Synthesis and Characterization of a Novel Modular Cadmium-Organic Framework with Biphenyl-4,4′-dicarboxylate

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We report the synthesis and structural characterization of a thermally stable and highly crystalline novel metal-organic framework with cadmium(II) ions. The crystal structure is formed by a threefold interpenetration of identical three-dimensional modular frameworks, assembled by the repetition of a binuclear secondary building unit. This unit contains 1,2-bis(4-pyridyl)ethane and introduces biphenyl-4,4′-dicarboxylate as an effective rigid large spacer between metal centres. Water molecules are hydrogen bonded to carboxylate groups and act as bridges between each independent framework. To the best of our knowledge, CUmof-1 is the first structure in which the paddlewheel motif is associated with a distribution of cavities in a concertina manner.

Introduction

Crystal engineering of polymeric coordination networks has advanced significantly since Hoskins and Robson reported the first such compounds.[1] The design and synthesis of highly ordered, porous, multi-dimensional metal-organic frameworks (MOFs) combining organic and inorganic properties is possible through the assembly of metal centres with di- or multitopic organic ligands. Consequently, features typical of purely inorganic frameworks, such as robustness, high thermal stability and a large variety of coordination geometries, can be achieved through very strong metal-to-ligand bonds (several hundreds of $kJ\cdot mol^{-1}$).[2] By closely controlling the molecular properties of the ligands, such as shape, functionality, flexibility and symmetry, frameworks with interesting and desirable properties can be created. A number of MOFs with attractive new topologies and containing several different metal centres (Cd, Co, Cu, Ni, Pt, Sn, Zn) have been reported. Many of these exhibit interesting properties, such as shape selectivity, clathration, molecular recognition, chirality, photoluminescence and unusual magnetic behaviour, and have potential applications in nonlinear optics, catalysis, and semiconductor physics.[2−23]

N,*N*′-donor spacer ligands with rod-like characteristics, such as 4,4′-bipyridine (BPY), have been extensively used.[24−30] 1,2-Bis(4-pyridyl)ethane (BPE),[6,31−33] can adopt the *gauche* and *anti* conformations which may induce supramolecular isomerism in coordination polymers.[34] Multifunctional organic molecules with one or more *exo* carboxylic acid groups have also been widely used as ligands, due to their rigidity and ability to coordinate to several metal centres in various modes.[9,22,35−37] The most common coordination forms are the unidentate, the chelating bidentate (both symmetrical and asymmetrical), several bridging systems and the free carboxylate anion.[38] Deprotonation of biphenyl-4,4′-dicarboxylic acid (H_2BPhDC) gives rise to a linear symmetrical ligand (BPhDC), which coordinates to metal ions in aqueous solutions. This ligand can serve as a bridge between metal centres because of its rigidity along the C_2 symmetry axis.

The use of large ligands such as BPhDC (ca. 10 Å between carboxylate groups) or BPE (ca. 9 Å between N-donor atoms) in MOFs increases the average distance between metal centres, leading to frameworks with large channels, cavities or windows. However, the presence of large cavities commonly leads to unusual materials, where the voids of one network are filled by one or more independent networks, which do not necessarily need to be identical or to have the same dimensionality.[27,39] Several structures reflecting these properties and containing BPE have been reported.[6,33,40−43] The design and synthesis of porous modular materials assembled by discrete aggregates (referred to as secondary building units, SBUs) has become an area of increasing interest.[12,36,44,45] This approach facilitates the design of crystal structures by selectively controlling the experimental conditions. For instance, optimal porosity of interpenetrated networks is achieved by controlling

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not only the length of the spacer but also the diameter of the repeat unit.[44]

In contrast to the extensive research focused on the use of mononuclear centres, coordination polymers containing bimetallic units (both homo- and heteronuclear) are little explored. These structural units have predictable coordination environments according to the type of ligands used, and can also exhibit attractive properties due to close metal-metal interactions. Cotton and co-workers made a contribution to this field,[46] and an unusual twofold interpenetrated $4^6 6^4$ network containing copper and the $Cr_2O_7^{2-}$ ion has been reported.[47]

