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Porous Polyrotaxane Coordination Networks Containing Two Distinct Conformers of a Discontinuously Flexible Ligand

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S Supporting Information

ABSTRACT: A new divergent homopiperazine-derived ligand N,N'-bis(4-carboxyphenyl)-1,4-diazacycloheptane H_2L has been prepared, containing a semirigid saturated heterocyclic core which is capable of providing multiple distinct bridging geometries. Reaction of H_2L with zinc acetate in DMSO gives a two-dimensional parallel interpenetrated polyrotaxane structure 1 in which the loops and *trans*-(ax,ax) twist chair conformers, respectively. By matching the distances between the solvated metal sites in the structure of 1, a related material 2 can be prepared incorporating the pillaring ligand *trans*-1,2-bis(4-pyridyl)ethylene **bpe**. Compound 2 displays a



similar polyrotaxane interpenetration mode, permitted by the presence of both *cis* and *trans* ligand conformers, but displays a three-dimensional 2.6⁹ topology related to the **dia** diamondoid network. The guest exchange and gas adsorption properties of both materials were investigated; while compound **1** displays poor stability to guest exchange and negligible gas uptake, the higher connectivity microporous compound **2** shows facile guest exchange and a surprisingly high CO₂ capacity of 12 wt % at 1 bar and 273 K, and a zero-loading enthalpy of adsorption of -32 kJ mol⁻¹. High-pressure adsorption isotherms also show moderate physisorption of H₂ and CH₄ within the material.

INTRODUCTION

The design and synthesis of functional coordination polymers is an area of undeniable interest in materials science and has seen enormous development in recent years.¹ Judicious ligand design has played a key role in many important developments in the field, with functionalities, such as photoluminescence, catalytic activity, guest recognition, and framework flexibility having been engineered into functional materials through the use of internally functionalized ligands.² In particular, framework flexibility engineered through conformational freedom of either the metal nodes or bridging ligands can lead to fascinating structural behavior.³ Nonetheless, ligands based on rigid aromatic core groups remain the dominant choice for the design and synthesis of porous coordination polymers.⁴ Although flexible ligands offer the possibility of unusual structural properties, the difficulty in predicting the extended structure of highly flexible architectures, and the tendency for flexible groups to distort to fill available void space, limits their applicability in many instances.⁵ Divergent ligands containing one or more flexible sp³ linker groups within their backbone are nonetheless relatively well-known, and tend to display a continuous range of bridging geometries related by one or more low-energy bond rotations.⁶ However, ligands with restricted flexibility can also be realized by incorporating saturated carbocyclic or heterocyclic functionality between

coordinating groups.⁷ To date, this approach has been most commonly employed using cyclohexane polycarboxylates,⁸ where conversion between diastereomers requires a chemical transformation, or 1,4-disubstituted piperazine species, where the diequatorial 1,4-substituted chair conformation is almost exclusively observed due to the large energy cost in adopting the other geometries.⁹ Currently, instances of divergent ligands capable of displaying structurally distinct, discontinuous and energetically similar bridging geometries under ambient conditions (without the need for, e.g., photochemical stimulus) remain uncommon. Nonetheless, the potential for fascinating and unique structural behavior exists in such systems.¹⁰ Herein, we report the synthesis of a semirigid ligand derived from 1,4diazacycloheptane, and the properties of two coordination polymers containing unusual polyrotaxane topologies permitted by the distinct geometric properties of the ligand.

RESULTS AND DISCUSSION

The ligand N,N'-bis(4-carboxyphenyl)-1,4-diazacycloheptane H_2L (Scheme 1) was prepared in good yield via hydrolysis of the reported nitrile precursor,¹¹ which was itself prepared by the reaction of 4-fluorobenzonitrile with homopiperazine.

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Scheme 1. Synthesis and Structure of H_2L , with Proton Numbering Scheme for ¹H NMR^{*a*}



^{*a*}Reagents and conditions: (i) 4-fluorobenzonitrile, DMSO, K_2CO_3 , 120 °C, 24 h; (ii) $HCl_{(aq),r}$ reflux, 48 h, then $KOH_{(aq),r}$ reflux, 12 h.

Examples of structurally characterized N,N'-diaryl-1,4-diazacycloheptanes are rare, with very few reports detailing solid-state structural studies on related compounds.¹² Of interest in such systems is the propensity for partial planarization of arylamine nitrogen atoms, hindered by the resulting ring strain, as well as the tendency for spontaneous interconversion of stereoisomers of saturated N-substituted nitrogen heterocycles. Structural investigation of related systems has shown that the dominant conformers can exhibit moderate energy barriers to interconversion.¹³ By these considerations, H₂L was expected to possess multiple stable conformations separated by nontrivial interconversion barriers. The very poor solubility of H_2L in common solvents necessitated the use of DMSO or DMSObased mixtures as the primary solvent for further reactions; attempts to react H₂L using DMF or other more common solvent mixtures returned only the unreacted ligand or poorly resolved mixtures.

