Inorg. Chem. **2002**, *41*, 2592–2597

Inorganic Chemistry
Article

$[Cd^{II}(bpdc)\cdot H_2O]_n$: A Robust, Thermally Stable Porous Framework through a Combination of a 2-D Grid and a Cadmium Dicarboxylate Cluster Chain (H_2bpdc = 2,2′-Bipyridyl-4,4′-dicarboxylic Acid)

Yen-Hsiang Liu,[†] Yi-Long Lu,[‡,†] Huang-Chun Wu,[†] Ju-Chun Wang,[§] and Kuang-Lieh Lu*,[†]

Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan, Republic of China, Department of Chemistry, National Changhua University of Education, Changhua 500, Taiwan, Republic of China, and Department of Chemistry, Soochow University, Taipei 100, Taiwan, Republic of China

Received November 21, 2001

The synthesis and characterization of a cadmium(II) coordination polymer, $[Cd(C_{12}H_6N_2O_4)\cdot H_2O]_n$ (**1**), is reported. A single-crystal X-ray analysis shows that compound **1** presents a noninterpenetrating three-dimensional porous host containing one-dimensional hydrophilic channels, where guest water molecules reside. The strategy in designing the 3-D framework architecture is based on a combination of two building subunits: a porous two-dimensional grid of (4,4) topology and a metal dicarboxylate cluster chain. Both subunits are assembled from the coordination of a cadmium ion with a three-connecting organic modular ligand, 2,2′-bipyridyl-4,4′-dicarboxylic acid (H_2bpdc). The results of thermogravimetric analysis and powder X-ray diffraction study show that the framework rigidity of compound **1** remains intact upon the removal of guest molecules, and maintains the thermal stability up to 440 °C. The second-row transition-metal ions are capable of engaging higher coordination modes (e.g., hepta- and octacoordination) because of their atomic sizes and intrinsic electron configurations. Our results show that the heptacoordinated cadmium center plays an important role in the overall framework rigidity and high thermal stability of compound **1**. Crystal data for **1**: $Cd(C_{12}H_6N_2O_4)\cdot H_2O$, triclinic, space group $P\bar{1}$, $a = 6.7843(5)$ Å, $b = 9.3299(7)$ Å, $c = 9.4439(7)$ Å, $\alpha = 104.629(1)^\circ$, $\beta = 92.324(1)^\circ$, $\gamma = 100.416(1)^\circ$, $Z = 2$.

Introduction

Open-framework coordination polymers are regarded as promising materials for applications in catalysis, separation, gas storage, and molecular recognition.[1−12] However, the control of pore size and shape, the occupation of counterions within the channels, the disruption of framework integrity in the absence of guests, and the thermal stability of the hosts are often serious challenges during preparation of these functional materials.

To overcome the above problems, the growing knowledge concerning the design of molecular building units[13−24] with

---

[*] To whom correspondence should be addressed. Phone: +886-2-27898518. Fax: +886-2-27831237. E-mail: lu@chem.sinica.edu.tw.

[†] Academia Sinica.

[‡] National Changhua University of Education.

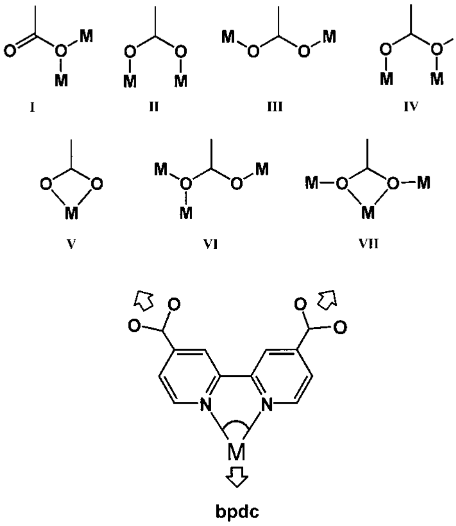
[§] Soochow University.

