Synthesis, Structural Characterization and Water Vapor Sorption Behavior of Two Ligands-ratio Dependent Supramolecular Networks, $[Cd(2,2'\text{-bpym})_{1.5}(BDC)]\cdot 0.5(2,2'\text{-bpym})\cdot 5H_2O$ and $[Cd(2,2'\text{-bpym})_{0.5}(BDC)(H_2O)_3]$

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Hydrogen atoms and guest H_2O are omitted for clarity.

Figure S4 (a) Thermogravimetric (TG) measurement of **1**. (b) Temperature-dependent powder X-ray diffraction patterns of **1** from room temperature to 200 °C and its simulation from single-crystal diffraction data. The baselines for each temperature were shifted for clarity.

Figure S5 (a) Thermogravimetric (TG) measurement of **2**. (b) Temperature-dependent powder X-ray diffraction patterns of **2** from room temperature to 200 °C and its simulation from single-crystal diffraction data. The baselines for each temperature were shifted for clarity.

Figure S6 (a) N_2 ad-/desorption isotherms of dehydrated species **1** at 77 K. (b) N_2 ad-/desorption isotherms of dehydrated species **2** at 77 K.

Table S1. Selected bond lengths (Å) and angle (°) around Cd(II) ion for **1**[a]

Cd–O(3)	2.205(1)	Cd–O(1)	2.345(2)
Cd–N(3)	2.358(2)	Cd–$N(2)_i$	2.408(2)
Cd–N(6)	2.445(2)	Cd–N(1)	2.451(2)
Cd–O(2)	2.622(2)		
O(3)–Cd–O(1)	87.87(6)	O(3)–Cd–N(3)	101.52(5)
O(1)–Cd–N(3)	125.13(6)	O(3)–Cd–$N(2)_i$	150.65(6)
O(1)–Cd–$N(2)_i$	84.81(6)	N(3)–Cd–$N(2)_i$	105.93(5)
O(3)–Cd–N(6)	101.20(6)	O(1)–Cd–N(6)	161.45(6)
N(3)–Cd–N(6)	69.26(5)	$N(2)_i$–Cd–N(6)	79.38(5)
O(3)–Cd–N(1)	82.57(5)	O(1)–Cd–N(1)	76.92(6)
N(3)–Cd–N(1)	157.40(5)	$N(2)_i$–Cd–N(1)	68.10(5)
N(6)–Cd–N(1)	88.14(5)	O(3)–Cd–O(2)	117.34(6)
O(1)–Cd–O(2)	51.72(6)	N(3)–Cd–O(2)	77.08(5)
$N(2)_i$–Cd–O(2)	79.33(5)	N(6)–Cd–O(2)	132.93(5)
N(1)–Cd–O(2)	121.10(5)		

[a]Symmetry transformations used to generate equivalent atoms: (i) –x, –y, 1–z.

Table S2. The parameters of O–H···N and O–H···O hydrogen bonds for **1**[a]

D–H (Å)	D···A(Å)	H···A(Å)	∠ D–H···Acceptor(°)
O(5)–H(5A)	O(5)···$N(7)_i$	H(5A)···$N(7)_i$	∠ O(5)–H(5A)···$N(7)_i$
0.782(4)	2.920(2)	2.152(4)	167.0(4)
O(5)–H(5B)	O(5)···O(7)	H(5B)···O(7)	∠ O(5)–H(5B)···O(7)
0.800(4)	2.824(2)	2.027(4)	173.8(4)
O(6)–H(6A)	O(6)···$O(2)_{ii}$	H(6A)···$O(2)_{ii}$	∠ O(6)–H(6A)···$O(2)_{ii}$
0.815(4)	2.868(2)	2.068(4)	167.1(4)
O(6)–H(6B)	O(6)···O(5)	H(6B)···O(5)	∠ O(6)–H(6B)···O(5)
0.802(4)	2.814(2)	2.014(4)	175.1(4)
O(7)–H(7A)	O(7)···$N(4)_{iii}$	H(7A)···$N(4)_{iii}$	∠ O(7)–H(7A)···$N(4)_{iii}$
0.806(4)	3.023(2)	2.227(4)	169.8(4)
O(7)–H(7B)	O(7)···$O(6)_{iv}$	H(7B)···$O(6)_{iv}$	∠ O(7)–H(7B)···$O(6)_{iv}$
0.805(4)	2.888(2)	2.091(4)	171.6(4)
O(8)–H(8A)	O(8)···$O(9)_v$	H(8A)···$O(9)_v$	∠ O(8)–H(8A)···$O(9)_v$
0.794(4)	2.744(2)	1.963(4)	167.6(4)
O(8)–H(8B)	O(8)···O(1)	H(8B)···O(1)	∠ O(8)–H(8B)···O(1)
0.806(4)	2.749(2)	1.944(4)	176.3(4)
O(9)–H(9A)	O(9)···O(8)	H(9A)···O(8)	∠ O(9)–H(9A)···O(8)
0.771(4)	2.726(2)	1.991(4)	159.3(4)
O(9)–H(9B)	O(9)···O(6)	H(9B)···O(6)	∠ O(9)–H(9B)···O(6)
0.760(4)	2.843(2)	2.085(4)	175.2(4)

