Supplementary Information

pH modulated assembly in the mixed-ligand system Cd(II)-dpstc-phen: structural diversity and luminescent properties

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Table S1. Selected Bond Lengths (Å) and Bond Angles (°) for **1-4**

1

Cd1—O2^{i}	2.2457 (14)	Cd1—O3	2.5237 (14)
Cd1—N1	2.2839 (16)	Cd1—O4	2.5316 (15)
Cd1—O3^{ii}	2.3461 (14)	Cd1—O1^{i}	2.5343 (15)
Cd1—N2	2.3632 (16)	O2^{i}—Cd1—O4	84.80 (5)
O2^{i}—Cd1—N1	172.91 (5)	N1—Cd1—O4	95.38 (5)
O2^{i}—Cd1—O3^{ii}	95.70 (6)	O3^{ii}—Cd1—O4	123.88 (5)
N1—Cd1—O3^{ii}	90.10 (5)	N2—Cd1—O4	82.79 (5)
O2^{i}—Cd1—N2	100.77 (6)	O3—Cd1—O4	51.08 (4)
N1—Cd1—N2	72.25 (6)	O2^{i}—Cd1—O1^{i}	54.54 (5)
O3^{ii}—Cd1—N2	149.97 (5)	N1—Cd1—O1^{i}	121.80 (5)
O2^{i}—Cd1—O3	81.34 (5)	O3^{ii}—Cd1—O1^{i}	88.15 (5)
N1—Cd1—O3	104.30 (5)	N2—Cd1—O1^{i}	81.36 (5)
O3^{ii}—Cd1—O3	73.43 (5)	O3—Cd1—O1^{i}	130.35 (5)
N2—Cd1—O3	133.66 (5)	O4—Cd1—O1^{i}	131.96 (5)

Symmetry codes: (i) -1+*x*, *y*, *z*; (ii) 1+*x*, *y*, *z*.

2

Cd1—O8^{i}	2.289 (4)	Cd2—O4	2.242 (4)
Cd1—O2^{ii}	2.313 (4)	Cd2—O6^{iii}	2.288 (4)
Cd1—O3	2.321 (4)	Cd2—O5^{i}	2.339 (4)
Cd1—N1	2.352 (4)	Cd2—N4	2.340 (5)
Cd1—N2	2.403 (4)	Cd2—O7^{i}	2.350 (4)
Cd1—O2	2.467 (4)	Cd2—N3	2.377 (5)
O8^{i}—Cd1—O2^{ii}	99.48 (15)	O4—Cd2—O6^{iii}	85.47 (16)
O8^{i}—Cd1—O3	92.92 (14)	O4—Cd2—O5^{i}	81.42 (15)

O2^{ii}—Cd1—O3	146.29 (13)	O6^{iii}—Cd2—O5^{i}	101.21 (14)
O8^{i}—Cd1—N1	171.67 (16)	O4—Cd2—N4	169.29 (17)
O2^{ii}—Cd1—N1	88.80 (16)	O6^{iii}—Cd2—N4	104.57 (17)
O3—Cd1—N1	79.57 (15)	O5^{i}—Cd2—N4	99.90 (16)
O8^{i}—Cd1—N2	111.17 (15)	O4—Cd2—O7^{i}	93.02 (15)
O2^{ii}—Cd1—N2	85.15 (14)	O6^{iii}—Cd2—O7^{i}	175.39 (13)
O3—Cd1—N2	119.28 (15)	O5^{i}—Cd2—O7^{i}	74.24 (13)
N1—Cd1—N2	70.15 (16)	N4—Cd2—O7^{i}	77.24 (16)
O8^{i}—Cd1—O2	80.71 (14)	O4—Cd2—N3	106.97 (17)
O2^{ii}—Cd1—O2	79.08 (14)	O6^{iii}—Cd2—N3	85.73 (17)
O3—Cd1—O2	72.14 (13)	O5^{i}—Cd2—N3	169.66 (16)
N1—Cd1—O2	100.17 (15)	N4—Cd2—N3	70.72 (17)
N2—Cd1—O2	161.75 (14)	O7^{i}—Cd2—N3	98.88 (16)

Symmetry codes: (i) *x*, -1+*y*, *z*; (ii) -*x*, -*y*, 1-*z*; (iii) -*x*, 1-*y*, 2-*z*.

3

Cd1—O3^{i}	2.221 (2)	O1—Cd2	2.298 (2)
Cd1—O4	2.332 (2)	N1—Cd2	2.335 (3)
Cd1—N3	2.356 (3)	Cd2—O8^{ii}	2.225 (3)
Cd1—N4	2.372 (3)	Cd2—N2	2.278 (3)
Cd1—O6^{ii}	2.416 (2)	Cd2—O6^{ii}	2.375 (2)
Cd1—O5^{ii}	2.504 (2)	Cd2—O2	2.442 (2)
O3^{i}—Cd1—O4	100.50 (9)	O8^{ii}—Cd2—N2	124.83 (10)
O3^{i}—Cd1—N3	152.35 (11)	O8^{ii}—Cd2—O1	100.63 (10)
O4—Cd1—N3	89.63 (10)	N2—Cd2—O1	130.61 (10)
O3^{i}—Cd1—N4	85.92 (11)	O8^{ii}—Cd2—N1	81.16 (10)
O4—Cd1—N4	78.53 (10)	N2—Cd2—N1	72.50 (11)
N3—Cd1—N4	70.84 (11)	O1—Cd2—N1	99.62 (10)