Here we report the synthesis and crystal structure of a novel MOF (CUmof-1) containing cadmium(II). The combination of H_2BPhDC with BPE and a cadmium(II) salt under hydrothermal conditions, and in the presence of a stoichiometric amount of triethylamine (TEA), gives a product containing a bimetallic SBU which self-assembles into a porous modular framework, interpenetrating in a threefold manner. The highly crystalline product was obtained in high yield (86.3%) using a carefully controlled temperature program for the synthesis. This was designed in order to overcome the limitations of hydrothermal synthesis, such as the formation of poorly crystalline products caused by the irreversible nature of the process,[24] and the fast kinetics of nucleation and crystal growth.[45]

Results and Discussion

Crystallography

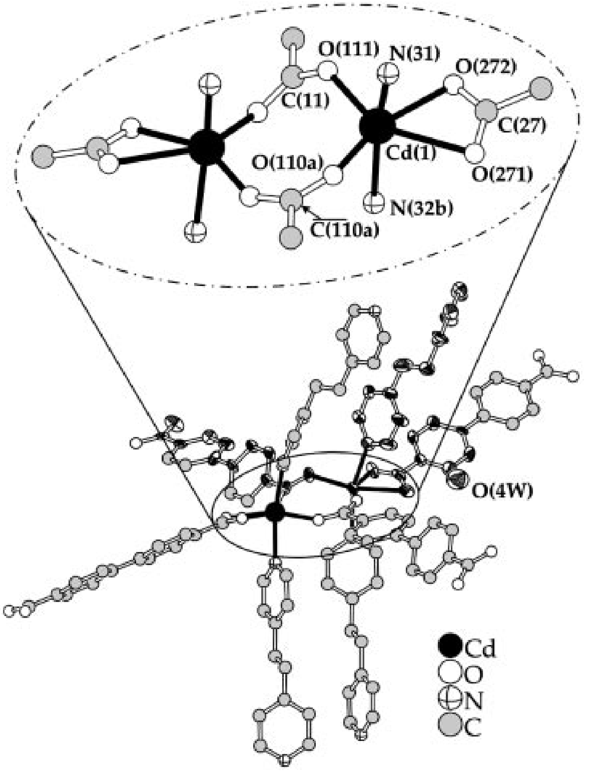


Figure 1. Binuclear building block in CUmof-1, showing the hexacoordinate environment of the cadmium centre; the top magnification shows in detail the two different coordination modes associated with the BPhDC ligand and responsible for the formation of the binuclear SBU; the distance between the metal centres is 4.375(1) Å; bond lengths and angles are given in Table 2; the atoms from the asymmetric unit are drawn as ellipsoids at 50% of probability; hydrogen atoms have been omitted for clarity

Table 1. Crystal data and structure refinement details

	CUmof-1
Formula	$C_{26}H_{22}CdN_2O_5$
Molecular weight	554.86
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	18.3846(14)
b (Å)	14.9260(2)
c (Å)	16.9890(2)
β (°)	93.897(7)
Volume (Å^3)	4651.1(4)
Z	8
D_c (g cm^{-3})	1.585
μ (Mo-K_α) (mm^{-1})	0.979
Crystal size (mm)	0.07×0.01×0.01
Crystal type	Colourless needles
θ range	3.52 to 22.47
Reflections collected	12300
Independent reflections	3018 (R_{int} = 0.238)
$R1$ [$I > 2\sigma(I)$]	0.0693
$wR2$ (all data)	0.0966