[a]Symmetry operations used to generate equivalent atoms: (i) 1–x, 1–y, 1–z; (ii) 1+x, y, z; (iii) –x, 1–y, 1–z; (iv) 1–x, –y, 1–z; (v) 1–x, –y, –z.

Table S3. π–π interactions (face-to-face) between pyrimidyl rings of 2,2'-bpym ligands in **1**[a]

Ring(i) → Ring(j)	Slip angle (i,j)/°	Interplanar (i,j) distance/ Å	Horizontal shift between the (i,j) ring centroids/Å	Distance between the (i,j) ring centroids/Å
R(1) → $R(1)_i$	12.8	3.293	0.749	3.377
R(2) → $R(3)_i$	22.3	3.325	1.367	3.595
R(1) → $R(3)_{ii}$	26.5	3.296	1.646	3.648

[a]R(i)/R(j) denotes the centroids of i-th/j-th of pyrimidyl/pyrimidyl rings; R(1) = N(5)–C(9)–N(6)–C(12)–C(11)–C(10); R(2) = N(3)–C(8)–N(4)–C(7)–C(6)–C(5); R(3) = N(7)–C(24)–N(8)–C(23)–C(22)–C(21). Symmetry code: (i) –x, 1–y, 1–z; (ii) –1+x, y, z.

Table S4. Selected bond lengths (Å) and angle (°) around Cd(II) ion for **2**[a]

Cd(1)–O(6)	2.300(2)	Cd(1)–O(2)	2.306(2)
Cd(1)–O(5)	2.339(2)	Cd(1)–O(7)	2.363(2)
Cd(1)–N(2)	2.369(2)	Cd(1)–O(1)	2.423(2)
Cd(1)–N(1)	2.438(2)		
O(6)–Cd(1)–O(2)	116.51(6)	O(6)–Cd(1)–O(5)	81.94(6)
O(2)–Cd(1)–O(5)	80.65(6)	O(6)–Cd(1)–O(7)	163.94(6)
O(2)–Cd(1)–O(7)	78.89(6)	O(5)–Cd(1)–O(7)	96.99(6)
O(6)–Cd(1)–N(2)	85.39(6)	O(2)–Cd(1)–N(2)	130.47(6)
O(5)–Cd(1)–N(2)	148.69(6)	O(7)–Cd(1)–N(2)	87.51(6)
O(6)–Cd(1)–O(1)	89.35(6)	O(2)–Cd(1)–O(1)	55.02(6)
O(5)–Cd(1)–O(1)	124.50(6)	O(7)–Cd(1)–O(1)	104.17(6)
N(2)–Cd(1)–O(1)	83.66(6)	O(6)–Cd(1)–N(1)	85.25(6)
O(2)–Cd(1)–N(1)	149.38(6)	O(5)–Cd(1)–N(1)	81.61(6)
O(7)–Cd(1)–N(1)	78.74(6)	N(2)–Cd(1)–N(1)	68.85(6)
O(1)–Cd(1)–N(1)	152.31(6)		

Table S5. The parameters of O–H···O hydrogen bonds for **2**[a]

D–H (Å)	D···A(Å)	H···A(Å)	∠ D–H···Acceptor(°)
O(5)–H(5A)	O(5)···$O(3)_i$	H(5A)···$O(3)_i$	∠ O(5)–H(5A)···$O(3)_i$
0.752(4)	2.796(2)	2.064(4)	164.6(4)
O(5)–H(5B)	O(5)···$O(7)_{ii}$	H(5B)···$O(7)_i$i	∠ O(5)–H(5B)···$O(6)_{ii}$
0.757(4)	2.865(2)	2.131(4)	163.2(4)
O(6)–H(6A)	O(6)···$O(3)_i$	H(6A)···$O(3)_i$	∠ O(6)–H(6A)···$O(3)_i$
0.776(4)	2.746(2)	2.020(4)	155.5(4)
O(6)–H(6B)	O(6)···$O(4)_{iii}$	H(6B)···$O(4)_{iii}$	∠ O(6)–H(6B)···$O(4)_{iii}$
0.704(4)	2.648(2)	1.961(4)	165.4(4)
O(7)–H(7A)	O(7)···$O(2)_{iv}$	H(7A)···$O(2)_{iv}$	∠ O(7)–H(7A)···$O(2)_{iv}$
0.792(4)	2.659(2)	1.908(4)	157.9(4)
O(7)–H(7B)	O(7)···$O(3)_v$	H(7B)···$O(3)_v$	∠ O(7)–H(7B)···$O(3)_v$
0.771(4)	2.749(2)	1.990(4)	167.9(4)

