A pillared-bilayer porous coordination polymer with 1D channel and 2D interlayer space, showing unique gas and vapor sorption

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Experimental Section:

Materials: All the reagents and solvents employed were commercially available and used as supplied without further purification. $Cd(NO_3)_2{\cdot}6H_2O$ and 2,3-pyridinedicarboxylic acid were obtained from the Aldrich Chemical Company. Azopyridine has been synthesized according to literature procedure.[1]

Synthesis of $\{[Cd_4(azpy)_2(pyrdc)_4(H_2O)_2].9H_2O)\}_n$ (1): An aqueous solution (25 ml) of Na_2pyrdc (1 mmol, 0.211 g) was mixed with an methanolic solution (25 ml) of azpy (1 mmol, 0.184 g) and stirred for 20 min. for mixing well. $Cd(ClO_4)_2{\cdot}6H_2O$ (1 mmol, 0.419 g) was dissolve in 50 mL water and 2 mL of this Cd(II) solution was slowly and carefully layered to the above mixed ligand solution. The reddish plate-like crystals were obtained after one month. The crystals were separated and washed with methanol water (1:1) mixture and dried. Yield, 80 %. Anal. calcd. for $C_{48}H_{50}N_{12}Cd_4O_{27}$: C, 34.39; H, 3.01; N, 10.02. Found: C, 34.04; H, 3.17; N, 9.65.

Bulk amount of **1** was prepared in powder form by direct mixing of the ligand solution with the metal solution and phase purity was checked by elemental analysis and comparing the powder X-ray diffraction (PXRD) pattern of the powder sample with the simulated data from single crystal.

Physical Measurements

The elemental analysis was carried out using a Flash 2000 Elemental Analyzer. IR spectrum of the compound was recorded on a Bruker IFS 66v/S spectrophotometer using the KBr pellets in the region 4000-400 cm^{-1}. Thermogravimetric analysis (TGA) was carried out using METTLER TOLEDO TGA850 instrument in the temperature range of 25 - 500 °C under nitrogen atmosphere (flow rate of 50 mL/min) at a heating rate of 5 °C/min. Powder X-ray diffraction (PXRD) pattern in different state of the samples were recorded on a Bruker D8 Discover instrument using Cu-$K\alpha$ radiation.

X-ray structure determination for 1: A suitable single crystal was mounted on a glass fiber and coated with epoxy resin and X-ray data was collected on a Rigaku Mercury Diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71069 Å) equipped with a CCD 2D detector. The size of the unit cells was calculated from the reflections collected on the setting angles of seven frames by changing of 0.5° for each frame. Three different settings were used and were changed by 0.5° per frame and intensity data were collected with a scan width of 0.5°. Empirical absorption correction by using REQABA was performed in both cases.[2] Structure of **1** was solved by direct methods using SIR-92 program[3] and expanded by using Fourier techniques.[4] All the non-hydrogen atoms including guest water molecules were refined anisotropically. The positions of all the hydrogen atoms were calculated and placed in ideal positions. All calculations were carried out using SHELXL 97[5], PLATON 99[6] and WinGX system, Ver 1.70.01.[7] Potential solvent accessible area or void space was calculated using the PLATON[6] multipurpose crystallographic software. Selected bond lengths, bond angles and hydrogen bonding parameters are displayed in Table S1 and S2 respectively.

References:

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Gas adsorption measurement:

The adsorption isotherms for N_2, (at 77K), and CO_2, CH_4 (at 195 K) gases were carried out by using an automatic volumetric adsorption apparatus (BELSORP 18; BEL Inc). The adsorption isotherms for H_2 (at 77 K) and Ar, O_2 (at 195 K) gases were measured by QUANTACHROME QUADRASORB *SI* analyzer. The solvent adsorption isotherms MeOH (at 293 K) and H_2O and EtOH (at 298 K) were measured by using BELSORP-aqua-3 volumetric adsorption instrument from BEL, Japan. A known weight (100-125 mg) of the as-synthesized sample was placed in the sample cell, then, prior to measurements, the sample was dried under high vacuum at 423 K for 12h to remove the solvated water molecules. The adsorbate was charged into the sample tube, and then the change of the pressure was monitored and the degree of adsorption was determined by the decrease in pressure at the equilibrium state. All operations were computer-controlled and automatic.

