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# Flexible porous coordination polymers constructed from 1,2-bis(4-pyridyl)hydrazine *via* solvothermal *in situ* reduction of 4,4'-azopyridine†

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Solvothermal reactions of  $Zn(NO_3)_2$ , 1,4-benzenedicarboxylic acid (H<sub>2</sub>bdc), and 4,4'-azopyridine (azpy) in different conditions yielded [Zn(bdc)(bphy)]·DMF·H<sub>2</sub>O (**1a**, bphy = 1,2-bis(4-pyridyl)hydrazine, DMF = *N*,*N*-dimethylformamide) and [Zn(bdc)(bphy)]·EtOH·H<sub>2</sub>O (**1b**) with two-fold interpenetrated **dmp** topology and [Zn<sub>2</sub>(bdc)<sub>2</sub>(bphy)]·1.5EtOH·H<sub>2</sub>O (**2a**) and [Zn<sub>2</sub>(bdc)<sub>2</sub>(bphy)]·DMA·1.5H<sub>2</sub>O (**2b**, DMA = *N*,*N*-dimethylacetamide) with two-fold interpenetrated **pcu** topology. The *in situ* reduction of azpy to bphy was confirmed by single-crystal structures and LC-MS analyses of the acid-digested crystalline samples, as well as controlled solvothermal experiments. Removal of the guest molecules in **1a**/**1b** and **2a**/**2b** converts the materials to guest-free phases [Zn(bdc)(bphy)] (**1**) and [Zn<sub>2</sub>(bdc)<sub>2</sub>(bphy)] (**2**), respectively, which were identified by PXRD. CO<sub>2</sub> sorption experiments performed at 195 and 298 K showed low porosity for **1** and gated sorption behavior for **2**. At 298 K, **2** exhibits high selectivity for adsorbing CO<sub>2</sub> over CH<sub>4</sub>.

## Introduction

During the last decade, porous coordination polymers (PCPs) rapidly emerged as a new type of porous materials and have attracted considerable attention from scientists in many research fields.1-3 These kinds of materials possess some advantages such as high crystallinity, tunability of pore character and structural flexibility, when compared with the conventional porous materials, i.e. zeolites and activated carbons.4-9 Flexible PCPs are of special interest because the host frameworks can show structural rearrangements during sorption processes. Such structural transformations may be guest-dependent, and consequently the adsorbents are able to distinguish different adsorbates with high selectivity. Therefore, flexible PCPs may find applications in chemical sensors, switches, gas separation, etc.10 Generally, framework flexibility is imparted by weak bonding interactions,<sup>11-13</sup> sliding of multiple networks,14-16 changing coordination geometries,17 and/or rotation around single coordination/covalent bonds.18,19 Presently, rational design and synthesis of flexible PCPs are basically based on choosing suitable ligands.

On the other hand, novel coordination structures with *in situ* generated ligands (especially those that are inaccessible by direct preparation) have attracted considerable attention not only in coordination chemistry but also in organic chemistry for discovery of new organic reactions.<sup>20–22</sup> To date, many metal/ligand reactions have been found and used to generate a large number of coordination polymers.<sup>23–27</sup> For example, we have discovered and elucidated several types of copper-mediated, oxidative ligand conversions under solvothermal conditions, such as hydroxylation of 2,2'-bipyridyl-like ligands<sup>28</sup> and one-pot syntheses of the 3,5-disubstituted-1,2,4-triazole from organonitriles and ammonia.<sup>29</sup> We have also utilized these reactions to synthesize a series of novel supramolecular architectures with interesting photoluminescent and porous properties.<sup>22</sup>

Herein, we report flexible PCPs constructed by reactions of 4,4'-azopyridine and 1,4-bezenedicarboxlic acid with  $Zn(NO_3)_2$ . Interestingly, 4,4'-azopyridine was found to be *in situ* reduced to a flexible ligand 1,2-bis(4-pyridyl)hydrazine, giving two PCPs crystallizing in four different crystal structures, which showed interesting framework flexibility and gas sorption properties.

