Electronic Supplementary Material (ESI)

Structural diversities of squarate-based complexes: photocurrent responses and thermochromic behaviours enchanced by viologens

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Supporting information

Table cation:

Figure cation:

Table S1 Selected Bond Lengths (Å) and Bond Angles (°) for 1-3

1			
Mg(1)-O(1)	2.092(3)	Mg(1)-O(1)#1	2.092(3)
Mg(1)-O(2)	2.074(3)	Mg(1)-O(2)#1	2.074(3)
Mg(1)-O(3)	2.046(3)	Mg(1)-O(3)#1	2.046(3)
C(1)-O(1)	1.263(4)	C(2)-O(2)	1.263(4)
C(1)-C(1)#2	1.455(5)	C(1)-C(1)#3	1.455(5)
O(1)-Mg(1)-O(3)	92.66(10)	O(1)-Mg(1)- O(3)#1	86.69(10)
O(2)#1-Mg(1)-O(3)	85.24(10)	O(2)-Mg(1)-O(3)#1	85.24(10)
O(3)#1-Mg(1)-O(3)	179.06(16)		
Symmetry codes: #1 z,-y-1/2,x; #2 -y,x-1/2,-z; #3 y+1/2,-x,-z; #4 x,-z-1/2,y #5 x,z,-y-1/2			
2			
Pr(1)-O(1)	2.468(3)	Pr(1)-O(2)	2.504(3)
Pr(1)-O(3)	2.480(3)	Pr(1)-O(4)	2.446(3)
Pr(1)-O(5)	2.478(4)	Pr(1)-O(6)	2.403(3)
Pr(1)-O(6)#2	2.809(3)	Pr(1)-O(7)	2.456(3)
Pr(1)-O(8)#1	2.474(3)	C(1)-O(1)	1.248(5)
C(2)-O(2)	1.263(5)	C(3)-O(4)	1.242(5)
C(4)-O(6)	1.267(5)		
O(6)-Pr(1)-O(4)	78.82(10)	O(6)-Pr(1)-O(7)	71.98(11)
O(4)-Pr(1)-O(7)	143.09(11)	O(6)-Pr(1)-O(1)	89.95(11)
O(6)-Pr(1)-O(5)	78.08(12)	O(4)-Pr(1)-O(5)	79.73(13)
O(4)-Pr(1)-O(3)	72.56(10)	O(7)-Pr(1)-O(3)	117.40(12)
O(5)-Pr(1)-O(3)	68.85(11)	O(6)-Pr(1)-O(2)	131.11(10)
O(4)-Pr(1)-O(2)	76.85(12)	O(7)-Pr(1)-O(2)	139.87(12)
O(1)-Pr(1)-O(2)	75.54(11)	O(8)#1-Pr(1)-O(2)	82.35(11)
O(5)-Pr(1)-O(2)	136.45(12)	O(3)-Pr(1)-O(2)	69.31(11)
O(6)-Pr(1)-O(6)#2	61.88(12)	O(4)-Pr(1)-O(6)#2	67.98(10)
O(7)-Pr(1)-O(6)#2	114.55(11)	O(1)-Pr(1)-O(6)#2	64.69(10)
Symmetry codes: #1 –x,-y,-z+1; #2 -x+1,-y,-z+1			
3			
Eu(1)-O(1)	2.401(6)	Eu(1)-O(2)	2.433(7)
Eu(1)-O(3)	2.376(6)	Eu(1)-O(4)	2.386(6)
Eu(1)-O(5)	2.451(6)	Eu(1)-O(6)	2.444(6)
Eu(1)-O(7)	2.451(8)	Eu(1)-O(8)	2.410(6)
Eu(2)-O(12)	2.345(6)	Eu(2)-O(13)	2.415(5)
Eu(2)-O(14)	2.458(6)	Eu(2)-O(15)	2.386(6)
Eu(2)-O(16)	2.407(6)	Eu(2)-O(17)	2.455(6)
Eu(2)-O(18)	2.401(6)	Eu(2)-O(19)	2.428(8)
C(1)-O(1)	1.237(9)	C(2)-O(2)	1.278(10)