Table S1 Bond distance (Å) and angles (º) for $\{[Cd_4(azpy)_2(pyrdc)_4(H_2O)_2]\cdot 9H_2O\}_n$ **(1)**

Cd1 -O1	2.4951(19)	Cd1 -O2	2.3380(18)
Cd1 -O5	2.4787(18)	Cd1 -O6	2.3925(18)
Cd1 -N5	2.415(2)	Cd1 -O4_d	2.3047(19)
Cd1 -N1_d	2.368(2)	Cd2 -O1W	2.387(2)
Cd2 -O3	2.2052(18)	Cd2 -O6	2.4490(18)
Cd2 -N2	2.333(2)	Cd2 -N6_b	2.437(2)
Cd2 -O7_e	2.323(2)	Cd2 -O8_e	2.730(3)
O1 -Cd1 -O2	54.03(6)	O1W -Cd2 -O3	80.15(7)
O1 -Cd1 -O5	129.76(7)	O1W -Cd2 -O6	85.10(7)
O1 -Cd1 -O6	83.98(7)	O1W -Cd2 -N2	90.25(7)
O1 -Cd1 -N5	136.74(7)	O1W -Cd2 -N6_b	164.81(7)
O1W -Cd2 -O7_e	75.03(9)	O1 -Cd1 -O4_d	85.74(7)
O1W -Cd2 -O8_e	122.76(9)	O1 -Cd1 -N1_d	97.20(7)
O3 - Cd2 -O6	76.20(7)	O2 -Cd1 -O5	132.00(6)
O3 -Cd2 -N2	144.51(7)	O2 -Cd1 -O6	85.04(6)
O3 -Cd2 -N6_b	92.62(8)	O2 -Cd1 -N5	83.19(7)
O3 -Cd2 -O7_e	108.96(8)	O3 -Cd2 -O8_e	128.24(8)
O2 -Cd1 -O4_d	79.33(7)	O6 -Cd2 -N2	68.94(6)
O2 -Cd1 -N1_d	140.94(7)	O6 -Cd2 -N6_b	80.19(8)
O5 -Cd1 -O6	53.45(7)	O6 -Cd2 -O7_e	157.96(8)
O5 -Cd1 -N5	81.95(8)	O6 -Cd2 -O8_e	142.91(9)
N2 -Cd2 -N6_b	87.98(8)	O4_d -Cd1 -O5	140.93(7)
O7_e -Cd2 -N2	101.20(8)	O5 -Cd1 -N1_d	85.99(6)
O8_e -Cd2 -N2	85.58(9)	O6 -Cd1 -N5	100.04(8)
O7_e -Cd2 -N6_b	120.10(9)	O8_e -Cd2 -N6_b	72.15(9)
O4_d -Cd1 -O6	164.32(7)	O7_e -Cd2 -O8_e	50.31(10)
O6 -Cd1 -N1_d	121.10(7)	O4_d -Cd1 -N5	79.56(8)
N1_d -Cd1 -N5	115.95(8)	O4_d -Cd1 -N1_d	71.96(7)

Symmetry code: b = -x,-y,-z; d = x,-y,1/2+z; e = x,1-y,-1/2+z

Table S2 Hydrogen bonds (Å / º) for $\{[Cd_4(azpy)_2(pyrdc)_4(H_2O)_2]\cdot 9H_2O\}_n$ **(1)**

O1W -- H2W1 .. O2W^{i}	0.8500	2.1600	2.904(3)	145.00
O2W -- H1W2 .. O1	0.8500	2.0700	2.842(3)	150.00
O2W -- H2W2 .. O1W	0.8500	2.2100	2.800(3)	127.00
O2W -- H2W2 .. O3W	0.8500	2.4000	2.841(3)	113.00
O3W -- H1W3 .. O7	0.8500	2.4900	2.974(4)	117.00
O3W – H1W3 .. O5	0.8500	2.5200	3.352(3)	167.00
O3W -- H2W3 .. O2W	0.8400	2.1600	2.841(3)	138.00
O4W -- H1W4 .. O5W	0.9900	1.9600	2.881(9)	154.00
O5W -- H1W5 .. O8^{ii}	0.9600	2.3700	2.980(6)	121.00
O5W -- H2W5 .. O6W	0.9700	1.9400	2.894(14)	169.00
O6W -- H2W6 .. O5W^{iii}	1.0300	2.5600	3.500(15)	152.00

Symmetry Code: i = 1/2-x,1/2-y,-z;; ii = -x,y,1/2-z; iii = -x,1-y,1-z.