Synthesis and Structure of *poly*-[Zn₂(L)₂(DMSO)] 1. Reaction of H₂L with zinc acetate in a 2:1 dimethyl sulfoxide:ethanol mixture at 100 °C gave colorless crystals of *poly*-[Zn₂(L)₂(DMSO)] 1 after 48 h, which were analyzed by single crystal X-ray diffraction using synchrotron radiation. The data were solved and the structural model refined in the triclinic space group $P\overline{1}$. The asymmetric unit contains two unique zinc(II) ions, both exhibiting tetrahedral coordination geometries, linked by three crystallographically unique bridging carboxylate groups, each coordinating in a μ_2 - κ O: κ O' coordination mode, shown in Figure 1. Zinc ion Zn1 is capped by another carboxylate group coordinating in a monodentate



Figure 1. Coordination environment in the structure of 1, with labeling scheme for metals and coordinating atoms. Hydrogen atoms and backbone disorder are omitted for clarity.

mode, while the fourth coordination site on Zn2 is occupied by the oxygen atom of a disordered DMSO ligand. The asymmetric unit of 1 contains one complete molecule of L and two additional halves of centrosymmetric L molecules. The acentric molecule of L adopts a twist-boat conformation with the two phenyl rings *cis*-(eq,ax) oriented, providing an interplanar angle of 84° between the two aromatic rings. The remaining L ligands, however, adopt twist-chair conformations with *trans*-diaxial oriented aromatic rings, in which the two aromatic rings on each molecule are parallel. The two conformers of L are shown in Figure 2. The overlapping of



Figure 2. (a) cis-(eq,ax) twist boat (top) and trans-(ax,ax) twist chair (bottom) conformers of L within the structure of 1. (b) Threading of a linear L group through the loop of an adjacent network. Hydrogen atoms and backbone disorder are omitted for clarity.

the noncentrosymmetric diazacycloheptane rings from these groups with crystallographic inversion elements complicates the geometric analysis of these conformers (Supporting Information); however, the relevant atom positions can be unambiguously resolved to show the overall geometry of each ligand.

Each dinuclear Zn_2 node connects into the extended network in two ways; the bent *cis*-oriented L groups provide two linkages between each pair of metal nodes, defining a rectangular loop of approximate (interatomic) dimensions 9 × 11 Å. The two linear *trans*-oriented L residues provide bridging between nodes in two directions, extending the looped structures into a 2-dimensional network. Interestingly, one of the linear L residues, which bridges two Zn_2 nodes with monodentate carboxylate groups, passes through the rectangular loop of an adjacent nonconnected network, shown in Figure 2.

The threading of a linear L ligand through the loop of an adjacent network extends the basic looped 2-dimensional network into a 2-fold parallel interpenetrated polyrotaxane network. This mode of interpenetration is the archetypal type IIIa polyrotaxane mode,¹⁴ where the otherwise trivial (6,3) network can instead be described by the 2.6⁵ topology, invoking

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2-membered rings to describe the interpenetration, shown in Figure 3. Only relatively minor $\pi - \pi$ and van der Waals



Figure 3. Polyrotaxane interpenetration mode observed between twodimensional sheets in the structure of 1, showing chemical connectivity (left) and topological representation (right) with networks colored separately. Hydrogen atoms and DMSO ligands are omitted for clarity.

interactions are observed between adjacent layers in the structure of **1**, and the loose packing of adjacent sheets results in undulating one-dimensional solvent channels, oriented parallel to the *c* axis. Although the contents of these channels could not be determined crystallographically, the combination of thermogravimetric and elemental analyses and the electron count provided by SQUEEZE¹⁵ suggests a void content of 3 DMSO molecules per Zn₂ unit (Supporting Information)

Synthesis and Structure of poly-[Zn₂L₂(bpe)_{0.5}] 2. The presence of a capping DMSO ligand preventing higher connectivity in the structure of 1 prompted an investigation into a pillaring approach to increasing the connectivity and stability of the material. Two dinuclear zinc nodes from adjacent sheets within the structure of 1 are oriented with DMSO ligands directed toward each other, with Zn-Zn separation of 11.609(5) Å, and an offset between the two parallel Zn-O bond vectors of 1.67 Å. These parameters are well-matched to bridging by trans-1,2-bis(4-pyridyl)ethylene bpe, which typically displays a bridging distance of ~13 Å, and provides an offset between the two parallel coordination bond vectors by virtue of the central trans-oriented double bond. Repeating the reaction of H₂L with zinc acetate at 100 °C in DMSO in the presence of bpe gave yellow block crystals after 48 h. Analysis by synchrotron X-ray diffraction provided a structural model of poly-[Zn₂L₂(bpe)_{0.5}] 2 in the triclinic space group $P\overline{1}$. The unit cell parameters of 2 are closely related to those observed in 1, with a $\sim 6\%$ decrease in volume (Table 1). The asymmetric unit of 2 contains an equivalent dinuclear zinc motif, with the DMSO ligand from 1 replaced by the pyridyl group of a **bpe** ligand, with a bridging distance of 13.218(4) Å, as shown in Figure 4. As was the case in 1, the L groups adopt two distinct geometries, with closely related structural parameters between the two compounds and equivalent bridging connectivity.

The similarities between the two compounds include the interpenetration of adjacent networks by threading of a linear *trans*-oriented L species through a rectangular Zn_2L_2 window defined by *cis*-oriented L residues. However, whereas $2D \rightarrow 2D$ parallel interpenetration was the result of these associations in 1, in 2 the 2-dimensional *poly*- $[Zn_2(L_2)]$ sheets are further linked by bridging **bpe** units. These additional linkages bridge metal nodes in the orthogonal direction to extend each network into 3 dimensions, resulting in an overall 2-fold interpenetrated 3-dimensional structure when considering the polyrotaxane

