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Colossal Trellislike Single-Crystal to Single-Crystal Structural Transformations in Two 1D Coordination Polymers

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1. INTRODUCTION

Coordination polymers (CPs) have attracted interest for more than three decades owing to their structural versatility, which often gives rise to distinctive chemical and physical properties.^{1,2} As a result, CPs have a range of potential applications, including the storage,³⁻⁵ separation,^{6,7} and sensing of small guest molecules,^{8,9} as well as catalysis¹⁰⁻¹² and magnetism.¹³⁻¹⁵ A fundamental understanding of the structureproperty relationships of CPs is essential for the rational design of dynamic functional materials based on such systems. Typically, these studies benefit substantially from structural transformations that occur in a single-crystal to single-crystal (SC-SC) manner. This is because routine structural solution from powder diffraction data using standard laboratory instrumentation is often a difficult process.^{1,16} However, the structural transformation of a crystal often introduces significant mechanical strain, leading to an increase in mosaicity or even to disintegration.¹ Therefore, SC-SC transformations are observed relatively infrequently for phase changes that involve large structural rearrangements at the molecular level.^{17–20} Although some 1D CPs are known to undergo SC-SC transformations,^{2,21–25} very few examples of substantial structural changes in such materials have been reported. Furthermore, many known 1D CPs do not possess large probe-accessible volumes (PAV)²⁶ because they often favor close-packed (or near close-packed) solid-state arrangements.

Owing to the toxicity of many volatile organic compounds (VOCs),^{27,28} materials that can capture various vapors are of interest to both fundamental research and industry. To mitigate costs, such materials should ideally be easy to prepare

and regenerable. Although viable low-cost options are available (e.g., activated carbons and zeolites), their preparation relies on calcination techniques and/or mining operations. Coordination compounds therefore present opportunities for the cyclable and environmentally friendly capture of VOCs if their preparation and regeneration can be optimized.^{29,30}

2. EXPERIMENTAL SECTION

2.1. Materials. Unless otherwise indicated, all reagents were obtained from commercial suppliers (Sigma-Aldrich, Alfa Aesar, Merck) and used without further purification.

2.2. Solvothermal Crystallization. $\{[Zn(bpdc)(bpy)] \cdot 2DMF\}_n$ (1) was prepared solvothermally. In a scintillation vial, equimolar amounts of the ligands 4,4'-biphenyldicarboxylic acid (bpdc, 0.30 mmol, 72.7 mg) and 2,2'-bipyridine (bpy, 0.30 mmol, 46.9 mg), along with $Zn(NO_3)_2 \cdot 6H_2O$ (0.40 mmol, 119.4 mg), were added to 5 mL of *N*,*N*-dimethylformamide (DMF) and sonicated until partially dissolved. The vial was heated at 80 °C in an oven for 4–7 days. Clear rod-shaped crystals were deposited in quantitative yield. $\{[Zn(bdc)(bpy)] \cdot DMF\}_n$ (2) was prepared in a manner similar to that for 1 from 1,4-benzenedicarboxylic acid (bdc, 0.1 mmol, 16.6 mg), bpy (0.1 mmol, 15.6 mg), and $Zn(NO_3)_2 \cdot 6H_2O$ (0.15 mmol, 44.8 mg) in 3 mL of DMF. Clear plates crystallized in quantitative yield.

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Figure 1. Crystal packing of (a) 1 and (b) 2 viewed along the crystallographic a axis. Guest molecules and hydrogen atoms are omitted. In (a) the major component of each ligand disorder is shown in green and the minor component in orange. The approximate atom to atom dimensions of each solvent-accessible aperture are shown.



Figure 2. Crystal packing of (a) **1a** and (b) **2a** viewed along the *a* axis. Dotted green lines in (a) illustrate $\pi \cdots \pi$ interactions between adjacent bpdc ligands (centroid–centroid 3.663(6) Å) and in (b) C–H $\cdots \pi$ interactions between adjacent bpy and bdc ligands (centroid–C 3.509(11) and 3.963(11) Å) are shown. Hydrogen atoms have been omitted for clarity.