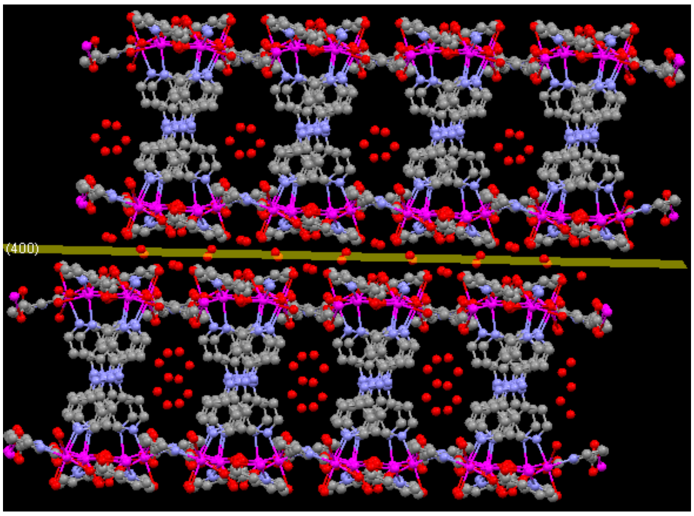

Fig. S1 View of the (400) crystallographic plane passing through inter-bilayer 2D space housing guest water molecules.

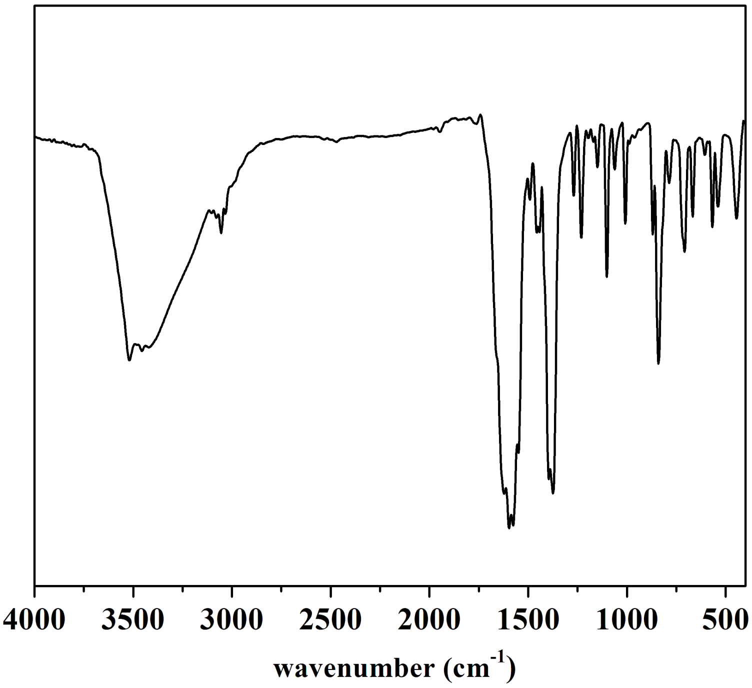

Fig. S2 IR spectrum for $\{[Cd_4(azpy)_2(pyrdc)_4(H_2O)_2]\cdot 9H_2O)\}_n$ **(1)**

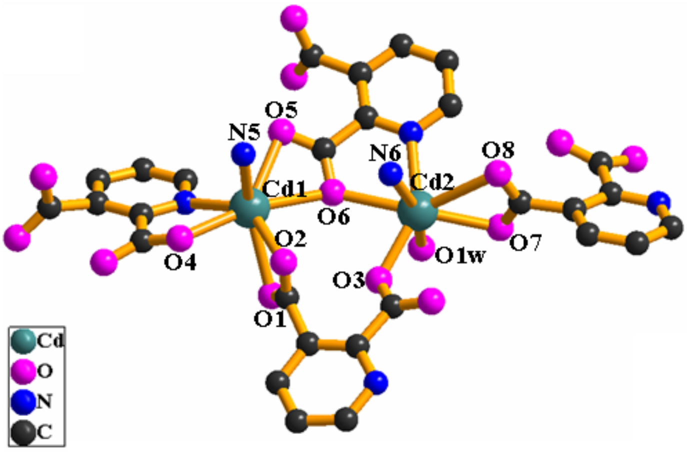

Fig. S3 View of the coordination environment around two different heptacoordinated Cd(II) with atom numbering scheme.