Single-crystal X-ray diffraction revealed a remarkable extended 3D structure with the molecular formula $[Cd(BPhDC)(BPE)(H_2O)]_n$ (CUmof-1) (Figure 1 and Table 1), which reflects the molar ratios in the synthesis mixture. The structure contains only one crystallographically unique metal centre coordinated to two BPE and three BPhDC ligands, in a geometry which is best described as a distorted octahedron (Figure 1 and Table 2). BPhDC acts as a bridging ligand with two different coordination modes. It also exhibits rod-like properties despite the internal rotations about the C_2 axis. In one of the coordination modes, each carboxylate group is coordinated to only one metal centre, forming an asymmetric chelate and imposing a Cd···Cd separation of 15.554(2) Å. Hydrogen bonds to the free water molecule maintain the C−O equivalence, although the respective Cd−O distances are slightly different (Table 2). The O−C−O angle [122.4(9)°] is also close to the expected value.[38] The aromatic rings in the chelating BPhDC are coplanar, forming an average dihedral angle of 16.1(9)° with the two crystallographically equivalent carboxylate groups. The second mode has each carboxylate forming a *syn-syn* bidentate bridge between the two cadmium centres with the Cd···Cd distance being 4.375(1) Å. This leads to the formation of a binuclear SBU with a paddlewheel-like structure, with the two bridging BPhDC ligands occupying the equatorial positions (Figure 1). The minimum separation between cadmium centres across this type of BPhDC rod is 14.926(1) Å. The oxygen atoms in the two carboxylate groups are approximately equidistant from the metal centres to which they are bound, with an average Cd−O distance of 2.22 Å (Table 2). The

Table 2. Bond lengths and angles

Bond lengths [Å][a]		Bond angles [°]	
Cd(1)−N(31)	2.349(7)	O(272)−Cd(1)−O(111)	91.8(2)
Cd(1)−N(32b)	2.310(7)	O(111)−Cd(1)−O(110)	114.4(2)
Cd(1)−O(110a)	2.227(7)	O(110a)−Cd(1)−O(271)	100.5(3)
Cd(1)−O(111)	2.215(6)	O(271)−Cd(1)−O(272)	53.0(2)
Cd(1)−O(271)	2.597(6)	N(31)−Cd(1)−N(32b)	157.6(3)
Cd(1)−O(272)	2.282(6)	N(31)−Cd(1)−O(271)	82.4(2)
C(11)−O(111)	1.258(8)	N(31)−Cd(1)−O(272)	83.4(2)
C(110)−O(110)	1.245(8)	N(31)−Cd(1)−O(110a)	80.2(2)
C(27)−O(271)	1.249(13)	N(31)−Cd(1)−O(111)	97.9(2)
C(27)−O(272)	1.258(12)	N(32b)−Cd(1)−O(271)	86.2(2)
O(4 W)···O(271)	2.974(13)	N(32)−Cd(1)−O(272)	104.9(2)
O(4 W)···O(271c)	3.190(11)	N(32b)−Cd(1)−O(110a)	83.0(3)
		N(32b)−Cd(1)−O(111)	102.5(2)
		O(271)−Cd(1)−O(111)	144.7(2)
		O(272)−Cd(1)−O(110a)	150.7(2)

[a] Symmetry codes: (a) *x*, 1 + *y*, *z*; (b) 1/2 + *x*, 1/2 − *y*, 1/2 + *z*; (c) 1/2 − *x*, 1/2 − *y*, 1 − *z*

dihedral angle between the two aromatic rings is 44.4(3)°. Although one carboxylic group is essentially coplanar with the benzene residue to which it is bound, the other is tilted by 25.6(3)° to the respective aromatic ring. The BPE ligands are *trans*-coordinated to the metal centres acting as axial linkers in a distorted *anti* conformation. The dihedral angle between the 4-pyridyl groups is 50.4(3)°.

The 3D assembly of the binuclear SBU gives a coordinatively bonded open framework (Figure 2). This structure has decorated square-grid perforated layers formed by dicarboxylate and cadmium ions, with each pair of opposite sides of the cavity containing one of the two previously discussed types of BPhDC (Figure 2, bottom perspective). The layers can be described as a 4.8^2 net,[48] a topology common to structures with the paddlewheel motif.[44] However, to the best of our knowledge, CUmof-1 is the first structure where this motif is associated with a distribution of the cavities in a concertina manner. The BPE axial linkers act as pillars between the 4.8^2 sheets, producing several types of channels. The most prominent channels run along the *b* direction of the unit cell and have a cross-section of ca. 8.0 × 12.1 Å^2 (Figure 2). A second type of perforated sheet can be described as a distorted rectangular 4^4 net, again presented in a concertina manner (Figure 2, top perspective). A BPE molecule acting as a pillar has also been found in other structures.[6,33]

The open framework can be seen as the [ABAB...] alternation, in the *ac* plane, of two different highly distorted cuboidal [Cd$_{16}$(BPhDC)$_8$(BPE)$_6$] units (Figure 3), which are mirror images of one another. Tao et al. have reported three frameworks resembling the CUmof-1 structure, with one of the structures containing cadmium ions.[49] However, in those cases the cuboidal units are significantly more regular, possibly due to the use of the 4,4′-bipyridine ligand, which is a more rigid pillar between the acid sheets.