2.3. Activation Procedures. Crystals of 1 were activated in the furnace of a thermogravimetric analyzer ($T_{max} = 180$ °C, ramp rate 5 °C min⁻¹, N₂ purge 40 mL min⁻¹) to yield single crystals of the guest-free phase 1a. Crystals of 2 were activated by supercritical CO₂ drying (T = 40 °C, $P \approx 100$ bar, $t \approx 4-6$ h) to yield single crystals of the guest-free phase 2a. Supercritical drying was carried out using a Tousimis Samdri PVT-3D critical point dryer.

2.4. Single-Crystal X-ray Diffraction. X-ray intensity data were recorded on a Bruker APEX II DUO or a Bruker D8 Venture diffractometer. The APEX II DUO was equipped with an Incoatec IµS molybdenum ($\lambda = 0.71073$ Å) microfocus X-ray source and a CCD area detector. The D8 Venture was equipped with an Incoatec I μ S 3.0 molybdenum (λ = 0.71073 Å) microfocus X-ray source and a Photon II CPAD detector. The diffractometers are equipped with Oxford Cryosystems cryostats (Cryostream 700 Plus and Cryostream 800 Plus, respectively). Data reduction and absorption corrections were carried out using the SAINT³¹ and SADABS³² programs, respectively. Unit-cell dimensions were refined on all data, and space groups were assigned on the basis of systematic absences and intensity statistics. The structures were solved using a dual-space algorithm employed by SHELXT.³³ Structure refinement was carried out with SHELXL-2018/3³⁴ using the X-Seed^{35,36} graphical user interface. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions using riding models. Illustrations of all crystal structures were generated using the programs POV-Ray³⁷ and Mercury.^{38–40}

2.5. Powder X-ray Diffraction (PXRD). A Bruker D2 Phaser powder diffractometer was used to record experimental diffractograms. The diffractometer utilizes a Bragg–Brentano geometry and Cu K α radiation (λ = 1.5418 Å) as the incident beam. The diffractometer was operated at 30 kV and 10 mA. Samples were placed on a rotating $(30^{\circ} \text{ min}^{-1})$ flat stage, and intensity data were recorded using a Lynxeye detector. Samples were finely ground (where necessary) using a mortar and pestle, loaded onto a zero-background sample holder, and leveled with a glass slide (where possible). Diffractograms were recorded under ambient conditions using a scanning range of 5–40°, a step size of 0.016°, and a scan speed of 0.8 s per step.

2.6. Gravimetric Vapor Sorption. A modified version of the vapor balance setup reported by Barbour and co-workers⁴¹ was used to carry out vapor sorption experiments. The system provides an accurate measure of the change in sample weight as a function of time. The vapor balance was enclosed in a temperature-controlled cabinet. The sample was placed in a perforated aluminum basket, which was suspended from the microbalance by a thin steel wire. A vacuum pump allowed the system to be evacuated dynamically to a pressure of 0.1 mbar. Typical sample sizes ranged from 15 to 30 mg, and the temperature was maintained at 23 °C. After introduction of the sample weight reached a plateau (indicating equilibrium). If required, the desorption profile could also be recorded by applying a dynamic vacuum.

3. RESULTS AND DISCUSSION

Here we report two analogous CPs, each consisting of distorted-octahedral zinc(II) nodes linked by means of a linear dicarboxylate ligand (either 4,4'-biphenyldicarboxylic acid (bpdc) or 1,4-benzenedicarboxylic acid (bdc)) and with the remaining two coordination sites occupied by a chelating

31.9%



30.3%

2,2'-bipyridine (bpy) ligand. This arrangement facilitates propagation of the coordination compound in only one dimension. {[Zn(bpdc)(bpy)]·2DMF}_n (1) and {[Zn(bdc)-(bpy)]·DMF}_n (2) (DMF = *N*,*N*-dimethylformamide) were prepared solvothermally in DMF. CPs 1 and 2 crystallize in the same space group (*P*2₁/*n* and *P*2₁/*c*, respectively) and exhibit analogous crystal packing motifs consisting of 1D "zigzag" strands that intercalate by means of $\pi \cdots \pi$ interactions between offset bpy moieties of neighboring strands to form large 1D channels (Figure 1).