O3^{i}—Cd1—O6^{ii}	99.02 (10)	O8^{ii}—Cd2—O6^{ii}	82.56 (9)
O4—Cd1—O6^{ii}	137.27 (8)	N2—Cd2—O6^{ii}	99.39 (10)
N3—Cd1—O6^{ii}	90.31 (10)	O1—Cd2—O6^{ii}	105.15 (9)
N4—Cd1—O6^{ii}	140.64 (9)	N1—Cd2—O6^{ii}	152.44 (9)
O3^{i}—Cd1—O5^{ii}	82.42 (9)	O8^{ii}—Cd2—O2	134.36 (9)
O4—Cd1—O5^{ii}	167.78 (9)	N2—Cd2—O2	96.11 (9)
N3—Cd1—O5^{ii}	82.76 (10)	O1—Cd2—O2	55.10 (8)
N4—Cd1—O5^{ii}	89.90 (9)	N1—Cd2—O2	135.54 (10)
O6^{ii}—Cd1—O5^{ii}	52.73 (8)	O6^{ii}—Cd2—O2	70.48 (8)
Symmetry codes: (i) -*x*, 1-*y*, -*z*; (ii) 1/2-*x*, 1/2+*y*, 1/2-*z*.			
4			
Cd1—O1	2.245 (3)	Cd2—O8	2.243 (3)
Cd1—O11	2.310 (3)	Cd2—O12	2.272 (4)
Cd1—N4	2.331 (3)	Cd2—N5	2.353 (4)
Cd1—N1	2.360 (3)	Cd2—N6	2.381 (4)
Cd1—N2	2.384 (3)	Cd2—N7	2.389 (4)
Cd1—N3	2.385 (3)	Cd2—N8	2.403 (4)
O1—Cd1—O11	106.84 (10)	O8—Cd2—O12	88.47 (13)
O1—Cd1—N4	97.75 (11)	O8—Cd2—N5	92.78 (12)
O11—Cd1—N4	101.63 (11)	O12—Cd2—N5	114.28 (15)
O1—Cd1—N1	99.20 (10)	O8—Cd2—N6	160.82 (13)
O11—Cd1—N1	88.59 (10)	O12—Cd2—N6	89.49 (14)
N4—Cd1—N1	156.73 (10)	N5—Cd2—N6	70.76 (14)
O1—Cd1—N2	88.81 (10)	O8—Cd2—N7	101.89 (12)
O11—Cd1—N2	156.17 (10)	O12—Cd2—N7	154.45 (14)
N4—Cd1—N2	93.69 (11)	N5—Cd2—N7	88.75 (13)
N1—Cd1—N2	70.90 (10)	N6—Cd2—N7	87.92 (13)

O1—Cd1—N3	166.65 (11)	O8—Cd2—N8	111.56 (12)
O11—Cd1—N3	82.71 (11)	O12—Cd2—N8	85.52 (17)
N4—Cd1—N3	70.74 (12)	N5—Cd2—N8	149.48 (14)
N1—Cd1—N3	90.20 (11)	N6—Cd2—N8	87.28 (14)
N2—Cd1—N3	85.30 (11)	N7—Cd2—N8	68.98 (16)

Table S2. List of π-π interactions in complexes **1-4**^{a}.

Complex **1**

Ring A	Ring B	Cg-Cg (Å)	Dihedral angel (°)	CgA_Perp(Å)	Slippage(Å)
R1	R2^{i}	3.8070	1.50	3.315	1.872
R1	R3^{ii}	3.4642	1.04	3.340	0.919
R2	R3^{i}	3.6672	0.50	3.338	1.519
R3	R3^{i}	3.4618	0.00	3.325	0.964

R1 = N(1)-C(17)-C(18)-C(19)-C(20)- C(21)

R2 =N(2)-C(22)-C(23)-C(26)-C(27)-C(28)

R3 = C(20)-C(21)-C(22)-C(23)-C(24)-C(25)

Symmetry codes: (i) -1-*x*, 1-*y*, 1-*z*, (ii) -*x*, 1-*y*, 1-*z*.

Complex **2**

Ring A	Ring B	Cg-Cg (Å)	Dihedral angel (°)	CgA_Perp(Å)	Slippage(Å)
R1	R3	3.8279	7.29	3.448	1.663
R1	R5^{i}	3.7476	0.96	3.298	1.780
R2	R6	3.6478	7.67	3.612	0.510
R3	R5	3.6892	6.87	3.360	1.202
R4	R6^{ii}	3.8484	2.99	3.320	1.946
R5	R5^{i}	3.8979	0.00	3.320	2.042
R6	R5	3.9192	8.32	3.507	1.749
R6	R6^{ii}	3.4601	0.03	3.377	0.754

R1 = N(1)-C(17)-C(18)-C(19)-C(20)-C(28)

R2 = N(2)-C(26)-C(25)-C(24)-C(23)-C(27)

R3 = N(3)-C(29)-C(30)-C(31)-C(32)-C(40)

R4 = N(4)-C(38)-C(37)-C(36)-C(35)-C(39)

R5 = C(20)-C(21)-C(22)-C(23)-C(27)-C(28)

R6 = C(32)-C(33)-C(34)-C(35)-C(39)-C(40)

Symmetry codes: (i) 1-*x*, -*y*, 1-*z*, (ii) 1-*x*, -*y*, 2-*z*.

complex **3**

Ring A	Ring B	Cg-Cg (Å)	Dihedral angel (°)	CgA_Perp(Å)	Slippage(Å)
R1	R2^{i}	3.7815	2.36	3.484	1.47

R1 = N(2)-C(26)-C(25)-C(24)-C(23)-C(28)

