

Three-Dimensional Porous Cd(II) Coordination Polymer with Large One-Dimensional Hexagonal Channels: High Pressure CH₄ and H₂ Adsorption Studies

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A new porous and hydrothermally stable three-dimensional (3D) coordination polymer $\{[\text{Cd}(\text{bpydb})] \cdot 6\text{H}_2\text{O}\}_n$ (**1**) has been synthesized under solvothermal condition from a new rigid ligand 4,4'-(4,4'-bipyridine-2,6-diyl) dibenzoic acid (H₂bpydb) and Cd(NO₃)₂ · 6H₂O. Single crystal X-ray analysis shows that **1** has a 5-connected 4⁴6⁶ vma net with one-dimensional (1D) hexagonal channels filled with water molecules. Integrity of the framework is maintained upon removal of the water molecules by heating to result in a porous framework. Low pressure N₂ and high pressure H₂ and CH₄ sorption studies along with water adsorption studies were performed on this framework.

Introduction

Synthesis and characterization of porous coordination polymers (PCPs) are motivated by the prospect of generating a wide variety of materials with potentially important applications. These structures can be rapidly and conveniently built using the modular or tinker-toy approach where topology of multidentate ligands, as well as the coordination characteristics of the metal ions direct the self-assembly process. The design of PCPs with increasing pore size carries increasing risk of interpenetration where voids associated with one framework are occupied by one or more frameworks causing disappearance of the intended voids. In some cases, however, the PCPs generate large voids or channels that are occupied by solvent molecules as guests. Expulsion of these guest molecules by heating often causes breakdown of the framework. However, if the integrity

of the framework is maintained, then porous open frameworks are formed that are potentially important in gas adsorption,¹ catalysis,² separation,³ and other applications.⁴ Therefore, design of ligands that may lead to structures retaining permanent porosity is still a challenge. The search for new linkers is also quite relevant as carboxylate based PCPs frequently exhibit low hydrothermal stability.⁵ One of the strategies to increase the stability could be the combination of different donors in the same linker. Several PCPs constructed from imidazolates or pyrazolates⁶ and carboxypyrazolates⁷ show high chemical stability. During the course of the present studies, an octacobalt cluster based (3,12)-connected porous framework has been reported⁸ based on our ligand.

Herein, we describe the synthesis of the tripodal ligand, 4,4'-(4,4'-bipyridine-2,6-diyl) dibenzoic acid (H₂bpydb) which comprises two different functional groups, namely, carboxylate and pyridine (Scheme 1). When reacted solvothermally with Cd(II), a three-dimensional (3D) coordination polymer with hexagonal channels is formed. The channels are not empty but are occupied by H₂O molecules. Removal of the H₂O molecules by heating leaves the integrity of the framework intact as the X-ray powder patterns before and after heat treatment do not

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(1) (a) Li, J.; Kuppler, R. J.; Zhou, H.-C. *Chem. Soc. Rev.* **2009**, 1477. (b) Murray, L. J.; Dincă, M.; Long, J. R. *Chem. Soc. Rev.* **2009**, 1294. (c) Ma, S.; Zhou, H.-C. *Chem. Commun.* **2010**, 44. (d) Fukushima, T.; Horike, S.; Inubushi, Y.; Nakagawa, K.; Kubota, Y.; Takata, M.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2010**, 49, 4820. (e) Yang, W.; Lin, X.; Blake, A. J.; Wilson, C.; Hubberstey, P.; Champness, N. R.; Schroder, M. *Inorg. Chem.* **2009**, 48, 11067. (f) Neogi, S.; Navarro, J. A. R.; Bharadwaj, P. K. *Cryst. Growth Des.* **2008**, 8, 1554.

(2) (a) Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* **2009**, 1248. (b) Lee, J. Y.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, 38, 1450. (c) Horike, S.; Dincă, M.; Tamaki, K.; Long, J. R. *J. Am. Chem. Soc.* **2008**, 130, 5854. (d) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, 404, 982. (e) Ohmori, O.; Fujita, M. *Chem. Commun.* **2004**, 1586. (f) Shultz, A. M.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. *J. Am. Chem. Soc.* **2009**, 131, 4204. (g) Dybtsev, D. N.; Nuzhdin, A. L.; Chung, H.; Bryliakov, K. P.; Talsi, E. P.; Fedin, V. P.; Kim, K. *Angew. Chem., Int. Ed.* **2006**, 45, 916. (h) Uemura, T.; Kitaura, R.; Ohta, Y.; Nagaoka, M.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2006**, 45, 4112. (i) Wu, C. D.; Lin, W. *Angew. Chem., Int. Ed.* **2007**, 46, 1075. (j) Henschel, A.; Gedrich, K.; Kraehnert, R.; Kaskel, S. *Chem. Commun.* **2008**, 4192. (k) Ingleson, M. J.; Barrio, J. P.; Bacsá, J.; Dickinson, C.; Park, H.; Rosseinsky, M. J. *Chem. Commun.* **2008**, 1287.