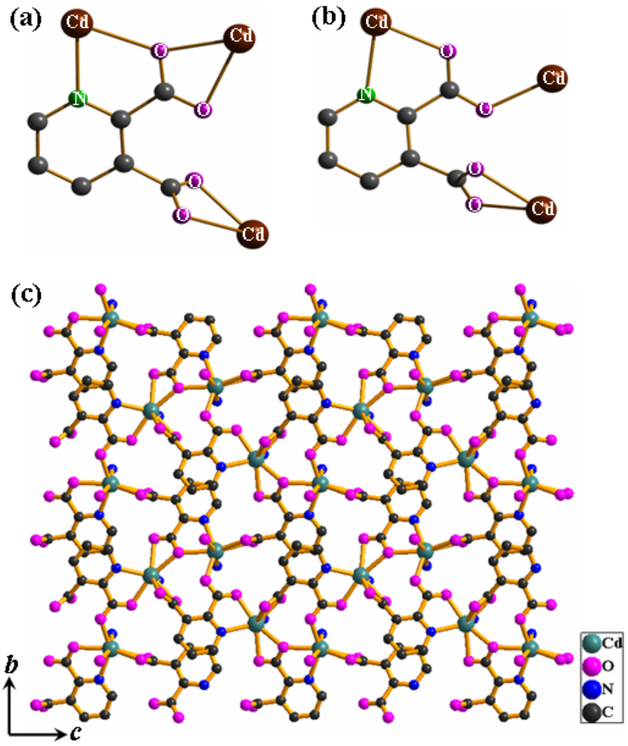

Fig. S4 (a-b) Different binding mode of pyridine-2,3-dicarboxylate with Cd(II); (c) View of the 2D $[Cd_4(pyrdc)_4(H_2O)_2]_n$ sheet in the crystallographic *bc* plane.

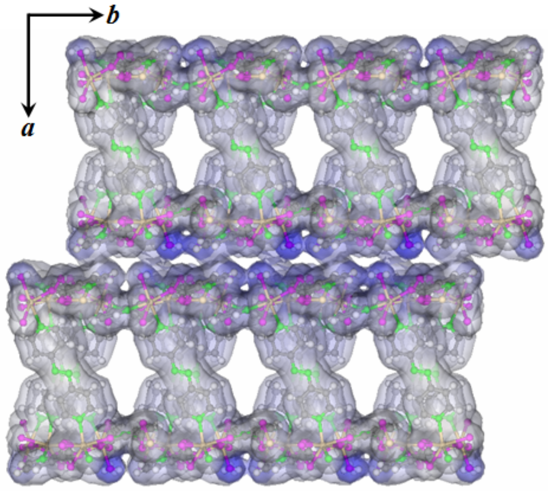

Fig. S5 View of the pore structure in 3D supramolecular framework formed by the sandwiched water molecules between the pillared-bilayer network.

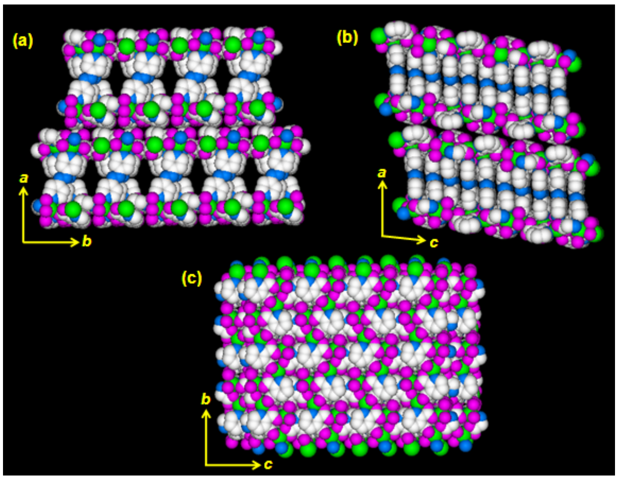

Fig. S6 View of the pillared-bilayer framework of **1** in CPK model: (a) along the crystallographic *c*-axis; (b) along the crystallographic *b*-axis; (c) along the crystallographic *a* –axis.