C(3)-O(5)	1.257(9)	C(4)-O(9)	1.246(11)
C(5)-O(10)	1.252(10)	C(6)-O(11)	1.228(9)
C(7)-O(12)	1.259(7)	C(8)-O(6)	1.275(8)
C(9)-O(20)	1.255(10)	C(10)-O(13)	1.246(8)
C(11)-O(14)	1.255(9)	C(12)- O(17)	1.262(8)
O(3)-Eu(1)-O(4)	80.4(2)	O(3)-Eu(1)-O(1)	76.4(2)
O(3)-Eu(1)-O(2)	75.6(2)	O(4)-Eu(1)-O(2)	75.1(2)
O(1)-Eu(1)-O(2)	75.6(2)	O(8)-Eu(1)-O(2)	72.8(2)
O(3)-Eu(1)-O(6)	143.61(16)	O(4)-Eu(1)-O(6)	72.5(2)
O(4)-Eu(1)-O(7)	139.1(2)	O(1)-Eu(1)-O(7)	73.4(2)
O(8)-Eu(1)-O(7)	85.0(3)	O(2)-Eu(1)-O(7)	144.81(16)
O(6)-Eu(1)-O(7)	76.4(3)	O(3)-Eu(1)-O(5)	74.0(2)
O(6)-Eu(1)-O(5)	76.3(2)	O(7)-Eu(1)-O(5)	70.8(2)
O(12)-Eu(2)-O(15)	143.2(2)	O(12)-Eu(2)-O(18)	73.6(2)
O(15)-Eu(2)-O(18)	141.60(18)	O(12)-Eu(2)-O(16)	111.6(3)
O(15)-Eu(2)-O(16)	81.2(2)	O(18)-Eu(2)-O(16)	71.2(2)
O(18)-Eu(2)-O(19)	76.8(3)	O(16)-Eu(2)-O(19)	138.3(2)
O(13)-Eu(2)-O(19)	74.3(2)	O(12)-Eu(2)-O(17)	141.4(2)
O(15)-Eu(2)-O(14)	75.8(2)	O(18)-Eu(2)-O(14)	119.7(3)
O(16)-Eu(2)-O(14)	74.8(2)	O(13)-Eu(2)-O(14)	75.6(2)
O(19)-Eu(2)-O(14)	146.17(16)	O(17)-Eu(2)-O(14)	140.6(2)

Table S2 Selected Bond Lengths (Å) and Bond Angles (°) for 4-6

4

Cd(1)-O(1)#1	2.2436(18)	Cd(1)-O(1)	2.2436(18)
Cd(1)-O(3)#2	2.3332(15)	Cd(1)-O(3)	2.3332(15)
Cd(1)-O(4)#1	2.277(2)	Cd(1)-O(4)	2.277(2)
C(1)-O(1)	1.259(3)	C(2)-O(2)	1.243(3)
O(1)#1-Cd(1)-O(4)#1	84.66(7)	O(1)-Cd(1)-O(4)	84.66(7)
O(1)-Cd(1)-O(4)#1	90.88(7)	O(1)#1-Cd(1)-O(4)	90.88(7)
O(1)#1-Cd(1)-O(3)#2	95.55(10)	O(1)-Cd(1)-O(3)#2	91.01(9)
O(1)#1-Cd(1)-O(3)	91.01(9)	O(1)-Cd(1)-O(3)	95.55(10)
O(1)#1-Cd(1)-O(1)	171.98(11)		