34.2%

In 1 the channels propagate along [100] and contain DMF guest molecules. Although it was not possible to model the guest molecules crystallographically, their presence and occupancies were determined by means of infrared spectroscopy and thermogravimetry (Figures S5 and S7), respectively. Each of the bpdc and bpy moieties is disordered over two positions (with site occupancy distributions of 50:50 and 62:38, respectively). The PAV (considering either component of the bpdc disorder) consists of approximately 45–46% of the total volume (Figure S2a,b).

On the basis of this promising "virtual porosity",⁴² CP 1 was activated (see the Experimental Section and the Supporting Information) with a view to investigating its guest inclusion properties. We note that precise control of the conditions is required to ensure that activation proceeds as a SC-SC process. Direct comparison of 1 with its apohost structure (1a) shows that activation preserves the space-group symmetry but results in dramatic contraction of the crystal, which results in a "virtually"⁴² nonporous apohost form, with apparent collapse of the 1D channels upon guest removal (Figure 2a).

During the transformation from 1 to 1a the *b* axis contracts substantially (by 34%), along with a slight contraction of the *c* axis (by 9%), with a total reduction of the unit-cell volume by ca. 39%. There are relatively few examples of SC-SC transformations that result in a structural contraction of similar magnitude⁴³⁻⁴⁶ and even fewer examples exceeding this value.⁴⁷ Notably, very few of these examples involve CPs, with most being 2D and 3D framework materials. Furthermore, activation results in ordering of the previously disordered ligands and could plausibly be due to the lack of free space in the close-packed apohost structure. To establish unequivocally that the transformation of 1 to 1a occurs as a SC-SC process, a crystal of 1 was activated *in situ* while it was mounted on a single-crystal diffractometer (Table S2 and Figure S1). This experiment also illustrated that the change in

size of the crystal corresponds to the changes in the unit-cell parameters (Table S3).

29.3%

The translations that accompany activation result in the formation of $\pi \cdots \pi$ interactions between adjacent bpdc linkers in **1a**. These interactions cause unusual contortion of the conceptually rigid bpdc ligand (Figures 2a and S3 and S4). A search of the Cambridge Structural Database⁴⁸ revealed that **1a** exhibits the largest deviation from linearity observed to date for bpdc and analogous ligands (Figure S4 and Table S4).

To investigate whether the guest-free form 1a would undergo further structural transformation upon reintroduction of guest molecules, a number of experiments (including exposure to possible guests in gas, liquid, or vapor form) were carried out, with various levels of success. Gas sorption was investigated using pressure-gradient differential scanning calorimetry (PG-DSC; see the Supporting Information).⁴ Exposure of 1a to 50 bar of CO₂, CH₄, and N₂ gas resulted in no structural changes or guest sorption (as determined by PG-DSC; Figure S26). Next, resolvation was carried out by immersing 1a in fresh DMF overnight. The material underwent a structural transformation to an open form (1')determined by means of powder X-ray diffraction (PXRD) to be structurally analogous to 1 (Figure S21). Single-crystal Xray diffraction (SCXRD) analysis of 1' was not possible, since the resolvation process resulted in disintegration of the crystals into a polycrystalline material. This is likely due to the large stress involved in structural transformation back to the open form 1'. Finally, vapor sorption was carried using a customized vapor balance,⁴¹ which monitors sample mass as a function of time during exposure to solvent vapor. In each vapor sorption experiment two cycles were carried out, each entailing sorption for 90 min followed by the application of a dynamic vacuum (desorption) for 90 min. A fresh sample of 1 was used for each vapor sorption experiment. Exposing 1a to vapors of tetrahydrofuran (THF), 1,4-dioxane, p-xylene, and toluene did not result in sorption (or structural transformation); no increase in sample mass was observed during 90 min of exposure, and the PXRD pattern was similar to that of 1a.