## **Experimental section**

#### Materials and general methods

Commercially available reagents were used as received without further purification. 4,4'-Azopyridine (azpy) was prepared according to a reported method (Fig. S1 and Fig. S2†).<sup>30</sup> ESI-MS spectra were measured on a SHIMADZU LCMS-2010A apparatus using an electrospray ionization source with MeOH as

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<sup>†</sup> Electronic supplementary information (ESI) available: PXRD patterns, TGA curve, additional plots, selected bond lengths and angles, and crystallographic data. CCDC reference numbers 822607–822610. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/c1dt10682a

the mobile phase. <sup>1</sup>H-NMR spectra were recorded on a Varian Mercury-Plus (300 MHz) spectrometer. Infrared spectra were recorded with a Bruker TENSOR 27 Fourier transform FT-IR spectrophotometer on KBr pellets in the range of 4000–400 cm<sup>-1</sup>. Elemental (C, H, and N) analyses were performed on a Perkin-Elmer 240 elemental analyzer. Thermogravimetry (TG) analyses were performed on a Netzsch TG 209 instrument in flowing N<sub>2</sub> with a heating rate of 10 °C min<sup>-1</sup>. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 AD-VANCE X-ray diffractometer with Cu-K $\alpha$  radiation. For variable-temperature PXRD measurements, the diffraction patterns at different temperatures were recorded after the sample had stayed at the respective temperature for 30 min in a N<sub>2</sub> atmosphere. CO<sub>2</sub> and CH<sub>4</sub> sorption measurements were performed with Belsorp-Max and Belsorp-HP automatic volumetric adsorption apparatus.

#### Synthesis

**[Zn(bdc)(bphy)]-DMF·H**<sub>2</sub>**O** (1a). An *N*,*N*-dimethylformamide (DMF) solution (9 mL) of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.074 g, 0.25 mmol), 1,4-benzenedicarboxylic acid (H<sub>2</sub>bdc, 0.042 g, 0.25 mmol), and azpy (0.046 g, 0.25 mmol) was sealed in a 15 mL Teflon-lined reactor and heated at 160 °C for 84 h, then cooled to room temperature. The products were washed with DMF and collected by filtration (0.0602 g, yield 37%). Anal. calcd. (%) for  $C_{21}H_{23}N_5O_6Zn: C, 49.76; H, 4.57; N, 13.82; found: C, 49.82; H,$ 4.52; N, 13.45. IR: 3239(m), 2510(w), 2481(w), 1621(w), 1618(s),1501(w), 1357(s), 1215(s), 1063(w), 1057(m), 1020(m), 828(m),750(m).

[Zn(bdc)(bphy)]-EtOH·H<sub>2</sub>O (1b). A similar synthesis procedure for 1a was adapted to prepare 1b, except that the DMF was replaced by EtOH (0.145 g, yield 90%). Anal. calcd. (%) for  $C_{20}H_{22}N_4O_6Zn$ : C, 50.06; H, 4.62; N, 11.68. found: C, 51.12; H, 4.36; N, 12.25. IR: 3245(m), 3141(w), 3040(w), 2998(w), 2791(w), 1616(s), 1501(w), 1359(s), 1216(s), 1061(m), 1020(s), 828(m), 750(m), 526(w).

 $[Zn_2(bdc)_2(bphy)]$ ·1.5EtOH·H<sub>2</sub>O (2a). An ethanol solution (9 mL) of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.0743 g, 0.25 mmol), H<sub>2</sub>bdc (0.042 g,

Table 1	Crystallographic	data and refinement	parameters for 1a	i, <b>1b</b> , <b>2a</b> and <b>2b</b>
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0.25 mmol), and azpy (0.023 g, 0.125 mmol) was sealed in a 15 mL Teflon-lined reactor and heated at 160 °C for 84 h, then cooled to room temperature. The product was washed with DMF and collected by filtration (0.1060 g, yield 76%). Anal. calcd. (%) for  $C_{29}H_{29}N_4O_{10.5}Zn_2$ : C, 47.56; H, 3.99; N, 7.65. found: C, 47.12; H, 3.54; N, 7.94. IR: 3390(m), 3022(w), 2480(w), 1634(s), 1566(m), 1389(s), 1201(w), 1016(w), 910(w), 826(m), 748(s), 552(m), 498(w).