Symmetry codes: #1 -x+1,-y+1,z; #2 -x+1,-y+1,-z+1

5

Cd(1)-O(10)	2.279(4)	Cd(1)-O(15)	2.318(5)
Cd(1)-O(17)	2.262(5)	Cd(1)-O(18)	2.221(5)
Cd(1)-O(19)	2.258(5)	Cd(1)-O(20)	2.336(5)
C(1)-O(1)	1.289(9)	C(2)-O(2)	1.277(9)
C(3)-O(3)	1.242(9)	C(4)-O(4)	1.236(9)
C(5)-O(5)	1.251(9)	C(6)-O(6)	1.245(10)
C(7)-O(7)	1.288(10)	C(8)-O(8)	1.267(9)

C(9)-O(9)	1.224(8)	C(10)-O(10)	1.254(8)
C(11)- O(11)	1.299(8)	C(12) O(12)-	1.240(8)
C(13)-O(13)	1.309(9)	C(14)-O(14)	1.254(8)
C(15)-O(15)	1.241(8)	C(16)-O(16)	1.240(8)
O(18)-Cd(1)-O(17)	91.7(3)	O(19)-Cd(1)-O(17)	95.7(2)
O(17)-Cd(1)-O(10)	95.95(18)	O(17)-Cd(1)-O(15)	90.59(18)
O(18)-Cd(1)-O(20)	86.0(3)	O(19)-Cd(1)-O(20)	86.5(2)
O(17)-Cd(1)-O(20)	176.7(2)		
6			
Cd(1)-O(12)	2.263(3)	Cd(1)-O(15)	2.271(3)
Cd(1)-O(18)	2.273(3)	Cd(1)-O(19)	2.282(3)
Cd(1)-O(20)	2.292(3)	Cd(1)-O(17)	2.322(3)
C(1)-O(1)	1.222(5)	C(2)-O(2)	1.248(5)
C(3)-O(3)	1.302(5)	C(4)-O(4)	1.239(5)
C(5)-O(5)	1.223(5)	C(6)-O(6)	1.250(5)
C(7)-O(7)	1.297(5)	C(8)-O(8)	1.255(4)
C(9)-O(9)	1.232(5)	C(10)-O(10)	1.249(5)
C(11)-O(11)	1.310(5)	C(12)-O(12)	1.259(5)
C(13)-O(13)	1.242(5)	C(14)-O(14)	1.231(5)
C(15)-O(15)	1.247(4)	C(16)-O(16)	1.302(5)
O(19)-Cd(1)-O(17)	177.39(9)	O(12)-Cd(1)-O(17)	85.67(9)
O(12)-Cd(1)-O(19)	96.64(10)	O(15)-Cd(1)-O(17)	82.21(9)
O(15)-Cd(1)-O(19)	95.70(10)	O(18)-Cd(1)-O(17)	86.59(11)
O(18)-Cd(1)-O(19)	94.78(11)	O(20)-Cd(1)-O(17)	90.24(10)
O(20)-Cd(1)-O(19)	88.32(10)		

Table S3 Hydrogen bridging details of 1, 4, 5, 6

Compound	D–H···A	D–H/Å	H···A/Å	D···A/Å	∠(D–H···A)/º	Symmetry codes
1	O(3)-H(3A)···O(2)	0.86	1.90	2.756(4)	172	1/2-y,x,z
	O(3)-H(3B)···O(3)	0.86	2.58	3.317(4)	144	-y,-1/2+z,1/2+x
4	O(3)-H(3)···O(10)	0.82	1.76	2.536(4)	156	1+x,1/2-y,1/2+z
	O(7)-H(7)···O(13)	0.82	1.77	2.541(4)	157	
	O(11)-H(11)···O(2)	0.82	1.73	2.499(4)	156	-1+x,1/2-y,-1/2+z
	O(16)-H(16)···O(6)	0.82	1.72	2.493(4)	157	
	O(17)-H(17A)···O(8)	0.89	1.95	2.843(4)	173	-1+x,1/2-y,-1/2+z
	O(17)-H(17B)···O(4)	0.89	1.89	2.781(4)	175	
	O(18)-H(18A)···O(4)	0.87	2.21	2.877(4)	133	-1+x,y,z
	O(18)-H(18B)···O(8)	0.87	1.90	2.712(4)	154	-1+x,1/2-y,-1/2+z
	O(19)-H(19A)···O(14)	0.90	1.89	2.752(4)	160	
	O(19)-H(19B)···O(9)	0.90	1.93	2.782(4)	156	
	O(20)-H(20A)···O(1)	0.88	1.89	2.723(4)	158	