Interpenetration occurs in CUmof-1 as in several other structures, and involves two identical frameworks filling the voids in another framework (Figure 4). This threefold inter-

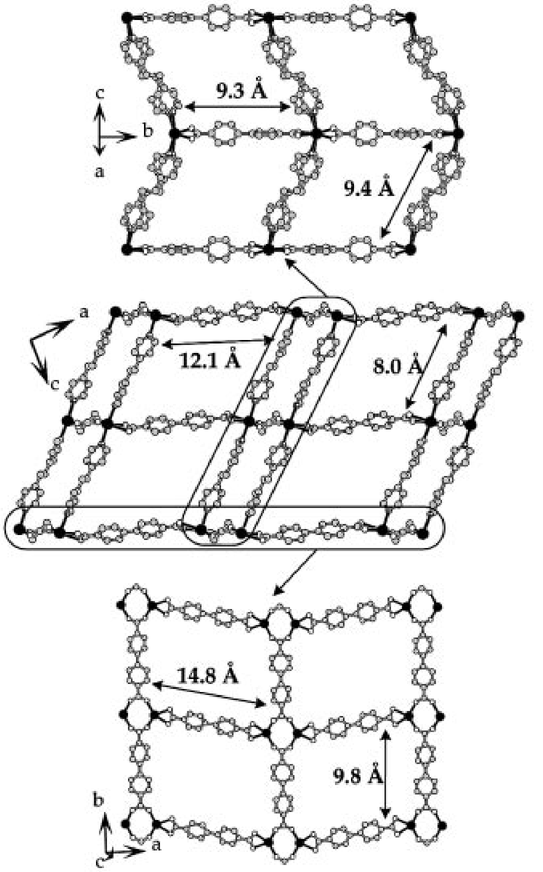


Figure 2. Overhead view along the crystallographic *b* axis of the framework constructed by assembly of the SBU; the structure has two types of perforated and interconnected concertina layers running along this axis, creating a porous 3D network; cavities inside each layer are shaded grey, and their dimensions are based on van der Waals radii; hydrogen atoms have been omitted for clarity

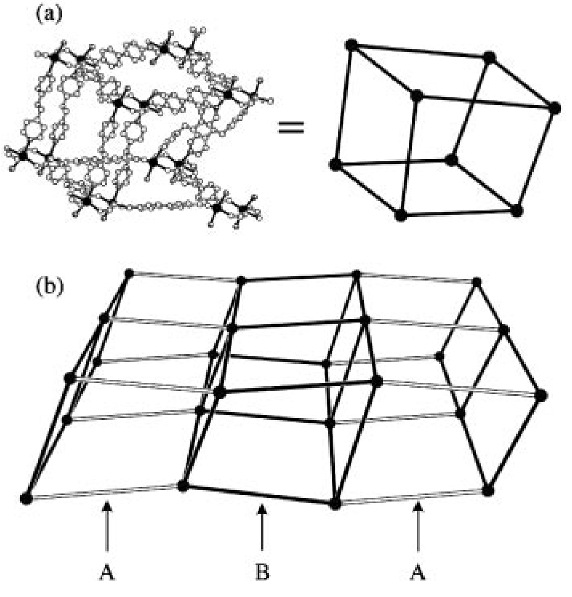


Figure 3. (a) The highly distorted cuboidal [Cd$_{16}$(BPhDC)$_8$(BPE)$_6$] unit and its simplified representation (a node is taken in the centre of each SBU); (b) The framework is constructed by [ABAB...] alternation in the *ac* plane of the two cuboidal units

penetration gives a nonporous material, as confirmed by nitrogen adsorption measurements (the adsorption isotherm of evacuated CUmof-1 reveals a BET surface area of about 2 m^2/g). The existence of an additional interpenetrating framework in CUmof-1 rather than the twofold interpenetration in the Cd-based compound reported by Tao et al.,[49] is probably the result not only of the greater length of the ligands, but also of the higher flexibility of BPE, which allows it to bend inside the cavities (Figure 4c). Such flexibility occurs in other MOF structures containing the BPE ligand: in NbO-like[42] and adamantoid networks,[43] layers[4,41] and chains.[32,41] We believe that this property of the BPE ligand is also responsible for the high distortion of the cuboidal units.