[Zn<sub>2</sub>(bdc)<sub>2</sub>(bphy)]-DMA-1.5H<sub>2</sub>O (2b). A procedure similar to that for 2a was utilized to prepare 2b by using *N*,*N*-dimethylacetamide (DMA) in place of ethanol (0.137 g, yield 92%). Anal. calcd. (%) for  $C_{30}H_{30}N_5O_{10.5}Zn_2$ : C, 47.45; H, 3.98; N, 9.22. found: C, 47.82; H, 3.26; N, 9.65. IR: 3301(m), 3200(w), 3104(w), 2939(w), 2877(w), 2014(m), 1698(s), 1514(m), 1447(s), 1262(s), 1142(m), 1041(w), 860(s), 546(s), 478(s), 415(m).

#### Crystallography

All the single-crystal XRD data were collected on a Bruker Apex CCD area-detector diffractometer with Mo-K $\alpha$  radiation at 293(2) K. The structures were solved by the direct or Patterson methods and refined by the full-matrix least-squares method on  $F^2$ using SHELXTL. All hydrogen atoms were placed geometrically and anisotropic thermal parameters were used to refine all non-hydrogen atoms of the frameworks. Most disordered guest molecules in compounds **1a–2b** could not be modeled and their electron density peaks were removed by the SQUEEZE route in PLATON, and the amount of them were determined by TG results and elemental analyses. The crystal data and structure refinement results for these compounds are listed in Table 1.

#### **Results and discussion**

#### Synthesis

Solvothermal reactions of  $Zn(NO_3)_2$ , 1,4-benzenedicarboxylic acid (H<sub>2</sub>bdc) and 4,4'-azopyridine (azpy) in different conditions yielded four crystalline products, [Zn(bdc)(bphy)]·DMF· H<sub>2</sub>O (1a), [Zn(bdc)(bphy)]·EtOH·H<sub>2</sub>O (1b), [Zn<sub>2</sub>(bdc)<sub>2</sub>(bphy)]· 1.5EtOH·H<sub>2</sub>O (2a), and [Zn<sub>2</sub>(bdc)<sub>2</sub>(bphy)]·DMA·1.5H<sub>2</sub>O (2b).

	1a	1b	2a	2b
Formula	$C_{21}H_{23}N_5O_6Zn$	$C_{20}H_{22}N_4O_6Zn$	$C_{29}H_{29}N_4O_{10.5}Zn_2$	$C_{30}H_{30}N_5O_{10}SZn_2$
F.W.	506.81	479.79	732.30	759.33
Space group	Fdd2	Pnna	$P\bar{1}$	$P\overline{1}$
a/Å	28.942(3)	29.50(2)	10.877(7)	10.9028(13)
b/Å	58.653(5)	14.724(13)	17.619(12)	10.9453(13)
c/Å	21.5267(19)	10.274(9)	20.499(14)	15.8533(18)
α (°)	90	90	110.788(12)	88.159(2)
β(°)	90	90	93.326(13)	80.542(2)
γ(°)	90	90	90.408(12)	85.314(2)
$V/Å^3$	36 542(6)	4463(7)	3665(4)	1859.6(4)
Ζ	64	8	4	2
$D_{\rm c}/{\rm g~cm^{-3}}$	1.474	1.428	1.327	1.356
$\mu/\mathrm{mm}^{-1}$	1.122	1.143	1.363	1.347
GOF	1.000	1.005	1.004	1.009
$R_1^a (I > 2\sigma)$	0.0664	0.0600	0.0544	0.0412
$wR_2^b$ (all data)	0.1868	0.1677	0.1469	0.1105
Flack parameter	0.461(9)			

<sup>*a*</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>*b*</sup>  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .

**1a/1b** and **2a/2b** were synthesized by feeding ratios  $Zn(NO_3)_2$ : H<sub>2</sub>bdc: azpy = 1:1:1 and 1:1:0.5, respectively. Different solvents resulted in inclusion of different guests. Though their synthetic conditions were only slightly different, all phases were obtained in high purity, which were confirmed by PXRD patterns (Fig. S8†). Evidence of the *in situ* reduction of azpy to bphy will be discussed below.

#### Structures

X-Ray crystallographic analyses revealed that 1a and 1b crystallize in the orthorhombic space groups Fdd2 and Pnna, respectively, with very different cell parameters. There are four independent  $Zn^{\scriptscriptstyle 2+}$  ions, four  $bdc^{\scriptscriptstyle 2-}$  ligands and four bphy ligands in the asymmetric unit of 1a, but 1b contains only two independent Zn<sup>2+</sup> ions (both lie on the twofold axes with half occupancy), one bdc<sup>2-</sup> and one bphy (in general positions with no imposed symmetry). The coordination modes between the Zn<sup>2+</sup> ions, bdc<sup>2-</sup> and bphy ligands in the two structures are basically similar (Fig. 1a). Each  $Zn^{2+}$  ion in 1a/1b is four-coordinated with two carboxylate O atoms [Zn-O 1.925(3)-2.187(3) Å] from two bdc<sup>2-</sup> ligands and two N atoms [Zn–N 2.004(3)–2.073(3) Å] from two bphy ligands in distorted tetrahedral geometries. The other two carboxylate O atoms form either weak coordination or non-bonding with the Zn ion [Zn–O 2.299(4)–2.915(3) Å] (Fig. S4 and Table S1<sup>†</sup>). Each bdc<sup>2-</sup> ligand bridges two Zn<sup>2+</sup> ions by its two carboxylate ends, and each bphy ligand links two Zn<sup>2+</sup> ions by its two pyridine nitrogen atoms. Based on the following facts, the ligand in 1a/1b should be bphy rather than the starting agent azpy. The N-N bond lengths [1.365(5)-1.440(5) Å] in **1a**/**1b** are in good accordance with reported values of those in free bphy [1.3934(14) Å] and other compounds containing N-N single bonds [1.368(15)-1.434(17) Å],<sup>30-36</sup> and are obviously longer than the typical N=N bond length [1.2513(15) Å] in azpy.<sup>36</sup> Furthermore, the absolute values of C-N-N-C torsion angles [89.3(5)-100.8(5)°] in 1a/1b are distinctly deviated from the planar configuration of C-N=N-C moieties in azpy (180°), but similar to the reported value for the free bphy [84.37(3)°] (Table 2). As depicted in Fig. 1b, bdc<sup>2-</sup> and bphy ligands can be regarded as 2-connected edges, while Zn<sup>2+</sup> ions can be treated as 4-connected vertexes, forming a 3D uninodal 4-connected **dmp** net (vertex symbol 6.6.6.6<sup>2</sup>.8<sup>3</sup>). This kind of net is rare and has been only observed in several coordination polymers.<sup>37</sup> Two such **dmp** nets interpenetrate in



Fig. 1 Perspective views of a typical coordination environment of the zinc atoms, the simplified topology networks (dmp and pcu) and the 3D packing structures with two-fold interpenetration for 1a/1b (a, b, c) and 2a/2b (d, e, f). (cyan sphere, red stick, and blue stick represent Zn, bdc<sup>2-</sup>, and bphy, respectively).

