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Interchanged Hysteresis for Carbon Dioxide and Water Vapor Sorption in a Pair of Water-Stable, Breathing, Isoreticular, 2-Periodic, Zn(II)-Based Mixed-Ligand Metal-Organic Frameworks

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S Supporting Information

ABSTRACT: We report the synthesis of two isoreticular mixed-ligand metal-organic frameworks (MOFs), namely, $[Zn(\mu_2-ia)(\mu_2-bpe)]_{\mu}$. nDMF (1) and $[Zn(\mu_2-mia)(\mu_2-bpe)]_n \cdot nDMF$ (2), where ia = isophthalate, mia = 5methoxyisophthalate, bpe = 1,2-bis(4-pyridyl)ethane, and DMF = N,N'dimethylformamide. Single-crystal X-ray diffraction studies revealed that the structures of 1 and 2 consist of a 2-periodic, layer sql motif. Structures exhibit entanglement through interpenetration of neighboring frameworks to form a two-dimensional bilayer. Variable-temperature powder X-ray diffraction studies confirmed both structures retain crystallinity upon desolvation up to ~500 K. Although structurally similar, activated samples of 1 and 2 showed differing gas and vapor sorption capabilities. Despite activated 2 having the higher actual void space, activated 1 showed significantly higher sorption for carbon dioxide at 195 K, as well as significant hysteresis upon desorption.



Empirical evidence points toward weaker bilayer...bilayer interactions, which allow the separation of the bilayers, illustrating that small changes in functional groups within an isoreticular pair of MOFs may have a large tuning effect on sorption properties.

■ INTRODUCTION

Metal-organic frameworks (MOFs), which may consist of 1periodic, 2-periodic, or 3-periodic coordination networks comprised of a metal coordinated to organic linkers, have attracted widespread attention for their porosity and potential applications in separation chemistry, catalysis, molecular sensing, and gas storage.¹⁻⁵ The coordination of a metal ion with two different ligands, as in the case of mixed-ligand MOFs, allows the possibility of direction-dependent pore variation^{6,7} and thus has exciting implications for offering chemists control over the behavioral characteristics of these MOFs.^{8–10} Single-crystal-to-single-crystal (SC-SC) transformation, intriguing solid-state phenomena whereby structural changes occur without loss of monocrystallinity, may yield some insight into breathing mechanisms of particular MOFs, where solvent molecules are exchanged.¹¹⁻¹⁵ Variable-temperature single-crystal X-ray diffraction (VT-SCXRD) may be used to test directly whether SC-SC transformations occur upon desolvation at higher temperatures and whether any structural changes are evident.^{16,17} The study of isoreticular MOFs, which have the same network topologies but differ in their constituent ligands (or metal ions), may prove useful in not only determining the influence of the ligand on pore dimensions but also in yielding insight into the influence of small changes in functional groups on properties such as gas or vapor sorption. Introducing a methoxy group on a ligand as an electron-donating group may be advantageous in interacting with partial positive charges on adsorbed molecules as has

recently been studied for a pair of ligand-originated MOF isomers, that is, where the two MOFs are constituted of ligands that are isomers of each other.¹⁸ The water stability of MOFs remain an important challenge in various industrial applications due to the ubiquitous nature of water in many processes, for example, the selective sorption of carbon dioxide in flue gas mixtures $(CO_2/N_2 = 85/15)$, where water is a major component.¹⁹ Recently, Das et al. reported a Co(II) and Cu(II)-based water-stable MOF, both of which were shown to be highly selective toward CO₂ sorption.^{20,21} Factors such as the absence of coordinatively unsaturated metal centers, interpenetration, and higher basicity of ligands have been implicated as structural features that may add to the water stability of MOFs.²²

In this study, we synthesized two isoreticular, Zn-based mixed-ligand MOFs that have 1,2-bis(4-pyridyl)ethane as the common ligand and differ only in the introduction of a methoxy functional group on the isophthalate ligand in the case of the second MOF. The two novel MOFs have the formula $[Zn(\mu_2-ia)(\mu_2-bpe)]_n \cdot nDMF(1)$ and $[Zn(\mu_2-mia)(\mu_2-ia)(\mu_2-ia))$ bpe)], nDMF(2), respectively, where ia = isophthalate, mia = 5-methoxyisophthalate, bpe = 1,2-bis(4-pyridyl)ethane, and DMF = N,N'-dimethylformamide. The isophthalate/1,2-bis(4pyridyl)ethane combination of ligands with Zn has been previously employed by Zaworotko et al. in the construction of

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2-periodic, non-interpenetrated and 3-periodic, interpenetrated nets.²³ However, in the case of 1 and 2 the 2-periodic coordination nets form twofold interpenetrated bilayers, which are interdigitated with neighboring bilayers. These are similar to the crystal structures for two Zn(II)-based, threefold interpenetrated, 2-periodic MOFs constructed with the related ligands phenylenediacrylate/5-ethoxyisophthalate and 1,2-bis-(4-pyridyl)ethene.^{24,25} Despite these similarities, 1 and 2 do exhibit important differences in terms of the degree of interpenetration and the location of the solvent molecules, which impart significantly larger potential void spaces on these structures. Despite the very close structural similarities of 1 and 2 to each other they display remarkably different sorption behaviors of carbon dioxide at low temperature with significant hysteresis observed for 1, a phenomenon that is switched within the pair in the case of water sorption.