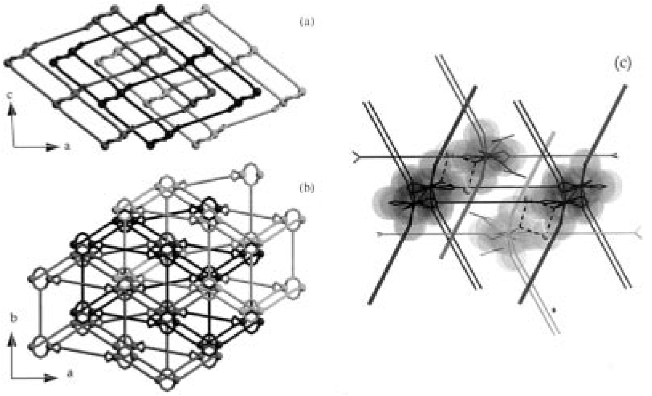


Figure 4. Crystal structure of CUmof-1, showing the presence of three interpenetrated networks, viewed along the (a) *b* and (b) *c* crystallographic axes; in view of the complexity of the structure, the aromatic rings have been omitted for clarity; for BPE the nitrogen atoms were connected directly one to each other [N(31) to N(32)], for BPhDC the connection is between the carboxylate carbon atoms [C(27) to C(27*x*), where *x* represents a different symmetry operation; C(11) to C(110)]; (c) projection showing two frameworks filling the voids of the third one; the van der Waals volume of the SBUs is also represented, along with the bridging water molecules and hydrogen bonds (dashed black lines)

Another remarkable feature of CUmof-1 is the structural function of the solvent molecules. Each individual framework is bridged to the other two by hydrogen bonding between the free water molecules and the O(271) bifurcated acceptor atoms (Figure 4c and Figure 5). These two strong O−H···O hydrogen bonds create an $R_4^2(8)$ motif with two different O···O distances (Table 2).

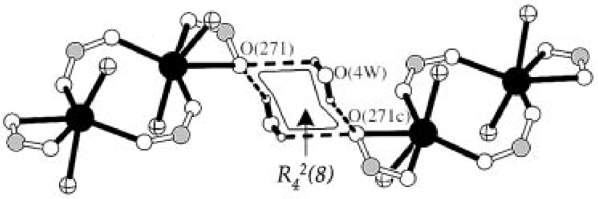


Figure 5. The chemical environment of the free solvent molecules, showing their function as bridges between different interpenetrated networks; bond lengths are given in Table 2

Other Techniques

The phase purity and crystallinity of the bulk were confirmed by a direct comparison between the experimental high-resolution PXRD pattern and a simulation based on the single-crystal X-ray diffraction results (see Supporting Information). This was also confirmed by elemental analysis. ^{113}Cd MAS NMR spectroscopy confirms the existence of only one cadmium site in CUmof-1, with a chemical shift of $\delta = 21.3$ ppm.

TGA shows a very slow and gradual release of approximately 0.71 water molecules per formula unit in the 28−140 °C temperature range. The slow kinetics of dehydration, along with the fact that not all the molecules were released, implies that the water is either strongly bonded or trapped inside the compact structure of CUmof-1. The two most significant weight losses occur between 330 and 440 °C, and are attributable to the complete oxidation of the sample to cadmium(II) oxide. This conclusion is supported by the 23.7% of residue which agrees with the expected value, considering the formation of a stoichiometric amount of CdO (23.1%). DSC analysis is in good agreement with the TGA, showing three endothermic processes corresponding to thermal decomposition of the MOF.