**1a** and **1b**, inducing the solvent accessible voids to 30.3% and 28.5%, respectively (Fig. 1c).<sup>38</sup> The void was occupied by one DMF and one water molecules per formula unit in **1a**, and one EtOH and one water molecules per formula unit in **1b**, which were confirmed by TG and elemental analyses for crystal

Table 2 Comparison of the N–N/N=N bond lengths and torsion angles in hydrazine/azo derivatives

Compounds	N–N bond length [Å]	C–N–N–C torsion angle [°]	Ref.
azobenzene	1.253(3)	180	31, 33, 34
4,4'-azopyridine	1.2513(15)	180	30, 31, 34, 36
1,2-bis(4-pyridyl)hydrazine	1.3934(14)	84.37(3)	30, 31, 34, 36
1,2-diphenylhydrazine	1.394(5)	75.59(7)	31, 33, 34
1,2-bis(4-pyridyl)hydrazine	1.387(1)	136.5(2)	this work
la la	N2–N3 1.431(5) N6–N7 1.365(5) N10–N11 1.440(5) N14–N15 1.424(6)	100.8(5), -89.6(5), -89.3(5), -96.2(6)	this work
1b	N2–N3 1.386(8)	-98.7(7)	this work
2a	N2–N3 1.371(6) N6–N7 1.375(8)	-142.9(7), 149.4(6)	this work
2b	N3A–N4A 1.419(16) N3B–N4B 1.364(14)	-142.0(13), 144.5(14)	this work

samples. Though 1a and 1b have the same topology, there are some slight differences for the detailed coordination environments of the Zn<sup>2+</sup> ions and conformations of the bphy ligands. The coordination configuration of each Zn<sup>2+</sup> ion is different from each other, especially in the Zn ··· O distances of the weak coordination and/or non-bonding interactions between the metal and the carboxylate O atoms. The conformations of bphy ligands are also similar, but deviations from the free bphy ligand are evident. According to ab initio calculations, the stable C-N-N-C torsion angle of free bphy is  $136.5(2)^\circ$ , but the values are -89.3(5), -89.6(5), -96.2(6), and  $100.8(5)^{\circ}$  in **1a** and  $-98.7(7)^{\circ}$  in **1b** (Fig. S5 and Table S2<sup>†</sup>). Accordingly, it is probably the size of the bigger guests which results in the more serious deformation of the bphy ligands (DMF in 1a and EtOH in 1b). Combination of slightly different coordination geometries and flexible ligands endows the framework with various conformations, resulting in the different crystallographic symmetries of 1a and 1b.

**2a** and **2b** both crystallize in the triclinic space group  $P\overline{1}$ , but the unit-cell volume of 2b is almost half that of 2a. There are four Zn<sup>2+</sup> ions, four bdc<sup>2-</sup> and two bphy ligands in the asymmetric unit of 2a, but 2b contains only half that of 2a (Fig. 1d). The N-N bond lengths [1.364(14)–1.419(16) Å] and the absolute values of C-N-N-C torsion angles [142.0(13)-149.4(6)°] in 2a/2b are also consistent with those for bphy (Fig. S7 and Table S4<sup>†</sup>). The coordination modes between each independent Zn2+ ions, bdc2ligands, and bphy ligands in 2a/2b are also basically similar. Each  $Zn^{2+}$  ion in 2a/2b is five-coordinated with four carboxylate O atoms [Zn–O 2.007(4)–2.061(4) Å] from four  $bdc^{2-}$  ligands and one N atom [Zn-N 1.993(4)-2.018(3) Å] from one bphy ligand in a square-pyramidal geometry (Fig. S6 and Table S3<sup>†</sup>). Two Zn<sup>2+</sup> ions are bridged by four carboxylate groups from four bdc<sup>2-</sup> ligands, leading to a paddle-wheel dinuclear unit. Each bdc2- ligand bridges two dinuclear units by its two carboxylate ends, extending to a 2D sql net, which are pillared by bphy to form a 3D elongated primitive pcu net (Fig. 1e).<sup>39,40</sup> The overall 3D structure of 2a/2b is composed of a pair of such pcu nets interpenetrated with each other, with voids of 40.3% in 2a and 37.3% in 2b, which are occupied by 1.5 EtOH and 1 H<sub>2</sub>O molecules per formula in 2a and 1 DMA and 1.5 H<sub>2</sub>O molecules per formula in **2b** (Fig. 1f). The reason for the structural discrepancies between 2a and 2b is similar to that mentioned for 1a/1b. Though there is no obvious difference in the Zn<sup>2+</sup> coordination environment, the C–N–N–C torsion angles in **2a**  $[142.9(7)-149.4(6)^{\circ}]$  are larger than that  $[136.5(2)^{\circ}]$  in the free bphy and those in **2b**  $[142.0(13)-144.5(14)^{\circ}]$ .