EXPERIMENTAL SECTION

Materials and Physical Measurements. All chemicals were acquired through commercial sources and used without further purification. Thermal analysis consisted of thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and hot stage microscopy (HSM). TGA was performed using a TGA Q500, and DSC was performed using a TA DSC25. HSM was performed using a Linkam THMS600 hot stage and Linkam TP92 control unit fitted to a Nikon SMZ-10 stereoscopic microscope. Crystals were placed on a coverslip under silicon oil to visualize solvent release using HSM. Images of thermal events were monitored with a Sony Digital Hyper HAD color video camera and visualized on the Soft Imaging System program analySIS. All thermal analyses were performed at a heating rate of 10 $^{\circ}$ C min⁻¹.

Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer in the $4-40^{\circ} 2\theta$ range. A step size rate of 0.015° sec⁻¹ was used, while X-rays were generated at 30 kV and 40 mA.

The gas and water vapor sorption experiments were performed using a Micromeritics 3Flex Surface Area Analyzer. The samples were prepared using a Micromeritics Flowprep with the flow of nitrogen over the samples for 12 h with continuous heating at 60 °C. Thereafter, samples were evacuated by heating at 200 °C for 3 h before the analysis started. The Brunauer–Emmett–Teller (BET) method was applied to data points where the slope of the Roquerol BET graph remained positive.

Preparation of $[Zn(\mu_2-ia)(\mu_2-bpe)]_n \cdot nDMF$ (1). The metal salt, Zn(NO₃)₂·6H₂O (100 mg, 0.34 mmol), was dissolved in 3 mL of H₂O and then stirred for 10 min. The organic linkers 1,2-bis(4byridyl)ethane (0.062 mg, 0.34 mmol) and isophthalic acid (0.056 mg, 0.34 mmol) were dissolved in a solvent solution of 4 mL of DMF and 2 mL of diethyl ether then stirred for 10 min. The solution of organic linkers was mixed with the metal salt solution with continuous stirring for a further 10 min followed by the addition of 0.2 μ L of H₂SO₄ acid (3 M) to aid dissolution. The resulting, clear solution was sealed in a 25 mL vial then heated in an oven at 90 °C for 48 h. Thereafter, the solution was cooled slowly to 30 °C at a rate of 10 °C per hour. Clear, block-shaped crystals were obtained within 10 d.

Preparation of $[Zn(\mu_2\text{-mia})(\mu_2\text{-bpe})]_n nDMF$ (2). The preparation followed a similar procedure to that of compound 1. The metal salt, $Zn(NO_3)_2$ ·6H₂O (100 mg, 0.34 mmol), was dissolved in 3 mL of H₂O and stirred for 10 min. The organic linkers 1,2-bis(4byridyl)ethane (0.062 mg, 0.34 mmol) and 5-methoxyisophthalic acid (0.066 mg, 0.34 mmol) were dissolved in 6 mL of DMF and then stirred for 10 min. The solution of organic linkers was mixed with the metal salt solution with continuous stirring followed by the addition of 0.2 μ L of H₂SO₄ acid (3 M). The resulting clear solution was sealed in a 25 mL vial and then heated in an oven at 90 °C for 48 h. Thereafter, the solution was cooled slowly to 30 °C at a rate of 10 °C per hour. Clear, block-shaped crystals were obtained immediately.

Single Crystal X-ray Diffraction Studies. For both 1 and 2, a suitable single crystal was mounted on a cryoloop using Paratone N oil. Single-crystal X-ray diffraction (SCXRD) data for each compound were collected using a Bruker Apex II DUO detector. Samples were irradiated with graphite monochromated Mo K α radiation of wavelength $\lambda = 0.71073$ Å generated at 50 kV and 30 mA. The Oxford Cryostream-700 unit maintained temperature control by streaming N_2 gas at a rate of 20 cm³ min⁻¹. Data reduction and unit cell refinement were performed with SAINT-Plus.²⁶ All intensity data were scaled and corrected for Lorentz-polarization and absorption effects using SADABS.²⁷ Structure solution and refinement were implemented using the crystallographic suite OLEX2.²⁸ The crystal structures were solved by SHELXT,²⁹ with subsequent refinement proceeding using the full-matrix least-square method, based on F^2 values against all reflections, including anisotropic displacement parameters for all non-H atoms, as employed in SHELXL-2018/3.³ All hydrogen atoms were placed using riding models (Csp^2-H) and $Csp^3 - H_{\text{methylene}}$: 0.93 Å, $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$; $Csp^3 - H_{\text{methyle}}$: 0.96 Å, $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C)$). X-Seed and MERCURY were used for generating high-quality images using POV-RAY, while MERCURY was also used to determine void spaces using a probe radius of 1.2 Å.31-33 Hirshfeld analyses of intermolecular interactions were performed with CrystalExplorer.34