(1) Min, K. S.; Suh, M. P. *Chem. Eur. J.* **2001**, *7*, 303.
(2) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim. K. *Nature* **2000**, *404*, 982.
(3) Noro, S.-I.; Kitagawa, S.; Kondo, M.; Seki, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 2081.
(4) Kiang, Y.-H.; Gardner, G. B.; Lee, S.; Xu, Z.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1999**, *121*, 8204.
(5) Tabares, L. C.; Navarro, J. A. R.; Salas, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 383.
(6) For recent papers on applications of porous metal−organic coordination polymers, see, for example, refs 1−5 and references therein. For other applications of metal−organic coordination polymers, see, for example, refs 7−12 and references therein.
(7) Coronado, E.; Clemente-Leon, M.; Galan-Mascaros, J. R.; Gimenez-Saiz, C.; Gomez-Garcia, C. J.; Martinez-Ferrero, E. *J. Chem. Soc., Dalton Trans.* **2000**, 3955.
(8) Chen, Z.-F.; Xiong, R.-G.; Abrahams, B. F.; You, X.-Z.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **2001**, 2453.
(9) Lu, J. Y.; Lawandy, M. A.; Li, J. *Inorg. Chem.* **1999**, *38*, 2695.
(10) Evans, O. R.; Lin, W. *Chem. Mater.* **2001**, *13*, 3009.
(11) Evans, O. R.; Lin, W. *Chem. Mater.* **2001**, *13*, 2705.
(12) Muthuraman, M.; Masse, R.; Nicoud, J.-F.; Desiraju, G. R. *Chem. Mater.* **2001**, *13*, 1473.
(13) Zaworotko, M. J. *Nature* **1999**, *402*, 242.
(14) Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3052.
(15) Pecoraro, V. L.; Bodwin, J. J.; Cutland, A. D. *J. Solid State Chem.* **2000**, *152*, 68.
(16) Holiday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022.
(17) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483.
(18) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759.
(19) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.
(20) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629.
(21) Lehn, J.-M. *Chem. Eur. J.* **2000**, *6*, 2097.
(22) Robson, R. *J. Chem. Soc., Dalton Trans.* **2000**, 3735.

10.1021/ic011192h CCC: $22.00

"preprogrammed" structural information and functionality, adopting the concept of supramolecular self-assembly,[25−27] has offered an efficient solution.[28−56] As exemplified by two porous coordination polymers, $\{Ni(L)(L')(NO_3)_2 \cdot 6C_6H_6\}_n$ and $\{Ni(L)(L'')(NO_3)_2 \cdot 8C_6H_6\}_n$ (L = 4,4′-bipyridine, L′ = 1,4-bis(4-pyridyl)benzene, L″ = 4,4′-bis(4-pyridyl)biphenyl), the porosity is generated on the basis of a two-dimensional metal−bipyridine grid building unit.[42] Their pore sizes and shapes can be tuned by altering the length of the bipyridine linker. Recently, investigations on the assembly of a metal−organic framework based on carboxylate linkers have led to a robust, thermally stable framework with large pores.[43−53,57] The benefits derived from the carboxylate moiety are (a) the inherent negative charge of the carboxylate groups compensates the charge induced by the metal cations and can mitigate the counterion effect and (b) the diverse coordination modes of the carboxylate groups provide potentials in the formation of metal−carboxylate clusters or bridging units (Chart 1), which can help enhance the robustness of the resulting network architectures. Some successful examples are a porous zinc(II) benzenedicarboxylate coordination polymer assembled on the basis of a $Zn_4(O)O_{12}C_6$ cluster unit[49] and a porous copper(II) 1,3,5,7-adamantanetetracarboxylate polymeric network constructed from a $Cu_2(O_2C)_4$ cluster unit.[45]

Chart 1



Our previous study based on the molecular building block approach has also led to two stable porous polymeric networks. On the basis of a dicobalt carboxylate cluster building unit, a rigid and thermally stable porous cobalt nicotinate polymeric network was generated.[57] A copper isonicotinate polymeric network possessing square channels is assembled on the basis of a combination of two building subunits, i.e., a metal−carboxylate bridging unit and a copper−isonicotinate square grid.[58]

In this paper, we report a new cadmium(II) coordination polymer, $[Cd(C_{12}H_6N_2O_4) \cdot H_2O]_n$ (**1**), by coordinating the cadmium ion with a three-connecting organic ligand, 2,2′-bipyridyl-4,4′-dicarboxylic acid (H_2bpdc). The H_2bpdc ligand bears two types of coordination sites: a 2,2′-bipyridyl chelating site and two carboxylate groups trans to the 2,2′-bipyridyl site (Chart 1), where they are arranged in a triangular fashion. The H_2bpdc compound and its derivatives are commonly studied in photochemistry and electron-transfer reactions,[59] but are less commonly exploited as modular building block ligands compared to polypyridine and polycarboxylate ligands.[60,61] The H_2bpdc molecule possesses diverse coordination capabilities upon reacting with