FT-IR and FT-Raman confirm the presence of the water molecule hydrogen bonded to the structure, and also the two organic ligands used in the synthesis. The typical antisymmetric (1577 cm^{-1}) and symmetric (1526 and 1400 cm^{-1}) stretching bands of carboxylate ions are also evident in the FT-IR spectrum. The respective $\Delta[\nu_{assym}(CO_2) - \nu_{sym}(CO_2)]$ values clearly indicate the presence of chelate (51 cm^{-1}) and bridging coordination modes (177 cm^{-1}) in CUmof-1 (Table 2), as is shown by the crystal structure.[38,50]

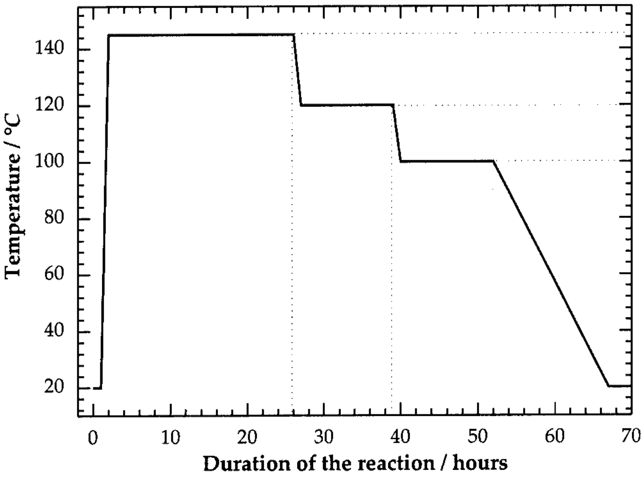
Conclusions

A novel modular coordination polymer with cadmium(II) ions was synthesised using a new organic bridging ligand, BPhDC, and a well-known flexible bidentate bridging molecule with two 4-pyridyl donor groups, BPE. A highly crystalline product was obtained using close control of the temperature in hydrothermal synthesis. The structure contains a single framework, assembled by the repetition of a binuclear SBU, which leads to the formation of BPhDC layers pillared by the BPE ligand. A cuboidal unit can also be isolated from the framework. Its distorted nature is attributed to the high flexibility of the BPE ligand. A threefold interpenetration leads to the formation of a nonporous compound, CUmof-1.

Experimental Section

Elemental analysis for C, N and H was performed on an Exeter Analytical CE-440 Elemental Analyser. The sample was combusted under oxygen at 975 °C for 1 minute, with He as the purge gas. TGA was carried out using Shimadzu TGA-50 and DSC on Shimadzu DSC-50 analyzers. Measurements were performed with a heating rate of 5 °C/min under a nitrogen atmosphere with a flow rate of 20 cm^3/min. The FT-IR spectrum was acquired using KBr pellets (Aldrich 99% +, FT-IR grade) on a Mattson 7000 FT-IR spectrometer. The FT-Raman spectrum was measured on a Bruker RFS 100 spectrometer with a Nd: YAG coherent laser (λ = 1064 nm). ^{113}Cd MAS NMR spectra were recorded at 88.71 MHz using a Chemagnetics CMX-400 spectrometer equipped with a 9.4 T magnet and zirconia rotors 7.5 mm in diameter spun in nitrogen at 5.0 kHz, using 6 µs pulse length and 180 s repetition time. Chemical shifts are quoted in ppm with respect to a 0.1 M aqueous solution of $Cd(NO_3)_2$.

Reagents: All chemicals are available from commercial sources and were used as received. The synthesis was carried out in a Teflon-lined autoclave under autogeneous pressure and static conditions (8 cm^3 total volume, filling rate 70%). The autoclave was obtained from Parr Instruments. The temperature profile used for the synthesis is described in Scheme 1.