RESULT AND DISCUSSION

Single Crystal X-ray Diffraction Studies. The unit cell parameters for MOFs 1 and 2 are very similar, as presented in Table 1, albeit that these compounds crystallize in different space groups. MOFs 1 and 2 are isoreticular, and therefore the description of the main structural features of 1 hold for 2 as

Table 1. Crystal and Refinement Data for MOFs 1 and 2

	1	2
ASU formula	C ₂₃ H ₂₃ N ₃ O ₅ Zn	C24H25N3O6Zn
formula weight	486.81	516.84
temperature/K	100.0	100.0
crystal system	orthorhombic	orthorhombic
space group	Pbca	Pbcn
a/Å	10.1799(8)	23.2656(12)
b/Å	17.9193(17)	10.1523(5)
c/Å	23.548(2)	19.7050(10)
α/deg	90	90
β /deg	90	90
γ/deg	90	90
volume/Å ³	4295.6(6)	4654.3(4)
Ζ	8	8
$ ho_{\rm calc}/{ m g~cm^{-3}}$	1.505	1.475
μ/mm^{-1}	1.185	1.101
F(000)	2016.0	2144.0
2θ range for data collection/deg	3.46 to 61.264	3.502 to 52.982
index ranges	$\begin{array}{l} -14 \leq h \leq 14, -25 \leq k \\ \leq 25, -33 \leq l \leq 33 \end{array}$	$\begin{array}{l} -29 \leq h \leq 29, -12 \leq k \\ \leq 12, -24 \leq l \leq 24 \end{array}$
reflections collected	151 995	66 730
independent reflections	$\begin{array}{l} 6627 \left[R_{\rm int} = 0.0903, \\ R_{\rm sigma} = 0.0296 \right] \end{array}$	$4817 [R_{int} = 0.0395, R_{sigma} = 0.0168]$
data/restraints/ parameters	6627/0/291	4817/0/310
goodness-of-fit on F ²	1.055	1.023
final R indexes $[I \ge 2\sigma(I)]$	$\begin{array}{l} R_1 = \ 0.0381, \ wR_2 = \\ 0.0978 \end{array}$	$\begin{array}{l} R_1 = 0.0261, \ wR_2 = \\ 0.0695 \end{array}$
final R indexes [all data]	$R_1 = 0.0487, wR_2 = 0.1039$	$\begin{array}{l} R_1 = 0.0321, \ wR_2 = \\ 0.0728 \end{array}$
largest diff peak/ hole/e Å ⁻³	0.69/-0.65	0.33/-0.34



Figure 1. (a) Coordination environment of Zn(II) in 1 with ASU atoms labeled. (b) 2-periodic framework of 1. (c, d) Bilayers in (c) 1 and (d) 2 formed by entanglement of neighboring 2-periodic frameworks that stack in an interdigitated fashion. DMF molecules, shown in space-fill mode. Hydrogen atoms are omitted for clarity.

well. The asymmetric unit (ASU) of 1 consists of a fully occupied Zn^{2+} cation, one neutral 1,2-bis(4-pyridyl)ethane ligand, one isophthalate ligand (5-methoxyisophthalate in the case of 2), and one fully occupied, uncoordinated DMF molecule (Figure 1a). The 2+ charge on the metal cation is balanced by the 2– charge on the doubly deprotonated ia ligand (mia ligand in 2). The Zn^{2+} cations are linked, as part of a 2-periodic framework (Figure 1b), through tetrahedral coordination via the two nitrogen atoms (N1 and N2) of the bpe ligands along the longest axis of 23.548 Å (23.266 Å in 2) as well as a single oxygen atom (O1 and O4) on of each the carboxylate groups of the isophthalate ligands along the

shortest axis of 10.180 Å (10.152 Å in 2). A single 2-periodic framework is entangled with its neighbor to form an interpenetrated bilayer (Figure 1c) with neighboring bilayers stacked in an interdigitated manner along the 17.919 Å axis (19.705 Å axis in 2).