---

(23) Ferey, G. *Chem. Mater.* **2001**, *13*, 3084.
(24) Kitagawa, S.; Kondo, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1735.
(25) Orr, G. W.; Barbour, L. J.; Atwood, J. L. *Science* **1999**, *285*, 1049.
(26) Kurth, D. G.; Fromm, K. M.; Lehn, J.-M. *Eur. J. Inorg. Chem.* **2001**, 1523.
(27) Desiraju, G. R. *Nature* **2001**, *412*, 397.
(28) For recent papers on functional porous metal−organic frameworks based on the 2-D building block approach, see, for example, refs 29−42 and references therein.
(29) Holman, K. T.; Pivovar, A. M.; Swift, J. A.; Ward, M. D. *Acc. Chem. Res.* **2001**, *34*, 107.
(30) Zaworotko, M. J. *Chem. Commun.* **2001**, 1.
(31) Yaghi, O. M.; Li, G.; Li, H. *Nature* **1995**, *378*, 703.
(32) Kondo, M.; Okubu, T.; Asami, A.; Noro, S.; Yoshitomi, T.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Seki, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 140.
(33) Zhang, S.-L.; Tong, M.-L.; Fu, R.-W.; Chen, X.-M.; Ng, S.-W. *Inorg. Chem.* **2001**, *40*, 3562.
(34) Kepert, C. J.; Prior, T. J.; Rosseinsky, M. J. *J. Solid State Chem.* **2000**, *152*, 261.
(35) Prior, T. J.; Rosseinsky, M. J. *Chem. Commun.* **2001**, 495.
(36) Russell, V. A.; Evans, C. C.; Li, W.; Ward, M. D. *Science* **1997**, *276*, 575.
(37) Biradha, K.; Hongo, Y.; Fujita, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3843.
(38) Kepert, C. J.; Rosseinsky, M. J. *Chem. Commun.* **1998**, 31.
(39) Aakeroy, C. B.; Beatty, A. M.; Lorimer, K. R. *J. Chem. Soc., Dalton Trans.* **2000**, 3869.
(40) De Munno, G.; Armentano, D.; Julve, M.; Lloret, F.; Lescouezec, R.; Faus, J. *Inorg. Chem.* **1999**, *38*, 2234.
(41) Zaman, M. B.; Smith, M. D.; zur Loye, H.-C. *Chem. Mater.* **2001**, *13*, 3534.
(42) Biradha, K.; Fujita, M. *Chem. Commun.* **2001**, 15.
(43) For recent articles on functional porous metal−organic frameworks based on the metal carboxylate building block approach, see, for example, refs 44−53 and references therein.
(44) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319.
(45) Kim, J.; Chen, B.; Reineke, T. M.; Li, H.; Eddaoudi, M.; Moler, D. B.; O'keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 8239.
(46) Mori, W.; Takamizawa, S. *J. Solid State Chem.* **2000**, *152*, 120.
(47) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148.
(48) Dong, Y.-B.; Smith, M. D.; zur Loye, H.-C. *Angew. Chem., Int. Ed.* **2000**, *39*, 4271.
(49) Lee, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276.
(50) Evans, O. R.; Lin, W. *Inorg. Chem.* **2000**, *39*, 2189.
(51) Seki, K. *Chem. Commun.* **2001**, 1496.
(52) Eddaoudi, M.; Li, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 1391.
(53) Kepert, C. J.; Rosseinsky, M. J. *Chem. Commun.* **1998**, 31.
(54) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638.
(55) Keller, S. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 247.
(56) Wang, Q.; Wu, X.; Zhang, W.; Sheng, T.; Lin, P.; Li, J. *Inorg. Chem.* **1999**, *38*, 2223.
(57) Liu, Y.-H.; Tsai, H.-L.; Lu, Y.-L.; Wen, Y.-S.; Wang, J.-C.; Lu, K.-L. *Inorg. Chem.* **2001**, *40*, 6426.
(58) Liu, Y.-H.; Lu, Y.-L.; Tsai, H.-L.; Wang, J.-C.; Lu, K.-L. *J. Solid State Chem.* **2001**, *158*, 315.
(59) Scandola, F.; Bignozzi, C. A.; Indelli, M. T. *Photosensitization and Photocatalysis Using Inorganic And Organometallic Compounds*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993.
(60) Schareina, T.; Schick, C.; Kempe, R. *Z. Anorg. Allg. Chem.* **2001**, *627*, 131.
(61) Schareina, T.; Schick, C.; Abrahams, B. F.; Kempe, R. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1711.

first-row transition-metal ions, and the overall framework architecture can be altered on the basis of the coordination habits of the metal ions.[60,61] In this context, a second-row transition metal, cadmium, is used. It was reported that the cadmium is able to engage higher numbers of coordination environments (e.g., hepta- and octacoordination) for its atomic size and intrinsic electron configuration.[62,63] On the basis of the characterization results, compound **1** presents a microporous 3-D network containing hydrophilic channels, where guest water molecules reside. The thermal stability and guest inclusion chemistry of **1** are also reported herein.