[a]Symmetry operations used to generate equivalent atoms: (i) −1+x, 1/2−y, −1/2+z; (ii) x, 1/2−y, −1/2+z; (iii) 1−x, −y, −z; (iv) x, 1/2−y, 1/2+z; (v) −1+x, 1/2−y, 1/2+z.

Table S6. Selected bond lengths (Å) and angle (°) around Cd(II) ion for **3**

Cd–O(4)	2.226(2)	Cd–O(2)	2.298(2)
Cd–O(5)	2.321(2)	Cd–N(4)	2.391(3)
Cd–N(1)	2.462(2)	Cd–O(1)	2.493(2)
O(4)–Cd–O(2)	116.60(9)	O(4)–Cd–N(5)	90.17(10)
O(2)–Cd–O(5)	139.85(8)	O(4)–Cd–N(4)	130.69(9)
O(2)–Cd–N(4)	97.38(8)	O(5)–Cd–N(4)	84.42(9)
O(4)–Cd–N(1)	77.07(9)	O(2)–Cd–N(1)	90.97(8)
O(5)–Cd–N(1))	125.55(9)	N(4)–Cd–N(1)	67.19(9)
O(4)–Cd–O(1)	142.90(9)	O(2)–Cd–O(1)	54.38(8)
O(5)–Cd–O(1)	86.00(8)	N(4)–Cd–O(1)	85.67(9)
N(1)–Cd–O(1)	133.37(8)		

Table S7. The parameters of O–H···N and O–H···O hydrogen bonds for **3**[a]

D–H (Å)	D···A(Å)	H···A(Å)	∠ D–H···Acceptor(°)
O(5)–H(5A) 0.887(4)	O(5)···O(6) 2.726(2)	H(5A)···O(6) 1.841(4)	∠ O(5)–H(5A)···O(6) 175.7(4)
O(5)–H(5B) 0.887(4)	O(5)···N(2)$_i$ 3.056(2)	H(5B)···N(2)$_i$ 2.233(4)	∠ O(5)–H(5B)··· N(2)$_i$ 154.2(4)
O(5)–H(5B) 0.887(4)	O(5)···N(3)$_i$ 3.072(2)	H(5B)···N(3)$_i$ 2.403(4)	∠ O(5)–H(5B)··· N(3)$_i$ 167.1(4)
O(6)–H(6A) 0.868(4)	O(6)···O(1)$_{ii}$ 2.850(2)	H(6A)···O(1)$_{ii}$ 1.996(4)	∠ O(6)–H(6A)···O(1)$_{ii}$ 167.9(4)
O(6)–H(6B) 0.886(4)	O(6)···O(8)$_{ii}$ 2.739(2)	H(6B)···O(8)$_{ii}$ 1.857(4)	∠ O(6)–H(6B)···O(8)$_{ii}$ 172.7(4)
O(7)–H(7A) 0.902(4)	O(7)···O(8)$_{iii}$ 2.880(2)	H(7A)···O(8)$_{iii}$ 2.119(4)	∠ O(7)–H(7A)···O(8)$_{iii}$ 141.5(4)
O(7)–H(7B) 0.899(4)	O(7)···O(1)$_{ii}$ 2.962(2)	H(7B)···O(1)$_{ii}$ 2.221(4)	∠ O(7)–H(7B)···O(1)$_{ii}$ 139.5(4)
O(8)–H(8A) 0.876(4)	O(8)···O(7)$_{iv}$ 2.880(2)	H(8A)···O(7)$_{iv}$ 2.302(4)	∠ O(8)–H(8A)···O(7)$_{iv}$ 123.5(4)

[a]Symmetry operations used to generate equivalent atoms: (i) 1/2–x, 3/2+y, 3/2–z; (ii) 3/2–x, 3/2+y, 3/2–z; (iii) 1–x, –y, 1–z; (iv) 1–x, –1–y, 1–z.