The topology of the nets in both MOFs, formed when the metal ions and centroids of the aromatic ia and mia rings are taken as nodes, may be described **sql** nets that are, according to terminology used by Carlucci, Proserpio and Blatov et al., 2-periodic and two-dimensional (2D), the latter indicating that there is no finite coordination in the third dimension.³⁵ Topologically, the entanglement is also referred to as two-

Table	2.	Crystal	and	Refinement	Data for	Water	-Exchang	ged and	d Deh	ydrated	Forms	of	1 an	d 1	2
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	1W	1′ (195 K)	1′ (298 K)	2W	2′ (195 K)	2' (298 K)
ASU formula	$C_{20}H_{20}N_2O_6Zn$	$\mathrm{C_{20}H_{16}N_2O_4Zn}$	$C_{20}H_{16}N_2O_4Zn$	$C_{21}H_{22}N_2O_7Zn$	$C_{21}H_{18}N_2O_5Zn$	$C_{21}H_{18}N_2O_5Zn$
formula weight	449.75	413.72	413.72	479.77	443.74	443.74
temperature/K	100(2)	195(2)	298(2)	100(2)	195(2)	298(2)
crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	Pbca	Pbca	Pbca	Pbcn	Pbcn	Pbcn
a/Å	10.113(2)	10.154(3)	10.134(3)	23.1978(11)	23.2246(13)	23.236(2)
b/Å	17.913(3)	17.786(4)	17.966(5)	10.1635(5)	10.1622(6)	10.1511(9)
c/Å	23.299(4)	23.447(6)	23.416(7)	19.3156(10)	19.4663(12)	19.5507(19)
$\alpha/{ m deg}$	90	90	90	90	90	90
β /deg	90	90	90	90	90	90
γ/deg	90	90	90	90	90	90
volume/Å ³	4220.8(13)	4234.6(18)	4263(2)	4554.1(4)	4594.3(5)	4611.4(7)
Ζ	8	8	8	8	8	8
$ ho_{ m calc}/ m g~cm^{-3}$	1.416	1.298	1.289	1.400	1.283	1.278
μ/mm^{-1}	1.201	1.184	1.176	1.121	1.100	1.095
F(000)	1856.0	1696.0	1696.0	1984.0	1824.0	1824.0
2θ range for data collection/deg	4.944 to 52.644	3.474 to 56.458	3.478 to 52.68	3.512 to 52.812	3.508 to 52.872	3.506 to 52.882
index ranges	$-5 \le h \le 12, -22 \le k$ $\le 14, -28 \le l \le 14$	$\begin{array}{c} -7 \leq h \leq 13, -14 \leq k \\ \leq 23, -13 \leq l \leq 31 \end{array}$	$\begin{array}{l} -12 \leq h \leq 6, -14 \leq k \\ \leq 22, -29 \leq l \leq 12 \end{array}$	$-20 \le h \le 29, -12 \le k \le 10, -24 \le l \le 17$	$-20 \le h \le 29, -10 \le k \le 12, -21 \le l \le 24$	$-29 \le h \le 20, -10 \le k \le 12, -24 \le l \le 21$
reflections collected	11 967	13 315	11 366	15 985	16 181	16 305
independent reflections	4284 $[R_{int} = 0.0692, R_{sigma} = 0.0754]$	5199 $[R_{int} = 0.1098, R_{sigma} = 0.1278]$	4325 $[R_{int} = 0.1186, R_{sigma} = 0.1232]$	4674 $[R_{int} = 0.0369, R_{sigma} = 0.0370]$	4702 $[R_{int} = 0.0441, R_{sigma} = 0.0453]$	4725 $[R_{int} = 0.0506, R_{sigma} = 0.0504]$
data/restraints/ parameters	4284/0/265	5199/0/244	4325/0/244	4674/0/287	4702/0/263	4725/0/263
goodness-of-fit on F ²	1.186	0.911	0.919	1.014	1.043	0.928
final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$\begin{array}{l} R_1 = \ 0.1044, \ wR_2 = \\ 0.2162 \end{array}$	$\begin{array}{l} R_1 = \ 0.0702, \ wR_2 = \\ 0.1533 \end{array}$	$R_1 = 0.0707, wR_2 = 0.1548$	$R_1 = 0.0415, wR_2 = 0.1319$	$\begin{array}{l} R_1 = \ 0.0418, \ wR_2 = \\ 0.1068 \end{array}$	$\begin{array}{l} R_1 = \ 0.0443, \ wR_2 = \\ 0.1301 \end{array}$
final R indexes [all data]	$\begin{array}{l} R_1 = \ 0.1421, \ wR_2 = \\ 0.2300 \end{array}$	$R_1 = 0.1833, wR_2 = 0.2053$	$\begin{array}{l} R_1 = \ 0.1906, \ wR_2 = \\ 0.2108 \end{array}$	$\begin{array}{l} R_1 = 0.0565, \ wR_2 = \\ 0.1442 \end{array}$	$\begin{array}{l} R_1 = \ 0.0638, \ wR_2 = \\ 0.1172 \end{array}$	$\begin{array}{l} R_1 = \ 0.0751, \ wR_2 = \\ 0.1521 \end{array}$
largest diff peak/ hole/e Å ⁻³	1.81/-1.38	0.57/-0.49	0.45/-0.35	1.47/-0.63	0.56/-0.38	0.58/-0.30

dimensional; that is, 2D bilayers are formed (Figures S1 and S2). Channels, occupied by DMF molecules, are formed down the shortest axis of both 1 and 2.