(3) (a) Das, M. C.; Bharadwaj, P. K. *J. Am. Chem. Soc.* **2009**, 131, 10942. (b) Cychoz, K. A.; R. Ahmad, R.; Matzger, A. J. *Chem. Sci.* **2010**, 1, 293.

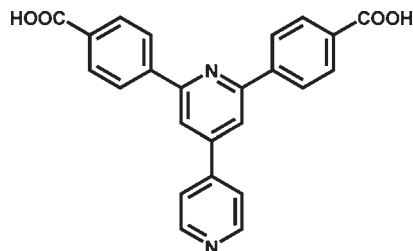
(4) (a) Min, K. S.; Suh, M. P. *J. Am. Chem. Soc.* **2000**, 122, 6834. (b) Fei, H.; Rogov, D. L.; Oliver, S. R. *J. Am. Chem. Soc.* **2008**, 132, 7202.

(5) (a) Cychoz, K. A.; Matzger, A. J. *Langmuir* **2010**, 26, 17198. (b) Küsgens, P.; Rose, M.; Senkova, I.; Fröde, H.; Henschel, A.; Siegle, S.; Kaskel, S. *Microporous Mesoporous Mater.* **2009**, 120, 325.

(6) Choi, H. J.; Dincă, M.; Dailly, A.; Long, J. R. *Energy Environ. Sci.* **2010**, 3, 117.

(7) Procopio, E. Q.; Linares, F.; Montoro, C.; Colombo, V.; Maspero, A.; Barea, E.; Navarro, J. A. R. *Angew. Chem., Int. Ed.* **2010**, 49, 7308.

(8) Hou, L.; Zhang, W.-X.; Zhang, J.-P.; Xue, W.; Zhang, Y.-B.; Chen, X.-M. *Chem. Commun.* **2010**, 6311.

Scheme 1. 4,4'-(4,4'-Bipyridine-2,6-diyl)dibenzoic acid (H₂bpydb)

show any significant change. Both methane and hydrogen adsorption properties of the resulting porous framework were studied. Also the water adsorption and the stability of the compound against moisture were examined. Use of PCPs as storage for energy carrier gases like methane⁹ and hydrogen¹⁰ have been actively pursued in several laboratories.

Experimental Section

Materials. The metal salt and other chemical reagents were procured from Aldrich and used as received. All the solvents were from S. D. Fine Chemicals, India. These solvents were purified following standard methods prior to use.

Synthesis of the Ligand. The ligand 4,4'-(4,4'-bipyridine-2,6-diyl)dibenzoic acid (bpydbH₂) has been synthesized in high yields via tandem Aldol condensation and Michael addition reactions of 4-pyridine carboxylaldehyde and 4-methyl acetophenone followed by cyclization and oxidation as described below.

(i). **Synthesis of 2,6-Di-*p*-tolyl-[4,4']bipyridinyl.** An aqueous solution of KOH (2.8 g, 50 mmol, 85%) was added into a solution of 4-pyridine carboxaldehyde (2.14 g, 20 mmol) and 4-methyl acetophenone (5.37 g, 40 mmol) in EtOH (100 mL) at 0 °C. The resulting solution was stirred for 2 h, and aq. NH₃ (60 mL, 29.3%) was then added. After the addition of aq. NH₃, the reaction mixture was allowed to warm up to room temperature (RT). It was then refluxed for 12 h. After this period, the mixture was cooled to 0 °C, and the solid formed was collected by filtration and washed with ice-cold EtOH (100 mL). Upon recrystallization from EtOH the desired product was obtained as a white crystalline solid. (Yield 51%). ¹H NMR (CDCl₃, 500 MHz): 8.79(broad, 1H; H_{Py}),

8.09–8.07 (d, *J* = 8.05 Hz, 2H; H_{Ar}), 7.82 (s, 1H; H_{Py}), 7.748–7.73 (d, 1H; *J* = 5.35 Hz, H_{Py}), 7.32–7.31 (d, *J* = 7.85 Hz, 2H; H_{Ar}), 2.43 (s, 3H; H_{Me}); IR (cm⁻¹, KBr pellet): 3103 (m), 2935 (m), 1599 (m), 1515 (m), 1305 (w); ESI-MS: *m/z* [M+H⁺] 337.16 (100%); calculated 336.16; Anal. Calcd for C₂₄H₂₀N₂: C, 85.68; H, 5.99; N, 8.33%. Found: C, 85.55; H, 5.91; N, 8.43%.

