Metal–Organic Framework

A Robust Porous Material Constructed of Linear Coordination Polymer Chains: Reversible Single-Crystal to Single-Crystal Transformations upon Dehydration and Rehydration**

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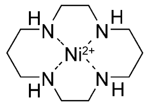
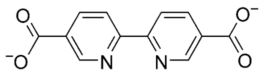
Metal–organic open-framework solids have been the focus of research interest because of their potential applications in molecular adsorption and separation processes,[1–4] ion exchange,[5,6] catalysis,[7,8] sensor technology,[9–11] and optoelectronics.[12] They can be designed and assembled to generate cavities or channels of various sizes and shapes by appropriate choice of the building blocks.[13–18] However, despite extensive studies, information on how to design and synthesize metal–organic frameworks (MOFs) with permanent porosity is still limited.[1,16,17] Moreover, applications of MOFs are scarce compared to zeolites. This is because 1) they often collapse when the guest molecules occupying the voids are removed, 2) they are in general thermally unstable compared with inorganic zeolites and are destroyed at high temperatures (> 200 °C) or even at low temperatures under vacuum, and 3) they are often soluble in solvents and dissociate into their building blocks.[3,4,13–15] Porous materials that retain their crystallinity during the reversible desorption/adsorption of guest molecules could be relevant as sensing devices.

Here we report a robust metal–organic open framework, namely, [Ni(cyclam)(bpydc)]·5 H_2O (**1**), which is constructed of linear coordination polymer chains made of the nickel–macrocyclic complex [Ni(cyclam)]$(ClO_4)_2$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) and 2,2′-bipyridyl-5,5′-dicarboxylate ($bpydc^{2-}$). Open framework **1** shows a reversible type I[19]



$[Ni(cyclam)]^{2+}$



$bpydc^{2-}$

N_2 gas sorption isotherm that indicates permanent microporosity (Langmuir surface area of 817 $m^2 g^{-1}$ and pore volume of 0.37 $cm^3 cm^{-3}$). It adsorbs H_2 gas up to 1.1 wt % at 77 K and 1 atm. The framework is thermally stable up to 300 °C. It differentiates phenol, pyridine, and benzene in isooctane. When solid **1** was dehydrated, its color changed from yellow to pink, and it returned to yellow on exposure to moisture. Interestingly, the single-crystal nature of **1** was retained during these reversible dehydration and rehydration processes. Although various linear coordination polymers have been prepared,[15,20] those exhibiting permanent porosity, gas adsorption, or selective guest binding are rare.[21]

The X-ray crystal structure of **1** is shown in Figure 1; crystallographic parameters are listed in Table 1. Each $bpydc^{2-}$ ligand binds two Ni^{II} ions in a bis-monodentate mode, and each Ni^{II} macrocyclic complex with a square-planar coordination geometry is coordinated to two carboxylate oxygen atoms of $bpydc^{2-}$ at *trans* positions, which results in a linear coordination polymer chain. The uncoordinated carbonyl oxygen atom of $bpydc^{2-}$ interacts with the secondary amine group of the macrocycle to form a hydrogen-bonded six-membered ring (O2···N1 3.010(6) Å, O2···H1–N1 137.7°), which reinforces the linear chain. The intrachain Ni···Ni separation is 15.56 Å. The $bpydc^{2-}$ ligand is planar and almost perpendicular to the coordination plane of the macrocycle (dihedral angle 85.1(1)°).

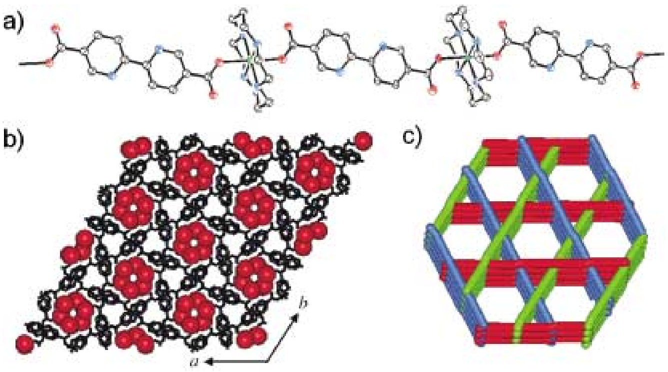


Figure 1. X-ray structure of **1**. a) Structure of the linear coordination polymer. b) View on the *ab* plane showing the linear coordination polymer chains extending in three directions; water guest molecules occupying the channels are depicted in CPK style (red). c) View showing the stacking of the linear chains, which generates 1D channels.