DESOLVATION STUDIES—THERMAL ANALYSIS AND VARIABLE-TEMPERATURE X-RAY DIFFRACTION ANALYSES

Thermal analysis and variable-temperature powder X-ray diffraction were employed to characterize MOFs 1 and 2 and also to assess the suitability of these compounds for sorption studies. Both compounds were found to be highly thermally stable. The TGA thermogram of 1 shows a mass loss of 13.72% in the broad temperature range of 292-558 K, which starts off gradually and peaks by ~398 K, representing the loss of one DMF molecule (calculated 14.91%), followed by a plateau over a nearly 75 K range before decomposition starts at 573 K (Figure S3). The TGA thermogram of 2 shows a mass loss of 13.60% (calculated 14.47%) for the DMF mass loss in the broad range of 290-540 K, which also starts gradually and peaks by 418 K, followed by a plateau over a nearly 50 K range before the onset of decomposition starts at 558 K (Figure S4). This mass loss was followed by decomposition of the compound with continued heating to 723 K. DSC and HSM analyses were used to confirm the thermal events described in the TGA thermograms (Figures S5-S8), while VT-PXRD analyses indicate that the MOF framework structures of the bulk material of 1 and 2 remain largely intact upon solvent removal and up to >500 K, inferred from the close agreement of the experimental PXRD patterns

to those calculated from the single-crystal structures (Figure S9). Desolvated crystals of 1 and 2 (hereinafter 1' and 2', respectively) for structure determination, obtained through SC-SC transformation, were accessed via slightly different methods. Crystals of 1 were heated on a hot stage to 573 K, with SCXRD analysis after 24 h (Table 2) revealing that water was absorbed from the atmosphere (1W hereinafter). Subsequent in situ heating of the same crystal on the singlecrystal X-ray diffractometer to 393 K removed the adsorbed water from the crystals to produce 1'. Heating crystals of 2 on a hot stage to 573 K with subsequent structure determination revealed the presence of significant electron density corresponding to DMF; thus, another method of obtaining 2' was investigated. Instead, as-synthesized crystals of 2 were placed in water, which underwent solvent exchange after two weeks (hereinafter 2W). SCXRD confirmed the water exchange, after which in situ removal of the adsorbed water in the same crystal was achieved by heating it to 393 K (hereinafter 2'). Interestingly, the water-exchange experiment on 1, by immersing crystals of 1 in water, showed that 1W is obtained after 1 d. For both 1' and 2', SCXRD data were collected at 195 and 298 K for direct comparison with sorption studies at these temperatures (Table 2). There were no significant connectivity or conformational changes observed for the processes $1 \rightarrow 1W \rightarrow 1'$ and $2 \rightarrow 2W \rightarrow 2'$ (Figure 2).

Void Space Analyses. Void space analyses were performed on potential void spaces of 1, 1W, 2, and 2W, that is, when the solvent coordinates are deleted, as well as on the actual void spaces of the desolvated structures (1' and 2')



Figure 2. Crystal structures (from left to right) of the as-synthesized MOFs 1 and 2 (at 100 K), their water-exchanged (at 100 K) and subsequent dehydrated structures (at 195 K with mapped void spaces shown in orange).

Table 3. Void Space Anal	lyses of Potential Void and Actu	al Void Spaces of MOFs 1 and 2
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	1^a	2 ^{<i>a</i>}	$1W^a$	$2W^{a}$	1′ (195 K)	2′ (195 K)	1′ (298 K)	2′ (298 K)
void space percent per unit cell (%)	18.6	18.3	14.5	14.2	14.9	15.5	15.4	15.6
absolute void space per unit cell (Å ³ /unit cell)	801	851	614	646	631	712	655	719
volume of unit cell (Å ³)	4296	4654	4221	4554	4235	4594	4263	4611
atomic mass unit (amu) per unit cell	3309.8	3549.9	3309.8	3549.9	3309.8	3549.9	3309.8	3549.9
void space per atomic mass unit (ų/amu)	0.242	0.240	0.186	0.182	0.191	0.201	0.198	0.203
void space per gram of MOF (cm ³ /g)	0.145	0.143	0.111	0.109	0.114	0.120	0.118	0.121
^{<i>a</i>} Solvent molecule coordinates are deleted.								