Table 1. Summary of Crystal and Refinement Statistics for Compounds 1 and 2

	1	2
empirical formula	$C_{40}H_{42}N_4O_9SZn_2$	$C_{44}H_{41}N_5O_8Zn_2\\$
formula weight	885.57	898.56
temp (K)	100	100
cryst syst	triclinic	triclinic
space group	$P\overline{1}$	$P\overline{1}$
a (Å)	10.766(2)	11.739(2)
b (Å)	12.993(3)	13.760(3)
c (Å)	20.035(4)	16.428(3)
α (deg)	76.46(3)	114.67(3)
β (deg)	85.52(3)	95.03(3)
γ (deg)	69.16(3)	92.65(3)
volume (Å ³)	2546.4(11)	2392.0(10)
Ζ	2	2
$\rho_{\rm calcd}~({\rm g/cm^3})$	1.155	1.248
$\mu \ (\mathrm{mm}^{-1})$	1.03	1.054
F(000)	916	928
radiation type	synchrotron $(\lambda = 0.7109)$	synchrotron ($\lambda = 0.7109$)
2\O range (deg)	4.792-52	2.748-55.882
reflns collected	53473	62638
independent reflns/ $R_{ m int}/R_{\sigma}$	9896 $[R_{int} = 0.1281, R_{\sigma} = 0.0678]$	11186 [$R_{int} = 0.0922$, $R_{\sigma} = 0.0516$]
reflns obs. $[I \ge 2\sigma(I)]$	7926	7766
data/restraints/ params	9896/128/625	11186/230/640
goodness-of-fit on F^2	1.044	1.042
final R indexes $[I \ge 2\sigma(I)]$	R1 = 0.0754, wR2 = 0.2102	$\begin{array}{l} \text{R1} = 0.0699, \\ \text{wR}_2 = 0.1868 \end{array}$
final R indexes [all data]	$\begin{array}{l} R1 = 0.0867, \\ wR_2 = 0.2196 \end{array}$	$\begin{array}{l} R1 = 0.1001, \\ wR_2 = 0.2080 \end{array}$
largest diff. peak/hole (e Å ⁻³)	1.21/-0.67	1.12/-1.22
CCDC deposition number	1487894	1487895
07 2n1 01 02 06 05 04 03 02 02 05		

Figure 4. Metal environment in the structure of 2 with labeling scheme for metal ions and coordinating atoms. Hydrogen atoms and backbone disorder are omitted for clarity.

interpenetration, shown in Figure 5. The topology of a single net in **2** is that of the *dia* diamondoid net (considering Zn_2 units as nodes), with looped connections on one out of every four linkages. As for **1**, however, since the interpenetration is such that the loops contain links from the other net passing through them, a 5-c net with 2.6° topology is more appropriate for a full description of the interpenetration. Although the inclusion of **bpe** groups reduces the available solvent-accessible volume somewhat compared to **1**, narrow one-dimensional channels remain in the structure of **2**, accounting for approximately 22% of the total unit cell volume (Figure 5).



Figure 5. (Top) Simplified schematic diagram showing the connectivity in compound 2; independent networks are colored red and blue, with linkages through **bpe** units colored green, showing the expansion from the 2-dimensional polyrotaxane structure of 1 to the three-dimensional network of 2. (Bottom) The calculated solvent-accessible area in the form of undulating one-dimensional channels within the structure of 2.

Gas Adsorption Studies. To probe the gas uptake properties of compounds 1 and 2, thermogravimetric analysis experiments were carried out. These experiments showed that neither of the as-synthesized compounds could be readily thermally activated, due to the low volatility of the DMSO guests. As such, both materials were soaked in a variety of exchange solvents to effect guest exchange to a more readily activated material. In the case of 1, both methanol and acetonitrile proved effective exchange solvents, with desolvation achieved at ~100 °C. Methanol exchange led to decomposition of the crystals, presumably by solvolysis of the metal sites. X-ray powder diffraction analysis of the MeCN-exchanged material showed some degree of crystallinity retention, albeit with conversion to a different crystalline phase, which is not necessarily surprising based on the expected flexibility of the bulk material. However, both CO_2 (273 K) and N_2 (77K) adsorption isotherms showed negligible uptake for the MeCN exchanged and thermally activated material (Supporting Information) suggesting that the solvent exchange and/or evacuation leads to the formation of a nonporous phase. This outcome is not unexpected for a low-dimensional material with no substantial interactions between layers.

Similar to 1, immersion of 2 in various solvents gave efficient exchange of the lattice DMSO and water molecules over 48 h, and thermogravimetric analysis showed that the exchange solvents were readily lost at low temperatures (Supporting Information). Using acetonitrile as the exchange solvent and with activation at 100 °C under dynamic vacuum overnight, CO_2 adsorption isotherms were carried out at 273, 298, and 308 K. These measurements, shown in Figure 6, revealed a relatively high CO_2 capacity for 2 of 68 cc(STP)/g at 273 K



Article



70

Figure 6. Low pressure CO_2 and N_2 adsorption isotherms for compound 2, measured in the pressure range 0-1 bar at the temperatures specified.

and 1 atm, corresponding to approximately 12 wt % uptake. The isosteric heat of adsorption for CO₂ was calculated from these data using a Virial equation (Supporting Information) and revealed a zero-loading value of approximately -32 kJ mol^{-1} , decreasing to approximately $-28 \text{ kJ} mol^{-1}$ at higher loading. These values are consistent with a relatively strong physisorption interaction, favored by the narrow channels in **2**.¹⁶ Nitrogen adsorption isotherms were measured at both 77 and 273 K in the pressure range 0–1 atm; only minimal uptake was observed at either temperature. CO2 is expected to be favored as a probe gas in such situations due to its smaller kinetic diameter compared to N2, as well as the much higher adsorption enthalpy for CO₂ dictating improved physisorption at higher temperatures. Excellent adsorption selectivity for CO₂ over N2 has been increasingly observed in ultramicroporous materials, which are now seen as a viable route toward various CO₂ separation technologies.¹⁷ Directly comparing the adsorbed quantities of CO2 and N2 from their singlecomponent isotherms at 273 K shows a volumetric ratio of adsorbed CO_2/N_2 which steadily decreases from a maximum of \sim 70 at 40 mbar flattening to a value of \sim 25 above 0.5 bar (Supporting Information).

