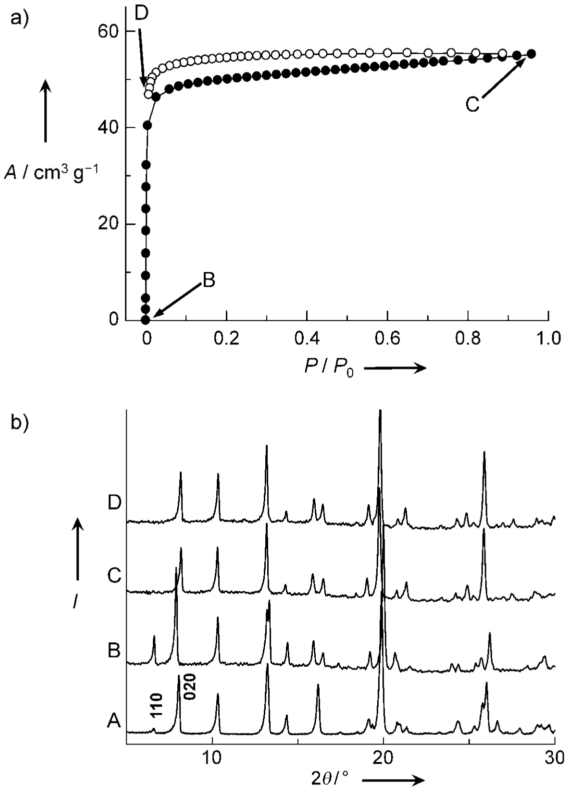

Figure 2. a) CO_2 adsorption (●) and desorption profiles (○) of **1** at 195 K. A: amount adsorbed at STP (standard temperature and pressure). P/P_0 is relative pressure; P_0 of CO_2 at 194.7 K is 101.3 kPa. b) A: XRPD pattern of as-synthesized **1**·*x*S measured at ambient temperature; B–D: XRPD patterns of **1** measured under CO_2 sorption conditions using Cu$_{K\alpha}$ radiation. Each pattern corresponds to the points labeled in (a).

of **2**. The high flexibility of **2** was also clearly observed by an in-situ coincident XRPD/adsorption measurement. First, the structure of **2** was significantly changed by removal of the guest molecule (Figure 3b, A and B). From point C to E, the peaks in the XRPD patterns considerably broaden and the crystallinity of **2** decreases, indicating that the crystal transformation occurs not in a cooperative fashion but rather in a non-uniform fashion in response to the accommodation of CO_2. Then, an apparent step is observed at the point E (ca. 125 $cm^3(STP)\,g^{-1}$), corresponding to 2.2 CO_2 per unit formula. Through the further adsorption of CO_2, the peaks, especially those assigned as 110 and 11–1, sharpen from point E to G, indicating that the structure becomes uniform. The saturated amount of CO_2 adsorption (at point G) is about 201 cm^3-(STP)g^{-1} (3.5 CO_2 per unit formula), which is about four times higher than that of **1**. The XRPD patterns of A and G are quite similar, which is indicative of the similar architecture of both states. Furthermore, to determine the precise structural change, we collected synchrotron XRPD data of desolvated **2** under 80 kPa of CO_2 atmosphere at BL02B2 and BL44B2 beamline in SPring-8[53,54] and determined the space group and refined cell parameters by Le Bail analysis (Supporting Information, Table S4).[55] The results show that the cell parameters of the frameworks at 0.8 of P/P_0 of CO_2 are quite close to those of as-synthesized **2**·*y*S. After the CO_2 adsorption and desorption, the structure of **2** can return to the initial state by immersion in DMF.

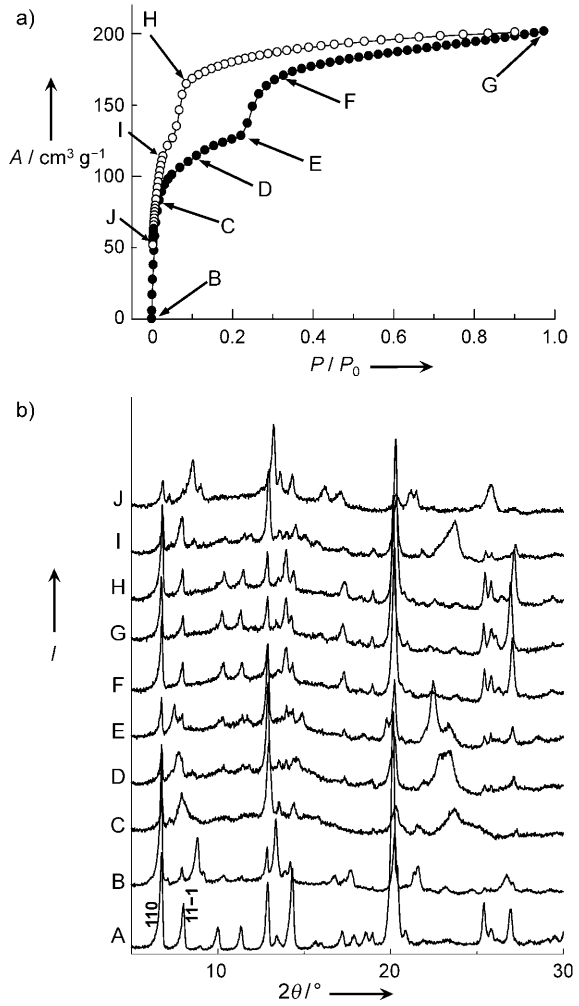

Figure 3. a) CO_2 adsorption (●) and desorption profiles (○) of **2** at 195 K. b) A: XRPD pattern of as-synthesized **2**·*y*S measured at ambient temperature. B–J: XRPD patterns of **2** measured under CO_2 sorption conditions using $Cu_{K\alpha}$ radiation. Each pattern corresponds to the points labeled in (a).

In conclusion, we have presented the usefulness of tuning the degree of interpenetration for designing flexible frameworks and stepwise sorption function. Although the two compounds had exactly the same chemical composition, they showed completely different adsorption behaviors and structural flexibilities, which was attributed to the difference in degree of interpenetration. Recent developments in the design of flexible porous frameworks and gate-opening-type sorption behaviors that are not categorized in the IUPAC classification have more important ramifications than we expected. Although many reports have particularly emphasized the surface properties based on structural components to date, this work clearly reveals that the architectural connectivity significantly impacts on the sorption behavior and is also quite important for tuning the structural flexibility and its sorption functions.

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[56] CCDC 746303 (**1**⋅xS), 746302 (**2**⋅yS), and CCDC 773219 (dried **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.