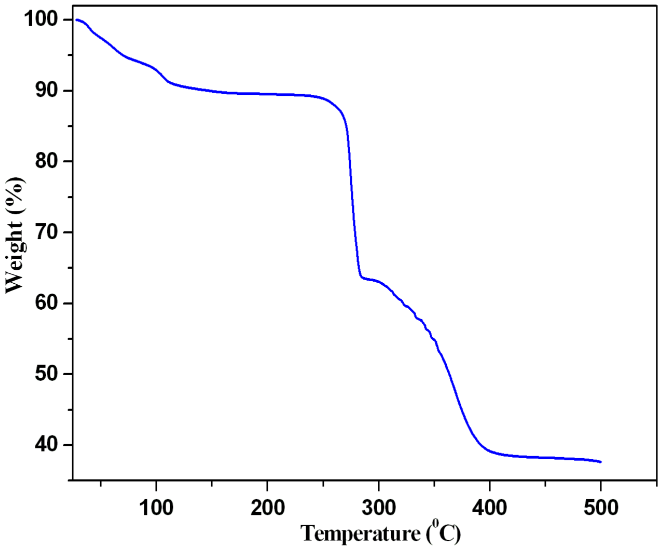

Fig. S7 TG analysis of **1** (room temperature – 500 °C) at heating rate of 2 °C min^{-1} under N_2 atmosphere.

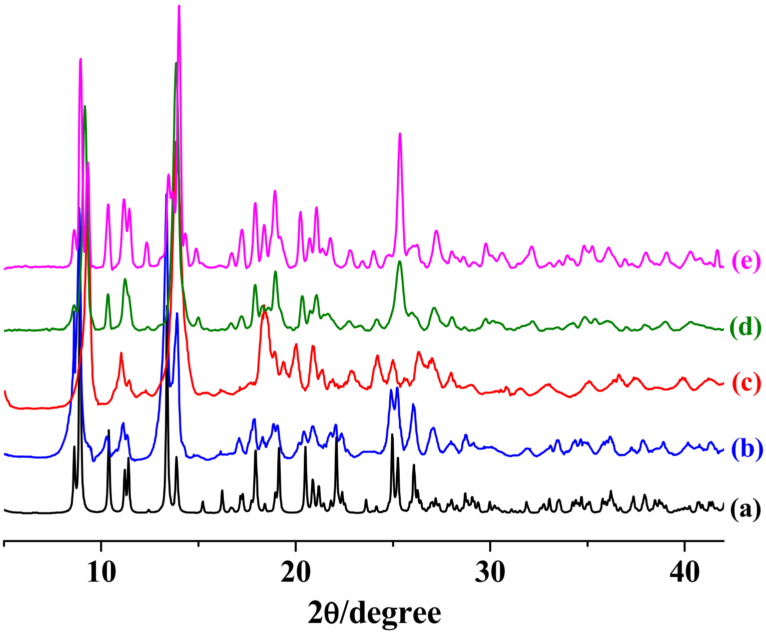

Fig. S8 PXRD pattern for **1** in different state; (a) simulated from the single crystal data; (b) assynthesized powder sample; (c) dehydrated sample at 150 ºC; (d) rehydrated sample and (e) MeOH exposed sample for 3 days.

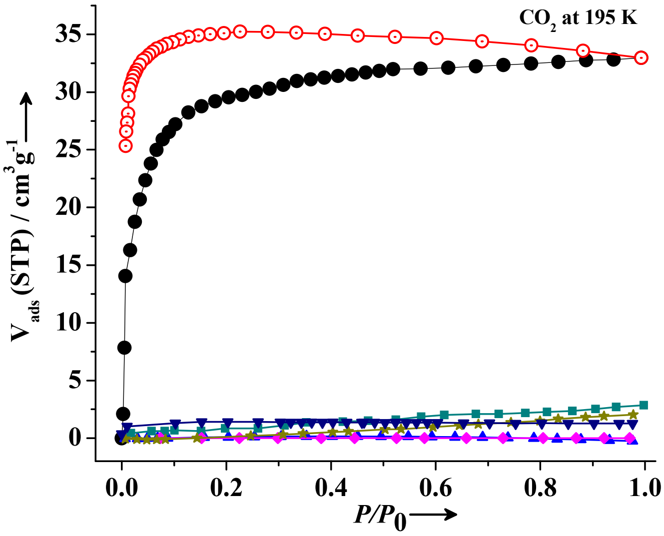

Fig. S9 Gas adsorption isotherms of **1′**: CO_2 (circles), O_2 (squares), Ar (triangles), CH_4 (diamonds) at 195 K and H_2 (stars), N_2 (inverted triangles) at 77 K. P_0 is the saturated vapor pressure (close symbols indicate adsorption and open symbols desorption)