Given the good performance for CO₂ adsorption displayed by 2 in the pressure range 0-1 bar, high-pressure adsorption isotherms for CO₂, CH₄, and H₂ were also measured, as shown in Figure 7. The CO₂ adsorption isotherm at high pressure (273 K) shows saturation at approximately 13 bar with a loading of 93 cc(STP)/g, or 15 wt %. Adsorption of H_2 at 77 K showed a maximum loading of 113 cc(STP)/g at 15 bar (1 wt %), while H₂ adsorption at 258 K gave a considerably lower maximum loading of 10 cc(STP)/g at 30 atm (Supporting Information). CH₄ adsorption carried out at 258 K revealed a maximum loading of 40 cc(STP)/g at 24 bar (approximately 2.5 wt %). Isosteric heat of adsorption calculations for CH₄ were carried out using isotherms measured at 258 and 273 K, and revealed a modest zero-loading enthalpy of adsorption of -23 kJ mol⁻¹, reducing to -18 kJ mol⁻¹ at saturation. Each isotherm displayed a smooth desorption curve corresponding closely to the adsorption branch. Following the adsorption experiments, X-ray powder diffraction analysis of the material was carried out (Supporting Information), which showed the crystallinity of the framework was retained throughout the solvent exchange, desolvation and adsorption process.



Figure 7. High pressure isotherms for CH_4 , CO_2 , and H_2 with desorption branches shown in gray. The negative slope for CO_2 and H_2 at pressures above the saturation pressure are ascribed to the well-known surface excess phenomenon discussed by Menon,¹⁸ and occur when the density of gas in the bulk phase approaches that of the adsorbed phase, causing the adsorbed quantity to be slightly underestimated.

Discussion. From the striking similarities in the behavior of L in the structures of 1 and 2, the two observed ligand conformers can be considered as accessible and robust linking tectons. A slight contraction in the interplanar angle within the cis-(eq,ax) conformer is observed in compound 2, at 68° compared with 84° in 1. This flexing behavior, presumably in response to the changes in the crystal packing properties of the two materials, is similar to that observed in other cleft-shaped molecules with saturated heterocyclic cores, the most obvious of which being the Tröger's Base motif.¹⁹ The crystal packing behavior of Tröger's Base analogues is also very often influenced by C-H··· π interactions involving the π system of the central cleft.²⁰ Similarly, in the case of compounds 1 and 2, such interactions are also present between the encapsulated homopiperazine ring and the surrounding aromatic groups, where at least one carbon atom from each of the four aromatic rings of the loop lies within 3.5 Å of a CH_2 carbon atom within. In the absence of strong electrostatic or classical hydrogen bonding templation, common for discrete rotaxanes,²¹ these interactions may play a role in directing the entanglement of the cis and trans conformers.

The gas adsorption behavior of 2 is relatively standard for narrow-pore porous coordination polymers; although the total adsorption capacity is short of that typically observed in rigid micro- and mesoporous frameworks, the higher enthalpy of adsorption for CO₂ leads to steeper uptake in the low pressure region, an important consideration for potential gas separation applications. Although the low pressure N₂ isotherm revealed negligible adsorption at 77 K, the material showed moderate uptake capacity for the smaller probe gas H₂ at 77 K and the similarly sized probe gas CH₄ at 258 K. These observations may imply a kinetic barrier to guest diffusion for N₂ at 77 K² although not to the same extent for the smaller probe molecule H₂ Excellent selectivity for CO₂ over CH₄, an important consideration for biogas applications, has previously been observed for flexible, narrow-pore materials;²³ however, in this instance the CO₂ and CH₄ adsorption isotherms are more comparable, with the molar ratio of adsorbed CO₂/CH₄ not exceeding ~5 across the loading range at 298 K.

We have prepared two related polyrotaxane networks 1 and 2 from a conformationally flexible diaryl-diazacycloheptane ligand L, and analyzed the structural, guest exchange and gas adsorption properties of each. In both cases, the presence of both trans-twist chair and cis-twist boat conformers of the ligand provided the necessary structural components to form both the rod and loop features of the interlocked structure. Compound 1, containing $2D \rightarrow 2D$ parallel interpenetrated networks, displayed poor gas adsorption characteristics, which we ascribe to structural collapse on evacuation. However, incorporation of the neutral pillaring ligand bpe provided the necessary structural reinforcement for the material to display permanent porosity, while retaining the key structural features observed in 1. These results represent progress in the use of discontinuous conformational flexibility in ligand design as a tool for engineering intricately entangled networks, with a view toward functional framework materials based on these structural features.

EXPERIMENTAL SECTION

Materials and Methods. All reagents and solvents were of reagent grade or better and were used as received from Sigma-Aldrich, Alfa Aesar or Merck. N,N'-bis(4-cyanophenyl)-1,4-diazacycloheptane was prepared according to published procedures.¹¹ NMR spectra were recorded on a Bruker AVANCE spectrometer operating at 400 MHz for ¹H and 100 MHz for ¹³C nuclei, with samples dissolved in d_{6} -DMSO. Melting points were recorded in air on an Electrothermal melting point apparatus and are uncorrected. Mass spectrometry was carried out using a Micromass Platform II ESI-MS instrument, with samples dissolved in Milli-Q water. Microanalysis was performed by the Campbell Microanalytical Laboratory, University of Otago, New Zealand, and the Science Centre, London Metropolitan University, London, England. Infrared spectra were obtained using an Agilent Cary 630 spectrometer equipped with an Attenuated Total Reflectance (ATR) sampler. Bulk phase purity of all crystalline materials was confirmed with X-ray powder diffraction patterns recorded with a Bruker X8 Focus powder diffractometer operating at Cu K α wavelength (1.5418 Å), with samples mounted on a zero-background silicon single crystal stage. Scans were performed at room temperature in the 2θ range 5–55° and compared with predicted patterns based on single crystal data. Thermogravimetric analyses were carried out using a Mettler-Toledo TGA/DSC 1 STARe instrument. Samples were heated at a rate of 5 $^{\circ}$ C min⁻¹ under a nitrogen purge flow of 30 mL min⁻¹. Gas adsorption experiments were carried out using a Micromeritics TriStar 3020 instrument (N2 and 0-1 atm CO2) or a Sieverts-type BELsorp-HP automatic gas sorption analyzer (H₂, CH₄, and high-pressure CO_2), using ultra high purity gases from BOC or Air Liquide. Nonideal gas behavior at high pressures of each gas at each measurement and reference temperature was corrected for. Source data were obtained from the NIST fluid properties Web site.²

