Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Structural diversity and properties of Zn^{II} and Cd^{II} complexes with a flexible dicarboxylate building block 1,3-phenylenediacetate and various heterocyclic co-ligands

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Table S1. Selected bond distances [Å] and angles [°] for compounds **1-6**

		1	
Zn(1)-O(1)	**1.951(2)**	**Zn(1)-N(2)**	**2.091(3)**
Zn(1)-O(3)#1	**2.028(2)**	**Zn(1)-O(4)#1**	**2.317(3)**
Zn(1)-N(1)	**2.067(2)**		
O(1)-Zn(1)-O(3)#1	**117.8(9)**	**O(3)#1-Zn(1)-O(4)#1**	**59.17(8)**
O(1)-Zn(1)-N(1)	**115.9(1)**	**N(1)-Zn(1)-O(4)#1**	**149.9(1)**
O(3)#1-Zn(1)-N(1)	**104.8(9)**	**N(2)-Zn(1)-O(4)#1**	**89.8(1)**
O(1)-Zn(1)-N(2)	**105.4(1)**	**N(1)-Zn(1)-N(2)**	**80.5(1)**
O(3)#1-Zn(1)-N(2)	**126.9(1)**	**O(1)-Zn(1)-O(4)#1**	**94.1(1)**
		2	
Zn(1)-O(2)	**1.945(4)**	**Zn(1)-N(2)**	**2.093(2)**
Zn(1)-O(3)#1	**1.965(4)**	**O(3)-Zn(1)#2**	**1.965(4)**
Zn(1)-N(1)	**2.053(4)**		
O(2)-Zn(1)-N(1)	**123.7(2)**	**O(2)-Zn(1)-O(3)#1**	**110.2(2)**
O(2)-Zn(1)-N(2)	**109.8(2)**	**O(3)#1-Zn(1)-N(1)**	**98.1(2)**
N(1)-Zn(1)-N(2)	**102.1(1)**	**O(3)#1-Zn(1)-N(2)**	**112.4(1)**
		3	
Zn(1)-O(4)#1	**1.939(1)**	**Zn(1)-N(2)#2**	**2.038(2)**
Zn(1)-O(1)	**1.967(2)**	**O(4)-Zn(1)#3**	**1.939(1)**
Zn(1)-N(1)	**2.032(2)**	**N(2)-Zn(1)#4**	**2.038(2)**
O(4)#1-Zn(1)-O(1)	**99.9(6)**	**O(4)#1-Zn(1)-N(2)#2**	**110.1(7)**
O(4)#1-Zn(1)-N(1)	**107.6(6)**	**O(1)-Zn(1)-N(2)#2**	**106.8(7)**
O(1)-Zn(1)-N(1)	**115.7(7)**	**N(1)-Zn(1)-N(2)#2**	**115.6(7)**

4

Cd(1)-O(9)#1	**2.210(2)**	**Cd(2)-O(5)#2**	**2.242(2)**
Cd(1)-O(4)	**2.302(2)**	**Cd(2)-O(7)**	**2.263(2)**
Cd(1)-N(1)	**2.332(2)**	**Cd(2)-N(3)**	**2.330(2)**
Cd(1)-N(2)	**2.340(2)**	**Cd(2)-N(4)**	**2.344(2)**
Cd(1)-O(8)	**2.421(2)**	**Cd(2)-O(3)**	**2.403(2)**
Cd(1)-O(3)	**2.551(2)**	**Cd(2)-O(8)**	**2.628(2)**
O(9)#1-Cd(1)-O(4)	**107.4(8)**	**O(5)#2-Cd(2)-O(7)**	**107.5(8)**
O(9)#1-Cd(1)-N(1)	**112.5(7)**	**O(5)#2-Cd(2)-N(3)**	**104.0(7)**
O(4)-Cd(1)-N(1)	**95.3(8)**	**O(7)-Cd(2)-N(3)**	**148.5(7)**
O(9)#1-Cd(1)-N(2)	**110.5(8)**	**O(5)#2-Cd(2)-N(4)**	**117.6(7)**
O(4)-Cd(1)-N(2)	**142.0(7)**	**O(7)-Cd(2)-N(4)**	**95.1(8)**
N(1)-Cd(1)-N(2)	**70.7(7)**	**N(3)-Cd(2)-N(4)**	**70.4(7)**
O(9)#1-Cd(1)-O(8)	**84.0(7)**	**O(5)#2-Cd(2)-O(3)**	**86.6(6)**
O(4)-Cd(1)-O(8)	**98.5(7)**	**O(7)-Cd(2)-O(3)**	**94.7(7)**
N(1)-Cd(1)-O(8)	**154.2(7)**	**N(3)-Cd(2)-O(3)**	**86.6(6)**
N(2)-Cd(1)-O(8)	**85.2(7)**	**N(4)-Cd(2)-O(3)**	**149.5(6)**
O(9)#1-Cd(1)-O(3)	**145.6(7)**	**O(5)#2-Cd(2)-O(8)**	**147.4(6)**
O(4)-Cd(1)-O(3)	**53.5(6)**	**O(7)-Cd(2)-O(8)**	**52.6(6)**
N(1)-Cd(1)-O(3)	**98.7(7)**	**N(3)-Cd(2)-O(8)**	**98.8(6)**
N(2)-Cd(1)-O(3)	**92.8(6)**	**N(4)-Cd(2)-O(8)**	**91.8(7)**
O(8)-Cd(1)-O(3)	**72.8(6)**	**O(3)-Cd(2)-O(8)**	**71.7(6)**