Table S8. π–π interactions (face-to-face) between pyrimidyl rings of 2,2'-bpym ligands and benzene ring of BDC^{2-} ligands in **1**[a]

Ring(i) → Ring(j)	Slip angle (i,j)/°	Interplanar (i,j) distance/ Å	Horizontal shift between the (i,j) ring centroids/Å	Distance between the (i,j) ring centroids/Å
R(1) → $R(2)_i$	25.6	3.338	1.596	3.700
R(3) → $R(1)_{ii}$	21.9	3.424	1.378	3.691

[a]R(i)/R(j) denotes the centroids of i-th/j-th of pyrimidyl/pyrimidyl rings; R(1) = N(1)–C(1)–C(2)–C(3)–N(2)–C(4); R(2) = N(3)–C(6)–C(7)–C(8)–N(4)–C(5); R(3) = C(13)–C(14)–C(15)–$C(13)_{iii}$–$C(14)_{iii}$–$C(15)_{iii}$. Symmetry code: (i) 1/2–x, 3/2+y, 3/2–z; (ii) 1/2+x, 1/2–y, 1/2+z; (iii) 3/2–x, 3/2+y, 5/2–z.

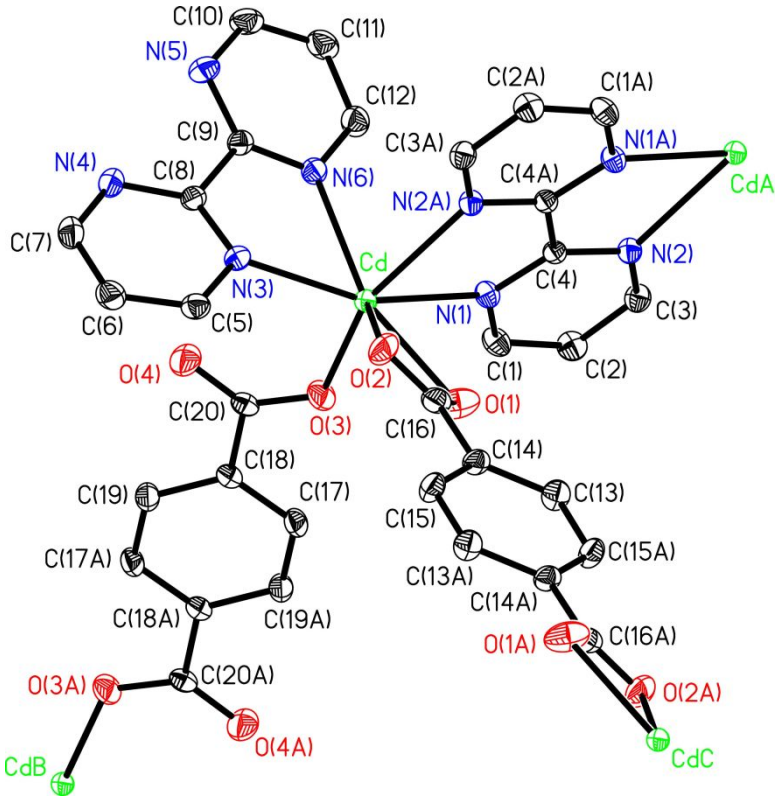


Figure S1. Coordination environments about Cd ion in $[Cd(2,2'\text{-bpym})_{1.5}(BDC)]\cdot 0.5(2,2'\text{-bpym})\cdot 5H_2O$ (**1**) with atom labelling scheme (ORTEP drawing, 50 % thermal ellipsoids). Hydrogen atoms, guest H_2O and bpym molecules are omitted for clarity.

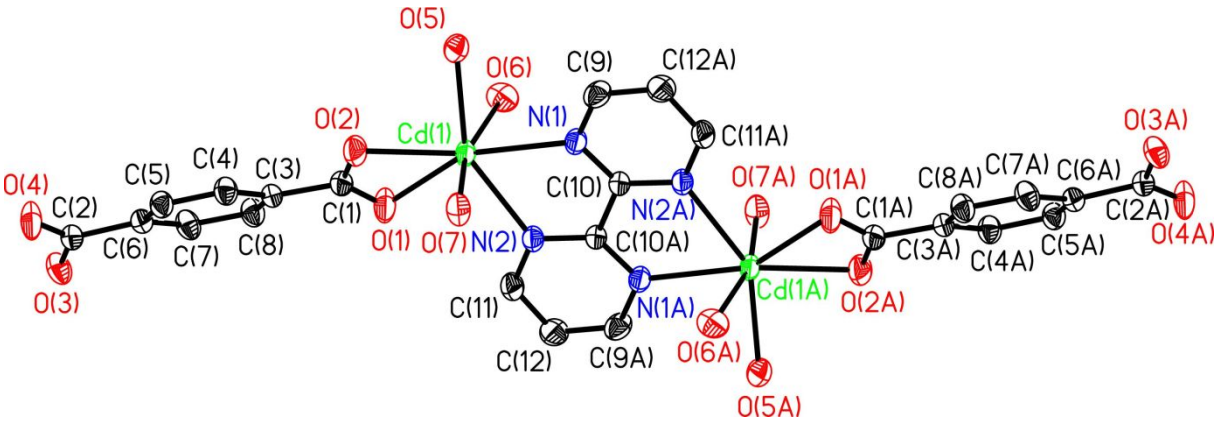


Figure S2. Coordination environments about Cd(1) ion in $[Cd(2,2'\text{-bpym})_{0.5}(BDC)(H_2O)_3]$ (**2**) with atom labelling scheme (ORTEP drawing, 30 % thermal ellipsoids). Hydrogen atoms are omitted for clarity.