R2 = N(4)-C(38)-C(37)-C(36)-C(35)-C(39)

Symmetry codes: (i) -*x*, 1-*y*, -*z*.

complex **4**

Ring A	Ring B	Cg-Cg (Å)	Dihedral angel (°)	CgA_Perp(Å)	Slippage(Å)
R1	R6^{i}	3.5988	0.68	3.407	1.159

R2	R2$^{\mathrm{ii}}$	3.8737	0.03	3.552	1.545
R3	R7$^{\mathrm{iii}}$	3.5412	1.75	3.428	0.888
R4	R8$^{\mathrm{iv}}$	3.6475	0.59	3.501	1.023
R5	R5$^{\mathrm{v}}$	3.8704	0.03	3.407	1.836
R5	R9$^{\mathrm{v}}$	3.4680	0.91	3.396	0.703
R6	R6$^{\mathrm{i}}$	3.7211	0.00	3.386	1.543
R8	R8$^{\mathrm{iv}}$	3.8167	0.00	3.514	1.489

R1 = N(1)-C(22)-C(23)-C(26)-C(27)-C(28)

R2 = N(2)-C(17)-C(18)-C(19)-C(20)-C(21)

R3 = N(4)-C(38)-C(37)-C(36)-C(35)-C(40)

R4 = N(5)-C(41)-C(42)-C(43)-C(44)-C(45)

R5 = N(8)-C(62)-C(61)-C(60)-C(59)-C(63)

R6 = C(20)-C(21)-C(22)-C(23)-C(24)-C(25)

R7 = C(32)-C(33)-C(34)-C(35)-C(40)-C(39)

R8 = C(44)-C(45)-C(52)-C(48)-C(47)-C(46)

R9 = C(56)-C(57)-C(58)-C(59)-C(63)-C(64)

Symmetry codes: (i) 2-*x*, 1-*y*, -*z*, (ii) 1-*x*, 1-*y*, -*z*, (iii) 1-*x*, -*y*, -*z*, (iv) 1-*x*, 1-*y*, 1-*z*, (v) 2-*x*, -*y*, 1-*z*.

[a]Cg-Cg = Distance between ring Centroids, CgA_Perp = Perpendicular distance of Cg(A) on ring B, Slippage = Distance between Cg(A) and Perpendicular Projection of Cg(B) on Ring A.

Table S3. List of C-H···π interactions in complex **4**[a].

D-H···*A*	*D*-H (Å)	H···*A* (Å)	∠*D*-H···*A* (°)
C19-H19···Cg(1)$^{\mathrm{i}}$	0.93	2.61	169
C25-H25···Cg(2)$^{\mathrm{i}}$	0.93	3.17	166
C55-H55···Cg(3)$^{\mathrm{ii}}$	0.93	3.16	164
C57-H57···Cg(4)$^{\mathrm{ii}}$	0.93	3.22	172

Ring 1 = N(3)-C(29)-C(30)-C(31)-C(32)-C(39)

Ring 2 = C(32)-C(33)-C(34)-C(35)-C(40)-C(39)

Ring 3 = N(6)-C(51)-C(50)-C(49)-C(48)-C(52)

Ring 4 = C(44)-C(45)-C(52)-C(48)-C(47)-C(46)

[a]Cg(A) = Centroid of ring A, symmetry codes: (i) 1-*x*, 1-*y*, -*z*, (ii) 1-*x*, 2-*y*, -*z*-1.

Table S4. Selected Hydrogen-bond Lengths (Å) and Angles (°) for **4**[a]

	D—H	H...A	D...A	D—H...A
O13—H13A...O4$^{\mathrm{i}}$	0.85	2.05	2.899 (5)	173.1
O13—H13B...O6	0.87	2.11	2.826 (5)	139.2
O14—H14A...O5	0.87	2.17	2.904 (6)	141.5
O14—H14B...O4$^{\mathrm{i}}$	0.86	2.11	2.950 (5)	165.2
O15—H15A...O1	0.87	2.11	2.971 (7)	174.3
O15—H15B...O17	0.87	2.05	2.859 (8)	153.3
O16—H16A...O15	0.89	2.06	2.946 (8)	169.8
O16—H16B...O5	0.89	1.92	2.805 (8)	170.6
O17—H17B...O3	0.88	2.03	2.832 (6)	152.5
O18—H18A...O14$^{\mathrm{ii}}$	0.90	2.11	2.897 (8)	145.4
O18—H18B...O3	0.86	2.03	2.863 (7)	164.2
O11—H11A...O2$^{\mathrm{iii}}$	0.85	2.15	2.792 (4)	132.6

O11—H11B...O4$^{\text{iii}}$	0.85	1.94	2.759 (4)	161.8
O12—H12B...O6$^{\text{iv}}$	0.85	2.05	2.638 (5)	125.3

[a] Symmetry codes: (i) *x*, -1+*y*, *z*; (ii) *x*, 1+*y*, *z*; (iii) -*x*, 2-*y*, -*z*; (iv) -*x*, 1-*y*, -1-*z*.