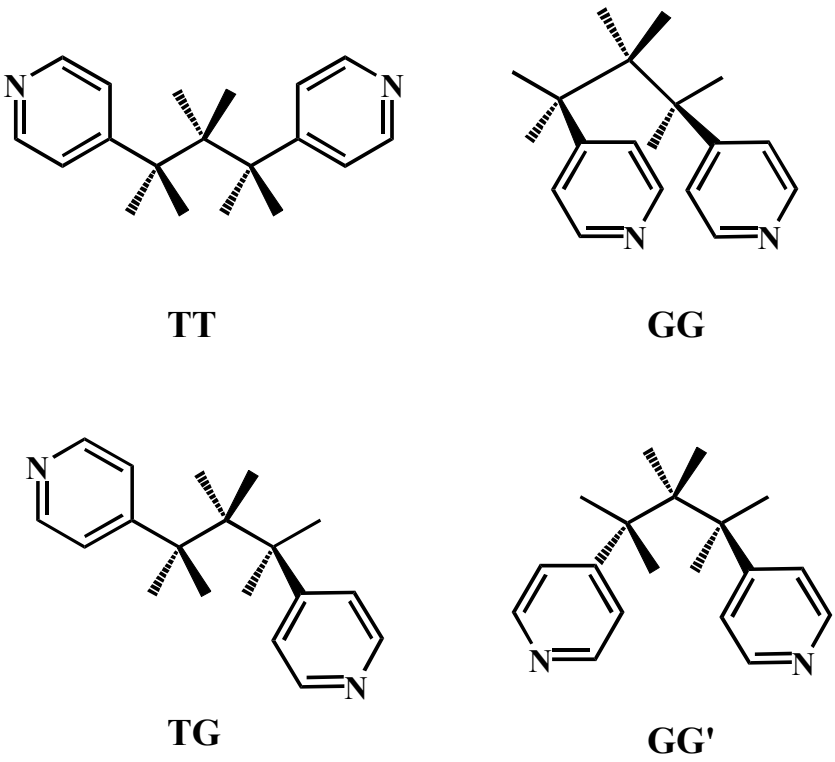
		5	
Cd(1)-N(1)	**2.301(2)**	**Cd(1)-O(1)**	**2.432(2)**
Cd(1)-N(2)#1	**2.334(2)**	**Cd(1)-O(2)**	**2.442(2)**
Cd(1)-O(5)	**2.367(2)**	**Cd(1)-O(4)#2**	**2.452(2)**
Cd(1)-O(3)#2	**2.368(2)**		
N(1)-Cd(1)-N(2)#1	**171.7(6)**	**O(1)-Cd(1)-O(2)**	**53.7(6)**
N(1)-Cd(1)-O(5)	**90.3(6)**	**N(2)#1-Cd(1)-O(2)**	**82.0(7)**
N(2)#1-Cd(1)-O(5)	**88.6(6)**	**O(5)-Cd(1)-O(2)**	**90.3(6)**
N(1)-Cd(1)-O(3)#2	**97.6(6)**	**O(3)#2-Cd(1)-O(2)**	**138.5(5)**
N(2)#1-Cd(1)-O(3)#2	**89.4(6)**	**N(1)-Cd(1)-O(4)#2**	**97.1(7)**
O(5)-Cd(1)-O(3)#2	**130.2(6)**	**N(2)#1-Cd(1)-O(4)#2**	**90.6(7)**
N(1)-Cd(1)-O(1)	**92.9(7)**	**O(5)-Cd(1)-O(4)#2**	**76.3(6)**
N(2)#1-Cd(1)-O(1)	**83.2(7)**	**O(3)#2-Cd(1)-O(4)#2**	**53.9(5)**
O(5)-Cd(1)-O(1)	**143.8(6)**	**O(1)-Cd(1)-O(4)#2**	**138.7(6)**
O(3)#2-Cd(1)-O(1)	**85.1(6)**	**O(2)-Cd(1)-O(4)#2**	**164.9(6)**
N(1)-Cd(1)-O(2)	**89.8(7)**		
		6	
Cd(1)-O(8)	**2.298(3)**	**Cd(1)-O(11)#1**	**2.380(3)**
Cd(1)-N(3)	**2.340(3)**	**Cd(1)-N(2)#2**	**2.389(3)**
Cd(1)-N(1)	**2.359(3)**	**Cd(1)-O(10)#1**	**2.552(3)**
O(10)-Cd(1)#3	**2.553(3)**	**O(11)-Cd(1)#3**	**2.381(3)**
N(2)-Cd(1)#2	**2.389(3)**	**O(8)-Cd(1)-N(3)**	**92.4(1)**
O(8)-Cd(1)-N(1)	**134.0(1)**	**N(1)-Cd(1)-N(2)#2**	**84.2(1)**
N(3)-Cd(1)-N(1)	**92.3(1)**	**O(11)#1-Cd(1)-N(2)#2**	**94.6(1)**
O(8)-Cd(1)-O(11)#1	**138.6(1)**	**O(8)-Cd(1)-O(10)#1**	**86.9(1)**
N(3)-Cd(1)-O(11)#1	**89.1(1)**	**N(3)-Cd(1)-O(10)#1**	**96.4(1)**
N(1)-Cd(1)-O(11)#1	**87.2(1)**	**N(1)-Cd(1)-O(10)#1**	**137.8(1)**
O(8)-Cd(1)-N(2)#2	**87.3(1)**	**O(11)#1-Cd(1)-O(10)#1**	**51.9(1)**
N(3)-Cd(1)-N(2)#2	**174.7(1)**	**N(2)#2-Cd(1)-O(10)#1**	**88.9(1)**