CP 2 packs in a manner analogous to that for 1, with DMF containing paired channels that are periodically interconnected to each other (Figures 3 and S2c; 31.9% PAV), also extending along [100]. Both of the ligands in 2 are ordered. The structural transformation from 2 to 2a involves considerable contraction along the *b* and *c* axes, resulting in a reduction in the unit-cell volume by ca. 22%. As for 1, activation of 2

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Figure 4. Vapor sorption (left) and desorption (right) profiles for **2a**. Two sorption–desorption cycles were carried out consecutively. Cycle 1 is shown in (a) and (b) and cycle 2 in (c) and (d). Insets show the first 10 min of sorption in (a) and (c) and the first 5 min of desorption in (b) and (d).

produces a "virtually nonporous" apohost form (2a). Structural translations accompanying activation result in the formation of C-H… π interactions between adjacent bpy and bdc ligands in 2a (Figure 2b), which cause slight contortion of the conceptually rigid bdc ligands.

PG-DSC $(1-50 \text{ bar of } CO_2, CH_4, \text{ and } N_2)$ of 2a showed no gas sorption or phase change events (Figure S27). Similarly to 1a, immersion of 2a in fresh DMF overnight resulted in a polycrystalline structural transformation to an open phase denoted 2' (Figure S22). In each case, exposure of 2a to vapors of THF, diethyl ether (DE), ethanol (EtOH), methanol (MeOH), and acetonitrile (ACN) resulted in uptake of the guest, from which we infer a structural transformation to an open phase denoted 2" (Figures 4 and S23 and S28). However, 2a did not appear to absorb vapors of 1,4-dioxane, pxylene, and cyclohexane within 90 min, implying that no structural transformation to an open form takes place in these instances. It is possible that these compounds are too sterically bulky for inclusion in the guest-accessible space, since they have the largest kinetic diameters of all the VOCs tested (Table S6). Furthermore, these vapors also do not appear to exchange with the DMF of the as-synthesized material 2, as determined by thermogravimetry (Figure S16). This suggests that a size-exclusion effect may prohibit the uptake of larger cyclic compounds.

The first vapor sorption cycle shows a latent period where the channels of 2a remain closed, after which the structure opens to allow uptake of the vapor (Figure 4a). The desorption profiles for THF and DE are stepped; an initial drop in guest occupancy occurs within the first few minutes (Figure 4b), followed by an inflection point after which the guest occupancy

decreases more rapidly. For the other sorbed vapors there is no notable inflection point. However, this may also be due to the relative speed of desorption. In some cases the guest occupancy does not return to zero (i.e., THF and DE), and thus the material might not revert completely to 2a because some portion remains open (2''). This was confirmed by PXRD of the desorbed materials in most cases (Figure S23), with the exception of MeOH and ACN. The diffractogram for each desorbed sample shows peaks at ca. $8^{\circ} 2\theta$, which corresponds to the major characteristic peak of the open form 2. However, the remainder of the diffractogram matches that of the guest-free material 2a. The relative intensities of the characteristic peaks of each form (open and closed) indicate that the sample consists predominantly of 2a. Heating the THF-desorbed sample at 75 °C under dynamic vacuum for several hours did not lead to any distinct change in the diffractogram (Figure S24). A subsequent thermogravimetric analysis confirmed that the material is guest-free at this point (Figure S17). Thus, the consecutive structural transformations between the closed and open forms result in bulk 2a never being entirely recovered. We believe that the remaining open phase then facilitates more rapid reopening to 2'' in consecutive sorption cycles. This phenomenon is observed in the second sorption cycle, which shows a reduced or no initial latent period in comparison to that of the first cycle for each solvent vapor (Figure 4c). The diffractograms of the samples post MeOH and ACN sorption reveal that the materials have entirely collapsed to closed forms and match that of 2a (Figure S23). This may be explained by the facile desolvation of these solvates of 2, which proved difficult to analyze via thermogravimetry (especially in the case of the MeOH solvate,

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Figure S13). However, the latent period in the second cycle of MeOH vapor sorption was notably diminished relative to the first cycle.