Experimental Section

Characterization. All powder X-ray diffraction (PXRD) data reported herein were recorded on a Siemens D5000 diffractometer at 40 kV and 30 mA for Cu Kα ($\lambda = 1.5406$ Å), with a step size of 0.02° in θ and scan speed of 1 s per step size. The elemental analysis was performed by use of a Perkin-Elmer 2400 elemental analyzer. A Perkin-Elmer TGA 7 analyzer was used to carry out the thermogravimetric (TG) analysis under flowing nitrogen at a heating rate of 3 °C/min for all measurements. The energy-dispersive X-ray (EDX) analysis was performed with a JEOL-2000 scanning electron microscope equipped with a KEVEX energy-dispersive X-ray spectrometer.

Synthesis. $Cd(NO_3)_2 \cdot 2.5H_2O$, triethylamine, ethylene glycol, and 2,2′-bipyridyl- 4,4′-dicarboxylic acid were purchased commercially and were used as received without further purification. The hydrothermal reactions were carried out under autogenous pressure in a Teflon-lined stainless steel Parr acid digestion bomb.

$[Cd(C_{12}H_6N_2O_4)\cdot H_2O]_n$ (1). The reaction of an aqueous solution (10 mL) containing $Cd(NO_3)_2 \cdot 2.5H_2O$ (0.2 mmol), H_2bpdc (0.2 mmol), and triethylamine (2 drops) at 180 °C for 96 h produced colorless columnar crystals and a white microcrystalline powder of **1** in a total yield of 62% based on cadmium. The solid product was washed by distilled water and isolated by suction filtration. The powder X-ray diffraction pattern of the powder sample agrees with the pattern simulated from the single-crystal diffraction data of **1** (vide infra). Elemental analysis confirmed the stoichiometry. Anal. Calcd: C, 38.68; H, 2.16; N, 7.52. Found: C, 38.19; H, 1.89; N, 7.25.

Crystallographic Determination. A suitable single crystal with dimensions of 0.40 × 0.42 × 0.38 mm for **1** was selected for indexing and intensity data collection. A total of 1350 frames constituting a hemisphere of X-ray intensity data were collected with a frame width of 0.3° in ω and a counting time of 90 s/frame, using a Bruker SMART CCD diffractometer. The first 50 frames were recollected at the end of data collection to monitor crystal decay. No significant decay was observed. The raw data frames were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using the SAINT program and for absorption using the SADABS program ($T_{min/max} = 0.743/0.884$).[64] The space group was determined to be $P\bar{1}$. Direct methods were used to solve the structure using the WINGX,[65] SHELX-97,[66] and PLATON[67] program packages. All non-hydrogen atoms and hydrogen atoms of the water molecules were located from the difference Fourier maps. Hydrogen atoms of the pyridyl rings were assigned by geometrical calculation and refined as a riding model. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares based on F^2 values on the basis of 1980 independent reflections out of 4522 reflections collected. The maximum and minimum peaks in the final difference maps were 2.978 and −0.886 e Å^{-3}. The largest residual density peak is close to the Cd atom. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1, and selected bond distances are provided in Table 2.

Table 1. Crystallographic Data for **1**

empirical formula	$Cd(C_{12}H_6N_2O_4)\cdot H_2O$	fw	372.6
a, Å	6.7843(5)	space group	$P\bar{1}$
b, Å	9.3299(7)	T, °C	25(2)
c, Å	9.4439(7)	λ, Å	0.71073
α, deg	104.629(1)	D_{calcd}, g/cm^3	2.184
β, deg	92.324(1)	μ, cm^{-1}	19.50
γ, deg	100.416(1)	R1^a [$I > 2\sigma(I)$]	0.0426
V, Å^3	566.52(7)	wR2^a (all data)	0.1165
Z	2		