Symmetry transformations used to generate equivalent atoms: For **1** #1: $-x + 2, -y + 2, -z$. For **2** #1: $x, y + 1, z$; #2: $x, y - 1, z$. For **3** #1: $-x + 3/2, y - 1/2, -z + 1/2$; #2: $x - 1, y, z - 1$; #3: $-x + 3/2, y + 1/2, -z + 1/2$; #4: $x + 1, y, z + 1$. For **4** #1: $-x + 2, -y, -z$; #2: $-x + 2, -y, -z + 1$. For **5** #1: $x - 1, y - 1, z$; #2: $-x, -y, -z + 2$. For **6** #1: $-x + 1/2, y + 1/2, -z + 3/2$; #2: $-x, -y + 1, -z + 2$; #3: $-x + 1/2, y - 1/2, -z + 3/2$.

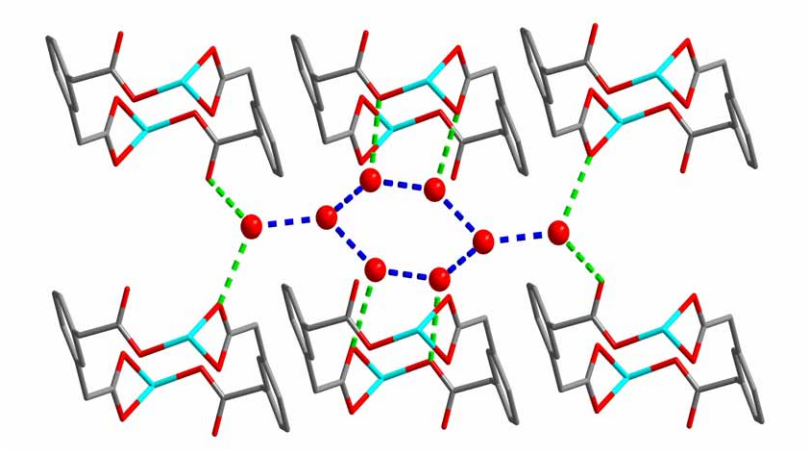
Table S2 Hydrogen bonding parameters for complexes **1** and **6**

D–H···A	H···A/Å	D···A/Å	<D–H···A/°
1			
O(5)–H(1W)···O(8)#2	1.93	2.746(5)	166
O(5)–H(2W)···O(4)#3	2.08	2.830(4)	150
O(6)–H(3W)···O(7)	1.96	2.768(5)	165
O(6)–H(4W)···O(5)	1.93	2.738(7)	165
O(7)–H(5W)···O(2)	2.01	2.788(4)	155
O(7)–H(6W)···O(3)#4	1.95	2.780(3)	174
O(8)–H(7W)···O(1)#5	1.98	2.801(3)	169
O(8)–H(8W)···O(6)	1.89	2.717(6)	167
6			
O(1)–H(1W)···O(3)	2.06	2.887(6)	169
O(1)–H(2W)···O(8)	2.15	2.937(5)	159
O(2)–H(3W)···O(1)	1.99	2.809(6)	168
O(2)–H(4W)···O(10)	2.24	3.051(6)	165
O(3)–H(5W)···O(9)#1	2.07	2.868(5)	164
O(3)–H(6W)···O(5)	1.85	2.705(1)	170
O(4)–H(7W)···O(5)	1.74	2.370(2)	131
O(4)–H(8W)···O(6)#5	2.34	3.058(2)	145
O(4)–H(8W)···O(2)	2.32	2.814(2)	119
O(6)–H(11W)···O(7)#6	1.86	2.463(1)	129
O(6)–H(12W)···O(4)#5	2.47	3.058(2)	129
O(7)–H(13W)···O(4)#7	1.93	2.426(2)	117
O(7)–H(14W)···O(7)#8	2.34	2.850(2)	119
O(5)–H(9W)···O(4)	1.93	2.370(2)	111
O(5)–H(10W)···O(5)#4	1.61	2.690(3)	171