Intriguingly, in all cases where vapor sorption occurred, the maximum guest occupancy attained far exceeded that expected (nearly double in some cases) from thermogravimetric analyses of the respective solvates. This was likely due to condensation of solvent on the sample during sorption (Figure S18). The presence of surface solvent may explain the inflection point observed during the desorption of certain solvent vapors. Under dynamic vacuum the surface solvent is removed relatively easily from the material, after which the included guest is then desorbed. Condensation did not occur during experiments with vapors that were not included (namely 1,4dioxane, cyclohexane, and p-xylene). Thus, the process of solvent deposition on the surface of the material seems to be connected to guest uptake. Although solvent uptake occurs rapidly, both solvent components (surface and guest) are readily removed from the material under reduced pressure.

The trends observed in each vapor sorption experiment are comparable, with the principal dissimilarity being the duration of the latent period before the onset of sorption. This is likely a consequence of several factors, including host-guest affinity (confined to relatively weak interactions), guest vapor pressure (Table S5), and guest kinetic diameters (Table S6). THF and DE have the highest vapor pressures under ambient conditions but also the largest kinetic diameters. Thus, relative to the other solvents investigated, these compounds display moderate latent periods for sorption and delayed desorption curves. Although ACN possesses one of the smallest kinetic diameters of the sorbed vapors, it also has one of the lowest vapor pressures. Since it is both sorbed and desorbed rapidly, its small kinetic diameter may facilitate its ease of movement in and out of the channels. MeOH and EtOH have the longest latent periods during both of the consecutive sorption cycles, and this is possibly related to their lower vapor pressures, since they also possess some of the smallest kinetic diameters. These vapors also desorb rapidly, which may also be attributed to the small kinetic diameters of these molecules. Thus, small molecules with high vapor pressures appear to be associated with shorter latent periods before sorption occurs, and they desorb with relative ease, with the opposite being true for larger molecules with lower vapor pressures.

The fact that only liquid DMF induces framework reopening in **1a** but both liquid DMF and certain solvent vapors induce a structural transformation in **2a** could be a consequence of the relative strengths of the supramolecular interactions that stabilize the two different structures. **1a** has notably stronger interactions ($\pi \cdots \pi$ interactions) than **2a** (C-H $\cdots \pi$). Subsequently, it is possible that there exists a smaller energy barrier in **2a** to overcome the interactions keeping the channel closed than in **1a**.

4. CONCLUSION

We have prepared two novel CPs with large solvent-accessible volumes in their as-synthesized forms. Upon activation these materials undergo colossal trellislike SC-SC contraction; the apohost forms display considerable contortion of the conceptually rigid dicarboxylic acid ligands, with **1a** exceeding all known examples of ligand contortion. Both apohost materials can be resolvated by immersion in DMF to recover their open phases. **2a** will also reopen when it is exposed to certain solvent vapors. The apohost material is largely or

entirely regenerable, with consecutive sorption cycles occurring at lower vapor pressures. Condensation of solvent vapor on the surface of the material allows for a much higher than expected equilibrium capacity. In some cases this increase is more than twice that expected. Furthermore, trends in the rapidity of the sorption and desorption cycles likely stem from trends in the kinetic diameter and vapor pressures of the individual solvents.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.1c00240.

Crystallization and activation procedures, FT-IR, singlecrystal X-ray diffraction, powder X-ray diffraction, vapor sorption, etc. (PDF)

Accession Codes

CCDC 1940574–1940578 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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REFERENCES

(1) Zhang, J.-P.; Liao, P.-Q.; Zhou, H.-L.; Lin, R.-B.; Chen, X.-M. Single-Crystal X-Ray Diffraction Studies on Structural Transformations of Porous Coordination Polymers. *Chem. Soc. Rev.* 2014, 43 (16), 5789–5814.

(2) Leong, W. L.; Vittal, J. J. One-Dimensional Coordination Polymers: Complexity and Diversity in Structures, Properties, and Applications. *Chem. Rev.* **2011**, *111* (2), 688–764.