[a] $R1 = \Sigma\{||F_o| - |F_c||\}/\{\Sigma|F_o|\}$. $wR2 = \{\{\Sigma[w(F_o^2 - F_c^2)^2]\}/\{\Sigma[w(F_o^2)^2]\}\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Cd(1)−O(2)#1	2.239(3)	O(2)−C(1)	1.263(6)
Cd(1)−N(1)	2.299(4)	O(3)−C(2)	1.240(6)
Cd(1)−N(2)	2.364(4)	O(4)−C(1)	1.237(6)
Cd(1)−O(1)#2	2.457(3)	N(1)−C(11)	1.341(7)
Cd(1)−O(3)#2	2.486(3)	N(1)−C(15)	1.355(6)
Cd(1)−O(1)#3	2.517(3)	N(2)−C(21)	1.341(6)
Cd(1)−O(3)#4	2.557(3)	N(2)−C(25)	1.347(6)
O(1)−C(2)	1.269(6)		
O(2)#1−Cd(1)−N(1)	154.86(14)	N(1)−Cd(1)−O(1)#3	80.88(12)
O(2)#1−Cd(1)−N(2)	92.82(13)	N(2)−Cd(1)−O(1)#3	88.63(11)
N(1)−Cd(1)−N(2)	70.74(13)	O(1)#2−Cd(1)−O(1)#3	71.39(12)
O(2)#1−Cd(1)−O(1)#2	80.32(12)	O(3)#2−Cd(1)−O(1)#3	102.78(10)
N(1)−Cd(1)−O(1)#2	123.05(13)	O(2)#1−Cd(1)−O(3)#4	81.27(11)
N(2)−Cd(1)−O(1)#2	151.78(12)	N(1)−Cd(1)−O(3)#4	81.35(11)
O(2)#1−Cd(1)−O(3)#2	101.32(12)	N(2)−Cd(1)−O(3)#4	94.86(11)
N(1)−Cd(1)−O(3A)#2	88.29(12)	O(1)#2−Cd(1)−O(3)#4	110.87(10)
N(2)−Cd(1)−O(3A)#2	154.38(12)	O(3)#2−Cd(1)−O(3)#4	66.76(11)
O(1)#2−Cd(1)−O(3)#2	53.08(10)	O(1)#3−Cd(1)−O(3)#4	159.62(12)
O(2)#1−Cd(1)−O(1)#3	118.67(12)		

[a] Symmetry transformations used to generate equivalent atoms: #1, $x, y + 1, z$; #2, $x, y, z - 1$; #3, $-x, -y + 1, -z + 1$; #4, $-x + 1, -y + 1, -z + 1$.

Results and Discussion

Compound **1** is successfully synthesized under hydrothermal conditions by reacting cadmium salts with bpdc ligands. The energy-dispersive X-ray analysis confirms the presence of cadmium atoms. On the basis of single-crystal X-ray diffraction and elemental analysis results, compound **1** is characterized with the formula $Cd(C_{12}H_6N_2O_4)\cdot H_2O$.

Structural Description. Single-crystal X-ray analysis reveals that **1** possesses a three-dimensional porous host framework possessing guest water molecules. (Figure 1). The crystallographic asymmetric unit contains one Cd(II) ion, one bpdc ligand, and one guest water molecule. Due to the atomic sizes and intrinsic electron configurations of second-row transition metals, the cadmium ions are able to engage higher

---

(62) Prasad, P. A.; Neeraj, S.; Natarajan, S.; Rao, C. N. R. *Chem. Commun.* **2000**, 1251.

(63) Vaidhyanathan, R.; Natarajan, S.; Rao, C. N. R. *Chem. Mater.* **2001**, *13*, 3524.

(64) *SMART/SAINT/ASTRO*, release 4.03; Siemens Energy & Automation, Inc.: Madison, WI, 1995.

(65) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(66) Sheldrick, G. M. *SHELX-97* (including SHELXS and SHELXL); University of Göttingen: Göttingen, Germany, 1997.

(67) Spek, A. L. *PLATON*; Utrecht University: Utrecht, The Netherlands, 2000.

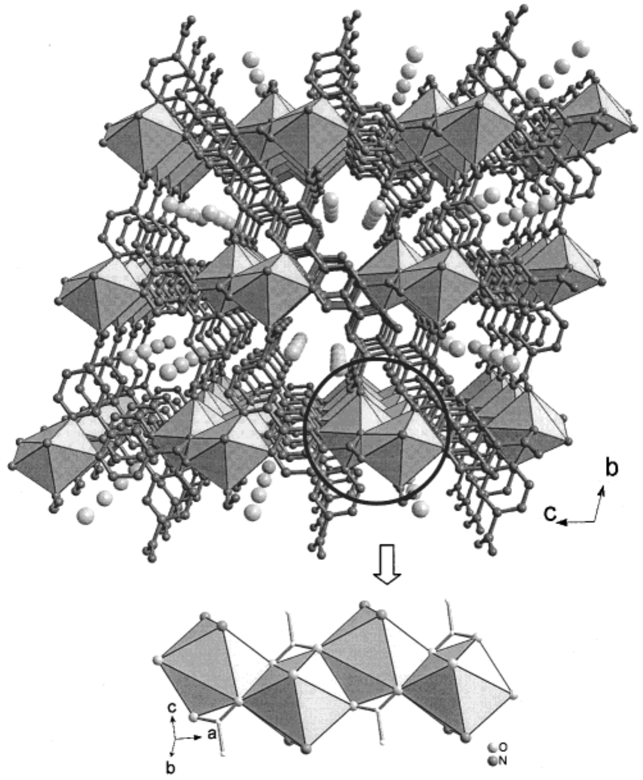


Figure 1. Perspective view of the porous framework of **1** along the (100) direction, showing elliptical-shaped hydrophilic channels where guest water molecules resided. Key: light-gray spheres, guest water molecules; edge-sharing polyhedra, $[CdN_2O_5]$.