Synthesis of H₂L1. A suspension of $N_{,N'}$ -bis(4-cyanophenyl)-1,4diazacycloheptane (3.20 g, 10.6 mmol) in concentrated hydrochloric acid (50 mL) was heated under reflux for 48 h. Following this period, the suspension was filtered, washed with 3×50 mL distilled water, and the solids were collected and suspended in a solution of potassium hydroxide (14 g, 250 mmol) in water (60 mL). This solution was heated at reflux for 12 h, and then cooled to room temperature and acidified with glacial acetic acid. The resulting white solids were filtered and exhaustively washed with water, followed by washing with methanol, and dried in air. Yield 2.69 g (74%). mp >300 °C; Found C, 63.03; H, 5.84; N, 7.74; Calculated for $C_{19}\dot{H}_{20}N_2O_4$ ·1.25H_2O C, 62.88; H, 6.25; N, 7.72%; $\delta_{\rm H}$ (DMSO- $d_{6\prime}$ 400 MHz) 1.97 (broad quint., 2H, ${}^{3}J = 5.6$ Hz, H³), 3.45 (broad t, 4H, ${}^{3}J = 5.5$ Hz, H²), 3.70 $(s, 4H, H^1)$, 6.79 (d, 4H, ${}^{3}J = 8.8$ Hz, H⁴), 7.73 (d, 4H, ${}^{3}J = 8.8$ Hz, H⁵), 12.05 (br, 2H, H⁶); $\delta_{\rm C}$ (DMSO- d_6 , 100 MHz) 22.87, 47.12, 47.92, 110.57, 117.12, 131.33, 150.63, 167.36; m/z (ESI⁻) 339.1

(100%, [M-H]⁻, calculated for $C_{19}H_{19}N_2O_4$ 339.1); ν_{max} (ATR, cm⁻¹) 2980m, 2901m, 2796m br, 2661m, 2559m br, 1664s, 1593s, 1521s, 1483w, 1461w, 1434m, 1404s, 1354m, 1318s, 1288s, 1225s, 1179s sh, 1128m, 1093w, 1031m, 964w, 928s, 829s, 767s, 695w.

Synthesis of *poly*-[Zn₂L₂(DMSO)] **1.** A mixture of zinc acetate dihydrate (40 mg, 180 μ mol) and H₂L (40 mg, 120 μ mol) in 6 mL of 2:1 DMSO:EtOH was dispersed by sonication and sealed in a glass vial, and heated at 100 °C. After 2 days, the resulting colorless crystals were isolated by filtration and washed with DMSO, and then EtOH. Yield 17 mg (33%). mp >300 °C; Found C, 49.34; H, 5.32; N, 5.18; calculated for C₄₀H₄₂N₄O₉S₁Zn₂·3(DMSO) C, 49.33; H, 5.40; N, 5.00%; ν_{max} (ATR, cm⁻¹) 3401w, 2927w, 1588s, 1539m, 1519m, 1387s, 1350s, 1329s, 1275m, 1245w, 1223w, 1194m, 1174w, 1148m, 1019s sh, 952m, 919m, 835m, 780s, 700m. Phase purity was confirmed with X-ray powder diffraction.

Synthesis of *poly*-[Zn₂L₂(bpe)] 2. A suspension of H₂L (40 mg, 120 μ mol), bpe (24 mg, 130 μ mol) and zinc acetate dihydrate (80 mg, 360 μ mol) in 4 mL of DMSO was heated in a sealed vial at 100 °C for 48 h. On cooling to room temperature, the yellow crystals were isolated by filtration, and washed with DMSO and ethanol. Yield 30 mg (56%). mp >300 °C; Found C, 51.56; H, 5.01; N, 6.23; calculated for C₄₄H₄₁N₅O₈Zn₂·3(DMSO)·2(H₂O) C, 51.37; H, 5.42; N, 5.99%; ν_{max} (ATR, cm⁻¹) 3411w br, 3059w, 2934w, 2825w, 1595s, 1545w, 1516m, 1387s, 1348s, 1329s, 1273w, 1245w, 1224m, 1192s, 1149m, 1074w, 1031m sh, 950w, 928m, 834m, 778s, 699m. Phase purity was confirmed with X-ray powder diffraction.