Table 1: Crystallographic parameters for **1**, **1′**, and **1″**.

Compound	**1**	**1′**	**1″**
space group	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$
a [Å]	26.143(1)	26.019(1)	26.136(2)
c [Å]	11.3245(3)	11.3009(4)	11.3231(4)
V [Å^3]	6702.7(4)	6625.6(4)	6698.4(8)
Ni–O [Å]	2.144(2)	2.119(2)	2.143(3)
av Ni–N [Å]	2.068(2)	2.067(2)	2.067(2)
Pyr–CO_2^- [°][a]	5.1(4)	2.4(3)	5.3(4)
Ni···Ni [Å][b]	8.438	8.403	8.436
C–H···π [Å][b]	3.687	3.670	3.685

[a] Dihedral angle between pyridine and carboxylate planes in the $bpydc^{2-}$ unit. [b] Shortest distance between nearest chains.

The structure contains three series of linear polymer chains extending in the [2,1,1], [1,2,−1], and [−1,1,1] directions (Figure 1 b and c). They are linked to one another by C–H–π interactions[22] between C2 of the macrocycle and the pyridyl ring of $bpydc^{2-}$ (distance between C2($x-y-1/3$, $x-2/3$, $-z+1/3$) and the centroid of the pyridine ring: 3.687 Å) and by hydrogen bonding with the guest water

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molecule (OW1···O2 2.801(8) Å). The shortest interchain Ni···Ni distance is 8.438 Å. The packing of 1D coordination polymer chains generates 1D channels with honeycomb-like openings of 10.0 Å diameter (effective size 5.8 Å). The channels are filled with guest water molecules. The packing of the rods have been mathematically analyzed.[23] Compound **1** exhibits a rod-packing mode corresponding to the double network of threefold braids, that is, a threefold braid of slanting rods is packed with inversion of the braid on translating in the *c* direction. In the present compound, however, the central vertical rod of the mathematical threefold braid is missing, and this creates the channel in **1**.

Compound **1** is insoluble in water and in common organic solvents. Thermogravimetric analysis on a crystalline sample of **1** showed loss of all guest water molecules at 25–110 °C. No chemical decomposition was observed up to 300°. The N_2 gas-sorption study revealed a reversible type I isotherm characteristic of a microporous material (Figure 2). The isotherm shows no hysterisis on desorption of gas from the pores. The Langmuir surface area and pore volume, estimated by applying the Langmuir and Dubinin–Raduskhvich equations, are 817 $m^2 g^{-1}$ and 0.37 $cm^3 cm^{-3}$, respectively. These values compare favorably to zeolites, whose pore volumes range from 0.18 to 0.47 $cm^3 cm^{-3}$.[24] In addition, the compound adsorbs H_2 gas up to 1.1 wt % (2.7 H_2 molecules per formula unit of host) at 77 K and 1 atm (Figure 2), which is superior to the best zeolite ZSM-5 (0.7 wt %).[25] Compared with MOF-5 (Langmuir surface area 2900 $m^2 g^{-1}$, pore volume 0.61 $cm^3 cm^{-3}$, H_2 gas uptake 4.5 wt %),[1a,b] **1** is inferior. However, **1** performs better than other recently published metal–organic open frameworks with respect to porosity and H_2 uptake capacity; for example, the $\{Mn(HCO_2)_2\}$ framework does not adsorb N_2 gas but adsorbs H_2 gas (0.9 wt %).[26]

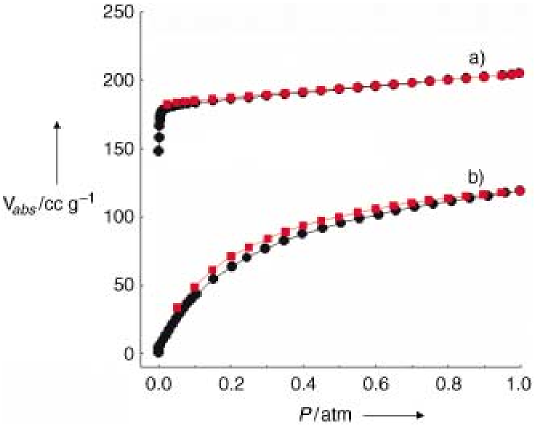

Figure 2. Gas-sorption isotherms for **1** (■ in red indicates desorption). a) N_2, b) H_2. $P_o(N_2)$ = 760 torr at 77 K.