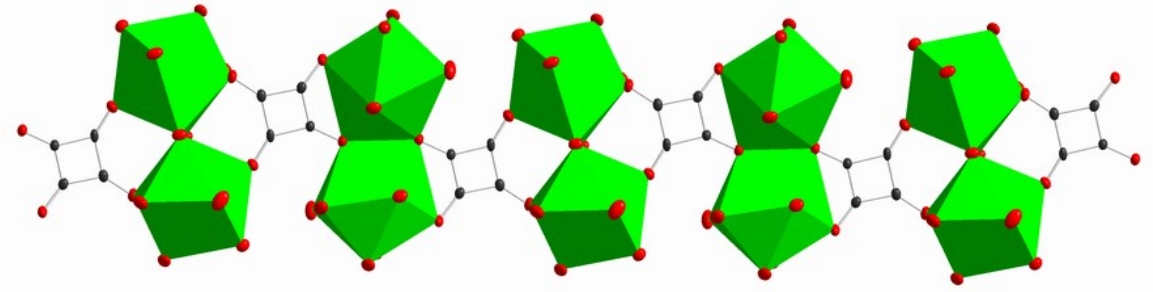
	O(20)-H(20B)···O(5)	0.88	1.88	2.742(4)	166	x,1/2-y,-1/2+z
5	O(2)-H(2)···O(7)	0.82	1.90	2.48(4(9)	127	x,-1+y,z
	O(13)-H(13)···O(12)	0.82	1.88	2.514(8)	133	
	O(17)--H(17A)···O(9)	0.92	1.90	2.764(8)	157	
	O(17)-H(17B)···O(16)	0.92	1.81	2.698(8)	161	
	O(17)-H(17B)···O(16)	0.93	2.50	3.222(4)	134	
	O(18)-H(18A)···O(5)	0.85	1.86	2.686(9)	164	
	O(18)-H(18B)···O(4)	0.85	2.10	2.670(9)	123	
	O(19)-H(19A)···O(6)	0.85	2.15	2.835(9)	137	-1+x,y,z
	O(19)-H(19B)···O(3)	0.85	2.47	2.818(9)	105	-1+x,y,z
	O(20)-H(20A)···O(6)	0.85	2.59	2.897(10)	102	
	O(20)-H(20B)···O(3)	0.85	2.56	2.842(9)	100	
	C(22)-(H22B)···O(3)	0.96	2.56	3.405(18)	148	-1+x,y,z
	C(22)-(H22C)···O(19)	0.96	2.44	3.386(12)	169	-x,1-y,-z
	C(23)-(H23)···O(16)	0.93	2.39	3.320(11)	174	
	C(24)-(H24)···O(9)	0.93	2.55	3.473(11)	175	
	C(26)-(H26)···O(9)	0.93	2.49	3.417(12)	175	1-x,1-y,1-z
	C(27)-(H27)···O(12)	0.93	2.43	3.259(13)	148	1-x,1-y,1-z
	C(28)-(H28A)···O(13)	0.96	2.57	3.437(12)	150	-x,-y,1-z
	C(28)-(H28C)···O(4)	0.96	2.59	3.318(11)	133	
6	O(3)-H(3)···O(10)	0.82	1.76	2.536(4)	156	-1+x,-1/2-y,-1/2+z
	O(7)-H(7)··O(13)	0.82	1.77	2.541(4)	157	
	O(11)-H(11)···O(2)	0.82	1.73	2.499(4)	156	1+x,-1/2-y,1/2+z
	O(16)-H(16)···O(6)	0.82	1.72	2.493(4)	157	
	O(17)-H(17A)···O(8)	0.89	1.95	2.842(4)	173	1+x,-1/2-y,1/2+z
	O(17)-H(17B)···O(4)	0.89	1.89	2.781(4)	175	
	O(18)-H(18A)···O(4)	0.87	2.21	2.877(4)	133	1+x,y,z
	O(18)-H(18B)···O(8)	0.87	1.90	2.712(4)	154	1+x,-1/2-y,1/2+z
	O(19)-H(19A)···O(14)	0.90	1.89	2.752(4)	160	
	O(19)-H(19B)···O(9)	0.90	1.93	2.782(4)	156	
	O(20)-H(20A)···O(1)	0.88	1.89	2.723(4)	158	
	O(20)-H(20B)···O(5)	0.88	1.88	2.742(4)	166	1+x,-1/2-y,1/2+z