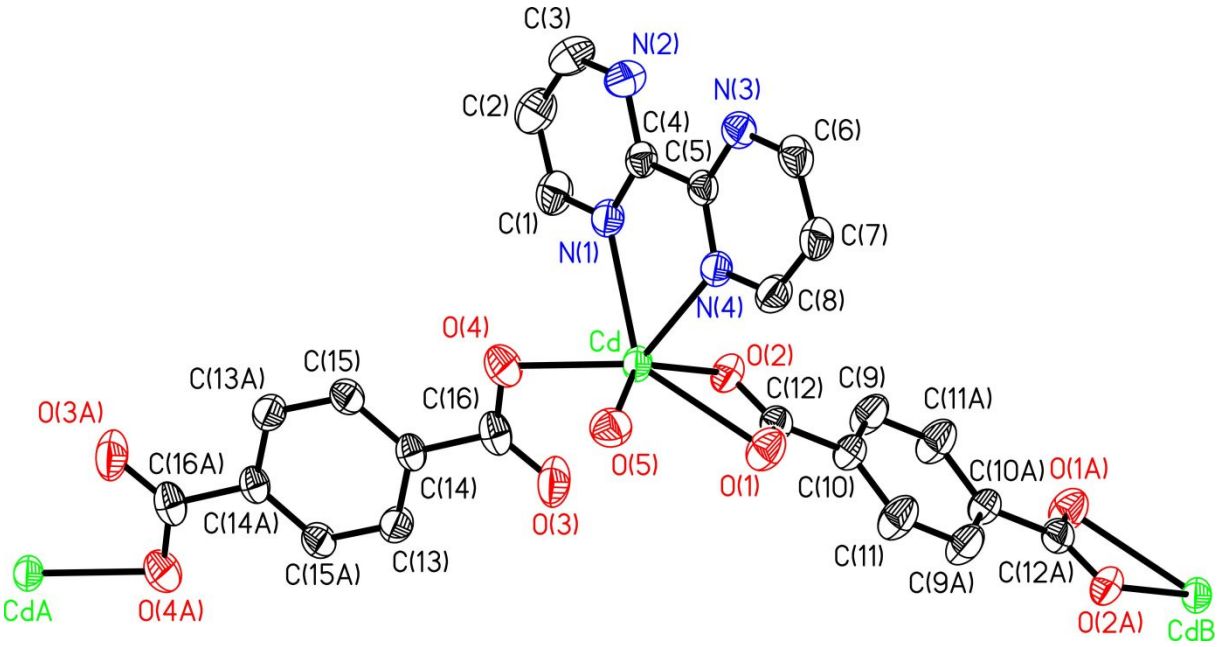
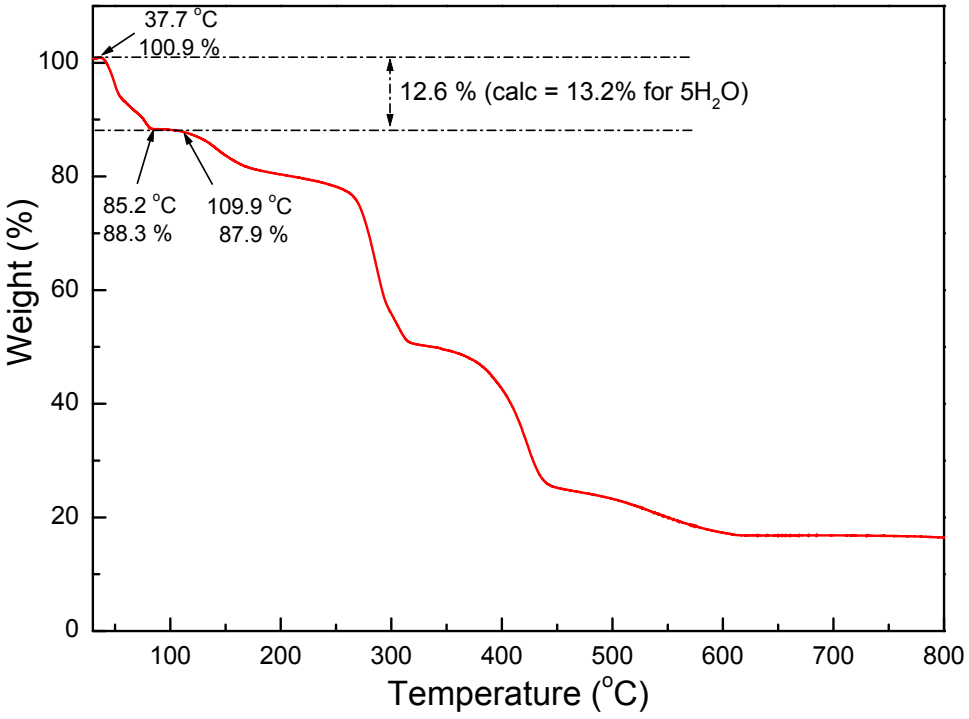