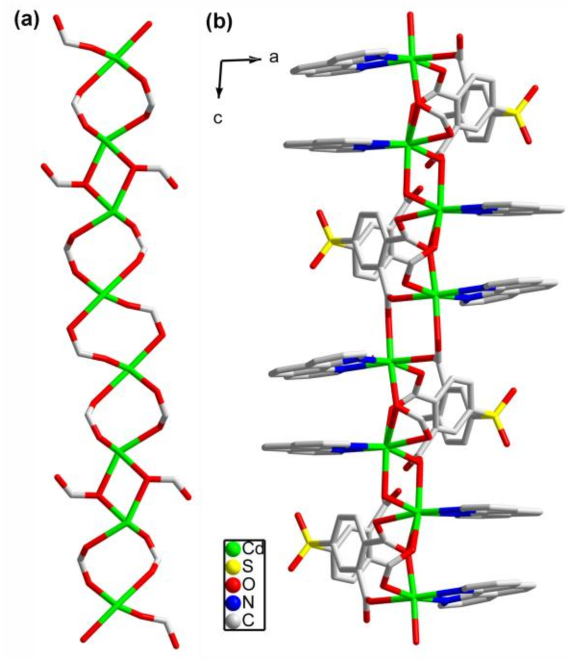

Figure S1. (a) The 1D Cd(II)-carboxylate chain in **2**. (b) The 2D layer of **2**, view along [0 1 0] direction.

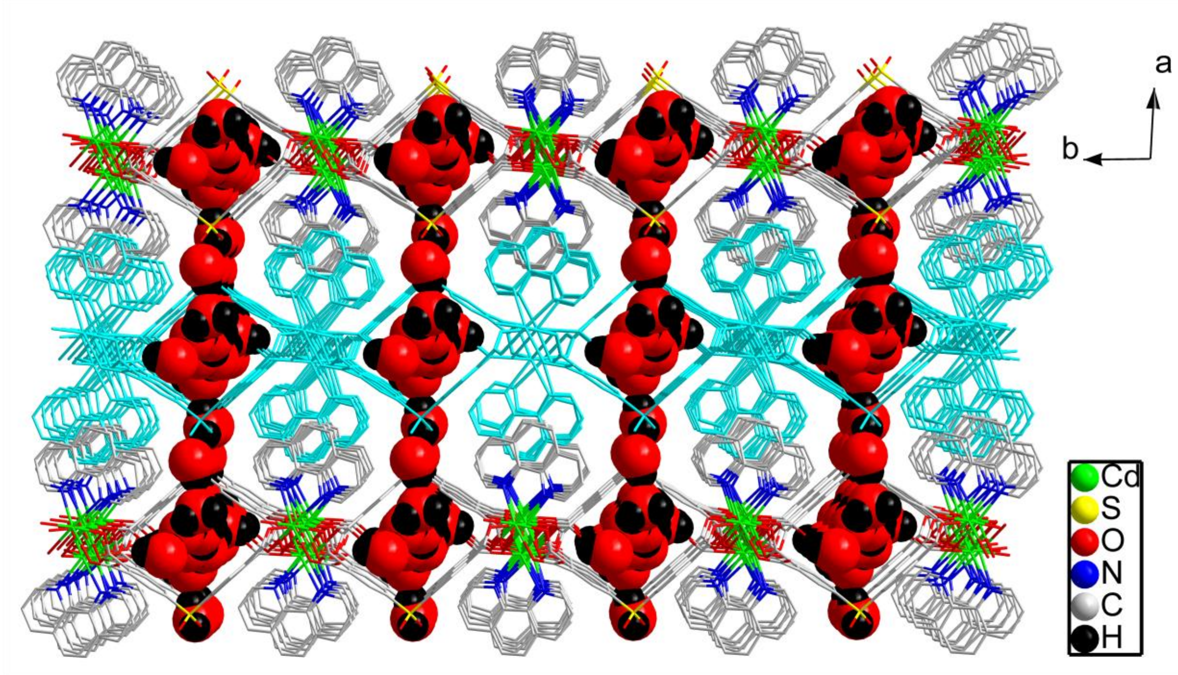

Figure S2. Illustration of the interpenetration mode of **2** from the [110] direction. One of the 2D metal-organic networks is highlighted in light blue, 2D water layers are represented in space-filling mode.