(3) Sumida, K.; Rogow, D. L.; Mason, J. A.; Mcdonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.; Long, R. Carbon Dioxide Capture in Metal-Organic Frameworks. *Chem. Rev.* **2012**, *112*, 724–781.

(4) D'Alessandro, D. M.; Smit, B.; Long, J. R. Carbon Dioxide Capture: Prospects for New Materials. *Angew. Chem., Int. Ed.* **2010**, 49 (35), 6058–6082.

(5) Mason, J. A.; Veenstra, M.; Long, J. R. Evaluating Metal– Organic Frameworks for Natural Gas Storage. *Chem. Sci.* **2014**, *5* (1), 32–51.

(6) Cadiau, A.; Adil, K.; Bhatt, P. M.; Belmabkhout, Y.; Eddaoudi, M. A Metal-Organic Framework-Based Splitter for Separating Propylene from Propane. *Science (Washington, DC, U. S.)* **2016**, 353 (6295), 137–140.

(7) Li, J.; Sculley, J.; Zhou, H. Metal-Organic Frameworks for Separations. *Chem. Rev.* 2012, *112*, 869–932.

(8) Yeung, M. C.-L.; Yam, V. W.-W. Luminescent Cation Sensors: From Host–Guest Chemistry, Supramolecular Chemistry to Reaction-Based Mechanisms. *Chem. Soc. Rev.* **2015**, *44* (13), 4192– 4202.

(9) You, L.; Zha, D.; Anslyn, E. V. Recent Advances in Supramolecular Analytical Chemistry Using Optical Sensing. *Chem. Rev.* **2015**, *115* (15), 7840–7892.

(10) Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C.-Y. Applications of Metal–Organic Frameworks in Heterogeneous Supramolecular Catalysis. *Chem. Soc. Rev.* **2014**, *43* (16), 6011–6061.

(11) Raynal, M.; Ballester, P.; Vidal-Ferran, A.; van Leeuwen, P. W. N. M. Supramolecular Catalysis. Part 1: Non-Covalent Interactions as a Tool for Building and Modifying Homogeneous Catalysts. *Chem. Soc. Rev.* **2014**, *43* (5), 1660–1733.

(12) Raynal, M.; Ballester, P.; Vidal-Ferran, A.; van Leeuwen, P. W. N. M. Supramolecular Catalysis. Part 2: Artificial Enzyme Mimics. *Chem. Soc. Rev.* **2014**, *43* (5), 1734–1787.

(13) Glaser, T. Rational Design of Single-Molecule Magnets: A Supramolecular Approach. *Chem. Commun.* **2011**, 47 (1), 116–130.

(14) Mihalčiak, J.; Bertová, P.; Růžičková, Z.; Moncol, J.; Segl'a, P.; Boča, R. Structure and Magnetism of Novel Dinuclear Cobalt(II) Complexes. *Inorg. Chem. Commun.* **2015**, *56*, 62–64.

(15) Dul, M. C.; Pardo, E.; Lescouëzec, R.; Journaux, Y.; Ferrando-Soria, J.; Ruiz-García, R.; Cano, J.; Julve, M.; Lloret, F.; Cangussu, D.; Pereira, C. L. M.; Stumpf, H. O.; Pasán, J.; Ruiz-Pérez, C. Supramolecular Coordination Chemistry of Aromatic Polyoxalamide Ligands: A Metallosupramolecular Approach toward Functional Magnetic Materials. *Coord. Chem. Rev.* **2010**, *254*, 2281–2296.

(16) Férey, G.; Serre, C.; Mellot-Draznieks, C.; Millange, F.; Surblé, S.; Dutour, J.; Margiolaki, I. A Hybrid Solid with Giant Pores Prepared by a Combination of Targeted Chemistry, Simulation, and Powder Diffraction. *Angew. Chem., Int. Ed.* **2004**, *43* (46), 6296–6301.

(17) Kawano, M.; Fujita, M. Direct Observation of Crystalline-State Guest Exchange in Coordination Networks. *Coord. Chem. Rev.* 2007, 251, 2592–2605.