Figure S3. Coordination environments about Cd ion in [Cd(2,2'-bpym)(BDC)(H_2O)]·3H_2O (**3**) with atom labelling scheme (ORTEP drawing, 50 % thermal ellipsoids). Hydrogen atoms and guest H_2O are omitted for clarity.



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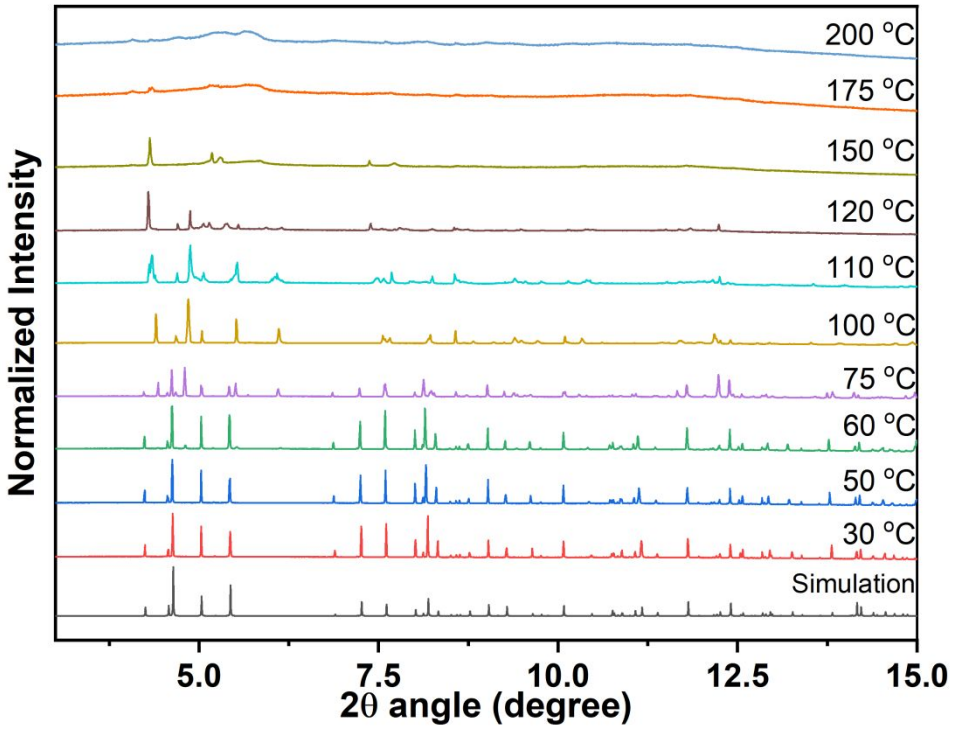
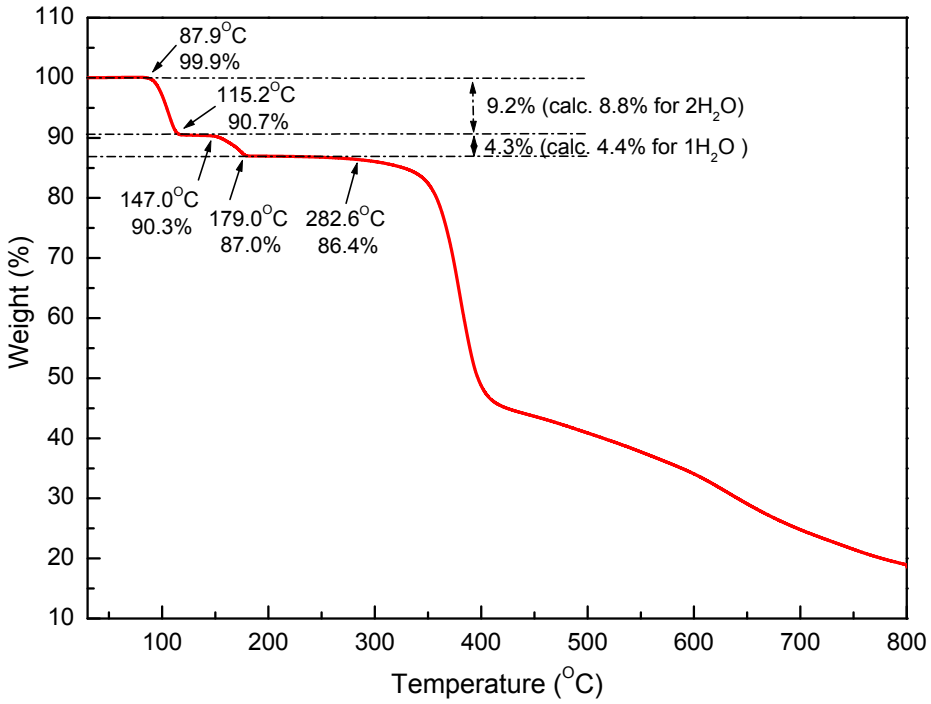