(ii). **Synthesis of 4,4'-(4,4'-Bipyridine-2,6-diyl) Dibenzoic Acid (bpydbH₂).** 2,6-Di-*p*-tolyl-[4,4']bipyridinyl (1.0 g, 2.98 mmol), concentrated HNO₃ (1 mL), and water (5 mL) were placed in a Parr Teflon-lined stainless steel autoclave which was heated under autogenous pressure to 180 °C for 24 h. The resulting yellow solid was washed with cold water (200 mL) and recrystallized in methanol to obtain the product as a bright yellow solid (Yield 86%). ¹H NMR (DMSO-*d*₆, 500 MHz): 8.82 (broad, 1H; H_{Py}), 8.43–8.42 (d, *J* = 3.5 Hz, 2H; H_{Ar}), 8.237 (broad, 1H; H_{Py}), 8.07 (d, *J* = 7.2 Hz, 2H; H_{Ar}), 7.98 (s, 1H; H_{Py}), ¹³C NMR (DMSO-*d*₆, 500 MHz): 167.63, 156.70, 145.61, 142.41, 134.93, 132.13, 130.36, 130.00, 127.78, 124.73, 118.99; IR (cm⁻¹, KBr pellet): 3068–2500 (broad), 1721(s), 1687 (s); ESI-MS: *m/z* [M+H⁺] 397.11 (100%); calculated 396.11; Anal. Calcd for C₂₄H₁₆N₂O₄: C, 72.72; H, 4.07; N, 7.07%. Found: C, 72.81; H, 4.12; N, 7.10%.

Preparation of {[Cd(bpydb)]_n·6H₂O}_n (1). A mixture containing bpydbH₂ (0.04 g, 0.10 mmol), Cd(NO₃)₂·4H₂O (0.031 g, 0.10 mmol), 3 mL of dimethylformamide (DMF), and 2 mL of EtOH was placed in a Teflon-lined autoclave, heated under autogenous pressure to 85 °C for 24 h, and then allowed to cool to room temperature at the rate of 1 °C per min. Triangular-shaped yellow crystals of **1** were collected and washed with DMF followed by acetone and finally dried in air. Yield ~40%. Anal. Calcd. for C₂₄H₂₆N₂O₁₀Cd: C, 46.88; H, 4.26; N, 4.56%. Found: C, 46.94; H, 4.31; N, 4.63%. IR (cm⁻¹): 3422 (broad), 1587(s), 1539(m), 1386(s).

Physical Measurements. Spectroscopic data were collected as follows: IR spectra (KBr disk, 400–4000 cm⁻¹) were recorded on a Perkin-Elmer Model 1320 spectrometer. X-ray powder patterns (CuK_α radiation, 3 deg/min scan rate, 293 K) were acquired using a Philips PW100 diffractometer. Thermogravimetric analysis (TGA) (5 °C/min heating rate under dinitrogen atmosphere) was performed with a Mettler Toledo Star System. ¹H NMR spectra were recorded on a JEOL JNM-LA500 FT instrument (500 MHz) in CDCl₃ and DMSO-*d*₆. Microanalyses for the compounds were obtained from CDRI, Lucknow, India.

Physisorption Measurements. N₂ and H₂ physisorption isotherms were measured at 77 K up to 1 bar pressure using a Quantachrome Autosorb1C apparatus. High-pressure H₂ adsorption measurements at 77 K up to 100 bar were performed using a volumetric BELSORP-HP apparatus. High pressure CH₄ adsorption was studied using a magnetic suspension balance (Rubotherm). The buoyancy corrections are performed as described earlier.^{9c} Water adsorption isotherms were measured with a Quantachrome Hydrosorb 1000 apparatus. High purity gases were used for the adsorption measurements (nitrogen: 99.999%, hydrogen: 99.999%, methane: 99.5%). Prior to all physisorption measurements, the samples were evacuated at 180 °C for 18 h.

X-ray Structural Studies. Single-crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized MoK_α radiation (0.71069 Å). The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The data integration and reduction were processed with SAINT^{11a} software. An empirical absorption correction was applied to the

(9) (a) Wu, H.; Zhou, W.; Yildirim, T. *J. Am. Chem. Soc.* **2009**, *131*, 4995. (b) Wood, C. D.; Tan, B.; Trewin, A.; Su, F.; Rosseinsky, M. J.; Bradshaw, D.; Sun, Y.; Zhou, L.; Cooper, A. I. *Adv. Mater.* **2008**, *20*, 1916. (c) Senkovska, I.; Kaskel, S. *Microporous Mesoporous Mater.* **2008**, *112*, 108. (d) Kondo, M.; Shimamura, M.; Noro, S.-i.; Minakoshi, S.; Asami, A.; Seki, K.; Kitagawa, S. *Chem. Mater.* **2000**, *12*, 1288. (e) Noro, S.-i.; Kitagawa, S.; Kondo, M.; Seki, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 2081. (f) Yang, W.; Lin, X.; Jia, J.; Blake, A. J.; Wilson, C.; Hubberstey, P.; Champness, N. R.; Schröder, M. *Chem. Commun.* **2008**, 359. (g) Lee, Y.-G.; Moon, H. R.; Cheon, Y. E.; Suh, M. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 7741. (h) Duren, T.; Sarkisov, L.; Yaghi, O. M.; Snurr, R. Q. *Langmuir* **2004**, *20*, 2683. (i) Bourrelly, S.; Llewellyn, P. L.; Serre, C.; Millange, F.; Loiseau, T.; Férey, G. *J. Am. Chem. Soc.* **2005**, *127*, 13519. (j) Kaye, S. S.; Dailly, A.; Yaghi, O. M.; Long, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 14176. (k) Kesani, B.; Cui, Y.; Smith, M. R.; Bittner, E. W.; Bockrath, B. C.; Lin, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 72. (l) Li, Y.; Yang, R. T. *J. Am. Chem. Soc.* **2006**, *128*, 8136.