Interestingly, **1** retains its single-crystal nature even after removal of the guest water molecules by heating the crystal at 150 °C under 10^{-5} torr for 2–40 h, which is accompanied by a color change from yellow to pink (Figure 3). The X-ray structure of the dehydrated crystal (**1′**) indicates that the porous framework structure constructed by packing of the linear chains is intact, and that only bond lengths and angles involving the Ni^{II} center and the carboxylate ligand are slightly changed (Table 1 and Supporting Information). This is contrary to our previous observation on a pillared bilayer open framework, which exhibits a spongelike behavior on removal of the guests.[4] The C–H–π interaction[22] between the linear chains in **1′** (C2($x-y-1/3$, $x-2/3$, $-z+1/3$)–centroid distance 3.670 Å) apparently sustains the porous framework structure. In general, Ni^{II} ions in an octahedral coordination geometry show a pink color, and those in square-planar environment result in a yellow color. The color change on dehydration may be partly attributable to shortening (by 0.025 Å) of the Ni–O(carboxylate) bond, which makes the Ni^{II} coordination environment in **1′** closer to octahedral compared to the hydrated solid (Table 1). In hydrated solid **1**, water guest molecules are involved in hydrogen bonding to the host framework through carbonyl oxygen atoms and C–H groups of the pyridyl rings of the bpydc ligand. However, these interactions cannot explain the yellow color in **1**, since the Ni^{II} ions in **1** still maintain the octahedral coordination geometry.

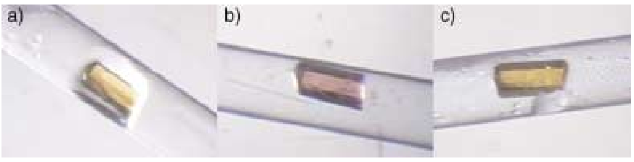

Figure 3. Photographs of a) original crystal **1** in the mother liquor, b) after evacuation of **1** at 150 °C and 10^{-5} torr for 2 h (**1′**), and c) after exposure of **1′** to water vapor for 5 min (**1″**).

When a dehydrated crystal of **1′** was exposed to air or water vapor the pink color of the crystal returned to yellow over a few minutes with retention of the single-crystallinity (Figure 3). Powder samples of **1′** instantly change color on exposure to air. The X-ray crystal structure of the rehydrated crystal **1″** was same as that of **1** (Table 1 and Supporting Information). In this regard, compound **1** is a new member of a relatively small group of molecular materials that reversibly desorbs guest molecules with retention of the original structure and single-crystallinity.[1a,16,27]

In isooctane the dehydrated host solid binds ethanol, phenol, pyridine, and benzene, for which Langmuir isotherms are observed (Figure 4), while it does not bind toluene. The amount of organic molecules bound to the solid at various guest concentrations was measured by GC, and the formation constant K_f and the number of binding sites (BS) for guest molecules in moles per gram of host $[BS]_0/\omega$ were estimated (Table 2). The K_f values indicate that the host binds guests in the order of ethanol ≈ phenol > pyridine > benzene. It is evident that the host favors guests that can form hydrogen bonds with its carbonyl groups, which are exposed to the channels.[4,28]

In conclusion, we have shown that a metal–organic framework having permanent porosity can be constructed by packing of linear coordination polymer chains. Framework **1** exhibits multiple functions: high porosity, hydrogen-storage capacity, and selective guest-binding ability. The framework exhibits reversible single-crystal to single-crystal transformation on dehydration and rehydration, which is accompanied by a fast color change of the crystal.