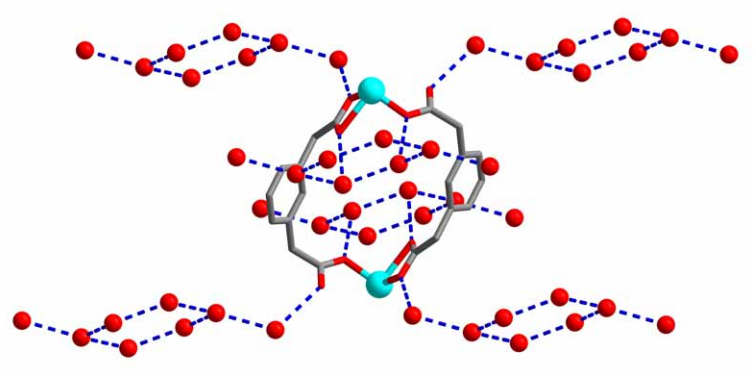
Symmetry codes: For **1** #1: -*x* + 2, -*y* + 2, -*z*; #2: -*x* + 2, -*y* + 1, -*z* + 2; #3: -*x* + 2, -*y* + 2, -*z* + 1; #4: *x* - 1, *y*, *z* + 1; #5: -*x* + 2, -*y* + 1, -*z* + 1. For **6** #1: -*x* + 1/2, *y* + 1/2, -*z* + 3/2; #2: -*x*, -*y* + 1, -*z* + 2; #3: -*x* + 1/2, *y* - 1/2, -*z* + 3/2; #4: -*x* + 1, *y*, -*z* + 3/2; #5: -*x* + 1/2, -*y* + 1/2, -*z* + 1; #6: *x*, *y* - 1, *z*; #7: -*x* + 1/2, -*y* + 3/2, -*z* + 1; #8: -*x*, -*y* + 2, -*z* + 1.



Scheme S1 Conformations of bpp in coordination complexes (T = trans and G =gauche).



(a)



(b)

Fig. S1. (a) Six binuclear molecules linked by one water cluster in complex **1**. (b) A binuclear molecule connecting six water clusters (the phen molecules are omitted for clarity).

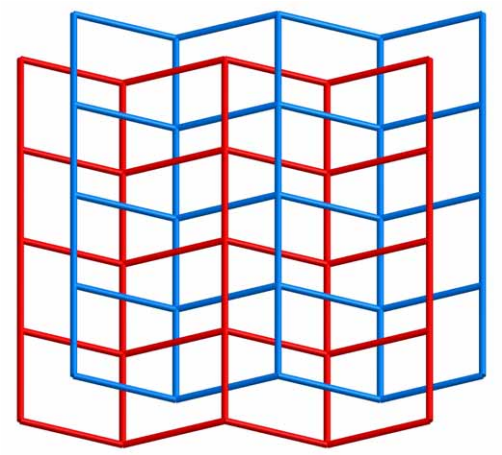


Fig. S2 Schematic illustration the 2-fold interpenetrating 2D network of complex **3**.

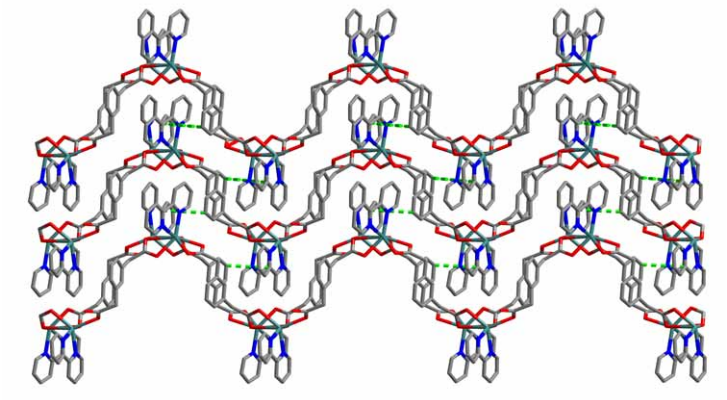


Fig. S3 2D layer of complex **4** through π-π stacking interactions.