determined at 195 and 298 K. The void space analyses on 1' and 2' were performed for direct comparison with sorption studies of the activated forms at these two temperatures, while the potential void space analysis served as a reference for conclusions that may be reached from the as-synthesized structures. The potential void spaces per unit cell for 1 (18.6% and 801 Å³) and 2 (18.3% and 851 Å³) are bigger than those of 1W (14.5% and 614 Å³) and 2W (14.2% and 646 Å³), respectively, indicating that the respective MOFs undergo a degree of "breathing" upon solvent exchange with water. This is further supported by smaller changes in the absolute void spaces when the MOFs are dehydrated. The void space in 2' is larger than in 1', which is counterintuitive, since at cursory inspection of the ligand one would expect the substitution of an H atom (in ia) by a bulkier methoxy group (in mia) to reduce the cavity size. Instead, the methoxy group is oriented in such a manner as not to protrude into the cavity, but instead it causes the bilayers in 2' to be further apart, as indicated by its ~19 Å axis, an increase of ~2 Å over the common axis in 1'. In our attempts to relate pore volumes to sorption studies

(which are typically reported in amount or volume of adsorbed gas per unit mass of activated material), we determined the void space per unit mass for each structure, since the molar masses of 1' and 2' are slightly different (Table 3). The table shows that the void space in 2' is large enough to offset its slightly higher molar masses so that the void space per unit mass of sample is also larger than that of 1' (5.3% larger at 195 K and 2.5% at 298 K). Thus, it would be expected that 2' would have a slightly higher sorption by mass for a given gas or vapor.

GAS AND VAPOR SORPTION STUDIES

At 298 K 1' and 2' both show appreciable CO₂ sorption, both exhibiting type-I isotherms (Figure 3). Despite an initial lag, 2' has the expected higher sorption with 39.3 cm³ (standard temperature and pressure (STP)) g^{-1} (0.78 CO₂ molecules per ASU) compared to 29.8 cm³ (STP) g^{-1} (0.55 CO₂ molecules per ASU) for 1' at 795 mmHg pressure. Initially, the same trend is observed at 195 K in terms of 2' having a higher uptake (64.4 cm³ (STP) g^{-1} at a pressure of 236 mmHg







Figure 4. C···C isolated interactions for curvedness property plotted onto Hirshfeld surface of (a) 1' (195 K) and (b) 2' (195 K) and fingerprint plots for (c) 1' (195 K) and (d) 2' (195 K).

corresponding to 1.28 CO₂ molecules per ASU) than 1' (53.6 cm³ (STP) g^{-1} at 236 mmHg corresponding to 0.99 CO₂ molecules per ASU). We note that sorption ratio of 2' to 1'(1.32) is significantly higher than the ratio of void space per unit mass of 2' to 1' (1.05), indicating that there are additional factors aiding the sorption of CO_2 in 2', the presence of the methoxy group possibly being one. However, after 275 mmHg pressure the isotherm of 1' has an inflection point and shows a marked increase in adsorption of CO₂ over a relatively short range up to 444 mmHg, after which it plateaus with an eventual uptake of 99.9 cm³ (STP) g^{-1} (1.84 CO₂ per ASU) at 709 mmHg pressure. This represents a near doubling of the amount of CO_2 that can be adsorbed by 1' over 2' at this temperature. Inflection points are usually indicative of structural changes, and a possible explanation is that the bilayers in 1' separate to accommodate, effectively, a second CO₂ molecule per ASU. However, this is difficult to justify in terms of isolated, intermolecular interactions alone for the structures of 1' and 2' at 195 K, since both structures have a C-H···O interaction in common between neighboring bilayers (C1-H1···O4 and C5-H5···O4 in 1' and 2', respectively), while 1', in fact, has an additional C–H $\cdots\pi$ interaction (C19– H19...N1-C1-C2-C3-C4-C5) between neighboring bilayers, which is absent in 2' (Tables S3 and S4). Hirshfeld surface analysis may provide some clue in that a greater percentage of C···H interactions (Table S5), which are generally attractive, are found in 2' than 1' (23.3% vs 22.4%), while 1' has a greater percentage of $H \cdots H$ interactions (36.9% vs 35.4%), which are generally repulsive. Furthermore, the mapping of the curvedness property onto the Hirshfeld surfaces indicate a red region over the phenyl ring of mia in 2', which is an indication of closer $\pi - \pi$ stacking interactions (Figure 4a,b). In both structures, the phenyl rings are the sections of the bilayers that interdigitate with those of neighboring bilayers. In 2' and 1', the centroids of the closest phenyl rings of neighboring bilayers are 3.843 and 4.054 Å apart, respectively. Also, in the fingerprint plots of the Hirshfeld surfaces, 2' has a "lighter blue" color at d_i and d_e of ~2.0 Å, indicating a larger percentage of interactions at distances associated with the π - π stacking regions (Figure 4c,d). The absence of these $\pi - \pi$ interactions in 1' may allow the relative movement of bilayers thus causing a second molecule of CO₂ per ASU to be adsorbed.