Scheme 1

Characterization: A suitable single crystal of CUmof-1 was mounted on a glass fibre, directly from the autoclave solution, using perfluoropolyether oil.[51] Data were collected on a Nonius Kappa CCD diffractometer with Mo-K_α graphite-monochromated radiation (λ = 0.7107 Å). The crystals were very thin needles and diffracted weakly: data were collected only to $\theta = 22.5°$ (equivalent to 0.93 Å resolution) and weak data at high angle contributes to a relatively large R_{int} value of 0.238). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms,[52,53] with multi-scan absorption corrections also being applied.[54] All hydrogen atoms bound to carbon were placed geometrically, and refined using a riding model with an isotropic displacement parameter fixed at 1.2-times U_{eq} for the atom to which they are connected. Bond length restraints were not applied, except for H(1O) and H(2O), associated with the water molecule, for which the O−H distances were restrained to be 0.85(1) Å and the H−O−H angle was also restrained to be 1.39(2) Å. These restraints ensure a chemically reasonable geometry for the water molecule. Cavity dimensions were calculated by overlapping rigid spheres with van der Waals radii for each element: Cd^{2+} 2.20 Å; O 1.52 Å; N 1.55 Å; C 1.7 Å. Hydrogen atoms were omitted in all cases for simplicity. Information concerning crystallographic data collection and structure refinement for CUmof-1 is summarised in Table 1, while selected bond lengths and angles are presented in Table 2. CCDC-178338 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

The PXRD pattern was measured at ambient temperature on a STOE STADI-P high-resolution diffractometer with Ge(111)-monochromated Cu-K_α radiation (λ = 1.5406 Å) and a position-sensitive detector covering 6° 2θ angle (40 kV, 40 mA). Data were collected using the step counting method (step 1.0°, time 150 s) in the $2° \leq 2\theta \leq 60°$ range. Theoretical PXRD calculations were performed using the STOE Win XPOW software package.[55]

Synthesis of CUmof-1: 1,2-Bis(4-pyridyl)ethane (BPE, 0.188 g, Aldrich), biphenyl-4,4′-dicarboxylic acid (H_2BPhDC, 0.244 g, Fluka) and triethylamine (TEA, 0.211 g, Avocado) were added to a solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.318 g, Aldrich) in distilled water (6.15 g) and the mixture was stirred thoroughly for 1 hour at ambient temperature. The suspension, with a composition of 1.00 H_2BPhDC:1.02 Cd^{2+}:1.01 BPE:2.07 TEA:339 H_2O, was autoclaved at 145 °C. A white crystalline product was obtained. Crystals suitable for single-crystal X-ray diffraction were separated manually and preserved in a portion of the autoclave aqueous solution. The powder was washed with 50 cm^3 distilled water and three times with 50 cm^3 absolute ethanol, and air-dried at 70 °C to give crystalline CUmof-1. This MOF proved to be air- and light-stable, as well as insoluble in distilled water and common organic solvents (ethanol, acetone, dichloromethane and toluene). The elemental composition found was: C 55.91%, H 3.85%, N 4.92%. The calculated composition was: C 56.30%, H 4.00%, N 5.05%. TGA (weight loss for an initial sample of 11.82 mg): 28−140 °C 2.3%; 330−380 °C 31.8% (DTG peak at 368 °C); 380−440 °C 41.6% (DTG peak at 435 °C). DSC data: three endothermic processes with peaks at 63, 371 and 433 °C. Selected FT-IR data (cm^{-1}): ν(O−H) 3664w and 3426 m,vb; ν(C−H) 3070w; overtones and combinations in substituted benzene rings, 1940w and 1815w; *p*-disubstituted benzene and pyridine rings ν(C=C) 1608vs, 1577vs, 1526vs, 1400vs,vb; ν(C−O) 1230m and 1175m; 1103w; 1071m; δ(=C−H) 1016m and 1006m; 963w; γ(O−H) 877w; *p*-substituted pyridine ring γ(C−H) 851s, 829s, 816s and 800m; *m*-substituted benzene ring ω(C−H) 773s; γ(C=O) 703m, 685m and 672m; pyridines δ(=C−H) 629w; *p*-disubstituted benzene ring δ and γ(=C−H) 547m, 528m; ρ[(C=O)−O] 493m; substituted benzenes γ(C−H) 420s. Selected FT-Raman data (cm^{-1}): ν(C−H) 3067 m; ν(C=C, pyridines and aromatic compounds) 1608vs; δ(O−H) 1415m; ν(C−O) 1295m and 1280m; 1141m; δ(=C−H) 1016w; γ(C−H) 861m and 846m; depolarized δ(C=C) 667w; 628w; 412w; 335w.

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