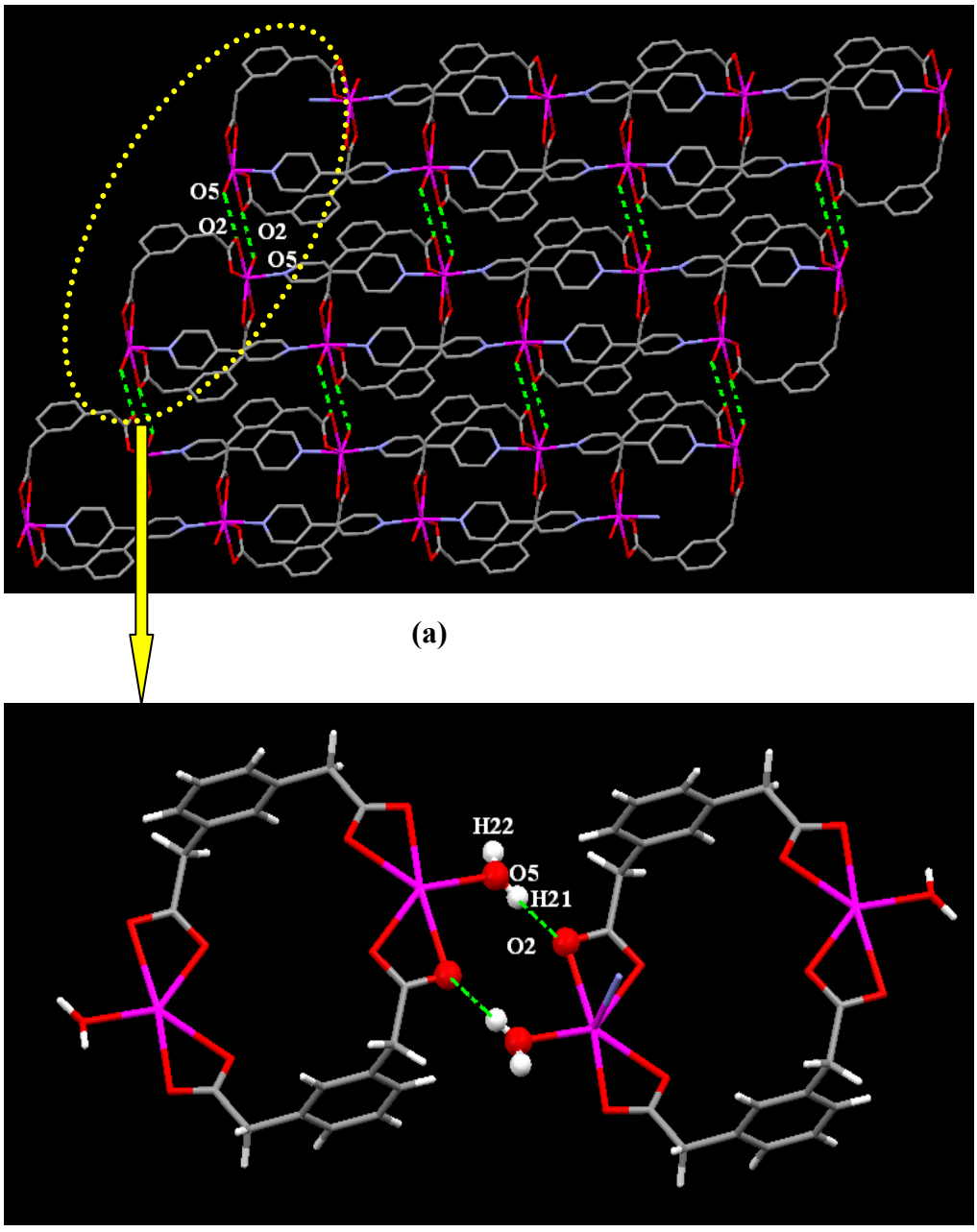
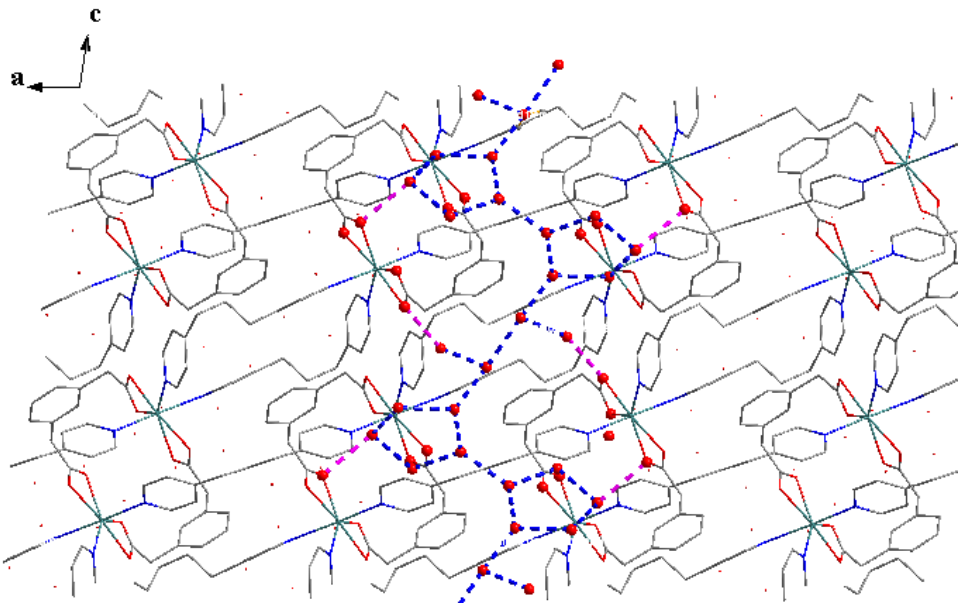
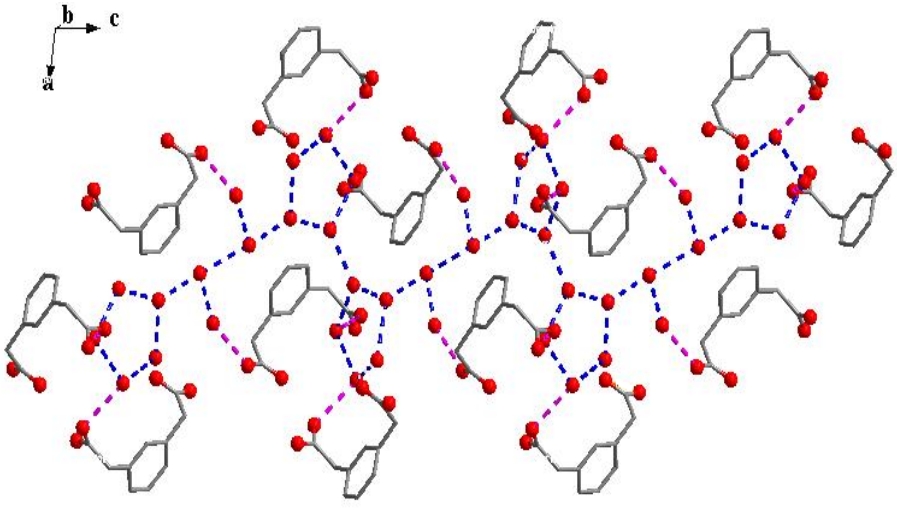


Fig. S4 (a) 2D supramolecular network of complex **5** through hydrogen bonding. (b) Schematic illustration of the hydrogen bonding motif [$R_2^2(8)$].