Table S4. *π–π* stacking interactions in this work (lengths in Å and angles in °)

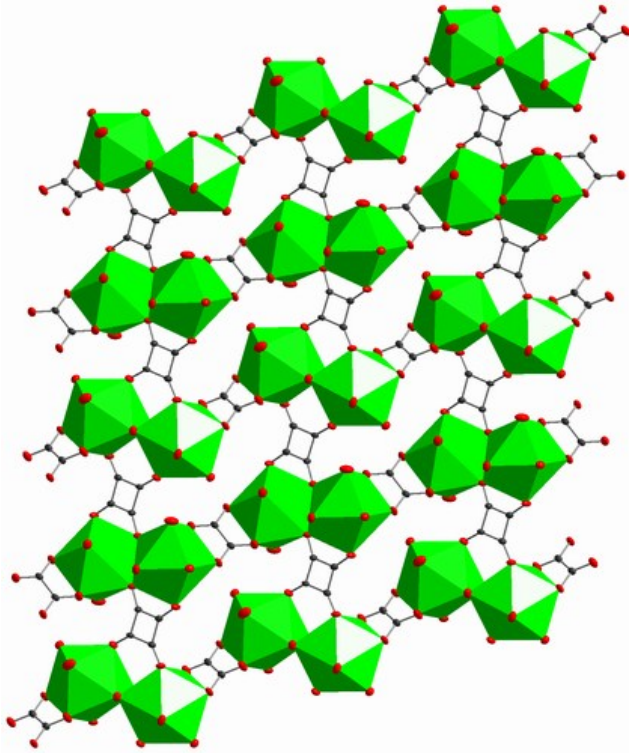
Compound	Cg(I)···Cg(J)	Symmetry code	Dist. Centroids	Dihedral angle	CgI_Perp dist.	CgJ_Perp dist.
1	Cg(1)→Cg(2)	x,-1/2-y,1/2+z	3.644(3)	4.3(3)	3.245(2)	3.1117(19)
	Cg(3)→Cg(4)	1+x,y,z	3.711(3)	11.3(3)	2.976(2)	3.3472(19)
	Ring Cg(1): C(9)→C(10)→C(11)→C(12)→;Ring Cg(2): C(5)→C(6)→C(7)→C(8)→					
	Ring Cg(3): C(13)→C(14)→C(15)→C(16)→;Ring Cg(4): C(1)→C(2)→C(3)→C(4)→					
5	Cg(1)→Cg(2)	-1+x,y,z	3.556(6)	3.6(6)	3.253(4)	3.158(4)
	Cg(3)→Cg(4)	x,1+y,z	3.578(6)	2.9(6)	3.248(4)	3.170(4)
	Ring Cg(1): C(13)→C(14)→C(15)→C(16)→;Ring Cg(2): C(1)→C(2)→C(3)→C(4)→					
	Ring Cg(3): C(9)→C(10)→C(11)→C(12)→;Ring Cg(4): C(5)→C(6)→C(7)→C(8)→					
6	Cg(1)→Cg(2)	-1+x,1/2-y,-1/2+z	3.675(3)	4.3(3)	3.1292(19)	3.2559(19)