(10) (a) Horcajada, P.; Serre, C.; Vallet-Regi, M.; Sebban, M.; Taulelle, F.; Férey, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 5974. (b) Rosi, N. L.; Eddaoudi, M.; Vodak, D. T.; Eckert, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127. (c) An, J.; Geib, S. J.; Rosi, N. L. *J. Am. Chem. Soc.* **2009**, *131*, 8376. (d) Furukawa, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **2009**, *25*, 8876. (e) Han, S. S.; Furukawa, H.; Yaghi, O. M.; Goddard, W. A. *J. Am. Chem. Soc.* **2008**, *130*, 11580. (f) Férey, G.; Latroche, M.; Serre, C.; Millange, F.; Loiseau, T.; Percheron-Guégan, A. *Chem. Commun.* **2003**, 2976. (g) Choi, H. J.; Dinca, M.; Long, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 7848. (h) Kanoo, P.; Matsuda, R.; Higuchi, M.; Kitagawa, S.; Maji, T. K. *Chem. Mater.* **2009**, *21*, 5860. (i) Chen, B.; Ma, S.; Zapata, F.; Lobkovsky, E. B.; Yang, J. *Inorg. Chem.* **2006**, *45*, 5718. (j) Gedrich, K.; Senkovska, I.; Baburin, I. A.; Mueller, U.; Trapp, O.; Kaskel, S. *Inorg. Chem.* **2010**, *49*, 4440. (k) Wang, X.-S.; Ma, S.; Sun, D.; Parkin, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 16474.

(11) (a) SAINT⁺, version 6.02; Bruker AXS: Madison, WI, 1999. (b) Sheldrick, G. M. *SADABS, Empirical Absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1997. (c) XPREP, version 5.1; Siemens Industrial Automation Inc.: Madison, WI, 1995. (d) Sheldrick, G. M. *SHELXTL Reference Manual*, version 5.1; Bruker AXS: Madison, WI, 1997. (e) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

collected reflections with SADABS^{11b} using XPREP.^{11c} The structure was solved by direct methods using SHELXTL^{11d} and refined on F^2 by full-matrix least-squares techniques using the SHELXL-97^{11e} program package. In compound **1**, atom OW(1), OW(2), OW(3), OW(4), OW(5), and OW(6) were refined isotropically, and all other non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the frameworks and water molecules could not be found in the difference Fourier maps. Therefore, all H atoms of framework **1** were placed in calculated positions using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. The crystal and refinement data are collected in Table 1.

Results and Discussion

Compound $\{[\text{Cd}(\text{bpydb})] \cdot 6\text{H}_2\text{O}\}_n$ (**1**) was synthesized by solvothermal reaction using $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and H_2bpydb

Table 1. Crystal and Structure Refinement Data for **1**

1	
formula	$\text{C}_{24}\text{H}_{14}\text{CdN}_2\text{O}_{10}$
formula weight	602.77
temperature	100 K
radiation	MoK_α
wavelength	0.71069 Å
crystal system	monoclinic
space group	Cc
a , Å	25.107(5)
b , Å	15.411(5)
c , Å	7.544(5)
α (deg)	90
β (deg)	106.999(5)
γ (deg)	90
V , Å ³	2791(2)
Z	4
ρ_{calc} g/cm ³	1.434
μ , mm ⁻¹	0.835
$F(000)$	1200
refl. collected	9025
R_{int}	0.0597
independent refl.	4333
refinement method	full-matrix least-squares on F^2
GOF	1.098
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0603$ $wR_2 = 0.1436$
R indices (all data)	$R_1 = 0.0855$ $wR_2 = 0.1864$

as starting materials in a mixture of DMF and ethanol (3:2 v/v) as solvent at 85 °C for 24 h. Once isolated, **1** is found to be air-stable and insoluble in common organic solvents as well as in water. A broad peak at 3422 cm^{-1} and strong absorption bands between 1587 and 1539 cm^{-1} in the IR spectrum of **1** are indicative of the presence of water molecules in the channels and of metal coordinated carboxylates, respectively (Supporting Information, Figure S7). Single crystal X-ray analysis shows that the structure can be converged successfully in the monoclinic space group Cc . The asymmetric unit consists of a Cd(II), one ligand, and six H_2O molecules. Each metal center shows distorted octahedral coordination geometry (Figure 1) with equatorial ligation from one pyridine, one monodentate, and one bridging carboxylate group from three different bpydb^{2-} units to form a two-dimensional (2D) (6,3)-connected layer. Axial coordination on each metal is provided by a carboxylate O from layers one above and the other below forming an overall 3D framework (Figures 2 and 3). The Cd–O bond distances lie in the range 2.199–2.483 Å while the Cd–N bond distance is 2.219 Å. All these bond distances are similar to those found in other octahedral Cd(II) complexes.¹² The layers are stacked in the $ABAB \cdots$ mode featuring 1D hexagonal channels of diameter ~ 10 Å (considering the van der Waals radii) viewed along the crystallographic c axis. This 3D framework can be described as a 5-connected vma net (RCSR symbol¹³) and Wells point symbol 4^6 , considering Cd(II) ions and bpydb^{2-} ligand as 5-connected nodes (Figures 4, 5 and 6).¹⁴ Coordination polymers possessing 5-connected nets are rare.¹⁵