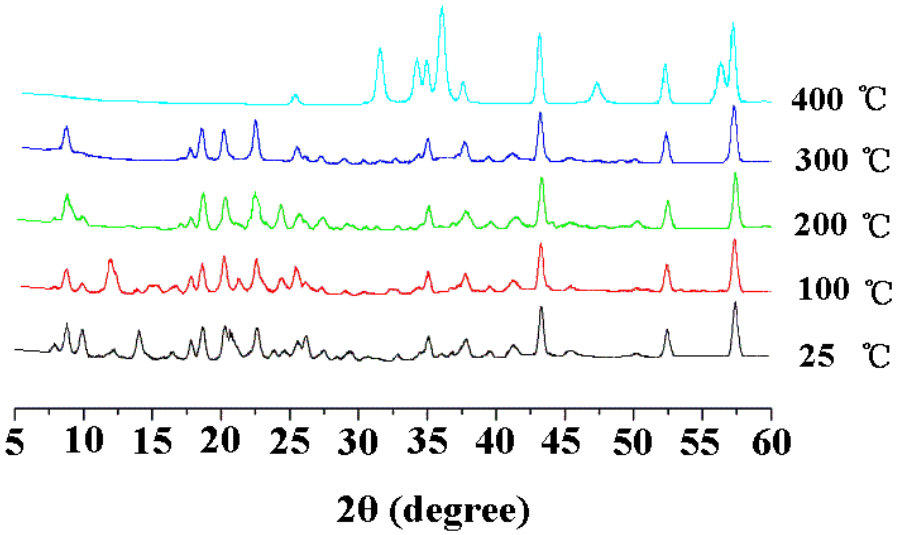


(a)

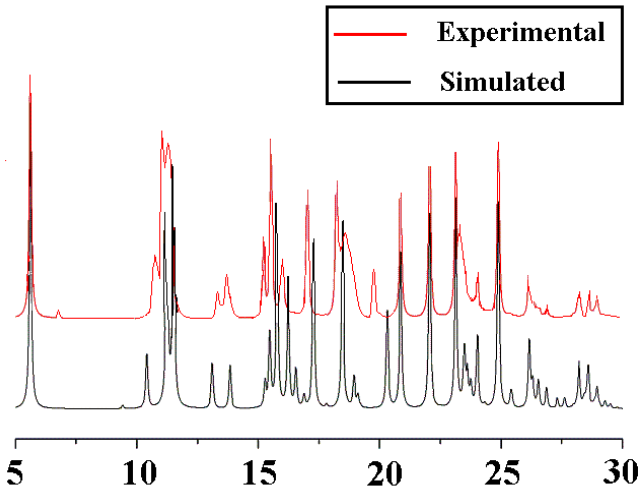


(b)

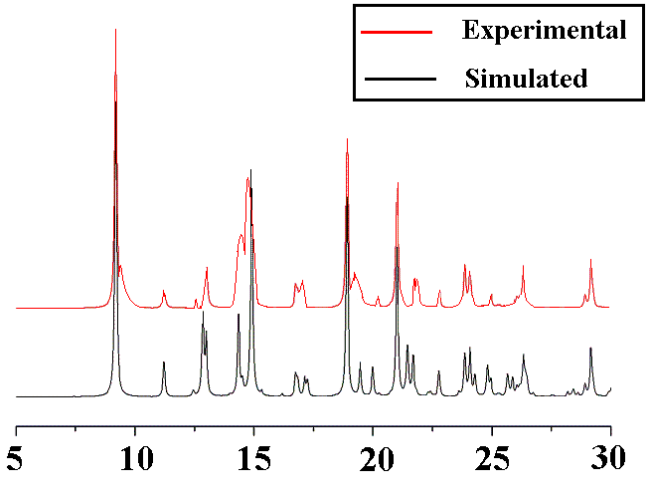
Fig. S5 (a) The water chains running through the 3D network (the purple broken lines: hydrogen bonds of the water chains anchored onto the 3D network). (b) Anchoring environment of the water chain in complex **6**.


400 ℃
300 ℃
200 ℃
100 ℃
25 ℃
5 10 15 20 25 30 35 40 45 50 55 60
2θ (degree)

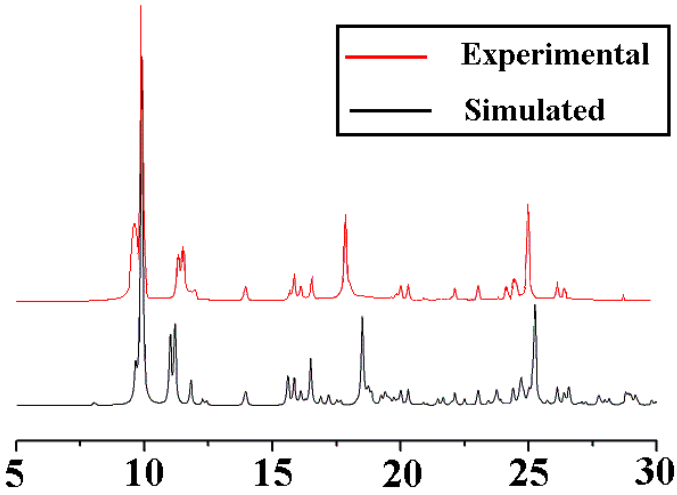
(a)