Cg(1)→Cg(3)	x,1/2-y,1/2+z	3.644(3)	4.3(3)	3.1123(19)	3.2448(19)	

Ring Cg(1): C(9)→C(10)→C(11)→C(12)→;Ring Cg(2): C(5)→C(6)→C(7)→C(8)→
Ring Cg(3): N(2) →C(22)→C(23)→C(24)→C(25)→C(26)→;

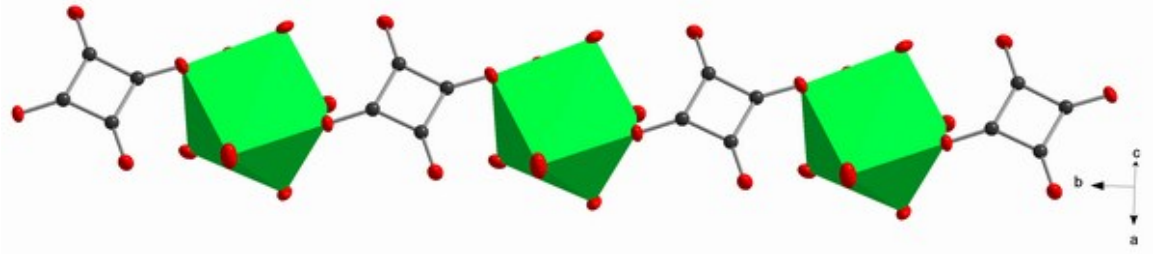


(a)

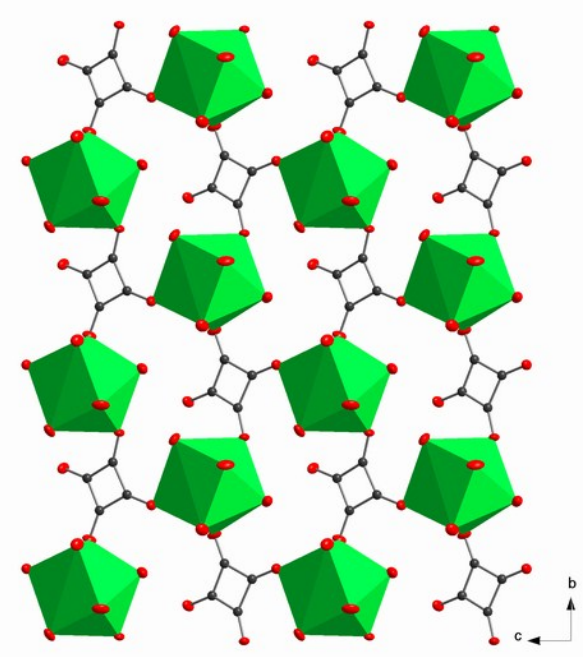


(b)

Fig. S1 (a) 1-D chain based on bridged; (b) 2-D layer via bridged oxalate ligands of 2

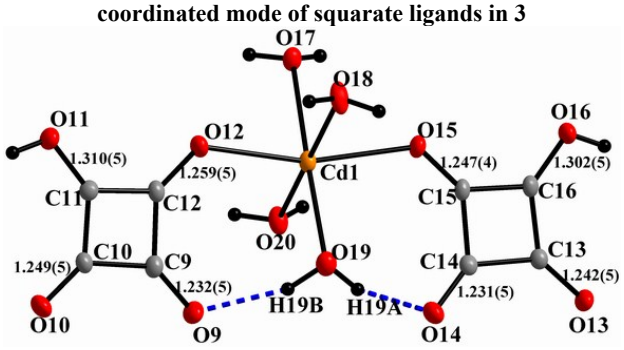


(a)