The solvent accessible volume calculated from the crystal structure using the PLATON routine¹⁶ is 40.5% of the total crystal volume. Thermogravimetric analysis of **1** shows a weight loss of 17.9% in the range, 40–100 °C that corresponds to the loss of six water molecules (calcd. 17.6%). No further weight loss is observed until 380 °C (Supporting Information, Figure S13). For gas adsorption studies, **1** was activated by heating at 180 °C under vacuum for 18 h. The PXRD patterns before and after heat treatment (Supporting Information, Figure S14) confirm that integrity of the framework is maintained upon solvent removal.

Adsorption Studies. To evaluate porosity of the activated **1**, gas adsorption measurements were carried out with N_2 , H_2 ,

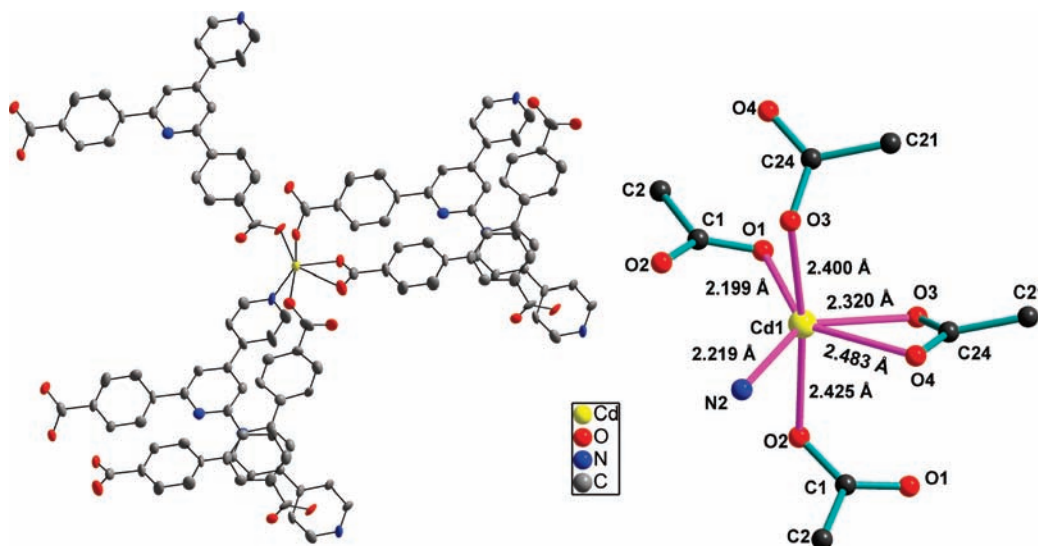


Figure 1. Perspective view of coordination environment of Cd(II) ion (left) showing the thermal ellipsoid (50% probability) and the bond lengths (right) in compound **1**. Hydrogen atoms are omitted for clarity.

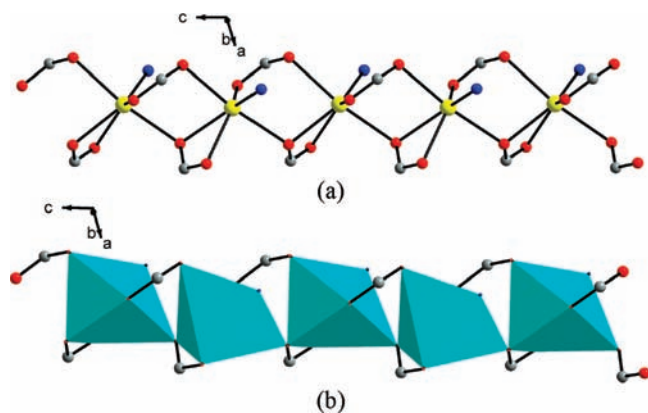


Figure 2. (a) View of **1**, showing extended chain of Cd(II) ions. (b) A polyhedral presentation of extended chain of Cd(II) ions.

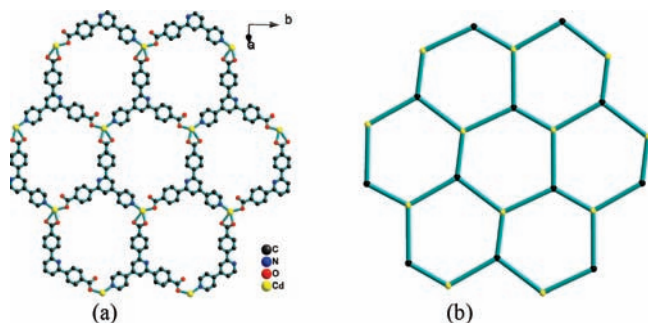


Figure 3. (a) Crystal structure showing 2D (6,3)-connected layer. (b) View of topological representation of (6,3)-connected layer of **1**.