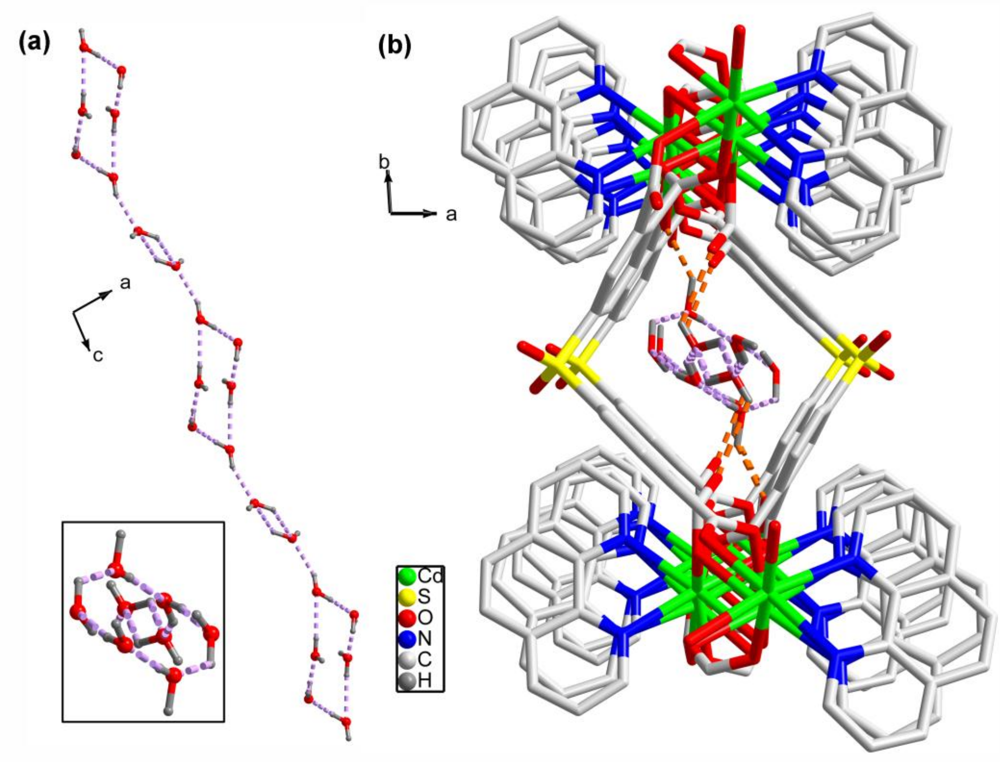

Figure S3. (a) The 1D water chain in **2** constructed from hexanuclear water clusters and dimers of O12. (b) The 1D water chain in the 1D channel of complex **2** stabilized by hydrogen bonding interactions, view along [0 0 1] direction. Violet dashed lines represent the hydrogen bonds between the water molecules; orange dashed lines represent the hydrogen bonds between the water chain and metal-organic host.

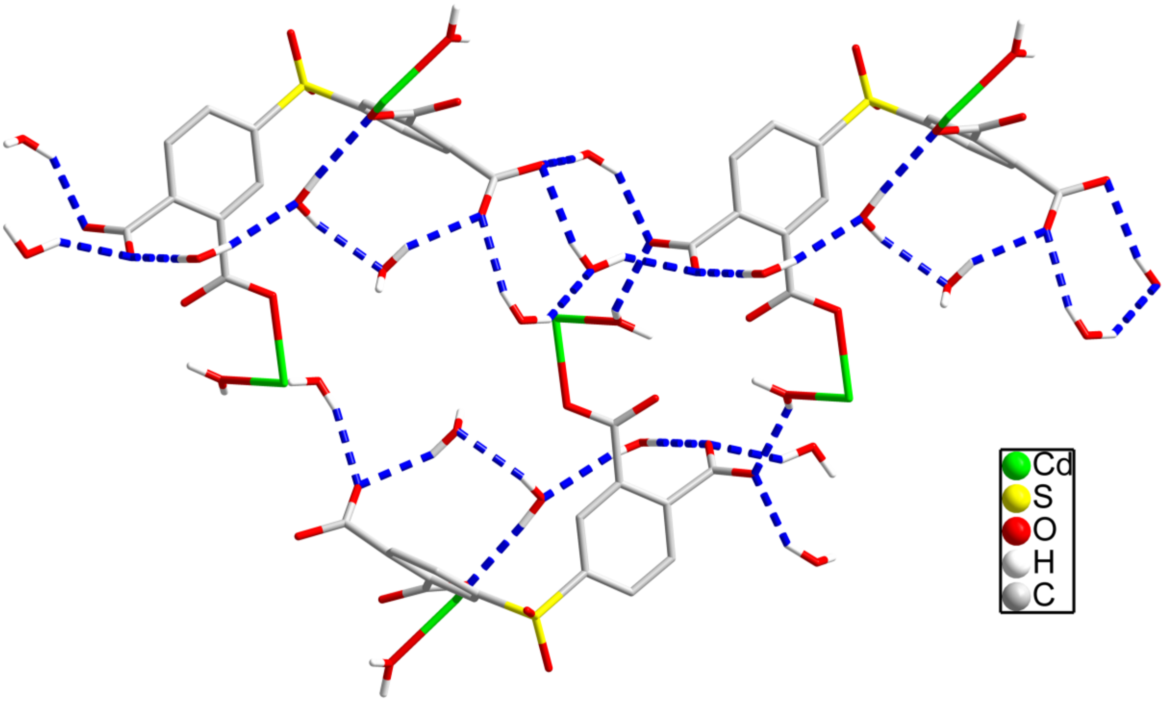

Figure S4. Illustration of the hydrogen-bonding interactions in complex **4** (the blue dashed lines represent the H-bonds and the phen ligands have been omitted for clarity)