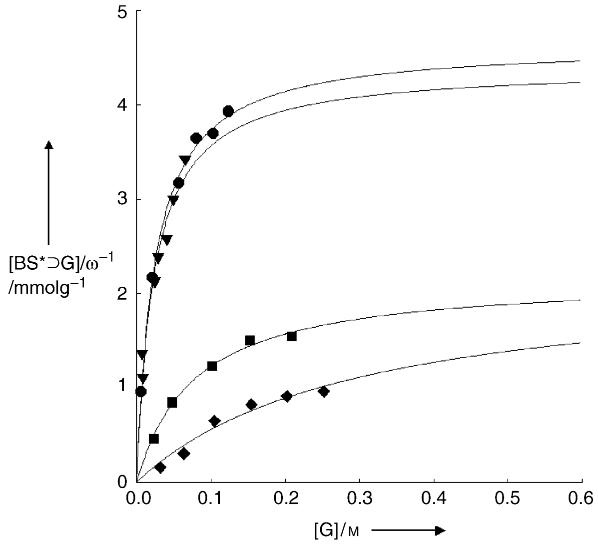

Figure 4. Binding of host solid **1** with the organic guests EtOH (●), PhOH (▼), pyridine (■), and benzene(◆). K_f, [G], and [BS⊃G]/ω are defined in the Experimental Section.

Table 2: Guest binding data for **1′**.[a]

	K_f [M^{-1}]	[BS]$_0$/ω [mmol g^{-1}]	GIC[b] [mol]
EtOH	41.1 ± 3.4	4.65 ± 0.11	2.33
PhOH	42.6 ± 10.7	4.41 ± 0.44	2.21
pyridine	12.9 ± 1.8	2.18 ± 0.12	1.09
benzene	3.37 ± 1.73	2.31 ± 0.71	1.11

[a] K_f and [BS]$_0$/ω indicate the binding constant and the binding capacity of host solid (per g) for guest molecules, respectively. [b] Guest inclusion capacity per formula unit of **1′**, [Ni(cyclam)(bpydc)].

Experimental Section

1: [Ni(cyclam)](ClO_4)$_2$ (0.314 g, 0.69 mmol) was dissolved in hot water (7 mL), and a hot aqueous solution (2 mL) of Na_2bpydc (0.199 g, 0.69 mmol) was added dropwise. The yellow solution was allowed to stand at room temperature until pale yellow crystals formed, which were filtered off, washed with water, and dried in air. Yield: 0.306 g, 75%. FTIR (Nujol mull): $\nu = 3370$ (m, br), 3195 (m), 1596 (s), 1537 (m), 1099 (s), 1022 (m), 837 (s), 783 (s) cm^{-1}; UV/Vis (diffuse reflectance): $\lambda_{max} = 510$ nm, 386 (sh) nm. Elemental analysis (%) calcd for $NiC_{22}H_{40}N_6O_9$: C 44.68, H 6.82, N 14.21; found: C 44.83, H 6.81, N 14.24.

1′: The single crystal **1** was isolated after the X-ray intensity data were collected at 293 K in the mother liquor. The crystal was introduced into a 0.5 mm glass capillary having an open end, which was inserted into the 9 mm cell of a gas sorption apparatus. It was heated at 150 °C under 10^{-5} torr for 2 h, and then cooled to room temperature under the same vacuum. The removal of all solvent guest molecules was checked by monitoring the out-gases. The cell was filled with He gas (1.0 atm). As soon as the capillary was removed, it was sealed for X-ray structure determination.

Gas-sorption study: Gas sorption was measured on a Quantachrome Autosorb-1 instrument. An exact amount of **1** was introduced into the gas sorption apparatus, and then the compound was dehydrated at 150 °C and 10^{-5} torr until all the guest molecules were removed from the pores. The N_2 gas-sorption isotherm was monitored at 77 K at each equilibrium pressure by the static volumetric method. The H_2 gas-sorption isotherm was measured by a similar procedure at 77 K.

Guest-binding study: The formation constant K_f for the complexes formed between a binding site (BS) of the insoluble host and a guest molecule (G) was defined as k_{ad}/k_{de} [Eqs. (1) and (2)] by analogy

$$\mathrm{BS} + \mathrm{G} \underset{k_{de}}{\overset{k_{ad}}{\rightleftharpoons}} \mathrm{BS} \supset \mathrm{G} \tag{1}$$

$$K_f = \frac{k_{ad}}{k_{de}} = \frac{[\mathrm{BS} \supset \mathrm{G}]}{[\mathrm{BS}]\,[\mathrm{G}]} \tag{2}$$

with the Langmuir isotherm for adsorption of gas molecules on solid surfaces.[4,28,29] The concentration of G bound to BS ([BS⊃G]) was plotted against [G], and K_f and [BS]$_0$/ω were estimated by analysis of the data according to Equations (3) and (4). In the experiment, the total concentration of guest ([G]$_o$) was varied to keep the θ values in the range of 20–80%.