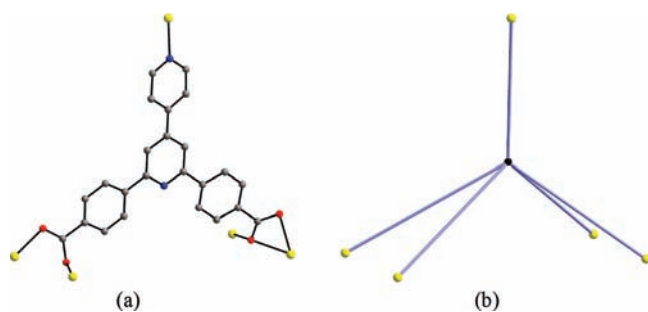


Figure 4. (a) View of coordination mode observed for the bpydbH₂ ligand. (b) 5-Connected ligand node in compound **1**.

and CH₄ under different experimental conditions. Unexpectedly, the nitrogen physisorption isotherm at 77 K (Figure 7) shows deviation from a typical type-I behavior. Initially it exhibits a steep rise at very low pressure region, suggesting porous nature of the framework. At p/p_0 of 0.7, the isotherm exhibits a sudden sharp rise and then attains saturation with

(12) Neogi, S.; Sharma, M. K.; Das, M. C.; Bharadwaj, P. K. *Polyhedron* **2009**, *28*, 3923.

(13) O'Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M. *Acc. Chem. Res.* **2008**, *30*, 1782, see also <http://rcsr.anu.edu.au/>.

(14) (a) The network topology was evaluated by the program "TOPOS-4.0", see: <http://www.topos.ssu.samara.ru/>; Blatov, V. A. *IUCr CompComm. Newsletter* **2006**, *7*, 4. (b) Blatov, V. A.; Shevchenko, A. P.; Serezhkin, V. N. *J. Appl. Crystallogr.* **2000**, *33*, 1193. (c) Blatov, V. A.; O'Keeffe, M.; Proserpio, D. M. *CrystEngComm* **2010**, *12*, 44.

(15) (a) Long, D. L.; Blake, A. J.; Champness, N. R.; Wilson, C.; Schröder, M. *J. Am. Chem. Soc.* **2001**, *123*, 3401. (b) Sun, H.-L.; Ma, B.-Q.; Gao, S.; Batten, S. R. *Cryst. Growth Des.* **2005**, *5*, 1331.

(16) Spek, A. L. *PLATON*; The University of Utrecht: Utrecht, The Netherlands, 1999.

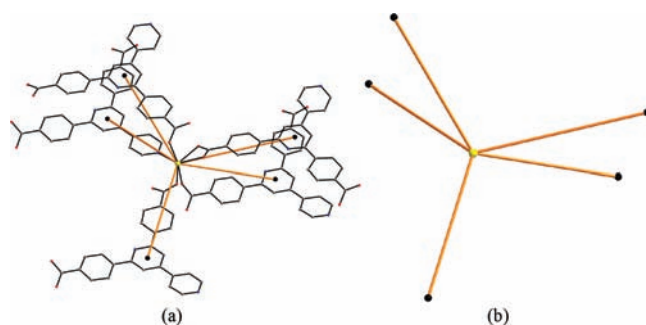


Figure 5. (a) View of coordination mode observed for Cd(II) ion. (b) 5-Connected metal node in compound **1**.

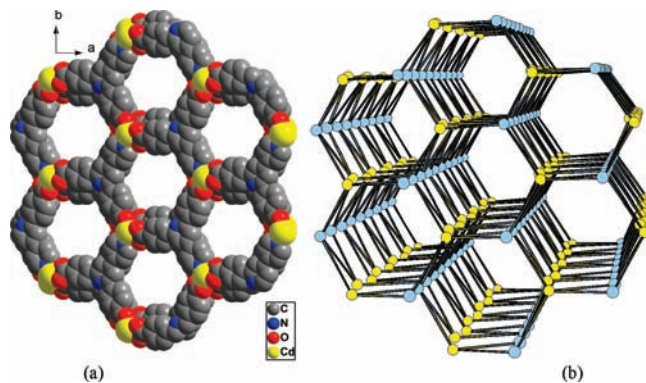


Figure 6. Crystal structure of **1**: (a) view of 1D hexagonal channels along c axis (guest molecules and H atoms are omitted for clarity). (b) view of the 5-connected vma net.

the adsorbed N₂ amount of 227 cm³ g⁻¹. A large hysteresis between the adsorption and desorption is observed revealing the trapping effect of the gas in the pores. The estimated Brunauer–Emmett–Teller (BET) surface area is 346 m² g⁻¹ (Supporting Information, Figure S15) while the total pore volume is 0.33 cm³ g⁻¹ ($p/p_0 = 0.7$) and 0.35 cm³ g⁻¹ (at $p/p_0 = 0.96$). The nitrogen adsorption measurements were performed three times on the same sample to examine the behavior of the framework **1** during the adsorption cycles and to exclude the possible network degradation (Supporting Information, Figure S16). The isotherms are extremely reproducible, which indicates the reversibility of adsorption/desorption and stability of the framework.