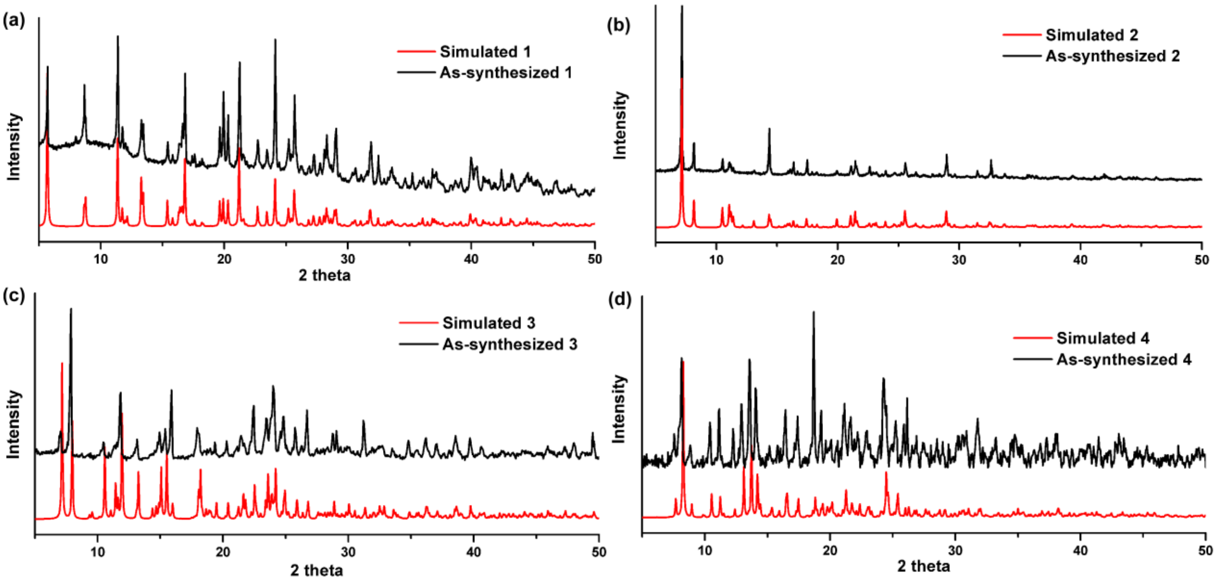

Figure S5. Powder X-ray diffraction patterns of the simulated and as-synthesized samples of **1**-**4**.

Estimation the acidity of the carboxylic groups on ligand H_4dpstc.

First, we suppose that the ligand is a monoprotic acid to compare the acidity among the four carboxylic groups. And due to the symmetry, the both phthalic groups are equally and we only need to discuss the two carboxylic groups of the phthalic groups. Because the sulphone group (SO_2) is an electron-withdrawing group, the carboxylic group on the benzene ring can be deprotonated more easily. At the same time, the electron-withdrawing effect of p-carboxylic group (4-COOH) is more obvious than that of m-carboxylic group (3-COOH). Therefore, the 4-COOH is easily to deprotonated than the 3-COOH. To check the conclusion, we use the *MarvinSketch* software to calculate the pKa values of the two carboxylic groups. To eliminate the influence of the other protonated carboxylic groups, we protect them as methyl ester groups (COOMe). The pKa values of the 3- and 4-COOH are calculated as 2.75 and 2.55, respectively, when the other three carboxylic groups are protected (Figure S6a, b). This result fits the inference well. Furthermore, we still wonder which carboxylic groups is the second most acidic. Use the same theory, we suppose that the ligand is a diacid and the 4-COOH is deprotonated. Because the deprotonated carboxylic group is an electron-donating group, it can make the other carboxylic groups become hard to get deprotonation. And electron-donating effect is most significant to the 3-COOH, but become weak to the carboxylic groups on the other phthalic group (3′- and 4′-COOH) because of the weak conjugation between the two benzene rings. Therefore, the 3′- and 4′-COOH are mainly affected by the electron-withdrawing effect of the SO_2 group. From this point, the acidity among these three carboxylic groups is 4′- > 3′- > 3-COOH. Equally, we calculate the pKa values of 4- and 3-COOH (4- and 3′-COOH, 4- and 4′-COOH at another two processes) simultaneously, with the other two carboxylic groups being protected. As the result, the pKa values of the 3-, 3′- and 4′-COOH are 5.08, 2.96 and 2.85 (the pKa values of the 4-COOH at three times are 2.25, 2.34 and 2.49, respectively) (Figure S6c-e). These results are also in accordance with the estimation we get previously. And when the 4- and 4′-COOH are all deprotonated, due to the strong electron-donating effect, the 3- and 3′-COOH would be relatively hard to be deprotonated. From the calculation above (when 4-COOH is deprotonated, the pKa value of 3-COOH is 5.08), the pKa values of remaining two carboxylic groups might locate at about 5. Therefore, the acidity of the 3- and 3′-COOH is the weakest among the four ones.

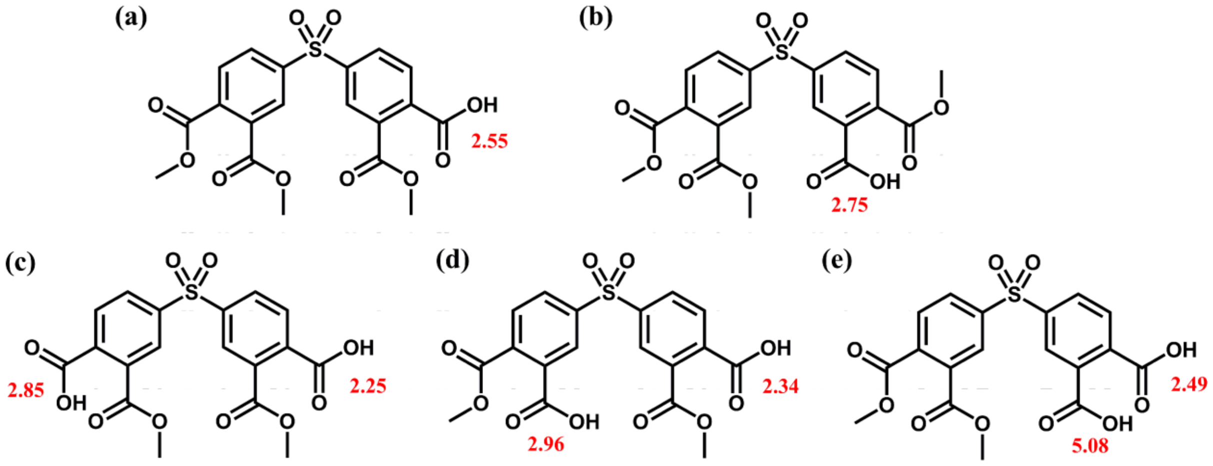

Figure S6. The pKa values calculated by *MarvinSketch* software and using the methyl ester groups (COOMe) to replace the protonated carboxylic groups (the numbers highlighted in red represent the pKa values)