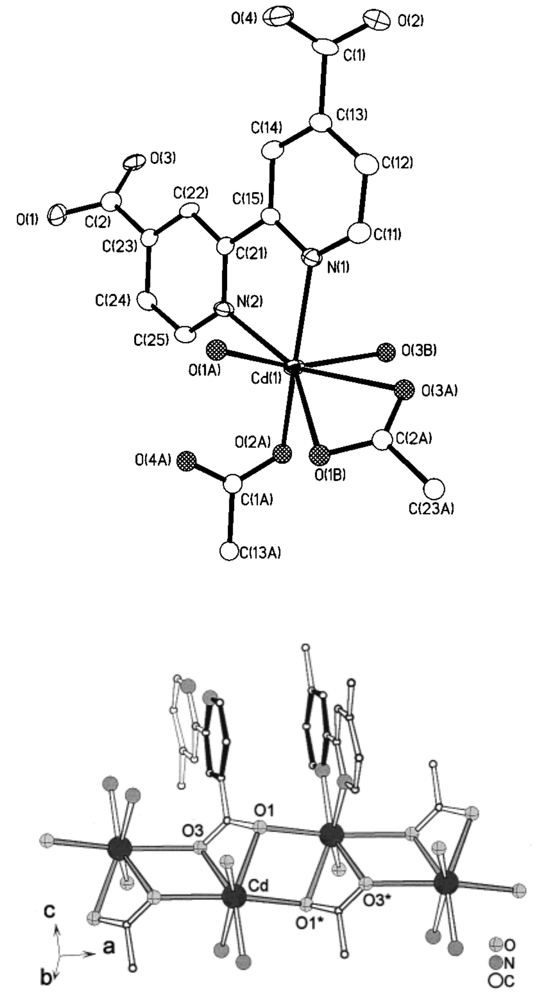


Figure 2. (a, top) Number scheme and coordination environment of the Cd center. Atoms in the asymmetric unit are represented at 40% ellipsoids. (b, bottom) Linking of cadmium ions into a cluster chain via carboxylate groups. Asterisks denote symmetry-equivalent atoms. Adjacent pyridyl rings that engaged the $\pi-\pi$ stacking interactions are highlighted in black.

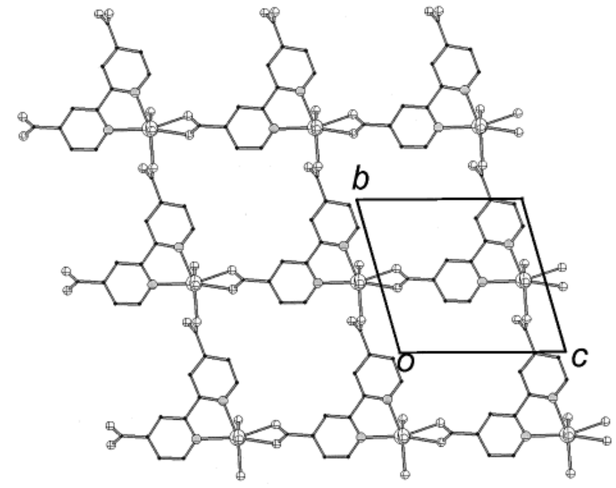


Figure 3. Perspective view of the Cd−bpdc sheet of (4,4) topology.

numbers of coordination modes (e.g., hepta- and octacoordination) while reacting with carboxylate ligands.[62,63] As in compound **1**, the cadmium ion adopts a heptacoordination environment, which is surrounded by two nitrogen atoms of the bipyridyl group and five oxygen atoms contributed from a monodentate carboxylate group and a chelating carboxylate group (Figure 2a). The charge neutrality is achieved by the two deprotonated carboxylate groups of the bpdc molecule. The chelation of the Cd(II) ion to the 2,2′-bipyridine site of the bpdc ligand restrains the planar conformation of the bipyridyl rings, as indicated by its dihedral angle (6.4°). Also shown in Figure 2b, the oxygen atoms (O1 and O3) of the chelating carboxylate groups act as bridging atoms connecting the neighboring cadmium centers. As a result, a tightly holding cadmium dicarboxylate cluster chain is formed (represented as an edge-sharing polyhedron in Figure 1).