Upon desorption, a very large hysteresis step was evident for 1' with a sharp decrease in sorption to the lower plateau only occurring as from 83 mmHg (92.2 cm³ (STP) g⁻¹ corresponding to 1.70 molecules of CO₂ per ASU) to 55 mmHg (53.6 cm³ (STP) g⁻¹ corresponding to 0.99 molecules of CO₂ per ASU), which is ~200 mmHg (or $P/P_0 \approx 0.25$) lower than the sharp increase on the adsorption run. The isosteric heats (Q_{st}) of CO₂ adsorption were also determined for 1' and 2' from isotherms obtained from 273 to 298 K (Figures S12). The Q_{st} values for 1' were in the range of 27.8–28.2 kJ mol⁻¹ up to a coverage of 29.7 cm³ (STP) g⁻¹, while those for 2' started lower at 25.1 kJ mol⁻¹ but increased to 29.7 kJ mol⁻¹ at 29.7 cm³ (STP) g⁻¹ coverage, which is consistent with the 2' sorption isotherms at different temperatures initially lagging behind, but eventually surpassing, those of 1'.

1' and 2' both displayed interesting water vapor sorption behaviors (Figure 5). For 1' the sorption is moderate up to $P/P_0 = 0.13$, where it has adsorbed 18.7 cm³ (STP) g⁻¹ (0.34 H₂O molecules per ASU), after which a sudden increase in



Figure 5. Adsorption and desorption isotherms for water vapor sorption for 1' and 2'.

sorption occurs with the next recorded point at $P/P_0 = 0.14$ showing an adsorption of 53.7 cm³ (STP) g^{-1} (0.99 H₂O molecules per ASU). Subsequently, the sorption starts to plateau, but an inflection point occurs at $P/P_0 = 0.18$ and adsorption of 66.5 cm³ (STP) g^{-1} (1.23 molecules of H_2O per ASU) indicates a structural change occurring allowing a rapid increase in sorption with the maximum sorption being 115.7 cm³ (STP) g⁻¹ (2.14 molecules of H₂O) at $P/P_0 = 0.81$. The desorption isotherm is virtually superimposable on the adsorption isotherm, showing no signs of hysteresis. The water sorption for 2' shows a similar trend to that of 1' but with some distinct differences. The first significant accelerated increase in sorption occurs at $P/P_0 = 0.10$, where 2' has adsorbed 17.2 cm³ (STP) g^{-1} (0.34 H₂O molecules per ASU). Thus, the pores of 2' are more hydrophilic than those of 1', as the same amount of water is adsorbed at a lower relative pressure than in 1', and therefore an indication that the pores of 2' are more polar.^{19,36} This could also be the reason that CO_2 sorption in 2' is higher than expected based on the void space analysis alone (except at 195 K, where structural changes in 1' allow the sorption of a second molecule of CO_2 per ASU), the methoxy group in 2' creating a more polar environment. Unlike, in the case of 1' the increase in sorption is more modest with the isotherm inflection point at P/P_0 = 0.17 indicating a sorption of 29.4 cm³ (STP) g^{-1} (0.58 H₂O molecules per ASU). However, after this point the accelerated increase in sorption is significant over a short range, with the isotherm starting to plateau at $P/P_0 = 0.24$, the maximum sorption of 105.6 cm³ (STP) g^{-1} (2.09 H₂O molecules per ASU) occurring at $P/P_0 = 0.82$. Unlike in the case of 1', 2' shows a significant degree of hysteresis with significant desorption only occurring at $P/P_0 = 0.10$ and sorption of 84.2 cm³ (STP) g^{-1} (1.67 H₂O molecules per ASU), the next desorption point at $P/P_0 = 0.09$ corresponding to a sorption of 24.9 cm³ (STP) g⁻¹ (0.49 H₂O molecules per ASU).

Post water vapor sorption PXRD patterns prove that both MOFs are water stable (Figure S13). After the water sorption experiments the same samples were tested for their affinities for atmospheric water by in situ TGA and VT-PXRD experiments. The samples were desolvated on the TGA equipment and exposed to the atmosphere, which showed that these rehydrated to their original water content after ~10 min (Figure S14). This rapid water sorption guided the in situ VT-PXRD experiments, where a sample of 1W and 2W were heated to 373 K and subsequently cooled to 298 K while being

exposed to the atmosphere. Because of the rapid sorption of water, only the range of $7-12.5^{\circ} 2\theta$ was measured over a scan period of ~ 1 min to visualize the peaks at $\sim 9.9^{\circ}$ (1W) and $\sim 9.2^{\circ}$ (2W), which were the most affected by dehydration and rehydration (Figure S15). These peaks are either absent or greatly diminished at 373 K; however, they return close to their original intensities after 10 min of cooling. These experiments lead us to believe that with the inevitable exposure of samples to the atmosphere after initial evacuation of the DMF molecules, the as-synthesized crystals of 1 and 2 proceed through a hydrated phase even before being activated for sorption, that is, $1/2 \rightarrow 1W/2W \rightarrow 1'/2'$.