X-ray Crystallography. Collection and refinement statistics are summarized in Table 1. All data sets were collected on the MX2 (1) or MX1 (2) beamlines at the Australian Synchrotron, Victoria, Australia,²⁵ operating at 17.4 keV ($\lambda = 0.7109$ Å) with data collections conducted using BluIce control software.²⁶ The diffraction data were reduced, processed and multiscan absorption corrections carried out using the XDS software suite,²⁷ and anomalous dispersion corrections for the nonstandard wavelength were made in the final refinement using Brennan and Cowan data.²⁸ All data sets were solved using direct methods with SHELXS²⁹ and refined on F^2 using all data by full matrix least-squares procedures with SHELXL-2015³⁰ within the OLEX-2 GUI.³¹ The functions minimized were $\Sigma w (F_0^2 - F_c^2)$, with w = $[\sigma^2(F_o^2) + aP_2 + bP]^{-1}$, where $P = [\max(F_o^2)^2 + 2(F_c^2)^2]/3$. Nonhydrogen atoms were refined with anisotropic displacement parameters, while most hydrogen atoms were included in calculated positions with isotropic displacement parameters either 1.2 or 1.5 times the isotropic equivalent of their carrier atoms. Because of restrictions on AFIX behavior involving highly disordered atoms split over multiple symmetry-related orientations, several CH₂ hydrogen atoms for the disordered diazacycloheptane residues were added manually in appropriate restrained positions and applied the appropriate U_{iso} dependencies.

Both data sets contained substantial regions of diffuse electron density, and the contribution of these regions to the observed structure factors was accounted for using the SQUEEZE routine within PLATON.¹⁵ The residual electron counts were compared with microanalysis and thermogravimetric analysis data to conclude reasonable solvent occupancies for the disordered regions. Crystallo-graphic formulas, F(000), calculated density and absorption coefficient are based on the crystallographically located atoms only.

Both structures contain substantially disordered framework groups, mostly involving the linear *trans*-chair conformers, which overlap crystallographic inversion elements with a noncentrosymmetric diazacycloheptane fragment. As such, these groups were modeled with both orientations overlapped, splitting all diazacycloheptane atoms and between two and ten attached phenyl atoms, depending on the degree of disorder with distance from the inversion center (Supporting Information). To maintain a chemically sensible structure for both disordered contributors in each case, various DFIX restraints were required, and the anisotropic displacement parameters were restrained to isotropic approximations, rigid body approximations, or constrained as equivalent to nearby atoms, as required. A complete list of restraints and constraints employed in each refinement and discussions of specific refinement strategies are given in the _refine_special_details and _olex2_refinement_description sections of each crystallographic information file.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b01713.

Additional figures, additional gas adsorption data and fitting parameters, thermogravimetric analysis plots, and X-ray powder diffraction patterns (PDF) Crystallographic information files for compounds 1 and 2 (CIF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

CCDC 1487894–1487895 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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REFERENCES

(1) Foo, M. L.; Matsuda, R.; Kitagawa, S. Functional Hybrid Porous Coordination Polymers. *Chem. Mater.* **2014**, *26*, 310–322. Seoane, B.; Castellanos, S.; Dikhtiarenko, A.; Kapteijn, F.; Gascon, J. Multi-scale crystal engineering of metal organic frameworks. *Coord. Chem. Rev.* **2016**, *307*, 147–187. Kumar, A.; Madden, D. G.; Lusi, M.; Chen, K.-J.; Daniels, E. A.; Curtin, T.; Perry, J. J., IV; Zaworotko, M. J. Direct Air Capture of CO₂ by Physisorbent Materials. *Angew. Chem., Int. Ed.* **2015**, *54*, 14372–14377. Cui, Y.; Li, B.; He, H.; Zhou, W.; Chen, B.; Qian, G. Metal-Organic Frameworks as Platforms for Functional Materials. *Acc. Chem. Res.* **2016**, *49*, 483–493.

(2) Almeida Paz, F. A.; Klinowski, J.; Vilela, S. M. F.; Tomé, J. P. C.; Cavaleiro, J. A. S.; Rocha, J. Ligand design for functional metal-organic frameworks. *Chem. Soc. Rev.* **2012**, *41*, 1088–1110. Lu, W.; Wei, Z.; Gu, Z.-Y.; Liu, T.-F.; Park, J.; Park, J.; Tian, J.; Zhang, M.; Zhang, Q.; Gentle, T., III; Bosch, M.; Zhou, H.-C. Tuning the structure and function of metal-organic frameworks via linker design. *Chem. Soc. Rev.* **2014**, *43*, 5561–5593.

(3) Krause, S.; Bon, V.; Senkovska, I.; Stoeck, U.; Wallacher, D.; Többens, D. M.; Zander, S.; Pillai, R. S.; Maurin, G.; Coudert, F.-X.; Kaskel, S. A pressure-amplifying framework material with negative gas adsorption transitions. *Nature* **2016**, *532*, 348–352.

(4) Chen, T.-H.; Popov, I.; Kaveevivitchai, W.; Miljanić, O. Š. Metal-Organic Frameworks: Rise of the Ligands. *Chem. Mater.* **2014**, *26*, 4322–4325.

(5) Hawes, C. S.; Chilton, N. F.; Moubaraki, B.; Knowles, G. P.; Chaffee, A. L.; Murray, K. S.; Batten, S. R.; Turner, D. R. Coordination polymers from a highly flexible alkyldiamine-derived ligand: structure, magnetism and gas adsorption studies. *Dalton Trans.* 2015, 44, 17494–17507. Yang, W.; Liu, C.; Ma, Q.; Wang, C.; Wang, H.; Jiang, J. Metallomacrocycle-supported interpenetration networks assembled from binary N-containing ligands. *CrystEngComm* 2016, 18, 3506–3512. Hawes, C. S.; Hamilton, S. E.; Hicks, J.; Knowles, G. P.; Chaffee, A. L.; Turner, D. R.; Batten, S. R. Coordination Chemistry and Structural Dynamics of a Long and Flexible Piperazine-Derived Ligand. *Inorg. Chem.* 2016, 55, 6692–6702.