#### Reduction of azpy to bphy

The reductions of aromatic azo compounds have been studied extensively and have focused on their electrochemical behavior by polarography, cyclic voltammetry, controlled-potential coulometry, electron spin resonance spectroscopy, and ultraviolet spectroscopy during the 1970s,<sup>31-35</sup> while few studies involving the reduction of 4,4'-azopyridine have been reported *via* other methods.<sup>36</sup> Launay's group reported the pH induced metal-to-ligand charge-transfer intramolecular redox reaction in an azpy/bphy system.<sup>30</sup> They also synthesized bphy by reducing azpy with granulated metallic Zn in ethanol and concentrated ammonia at 80 °C under argon. Williams *et al.* introduced azpy to synthesize hydrazopyridiniumcontaining [2]catenanes, and observed the reduction of azpy to hydrazopyridinium.<sup>41</sup> Recently, Beckhaus *et al.* isolated bphy as a byproduct using azpy as starting material.<sup>36</sup> Whereas, the reason for the reduction of azpy was unclear in the latter two examples.

Although X-ray crystallographic analysis strongly suggested the presence of bphy ligands in the four obtained crystal structures, we performed LC-MS analysis on the acid digested sample and control experiments to further confirm the *in situ* reduction of azpy (Scheme 1). Acetic acid was used to decompose the crystalline compounds, and then the resultant solution was analyzed by LC-MS, showing clearly one peak of bphy instead of azpy (Fig. S3†). Meanwhile, we also treated a sample of the starting material azpy with the above-mentioned conditions for LC-MS measurement, and the results showed azpy remained intact. Therefore it was confirmed that the ligands in **1a**, **1b**, **2a** and **2b** are bphy rather than azpy, and azpy was reduced to bphy during the reaction processes.



Scheme 1 Reduction of azpy into bphy.

In view of the lack of reduction ability for zinc nitrate and terephthalic acid, we speculated that the employed solvents were critical for the *in situ* reducing of azpy into bphy under solvothermal conditions. Different solvents including pure water were reacted with azpy under solvothermal condition without the addition of zinc ions or H<sub>2</sub>bdc ligands. LC-MS analysis indicated that the reduction of azpy to bphy can be furnished at 160 °C in water.

#### Framework stability

The TG curves show that **1a** releases one H<sub>2</sub>O molecule per formula unit (observed 3.8%, calc. 3.6%) below 145 °C and subsequently one DMF (observed 17.0%, calc. 16.7%) before 210 °C. **1b** shows a 9.3% of weight loss at about 90 °C and another 3.7% weight loss before 135 °C, which are respectively corresponding to an EtOH molecule (calc. 9.1%) and a water molecule (calc. 3.5%) per formula unit. **1a** and **1b** decompose similarly above 320–330 °C. (Fig. S9†). **2a** loses all its guest molecules (15.0%, calc. 14.6%) per formula unit. A step in weight loss before 190 °C is observed for **2b**, which is ascribed to the release of 1 DMA and 1.5 water molecules per formula unit (14.0%, calc. 13.7%). **2a** and **2b** also decompose similarly around 340–350 °C (Scheme 2).