$$\theta = \frac{[\mathrm{BS} \supset \mathrm{G}]}{[\mathrm{BS}]_0} = \frac{[\mathrm{G}]}{\left([\mathrm{G}] + \frac{1}{K_f}\right)} \tag{3}$$

$$\frac{[\mathrm{BS} \supset \mathrm{G}]}{\omega} = \frac{\left(\frac{[\mathrm{BS}]_0}{\omega}\right)[\mathrm{G}]}{\left([\mathrm{G}] + \frac{1}{K_f}\right)} \tag{4}$$

If θ is defined as the fractional coverage then where ω is the amount of host solid per unit volume of the solution (mg mL^{-1}).

Pale pink crystals of **1′** were dried in a Schlenk tube at 80–100 °C under vacuum for 2–3 h. The solid (20.0–36.0 mg) was weighed exactly and immersed in a measured volume of isooctane (1–2 mL) containing ethanol, phenol, pyridine, or benzene for 16–20 h at 20 °C. The initial concentrations of ethanol, phenol, pyridine, and benzene were varied in the ranges of $(0.206–2.57) \times 10^{-1}$ M, $(0.222–1.27) \times 10^{-1}$ M, $(0.198–2.37) \times 10^{-1}$ M, and $(0.337–2.81) \times 10^{-1}$ M, respectively, to keep the saturation values θ in the range of 20–80%. The concentration change of the organic guest was measured by GC, with dodecane as internal standard. The GC system was fitted with a 30 m × 0.32 mm × 0.25 μm cross-linked polydimethylsiloxane capillary column and interfaced with a GC ChemStation. The column temperature was programmed from 80 °C (3 min) to 140 °C (2 min) at a rate of 30 °C min^{-1}. A flame-ionization detector was used.

X-ray crystallography: Diffraction data for **1**, the dehydrated crystal **1′**, and the rehydrated crystal **1″** were collected with an Enraf Nonius Kappa CCD diffractometer ($Mo_{K\alpha}$, $\lambda = 0.71073$ Å, graphite monochromator). Crystal data for **1**: $NiC_{22}H_{40}N_6O_9$, $M_r = 591.31$, trigonal, space group $R\bar{3}$, $a = 26.143(1)$, $c = 11.3245(3)$ Å, $V = 6702.9(4)$ Å^3, $Z = 9$, $T = 293$ K, $R_1 = 0.0662$ ($I > 2\sigma(I)$), $wR_2(F^2) = 0.1981$ ($I > 2\sigma(I)$), GOF = 1.109. Although microanalysis and thermogravimetric analysis indicate that the compound contains five water molecules per formula unit, only four water molecules could be located in the structure because of disorder. Full-site occupancy was assigned to OW1 because it forms a hydrogen bond with the carbonyl oxygen atom of the host and adjacent OW1 molecules, and 2/3 and 1/3 site occupancy factors were assigned to OW2 and OW3, respectively. Crystal data for **1′**: $NiC_{22}H_{30}N_6O_4$, $M_r = 501.23$, trigonal, space group $R\bar{3}$, $a = 26.019(1)$, $c = 11.3009(4)$ Å, $V = 6625.6(4)$ Å^3, $Z = 9$, $T = 293$ K, $R_1 = 0.0503$ ($I > 2\sigma(I)$), $wR_2(F^2) = 0.1391$ ($I > 2\sigma(I)$), GOF = 1.210. Crystal data for **1″**: $NiC_{22}H_{40}N_6O_9$, $M_r = 591.31$, trigonal, space group $R\bar{3}$, $a = 26.136(2)$, $c = 11.3231(4)$ Å, $V = 6698.4(8)$ Å^3, $Z = 9$, $T = 293$ K, $R_1 = 0.0622$ ($I > 2\sigma(I)$), $wR_2(F^2) = 0.1749$ ($I > 2\sigma(I)$), GOF = 1.110. Crystallographic data for **1**, **1′**, and **1″** are summarized in the Supporting Information.

CCDC 224802 (**1**), 224803 (**1′**), and 224804 (**1″**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union

Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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