The three-dimensional polymeric structure of **1** can be described in terms of two building subunits: a cadmium dicarboxylate cluster chain as mentioned above and a 2-D porous grid of (4,4) topology. As shown in Figure 3, assembly of the rigid, panel-like cadmium−bpdc units leads to an extended porous sheet of (4,4) net topology along the *bc*-plane. The Cd−Cd separations are 9.33 and 9.44 Å along the *b*- and *c*-axes, respectively. The separation between neighboring cadmium−bpdc (4,4) nets is ca. 3.33 Å, and pyridyl rings of adjacent sheets form $\pi-\pi$ stacking interactions. This results in the combination of the two building subunits to generate a three-dimensional polymeric network. The arrangement of the neighboring cadmium−bpdc nets within the 3-D network entails a center of symmetry that is inherent to the space group $P\bar{1}$ and leads to 1-D elliptical-shaped hydrophilic channels along the *a*-axis (Figure 4). The guest water molecules reside in the channels and form O−H···O hydrogen-bonding interactions (e.g., O(5)···O(2A) 2.96

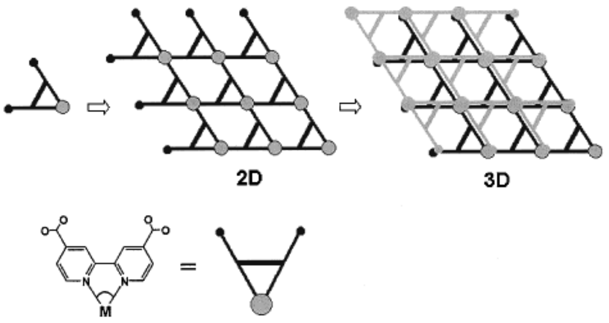


Figure 4. Diagram showing the arrangement of 2-D grids and 1-D channels.

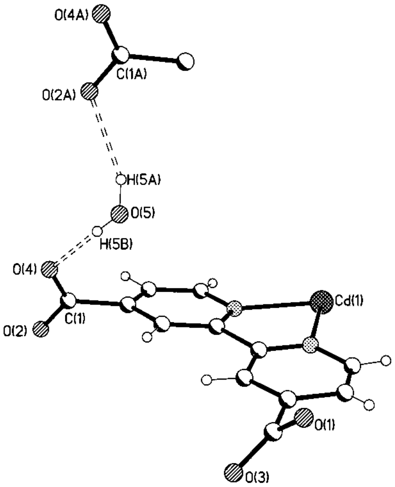


Figure 5. A part of the packing diagram showing the hydrogen-bonding interactions between the guest water molecule and host carboxylate groups.

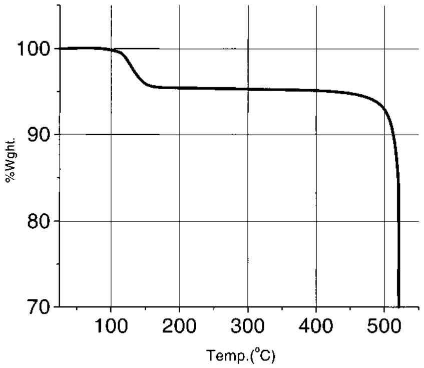


Figure 6. Thermogravimetric diagram of **1**.

Å and O(5)···O(4) 2.91 Å) with the uncoordinated framework carboxylate oxygens that protrude into the channels (Figure 5). A PLATON analysis indicates that the host framework is quite dense (9% of the unit cell volume is solvent accessible).[67]

Thermal Stability Analysis. TG analysis of compound **1** is consistent with the crystallographic observations (Figure 6). The framework releases the guest water molecules (calcd 4.8%, found 4.9%) between 40 and 170 °C. Above 170 °C, the guest-free compound shows no weight loss until it reaches 440 °C. To further test the thermal stability of compound **1**, powder samples were examined by powder X-ray diffraction analysis. Two freshly ground samples of **1** were heated in air at 350 °C for 5 h and 410 °C for 3 h, respectively, and