(18) Vittal, J. J. Supramolecular Structural Transformations Involving Coordination Polymers in the Solid State. *Coord. Chem. Rev.* 2007, 251, 1781–1795.

(19) Kole, G. K.; Vittal, J. J. Solid-State Reactivity and Structural Transformations Involving Coordination Polymers. *Chem. Soc. Rev.* **2013**, 42 (4), 1755–1775.

(20) Mukherjee, S.; Joarder, B.; Desai, A. V.; Manna, B.; Krishna, R.; Ghosh, S. K. Exploiting Framework Flexibility of a Metal-Organic Framework for Selective Adsorption of Styrene over Ethylbenzene. *Inorg. Chem.* **2015**, *54* (9), 4403–4408.

(21) Mori, W.; Hoshino, H.; Nishimoto, Y.; Takamizawa, S. Synthesis and Gas Occlusion of New Micropore Substance Rhodium-(II) Carboxylated Bridged by Pyrazine. *Chem. Lett.* **1999**, *28*, 331–332.

(22) Takamizawa, S.; Nakata, E. I.; Yokoyama, H. Synthesis of Novel Copper (II) Benzoate Pyrazine and Its Phase Transition Induced by CO2 Adsorption. *Inorg. Chem. Commun.* **2003**, *6* (6), 763–765.

(23) Takahashi, K.; Hoshino, N.; Takeda, T.; Noro, S. I.; Nakamura, T.; Takeda, S.; Akutagawa, T. Structural Flexibilities and Gas Adsorption Properties of One-Dimensional Copper(II) Polymers with Paddle-Wheel Units by Modification of Benzoate Ligands. *Inorg. Chem.* **2015**, *54* (19), 9423–9431.

(24) Nagarathinam, M.; Vittal, J. J. Anisotropic Movements of Coordination Polymers upon Desolvation: Solid-State Transformation of a Linear 1D Coordination Polymer to a Ladderlike Structure. *Angew. Chem., Int. Ed.* **2006**, 45 (26), 4337–4341.

(25) Dutta, B.; Sinha, C.; Mir, M. H. The Sunlight-Driven Photosalient Effect of a 1D Coordination Polymer and the Release of an Elusive Cyclobutane Derivative. *Chem. Commun.* **2019**, 55 (74), 11049–11051.

(26) van Heerden, D. P.; Barbour, L. J. Guest-Occupiable Space in the Crystalline Solid State: A Simple Rule-of-Thumb for Predicting Occupancy. *Chem. Soc. Rev.* **2021**, *50* (2), 735–749.

(27) Bale, A. S.; Meacham, C. A.; Benignus, V. A.; Bushnell, P. J.; Shafer, T. J. Volatile Organic Compounds Inhibit Human and Rat Neuronal Nicotinic Acetylcholine Receptors Expressed in Xenopus Oocytes. *Toxicol. Appl. Pharmacol.* **2005**, 205, 77–88.

(28) Boeglin, M. L.; Wessels, D.; Henshel, D. An Investigation of the Relationship between Air Emissions of Volatile Organic Compounds and the Incidence of Cancer in Indiana Counties. *Environ. Res.* **2006**, 100, 242–254.

(29) Vellingiri, K.; Kumar, P.; Kim, K. Coordination Polymers: Challenges and Future Scenarios for Capture and Degradation of Volatile Organic Compounds. *Nano Res.* **2016**, *9* (11), 3181–3208.

(30) Mukherjee, S.; Sensharma, D.; Qazvini, O. T.; Dutta, S.; Macreadie, L. K.; Ghosh, S. K.; Babarao, R. Advances in Adsorptive Separation of Benzene and Cyclohexane by Metal-Organic Framework Adsorbents. *Coord. Chem. Rev.* **2021**, *437*, 213852.

(31) SAINT Data Collection Software; Bruker AXS Inc.: Madison, WI, 2016.

(32) SADABS Data Correction Software; Bruker AXS Inc.: Madison, WI,2016.