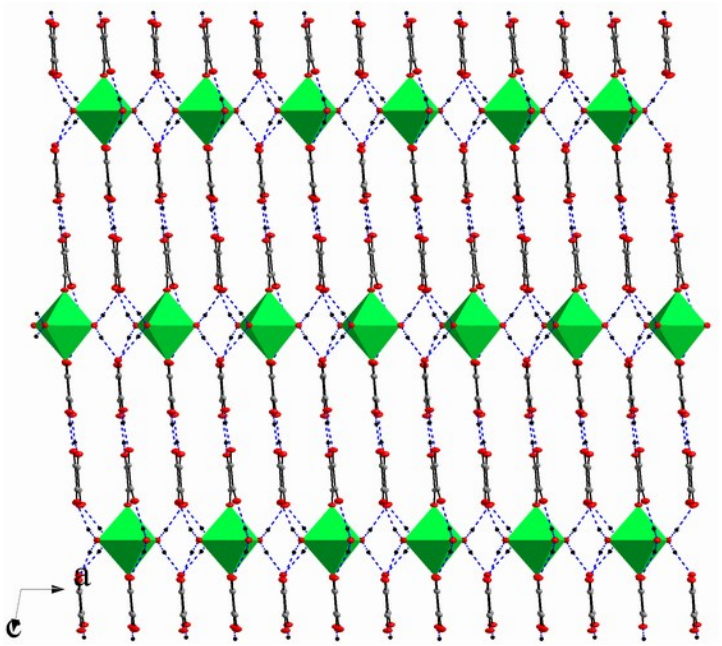


(b)

Fig. S2 (a) a 1-D chain bridged by squarate ligands; (b) 2-D mono-layer constructed from the μ_3-connected coordinated mode of squarate ligands in 3

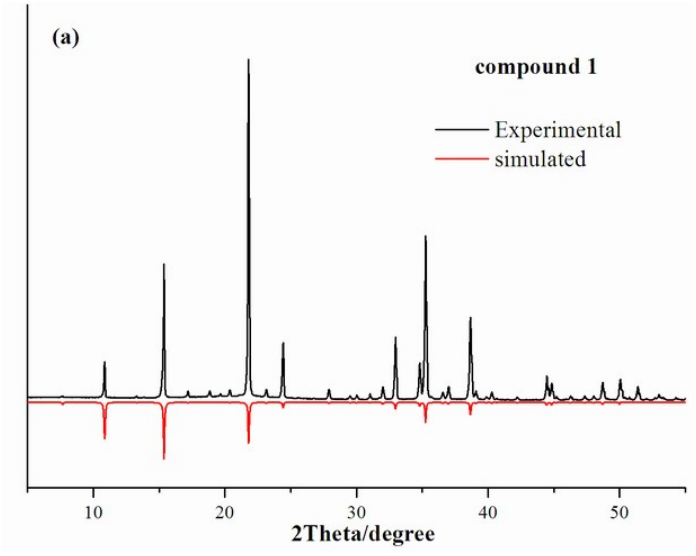


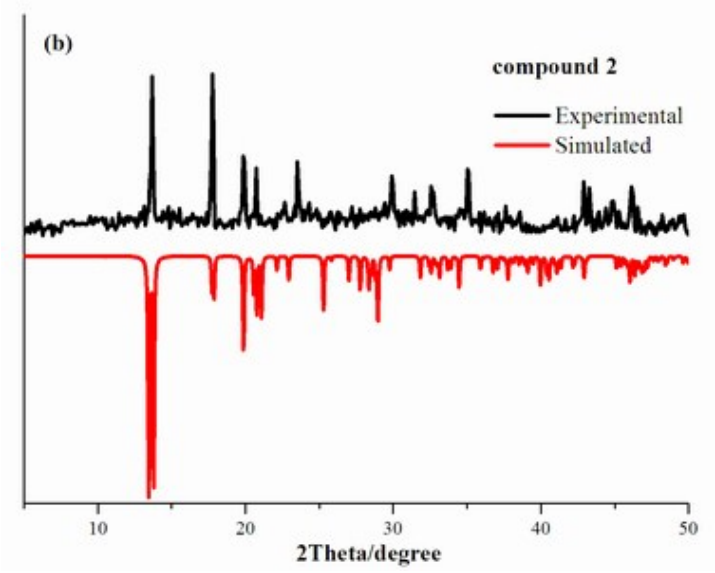
(a)