Experimental
Simulated
5 10 15 20 25 30

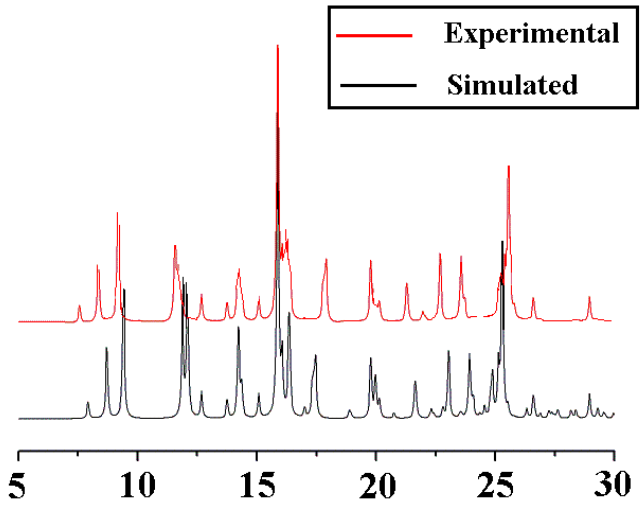
(b)


Experimental
Simulated
5
10
15
20
25
30

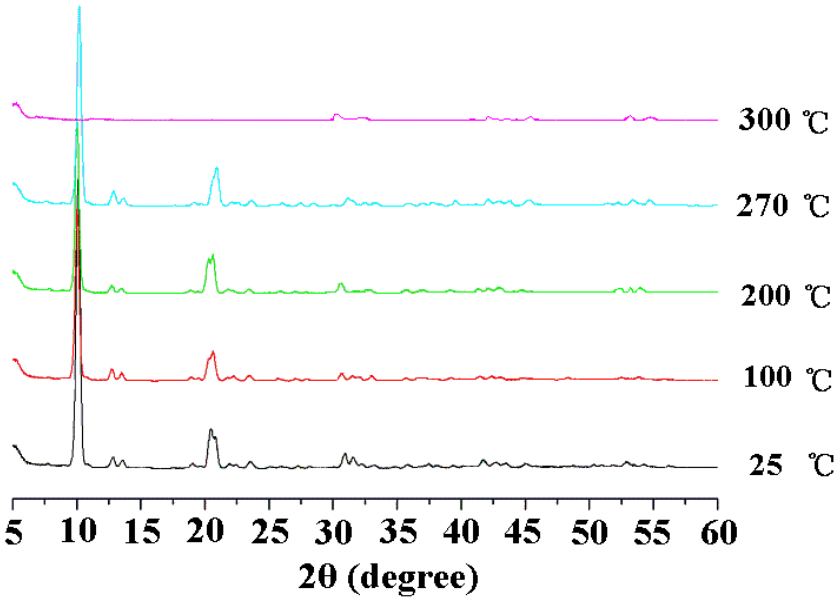
(c)


Experimental
Simulated
5
10
15
20
25
30

(d)

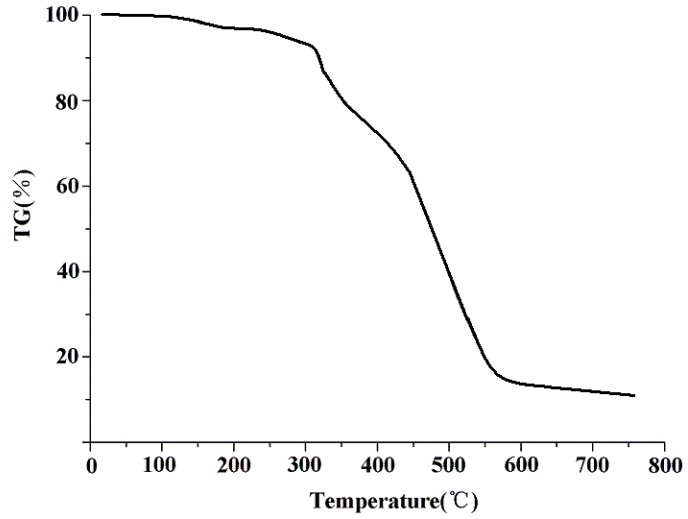


(e)

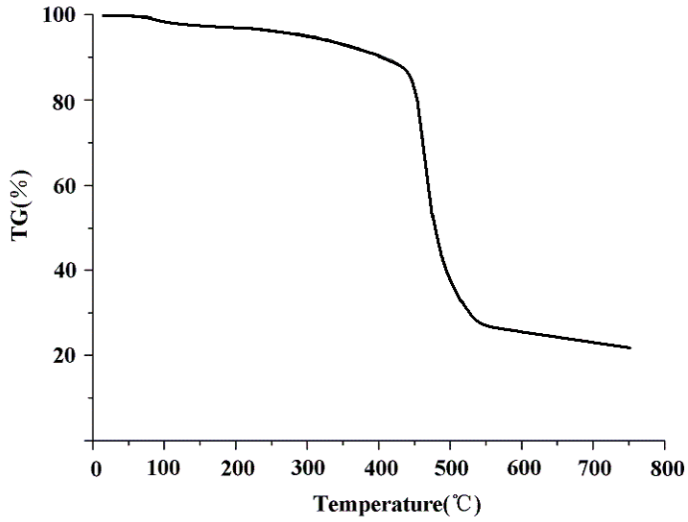


(f)