(b)

Figure S4. (a) Thermogravimetric (TG) measurement of **1**. (b) Temperature-dependent powder X-ray diffraction patterns of **1** from room temperature to 200 °C and its simulation from single-crystal diffraction data. The baselines for each temperature were shifted for clarity.



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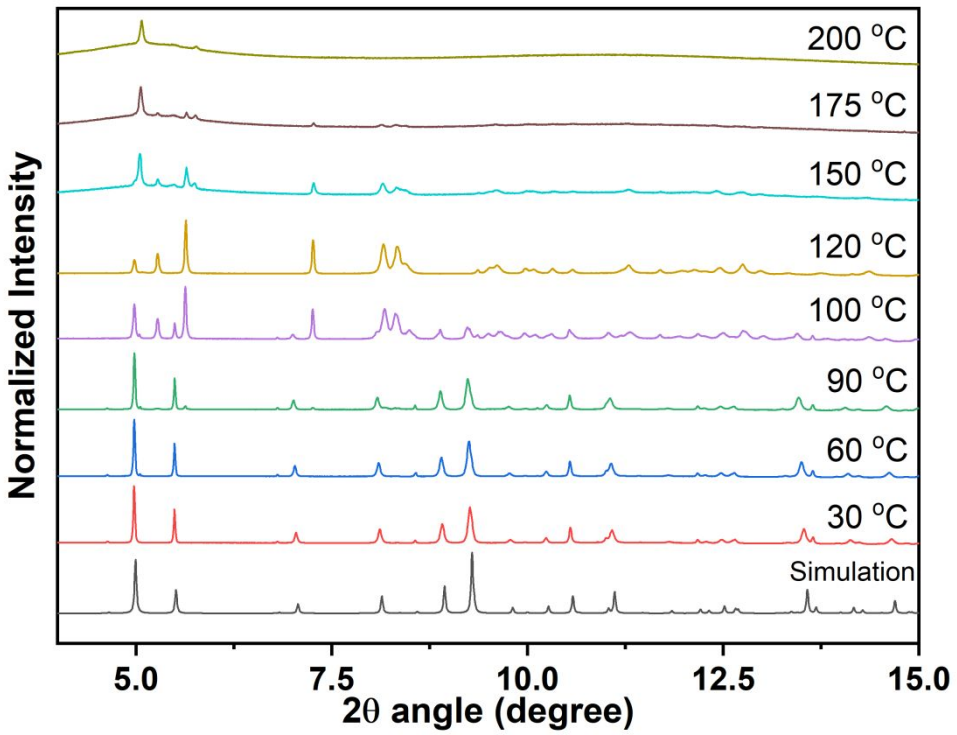
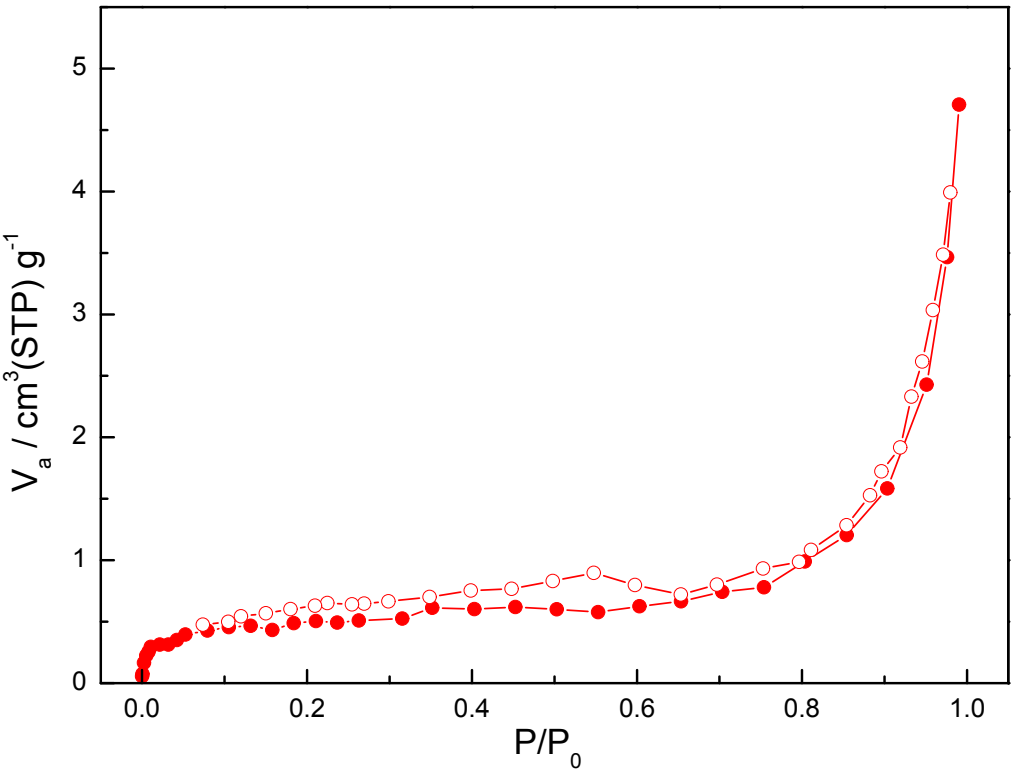