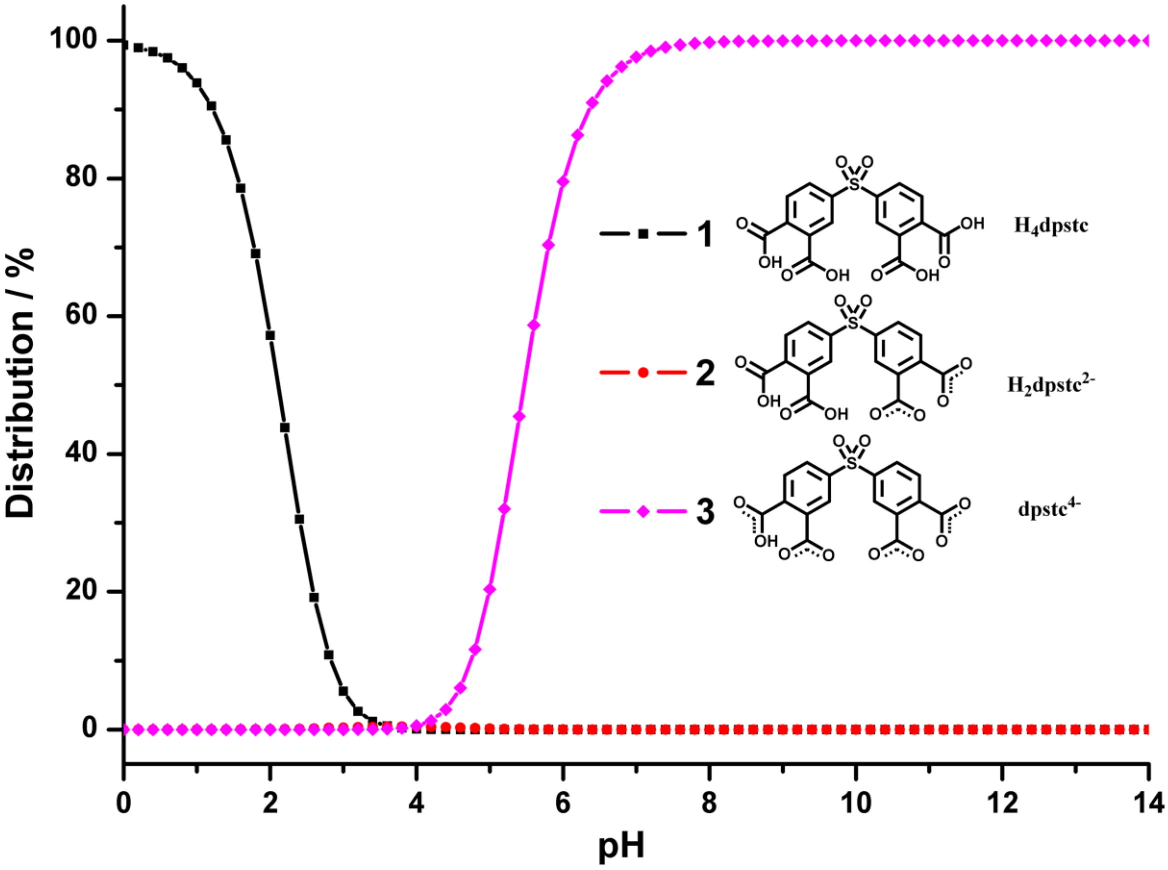

Figure S7. Distribution of partial and fully deprotonated ligand species in aqueous solution with varies pH values