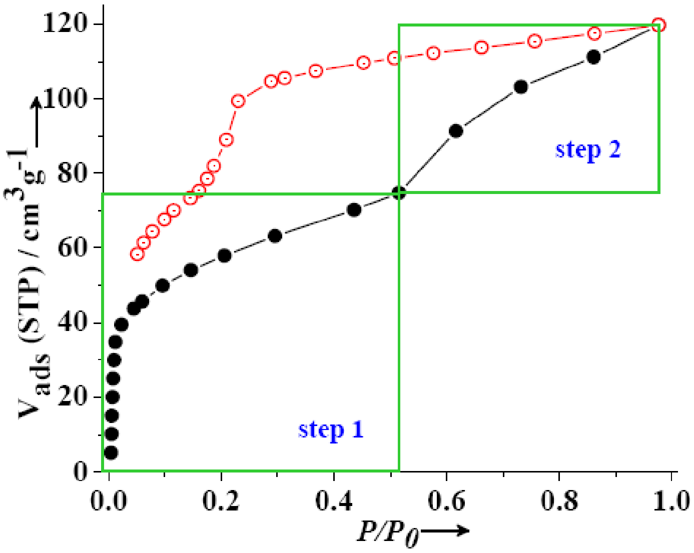

Fig. S10 H_2O sorption isotherm at 298 K; black curves indicate sorption and red curves indicate desorption.

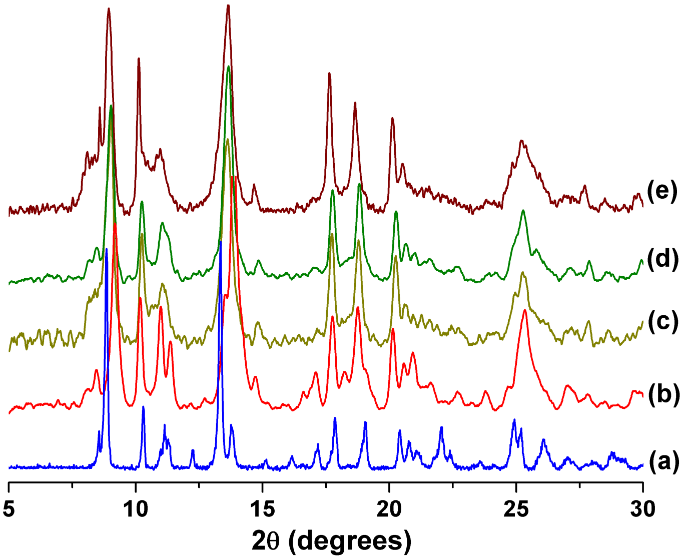

Fig. S11 PXRD pattern for **1** in different state; (a) assynthesized powder sample; (b) dehydrated sample at 150 ºC; (c, d, e) **1′** at $P/P_0 \sim 0.12, 0.68, 1$ during H_2O adsorption experiments, respectively.

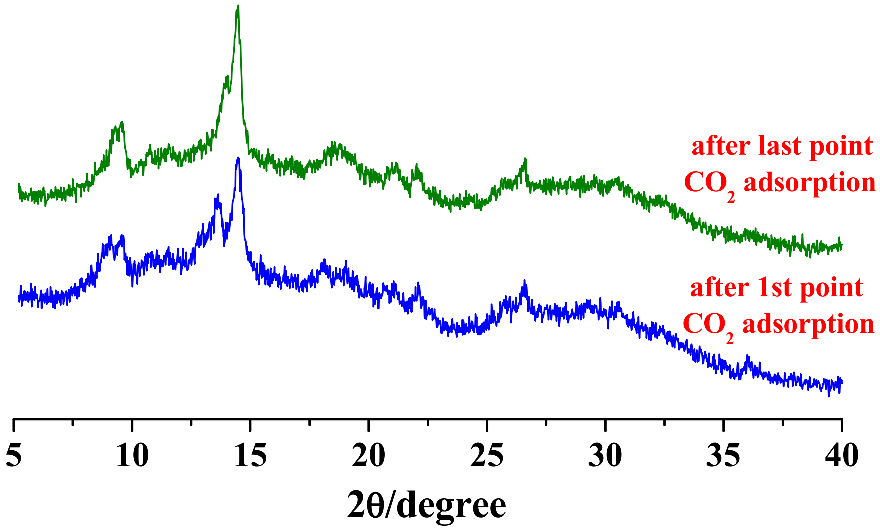

Fig. S12 *In situ* PXRD patterns recorded during CO_2 adsorption at 195 K.