 \hat{N}_2 sorption isotherms at 77 K for 1' and 2' were not deemed appropriate to determine internal surface areas by BET analysis, as the shape of the isotherms did not conform to a type-I isotherm even though SC-SC transformations, SCXRD analyses, and sorption experiments with water and carbon dioxide indicate that 1' and 2' are microporous. This is supported by the relatively low BET analysis surface areas calculated from N₂ sorption data, which were 40 m² g⁻¹ and 72 $m^2 g^{-1}$ for 1' and 2', respectively. Bae et al. showed that, in the absence of reliable N₂ sorption data, CO₂ sorption at 273 K could be used to determine BET surface areas of ultramicroporous MOFs with pore diameters of less than 7 Å.³⁷ In this work, the CO₂ sorption isotherms at 273 K revealed virtually identical BET surface areas of 187 and 188 $m^2 g^{-1}$ for 1' and 2', respectively. The 298 K single-crystal structures of the desolvated forms (taken as the SCXRD analyses closest in temperature to those of the BET isotherms used), revealed channel diameters of 3.8 \times 4.9 Å² and 4.9 \times 4.6 Å² for 1' and $\mathbf{2}'$, respectively.³⁸ There is some controversy around the use of CO₂ sorption for determining BET surface areas;³⁹ however, we include these results in this work to compare sorption values 1' and 2' but also to show that CO_2 is more able to penetrate the structures than N₂. H₂ sorption was low for both MOFs, with 2' performing slightly better than 1' at 0.17 versus 0.11 wt % (Figure S16).

CONCLUSION

In conclusion, two isoreticular, mixed-ligand, 2-periodic MOFs were synthesized using $Zn(NO_3)_2 \cdot 6H_2O_1$, 1,2-bis(4-pyridyl)ethane and either isophthalic acid (in the case of 1) or 5methoxyisophthalic acid (in the case of 2). Single-crystal structures of the activated, desolvated forms (1' and 2') could be obtained through an intermediate, hydrated phase in each case. Despite their similar structures, 1' and 2' showed marked differences in their carbon dioxide sorption behaviors at 195 K. At this temperature, 1' adsorbs a second CO₂ molecule per ASU attributed to structural changes as indicated by an inflection point in its isotherm. We suggest that interbilayer separation, that is, through a "breathing" effect, may be the type of structural change that aids the sorption of this second CO₂ molecule per ASU. Void space analyses indicate that pore volumes, as well as unit cell axes along the bilayer stacking direction, change through the $1/2 \rightarrow 1W/2W \rightarrow 1'/2W$ transformations, suggesting that inter-bilayer separation is a plausible explanation. The methoxy group may initially aid carbon dioxide and water sorption in 2' (initial sorption is higher for 2' than for 1' in both cases); however, it may be indirectly responsible for retarding inter-bilayer separation in 2'. That transformations are more difficult in 2 is further supported by the empirical observations that direct SC-SC desolvation of 2 was not possible, whereas it was for 1.

Furthermore, complete water exchange with the as-synthesized crystals 2, to produce 2W, occurred over two weeks, whereas the same experiment on 1 (to produce 1W) was complete after 1 d. We have on a previous occasion shown that low-temperature CO_2 dioxide isotherms can reveal different sorption behaviors when compared to room-temperature sorption, possibly due to increased interaction strengths at lower temperatures.⁴⁰ The low-temperature sorption experiments show the utility of investigating these possibilities in the absence of high-pressure, room-temperature carbon dioxide sorption experiments. The carbon dioxide and water-sorption hysteresis behaviors are interchanged in the isoreticular MOF pair, possibly pointing to different modes of interaction of water and carbon dioxide molecules when adsorbed into the MOFs.

This work highlights that sorption behavior of isoreticular MOFs, even in the case of such closely related MOFs as described in this work, can be very different and may depend on a multitude of factors such as chemical functionality and "breathability", which may come into effect at different pressures. Therefore, continued investigation of subtle changes in MOF structures and their effects on properties such as gas sorption is warranted.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b03148.

Structural and thermal analysis of MOFs such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and hot stage microscopy (HSM) and variable temperature powder X-ray diffraction (VT-PXRD) are included along with several tables of supramolecular hydrogen bonding interactions in the frameworks. Adsorption and desorption isotherms are provided for gases N₂, H₂, and CO₂ (at different temperatures), as well as water vapor. The CO₂ heat of adsorption plots for both the frameworks are also provided (PDF)

Accession Codes

CCDC 1877607–1877614 contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via www. ccdc.cam.ac.uk/data_request/cif [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: + 44(0)1223– 336033; e-mail: deposit@ccdc.cam.ac.uk.

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