(b)

Figure S5. (a) Thermogravimetric (TG) measurement of **2**. (b) Temperature-dependent powder X-ray diffraction patterns of **2** from room temperature to 200 °C and its simulation from single-crystal diffraction data. The baselines for each temperature were shifted for clarity.



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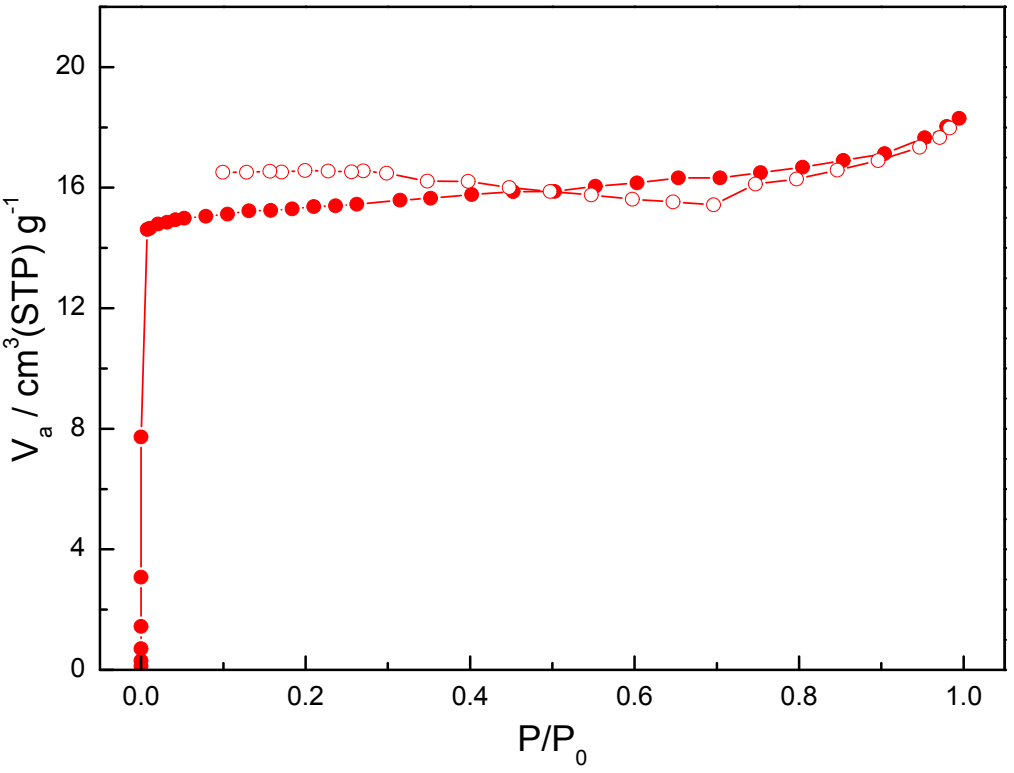

(b)

Figure S6. (a) N_2 ad-/desorption isotherms of dehydrated species **1** at 77 K. (b) N_2 ad-/desorption isotherms of dehydrated species **2** at 77 K.