(33) Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71*, 3–8.

(34) Sheldrick, G. M. SHELXS Version-2018/3 and SHELXL Version-2018/3: Programs for Crystal Structure Solution and Refinement; University of Göttingen: Göttingen, Germany. 2018.

(35) Barbour, L. J. X-Seed - A Software Tool for Supramolecular Crystallography. J. Supramol. Chem. 2001, 1 (4–6), 189–191.

(36) Barbour, L. J. X-Seed 4: Updates to a Program for Small-Molecule Supramolecular Crystallography. J. Appl. Crystallogr. 2020, 53, 1141–1146.

(37) *POV-Ray for Windows*; Persistence of Vision Raytracer Pty. Ltd.: Williamstone, 2004.

(38) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; Van De Streek, J. Mercury: Visualization and Analysis of Crystal Structures. *J. Appl. Crystallogr.* **2006**, 39 (3), 453–457.

(39) Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; Van De Streek, J.; Wood, P. A. Mercury CSD 2.0 - New Features for the Visualization and Investigation of Crystal Structures. *J. Appl. Crystallogr.* **2008**, *41* (2), 466–470.

(40) MacRae, C. F.; Sovago, I.; Cottrell, S. J.; Galek, P. T. A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G. P.; Stevens, J. S.; Towler, M.; Wood, P. A. Mercury 4.0: From Visualization to Analysis, Design and Prediction. *J. Appl. Crystallogr.* **2020**, *53*, 226–235.

(41) Barbour, L. J.; Achleitner, K.; Greene, J. R. A System for Studying Gas-Solid in Controlled Atmospheres Reaction Kinetics. *Thermochim. Acta* **1992**, 205, 171–177.

(42) Barbour, L. J. Crystal Porosity and the Burden of Proof. *Chem. Commun.* **2006**, No. 40, 1163–1168.

(43) Chen, C.; Goforth, A. M.; Smith, M. D.; Su, C.-Y.; Zur Loye, H.-C. [Co2(Ppca)2(H2O)(V4O12)0.5]: A Framework Material Exhibiting Reversible Shrinkage and Expansion through a Single-Crystal-to-Single- Crystal Transformation Involving a Change in the Cobalt Coordination Environment. *Angew. Chem., Int. Ed.* **2005**, *44*, 6673–6677.

(44) Kaneko, W.; Ohba, M.; Kitagawa, S. A Flexible Coordination Polymer Crystal Providing Reversible Structural and Magnetic Conversions. J. Am. Chem. Soc. 2007, 129, 13706–13712. (45) Bernini, M. C.; Gándara, F.; Iglesias, M.; Snejko, N.; et al. Reversible Breaking and Forming of Metal – Ligand Coordination Bonds: Temperature-Triggered Single-Crystal to Single-Crystal Transformation in a Metal – Organic Framework. *Chem.-Eur. J.* **2009**, *15*, 4896–4905.

(46) Demessence, A.; Long, J. R. Selective Gas Adsorption in the Flexible Metal – Organic Frameworks Cu(BDTri)L (L = DMF, DEF). *Chem. - Eur. J.* **2010**, *16*, 5902–5908.

(47) Zhang, Y.; Zhang, X.; Lyu, J.; Otake, K.; Wang, X.; Redfern, L. R.; Malliakas, C. D.; Li, Z.; Islamoglu, T.; Wang, B.; Farha, O. K. A Flexible Metal–Organic Framework with 4-Connected Zr6 Nodes. J. Am. Chem. Soc. **2018**, 140, 11179–11183.

(48) Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. The Cambridge Structural Database. *Acta Crystallogr.* **2016**, 72 (2), 171–179.

(49) Feldmann, W. K.; White, K.-A.; Bezuidenhout, C. X.; Smith, V. J.; Esterhuysen, C.; Barbour, L. J. Direct Determination of Enthalpies of Sorption Using Pressure-Gradient Differential Scanning Calorimetry: CO2 Sorption by Cu-HKUST. *ChemSusChem* **2020**, *13* (1), 102–105.