(6) Lin, Z.-J.; Lii, J.; Hong, M.; Cao, R. Metal-organic frameworks based on flexible ligands (FL-MOFs): structures and applications. *Chem. Soc. Rev.* 2014, 43, 5867–5895. Schneemann, A.; Bon, V.; Schwedler, I.; Senkovska, I.; Kaskel, S.; Fischer, R. A. Flexible metal-organic frameworks. *Chem. Soc. Rev.* 2014, 43, 6062–6096.

(7) Niekiel, F.; Lannoeye, J.; Reinsch, H.; Munn, A. S.; Heerwig, A.; Zizak, I.; Kaskel, S.; Walton, R. I.; de Vos, D.; Llewellyn, P.; Lieb, A.; Maurin, G.; Stock, N. Conformation-Controlled Sorption Properties and Breathing of the Aliphatic Al-MOF [Al(OH)(CDC)]. *Inorg. Chem.* **2014**, *53*, 4610–4620.

(8) Niekiel, F.; Ackermann, M.; Guerrier, P.; Rothkirch, A.; Stock, N. Aluminum-1,4-cyclohexanedicarboxylates: High-Throughput and Temperature Dependent in Situ EDXRD Studies. *Inorg. Chem.* **2013**, *52*, 8699–8705. Qiblawi, S. H.; LaDuca, R. L. Control of water molecule aggregations in copper 1,4-cyclohexanedicarboxylate coordination polymers containing pyridyl-piperazine type ligands. *J. Mol. Struct.* **2014**, *1058*, 163–172. Lannoeye, J.; Van de Voorde, B.; Bozbiyik, B.; Reinsch, H.; Denayer, J.; de Vos, D. An aliphatic copper metal-organic framework as versatile shape selective adsorbent in liquid phase separations. *Microporous Mesoporous Mater.* **2016**, *226*, 292–298.

(9) Ju, H.; Lee, E.; Kim, S.; Park, I.-H.; Lee, J.-H.; Lee, S. S. Cationdirected assembly of polyrotaxane and polycatenane. *CrystEngComm* **2016**, *18*, 2621–2625. Beeching, L. J.; Hawes, C. S.; Turner, D. R.; Batten, S. R. The influence of anion, ligand geometry and stoichiometry on the structure and dimensionality of a series of Ag¹bis(cyanobenzyl)piperazine coordination polymers. *CrystEngComm* **2014**, *16*, 6459–6468. Robinson, M. E.; Mizzi, J. E.; Staples, R. J.; LaDuca, R. L. Structural Chemistry and Properties of Metal Oxalates Containing a Long-Spanning Dipyridyl Ligand: Chain, Interpenetrated Diamondoid, Threaded-Loop Layer, and Self-Penetrated Topologies. *Cryst. Growth Des.* **2015**, *15*, 2260–2271. Xu, B.; Lin, X.; He, Z.; Lin, Z.; Cao, R. A unique $2D \rightarrow 3D$ polycatenation cobalt(II)-based molecule magnet showing coexistence of paramagnetism and canted antiferromagnetism. *Chem. Commun.* **2011**, *47*, 3766–3768.

(10) Mowat, J. P. S.; Groves, J. A.; Wharmby, M. T.; Miller, S. R.; Li, Y.; Lightfoot, P.; Wright, P. A. Lanthanide N,N'-piperazine-bis-(methylenephosphonates) (Ln = La, Ce, Nd) that display flexible frameworks, reversible hydration and cation exchange. *J. Solid State Chem.* **2009**, *182*, 2769–2778.

(11) Donkor, I. O.; Huang, T. L.; Tao, B.; Rattendi, D.; Lane, S.; Vargas, M.; Goldberg, B.; Bacchi, C. Trypanocidal Activity of Conformationally Restricted Pentamidine Congeners. *J. Med. Chem.* **2003**, *46*, 1041–1048.

(12) Pochodylo, A. L.; Wang, C. Y.; LaDuca, R. L. Layered and selfpenetrated cadmium isophthalate and 5-methylisophthalate coordination polymers containing bis(4-pyridylformyl)piperazine or bis(4pyridylmethyl)homopiperazine ligands. *Inorg. Chim. Acta* 2011, 370, 449–455. Ramirez-Montes, P. I.; Ochoa, M. E.; Rodríguez, V.; Santillan, R.; García-Ortega, H.; Rodríguez, P.; Farfán, N. Synthesis, characterization and X-ray analysis of new N,N'-disubstituted-1,4diazepanes. *Tetrahedron Lett.* 2012, 53, 5887–5890. (13) Cox, C. D.; McGaughey, G. B.; Bogusky, M. J.; Whitman, D. B.; Ball, R. G.; Winrow, C. J.; Renger, J. J.; Coleman, P. J. Conformational analysis of N,N'-disubstituted-1,4-diazepane orexin receptor antagonists and implications for receptor binding. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 2997–3001.

(14) Yang, J.; Ma, J.-F.; Batten, S. R. Polyrotaxane Metal-Organic Frameworks (PMOFS). *Chem. Commun.* **2012**, *48*, 7899–7912.

(15) Spek, A. L. PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 9–18.