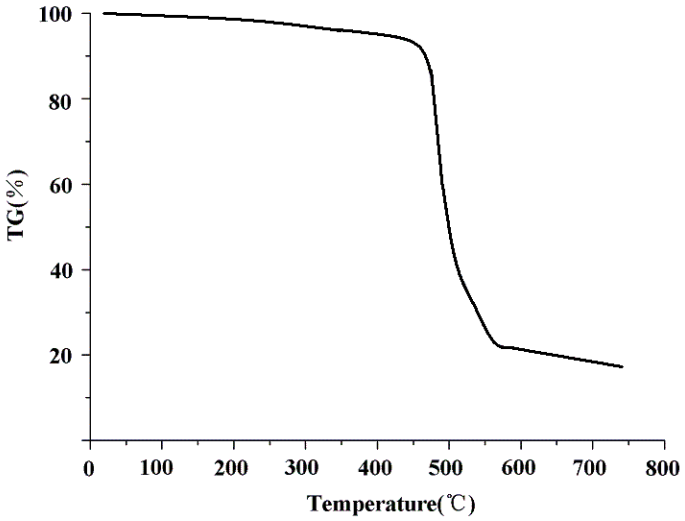
Fig. S6 PXRD patterns of complexes **1-6**: (a) for **1** at different temperatures; (b), (c), (d), and (e) for **2, 3, 4,** and **5** at room temperature; (f) for **6** at different temperatures.


100
80
60
40
20
TG(%)
0
100
200
300
400
500
600
700
800
Temperature(℃)

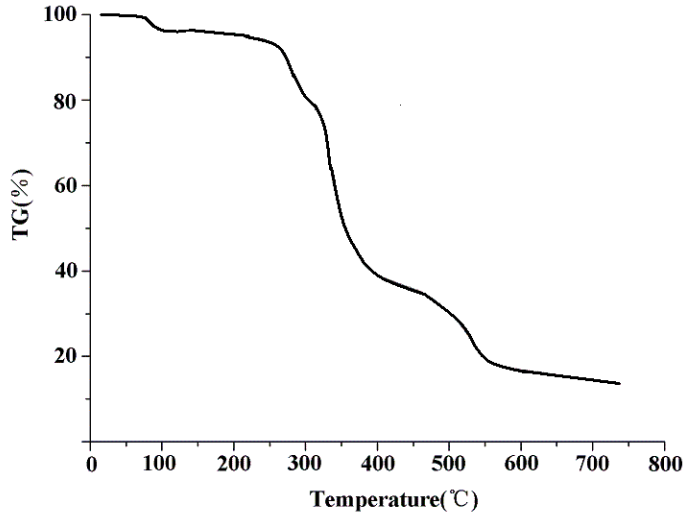
(a)


100
80
60
40
20
TG(%)
0
100
200
300
400
500
600
700
800
Temperature(℃)

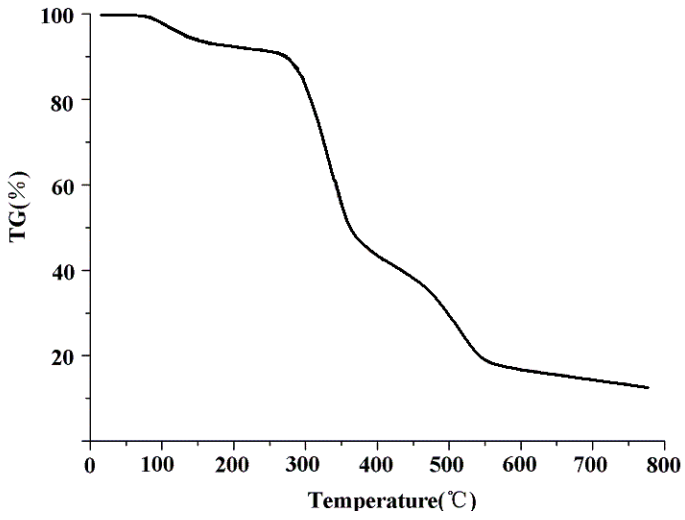
(b)


100
80
60
40
20
TG(%)
0
100
200
300
400
500
600
700
800
Temperature(℃)

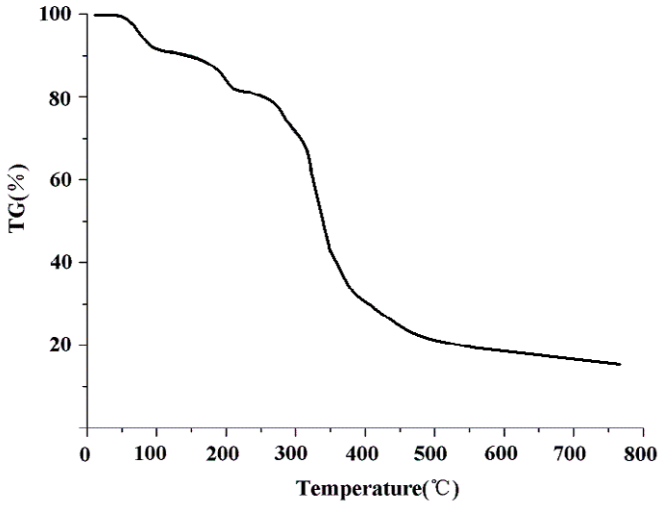
(c)



(d)



(e)



(f)

Fig. S7 TGA curves for complexes **1-6** (from **a** to **f**).