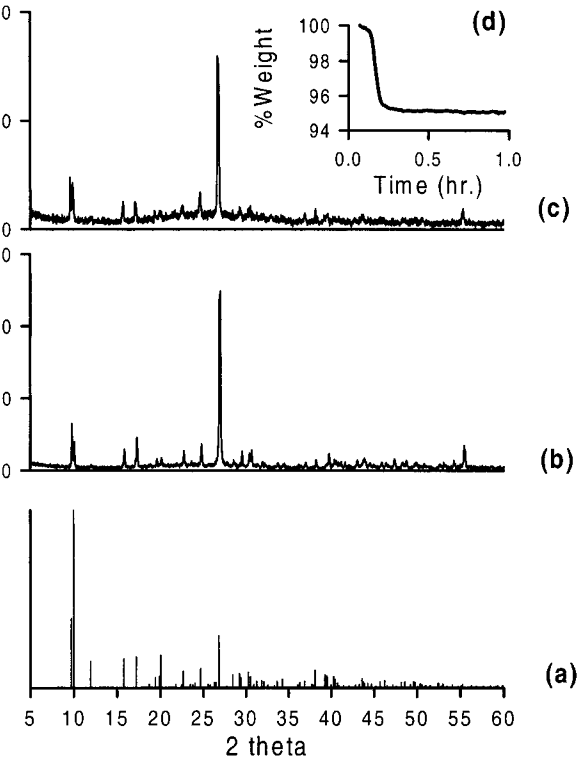


Figure 7. (a) Simulated PXRD pattern. (b) PXRD pattern of a freshly ground sample of **1**. (c) PXRD pattern after heating of **1** at 150 °C for 4 h, followed by exposure to moist air at room temperature for 20 h. (d) TG curve of the heat treatment at 150 °C, showing a weight loss and a flat baseline.

then naturally cooled to room temperature. The existence of major peaks from the PXRD patterns of the two heated samples showed no change in the diffraction peak position of 2θ in both the cases. The results indicate that the framework architecture was able to survive the heat treatment and proved to be thermally stable. The relatively dense framework as indicated by PLATON analysis may attribute to its stability.

Removal of Guests. The existence of a wide plateau area (ca. 270 °C duration) observed in the TG curve of compound **1** indicates that the framework is quite stable and allows for a guest desorption−sorption study. A freshly ground sample of **1** was heated at 150 °C for 4 h until a stable flat baseline of the TG curve was observed (Figure 7). The sample was then naturally cooled to room temperature by being exposed to a moist atmosphere for 20 h. No marked change in the diffraction peak position of 2θ (Figure 7b,c), as compared to the simulated powder patterns from single-crystal diffraction results (Figure 7a), indicates that the framework integrity of **1** remains intact upon removal of the guest molecules.

The coordination habit of the metal ions with the bpdc ligand has a profound effect on the overall framework rigidity and thermal stability in comparing compound **1** with the 3-D porous manganese(II)−bpdc coordination polymer [Mn(bpdc)]$_n$ (**2**).[60] For compound **2**, the second-row manganese ion adopts a hexacoordination environment with the bpdc ligand and results in a one-dimensional manganese μ_2-dicarboxylate bridging chain (Figure 8). The adjacent bipyridyl rings in **2** are separated by about 3.72 Å. The Mn(II)−

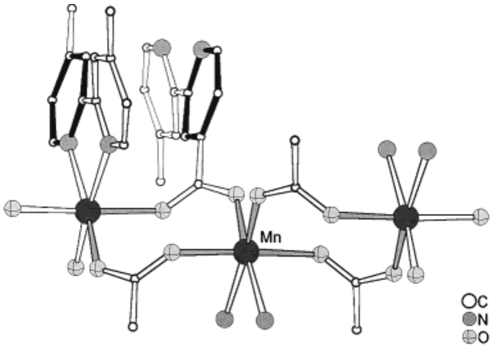


Figure 8. Perspective view of the μ_2-dicarboxylates chain of the Mn(II)-bpdc compound.

bpdc polymeric network remains thermally stable up to 310 °C. A temperature difference of ca. 130 °C is observed between the thermally stable phases of compounds **1** and **2**. A search of the literature shows that compound **1** is among the highest thermally stable phases of the three-dimensional porous transition-metal−bpdc coordination polymers reported so far.[60,61]

Conclusions

The assembly of the framework possessing large channels remains challenging. The large void spaces within the framework tend to form an interpenetrating network. However, it is promising to assemble a rigid 3-D array with tailored porosity based on a suitable combination of building subunits. The character of the rigid conformation, panel shape, and multidentation capability of the organic ligands and the coordination nature of the metal ions play an important role in facilitating the formation of a robust, thermally stable, and nonpenetrating framework with open channels. It would be profitable to explore other related architectures by employing this strategy, for example, the enlargement of the "arms" of the carboxylate ends of the bpdc ligands by employing phenyl moieties. This will enhance the $\pi-\pi$ interaction capability and alter the channel shape. Work in this direction is in progress.

Acknowledgment. We are grateful for funding from the Academia Sinica and the National Science Council of Taiwan, Republic of China.

Supporting Information Available: Two figures showing the powder X-ray diffraction patterns for the heated samples of **1** and the X-ray crystallographic file in CIF format for the structure of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC011192H