The hydrogen gas uptake studied at 77 K and up to 1 bar exhibits a typical reversible type-I isotherm with a capacity of 0.87 wt % (97 cm³ g⁻¹). At high pressure (43 bar) and 77 K hydrogen uptake of 1.6 wt % (Figure 8) is observed. Likewise, methane also exhibits a classical type-I adsorption isotherm up to 130 bar at 298 K (Figure 9). The maximum amount adsorbed is 58 mg g⁻¹ at 80 bar. The gravimetric methane uptake of **1** is lower than for the best PCPs like MIL-101 (239 mg g⁻¹ at 80 bar),¹⁷ DUT-6 (230 mg g⁻¹ at 100 bar),¹⁸ or MOF-210 (264 mg g⁻¹ at 80 bar).¹⁹ However, because of the relatively high

(17) Llewellyn, P. L.; Bourrelly, S.; Serre, C.; Vimont, A.; Daturi, M.; Hamon, L.; Weirald, G. D.; Chang, J.-S.; Hong, D.-Y.; Hwang, Y. K.; Jung, S. H.; Férey, G. *Langmuir* **2008**, *24*, 7245.

(18) Klein, N.; Senkova, I.; Gedrich, K.; Stoeck, U.; Henschel, A.; Mueller, U.; Kaskel, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 9954.

(19) Furukawa, H.; Ko, N.; Go, Y. B.; Aratani, N.; Choi, S. B.; Choi, E.; Yazaydin, A. O.; Snurr, R. Q.; O'Keeffe, M.; Kim, J.; Yaghi, O. M. *Science* **2010**, *329*, 424.

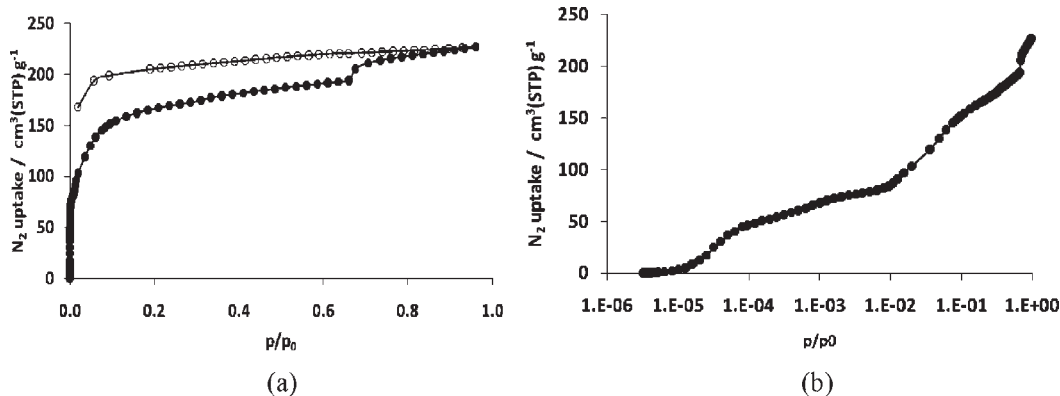


Figure 7. Nitrogen physisorption isotherm of activated **1** at 77 K (adsorption/desorption ●/○) in (a) linear scale and (b) logarithmic scale.

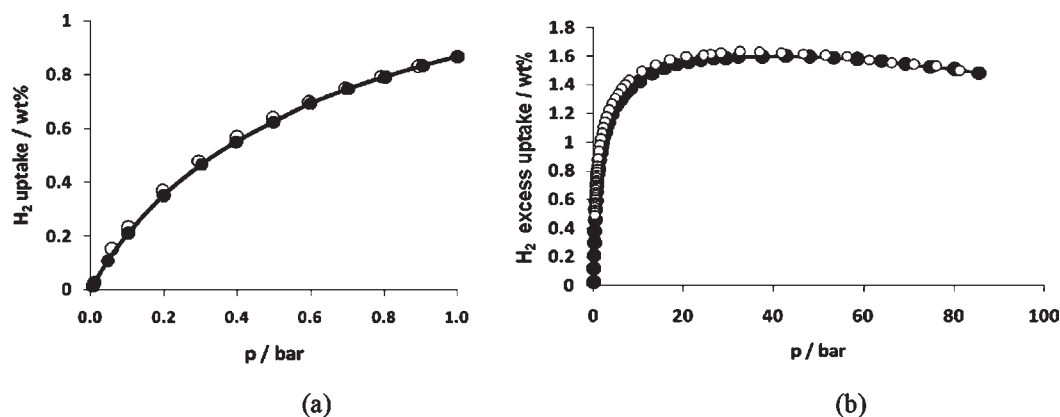


Figure 8. Hydrogen physisorption isotherms of activated **1** (a) at 77 K up to 1 bar, and (b) at 77 K up to 100 bar (adsorption/desorption ●/○).