The guest-free phases of **1a** and **1b** show new and similar PXRD patterns, confirming they have the same flexible frameworks, *i.e.*, **1** (Fig. S10†). When **1** adsorbs DMF or EtOH, **1a** or **1b** is recovered, respectively, whatever sample **1** was obtained. Analogously, **2a** and **2b** could be also transformed to the same activated phase of **2** after complete removal of their guests, but the crystallinity of **2** obtained from **2b** was poor (Fig. S11†). **2a** can be recovered from **2** by adsorption of EtOH, but **2b** can be hardly recovered even



Scheme 2 Relationships between 1a/1b, 1, 2a/2b and 2.

by exposing **2** to DMA vapor for several days. The reason may be that the DMA guests in **2b** were difficult to remove because of their large molecular size and high boiling points, making the framework partially collapse during activation.

#### Sorption studies

CO<sub>2</sub> sorption isotherms of 1 and 2 were measured at 195 K (Fig. 2). The  $CO_2$  uptake of 1 increased with increasing pressure and reach 25.6 cm<sup>3</sup> g<sup>-1</sup> at  $P/P_0 = 1$ . The low porosity indicated the coordination frameworks of 1a/1b were severely deformed into a relatively condensed phase after guest removal, which could be hardly opened by CO<sub>2</sub>. In contrast, 2 exhibited an interesting stepwise adsorption at 195 K. The adsorption isotherm gradually reached an uptake of 45.7 cm<sup>3</sup> g<sup>-1</sup> at  $P/P_0 = 0.1$ , indicating low porosity of 2, but being higher than 1. Then, it sharply increased to reach saturation at about  $P/P_0 = 0.3$ , indicating that the abrupt expansion of the framework largely extended the porosity. From the saturation uptake of 193 cm<sup>3</sup> g<sup>-1</sup>, the pore volume of 2 was calculated to be 0.34 cm<sup>3</sup> g<sup>-1</sup>, being similar to the calculated result of 0.35 cm<sup>3</sup> g<sup>-1</sup> from the single-crystal structure of **2a**. The isotherm of 2 showed a clear hysteresis, where desorption occurred at  $P/P_0$ < 0.05, being similar to reported sorption behavior of flexible frameworks.42



Fig. 2 Adsorption isotherms of  $CO_2$  at 195 K for 1 and 2.

Considering the gating sorption behavior of **2** may be utilized to selectively separate different gases,  $CO_2$  and  $CH_4$  sorption isotherms were also measured at 298 K with pressures up to 40 bar (Fig. 3). The  $CO_2$  isotherm is similar to that measured at 195 K and an uptake of 160 cm<sup>3</sup> g<sup>-1</sup> is reached at 40 bar. In contrast, almost no  $CH_4$  can be adsorbed up to 40 bar. Consequently, the  $CO_2/CH_4$  adsorption ratio is extremely large, which results from the fact that the flexible structure can be selectively opened by only  $CO_2$ . Common porous materials based on adsorption affinity only have relatively low selectivities. Finally, PXRD patterns of the samples after  $CO_2/CH_4$  sorption experiments matched well with **2**, indicating the reversibility of structure transformation during adsorption and desorption (Fig. S12†).



Fig. 3 Adsorption isotherms of  $CO_2$  and  $CH_4$  for 2 at 298 K and 0–40 bar.

#### Conclusions

In situ formation of 1,2-bis(4-pyridyl)hydrazine from reduction of 4,4'-azopyridine under solvothermal conditions has been found in the syntheses of two new porous coordination polymers crystallized as four crystalline phases. Inclusion of slightly different solvents distinctly changes the total symmetry of the framework, indicating flexibility in the frameworks and ligands. Depending on the topologies, the two types of frameworks exhibited very different sorption behaviors, one of which showed interesting gating adsorption of  $CO_2$ , which can be utilized to efficiently separate  $CO_2$  from CH<sub>4</sub>.

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