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

(17) Chen, K.-J.; Madden, D. G.; Pham, T.; Forrest, K. A.; Kumar, A.; Yang, Q.-Y.; Xue, W.; Space, B.; Perry, J. J. P., IV; Zhang, J.-P.; Chen, X.-M.; Zaworotko, M. J. Tuning Pore Size in Square-Lattice Coordination Networks for Size-Selective Sieving of CO₂. *Angew. Chem., Int. Ed.* **2016**, *55*, 10268–10272. Scott, H. S.; Ogiwara, N.; Chen, K.-J.; Madden, D. G.; Pham, T.; Forrest, K.; Space, B.; Horike, S.; Perry, J. J. P., IV; Kitagawa, S.; Zaworotko, M. J. Crystal engineering of a family of hybrid ultramicroporous materials based upon interpenetration and dichromate linkers. *Chem. Sci.* **2016**, *7*, 5470– 5476. McCormick, L. J.; Duyker, S. G.; Thornton, A. W.; Hawes, C. S.; Hill, M. R.; Peterson, V. K.; Batten, S. R.; Turner, D. R. Ultramicroporous MOF with High Concentration of Vacant Cu^{II} sites. *Chem. Mater.* **2014**, *26*, 4640–4646.

(18) Menon, P. G. Adsorption at high pressures. *Chem. Rev.* **1968**, *68*, 277–294.

(19) Sergeyev, S. Recent Developments in Synthetic Chemistry, Chiral Separations, and Applications of Tröger's Base Analogues. *Helv. Chim. Acta* **2009**, *92*, 415–444.

(20) Kim, E.-I.; Paliwal, S.; Wilcox, C. S. Measurements of Molecular Electrostatic Field Effects in Edge-to-Face Aromatic Interactions and CH- π Interactions with Implications for Protein Folding and Molecular Recognition. J. Am. Chem. Soc. **1998**, 120, 11192–11193. Hawes, C. S.; Fitchett, C. M.; Batten, S. R.; Kruger, P. E. Synthesis and structural characterisation of a Co(II) coordination polymer incorporating a novel dicarboxy-Trögers base/bis-pyrazole mixed ligand system. Inorg. Chim. Acta **2012**, 389, 112–117.

(21) Beves, J. E.; Blight, B. A.; Campbell, C. J.; Leigh, D. A.; McBurney, R. T. Strategies and Tactics for the Metal-Directed Synthesis of Rotaxanes, Knots, Catenanes and Higher Order Links. *Angew. Chem., Int. Ed.* **2011**, *50*, 9260–9327. Langton, M. J.; Robinson, S. W.; Marques, I.; Félix, V.; Beer, P. D. Halogen bonding in water results in enhanced anion recognition in acyclic and rotaxane hosts. *Nat. Chem.* **2014**, *6*, 1039–1043.

(22) Sircar, S.; Wu, H.; Li, J.; Lueking, A. D. Effect of Time, Temperature and Kinetics on the Hysteretic Adsorption-Desorption of H₂, Ar and N₂ in the Metal-Organic Framework $Zn_2(bpdc)_2(bpee)$. *Langmuir* 2011, 27, 14169–14179. de Jonge, H.; Mittelmeijer-Hazeleger, M. C. Adsorption of CO₂ and N₂ on Soil Organic Matter: Nature of Porosity, Surface Area, and Diffusion Mechanisms. *Environ. Sci. Technol.* 1996, 30, 408–413.

(23) Noro, S.; Matsuda, R.; Hijikata, Y.; Inubushi, Y.; Takeda, S.; Kitagawa, S.; Takahashi, Y.; Yoshitake, M.; Kubo, K.; Nakamura, T. High CO_2/CH_4 Selectivity of a Flexible Copper(II) Porous Coordination Polymer under Humid Conditions. *ChemPlusChem* **2015**, *80*, 1517–1524. Noro, S.; Hijikata, Y.; Inukai, M.; Fukushima, T.; Horike, S.; Higuchi, M.; Kitagawa, S.; Akutagawa, T.; Nakamura, T. Highly Selective CO_2 Adsorption Accompanied with Low-Energy Regeneration in a Two-Dimensional Cu(II) Porous Coordination Polymer with Inorganic Fluorinated PF₆⁻ Anions. *Inorg. Chem.* **2013**, *52*, 280–285. Couck, S.; Denayer, J. F. M.; Baron, G. V.; Rémy, T.; Gascon, J.; Kapteijn, F. An Amine-Functionalized MIL-53 Metal-Organic Framework with Large Separation Power for CO_2 and CH_4 . *J. Am. Chem. Soc.* **2009**, *131*, 6326–6327.

(24) Thermophysical Properties of Fluid Systems. http://webbook. nist.gov/chemistry/fluid/ (accessed March 3, 2015). (25) Cowieson, N. P.; Aragao, D.; Clift, M.; Ericsson, D. J.; Gee, C.; Harrop, S. J.; Mudie, N.; Panjikar, S.; Price, J. R.; Riboldi-Tunnicliffe, A.; Williamson, R.; Caradoc-Davies, T. MX1: a bending-magnet crystallography beamline serving both chemical and macromolecular crystallography communities at the Australian Synchrotron. J. Synchrotron Radiat. **2015**, *22*, 187–190.

(26) McPhillips, T. M.; McPhillips, S. E.; Chiu, H.-J.; Cohen, A. E.; Deacon, A. M.; Ellis, P. J.; Garman, E.; Gonzalez, A.; Sauter, N. K.; Phizackerley, R. P.; Soltis, S. M.; Kuhn, P. Blu-Ice and the Distributed Control System: software for data acquisition and instrument control at macromolecular crystallography beamlines. *J. Synchrotron Radiat.* **2002**, *9*, 401–406.

(27) Kabsch, W. J. Automatic processing of rotation diffraction data from crystals of initially unknown symmetry and cell constants. *J. Appl. Crystallogr.* **1993**, *26*, 795–800.

(28) Brennan, S.; Cowan, P. L. A suite of programs for calculating xray absorption, reflection, and diffraction performance for a variety of materials at arbitrary wavelengths. *Rev. Sci. Instrum.* **1992**, *63*, 850– 853.

(29) Sheldrick, G. M. A short history of SHELX. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112–122.

(30) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3–8.

(31) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.