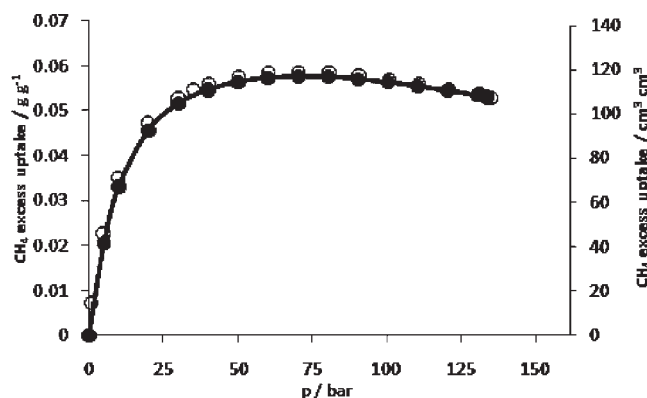


Figure 9. Excess methane physisorption isotherm of activated **1** at 77 K up to 130 bar (adsorption/desorption ●/○).

crystallographic density of **1** (1.43 g cm^{-3}), the maximal volumetric methane storage capacity exceeds that of mentioned PCPs. For example, the volumetric methane uptake of MOF-210 is reported to be $92 \text{ cm}^3 \text{ cm}^{-3}$ whereas for **1** it is significantly higher at the same pressure ($117 \text{ cm}^3 \text{ cm}^{-3}$). For PCN-14, a volumetric methane

(20) Ma, S.; Sun, D.; Simmons, J. M.; Collier, C. D.; Yuan, D.; Zhou, H.-C. *J. Am. Chem. Soc.* **2008**, *130*, 1012.

(21) (a) Bureekaew, S.; Shimomura, S.; Kitagawa, S. *Sci. Technol. Adv. Mater.* **2008**, *14108*. (b) Klein, N.; Herzog, C.; Sabo, M.; Senkowska, I.; Getzschmann, J.; Paasch, S.; Lohe, M. R.; Brunner, E.; Kaskel, S. *Phys. Chem. Chem. Phys.* **2010**, *12*, 11778. (c) Serre, C.; Millange, F.; Thouvenot, C.; Nogués, M.; Marsolier, G.; Louer, D.; Férey, G. *J. Am. Chem. Soc.* **2002**, *124*, 13519.

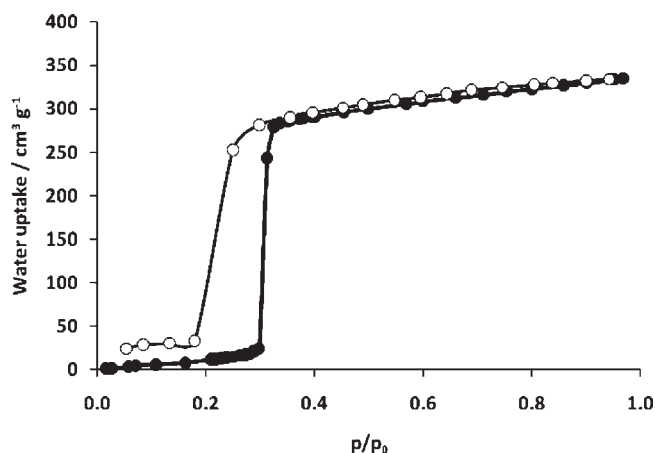


Figure 10. Water physisorption isotherms of **1** at 298 K (adsorption/desorption ●/○).

storage capacity of $220 \text{ cm}^3 \text{ cm}^{-3}$ at 35 bar has been reported²⁰ which is one of the best storage materials concerning the volumetric uptake.

The water adsorption experiment was run three times on the same sample to estimate the water affinity and stability of **1** against moisture. Between measurements, the sample was evacuated at 473 K for 16 h. Up to p/p_0 of 0.3, almost no water uptake is observed, followed by a steep uptake and saturation (Figure 10). Such isotherms are typical for flexible, so-called “gate pressure” MOFs,

which can adsorb a substantial amount of gas only above a fixed pressure, named the gate pressure.²¹

The reproducibility of the isotherms without changes in uptake or isotherm shape points at the high stability of the sample. The pore volume derived from the water adsorption isotherm at p/p_0 of 0.97 is found to be $0.27 \text{ cm}^3 \text{ g}^{-1}$. The PXRD patterns after nitrogen and water adsorption experiments show same changes in some of the reflection intensities. (Supporting Information, Figure S14). The PXRD pattern after the adsorption experiment shows that some peaks are shifted toward the lower 2θ values indicating expansion of the channels. It is not fully understood which changes in structure of **1** occur in response to adsorption of guest molecules, and further studies are needed.

Conclusion

In summary, we have successfully constructed a stable 3D porous coordination polymer with Cd(II) and a new ligand

containing hexagonal 1D nanosized channels occupied by water molecules. Integrity of the structure is maintained upon removal of the guest water molecules to afford a porous structure that exhibits N_2 , H_2 , CH_4 , and H_2O adsorption properties.

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Supporting Information Available: Experimental details, ^1H and ^{13}C NMR spectra, ESI mass spectra, IR spectra, additional figures, tabulated physisorption isotherms and X-ray crystallographic file (CIF) of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.