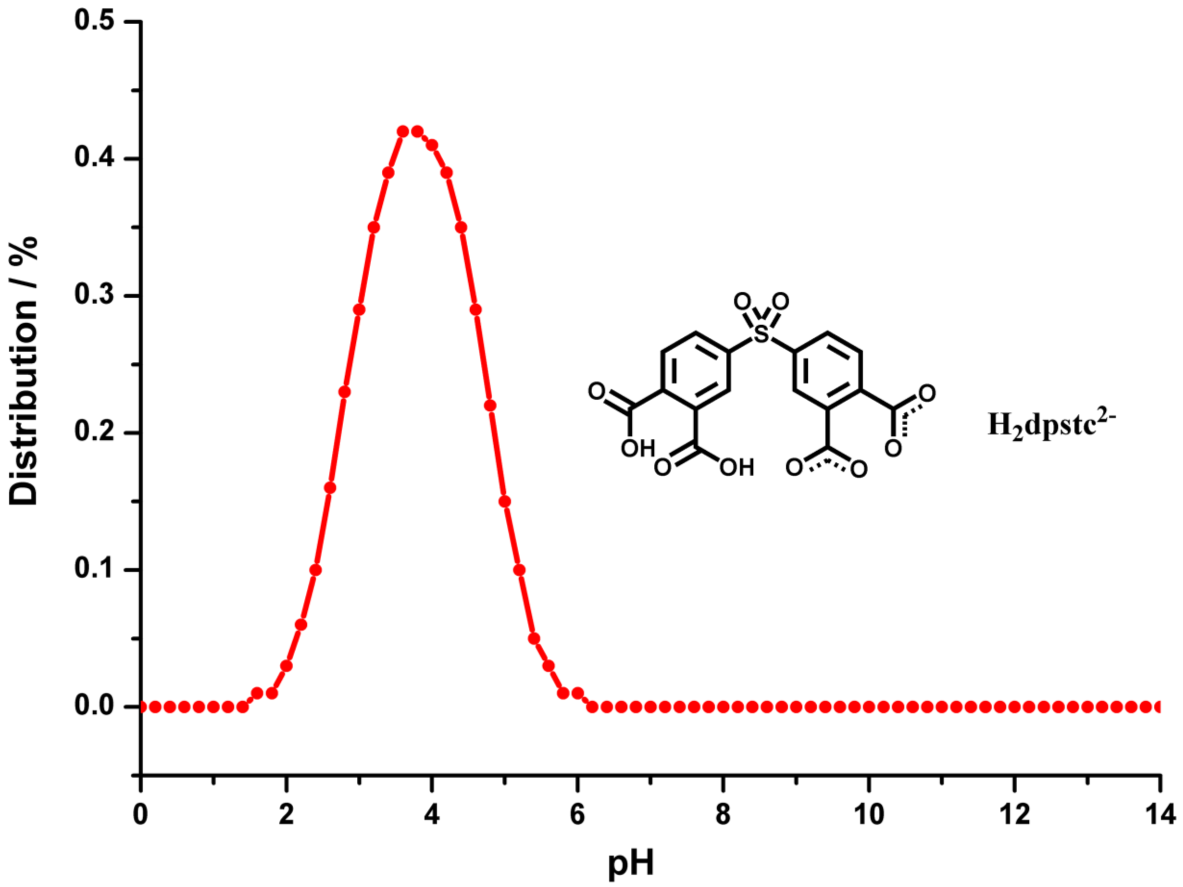

Figure S8. Distribution of partial deprotonated ligand species H$_2$dpstc^{2-} in aqueous solution with varies pH values

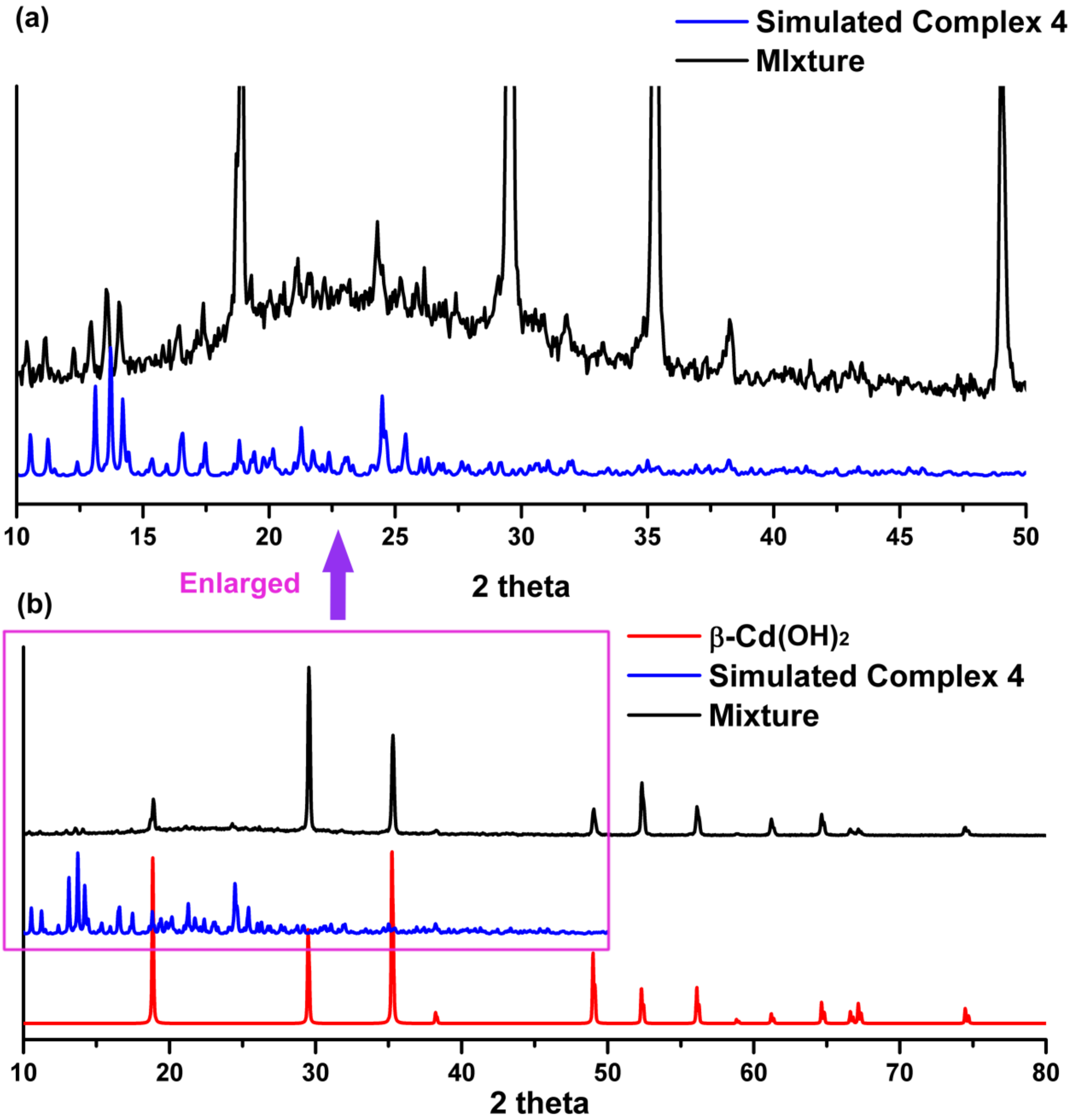

Figure S9. Powder X-ray diffraction patterns of the simulated β-Cd$(OH)_2$, complex **4** and as-synthesized the mixture of the reaction.