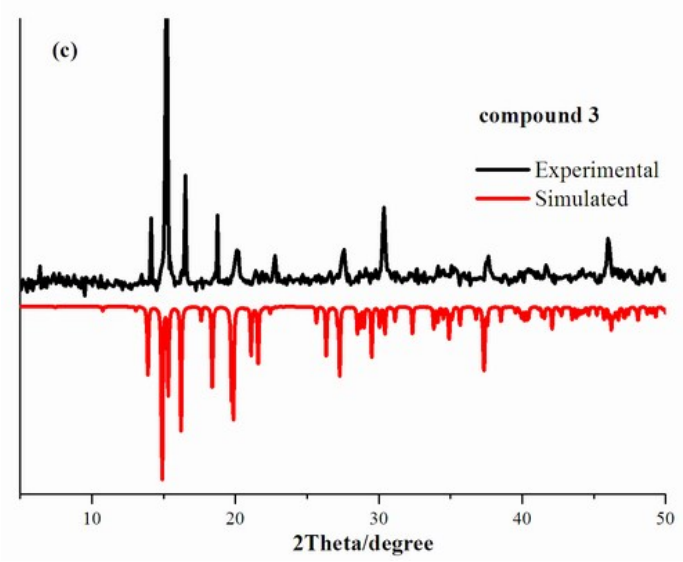


(b)

Fig. S3 (a) Structure of $[Cd(C_2HO_4)_2(H_2O)_4]$ cluster showing intra-molecular hydrogen bonds in 6; (b) structure of $\{[Cd(C_2HO_4)_2(H_2O)_4]\cdot 2(C_2HO_4)\}^{2-}$ layer constructed from intermolecular hydrogen bonds and π-π stacking interactions of 6




(b)
compound 2
Experimental
Simulated
10
20
30
40
50
2Theta/degree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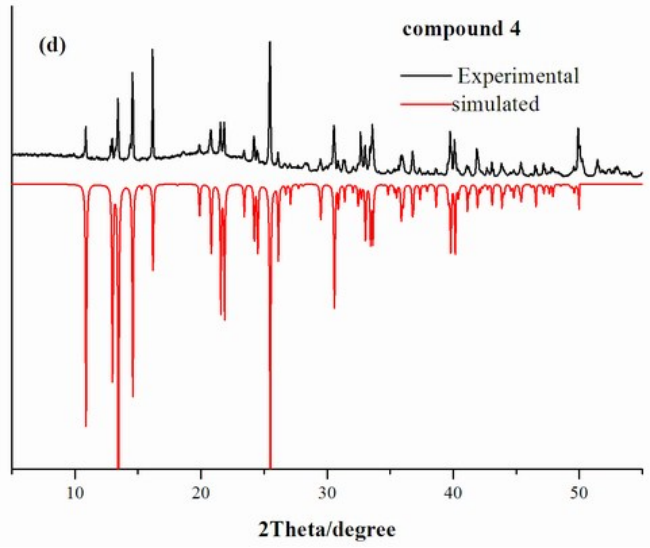
compound 3
Experimental
Simulated
10
20
30
40
50
2Theta/degree


(d)
compound 4
Experimental
simulated
10
20
30
40
50
2Theta/degree

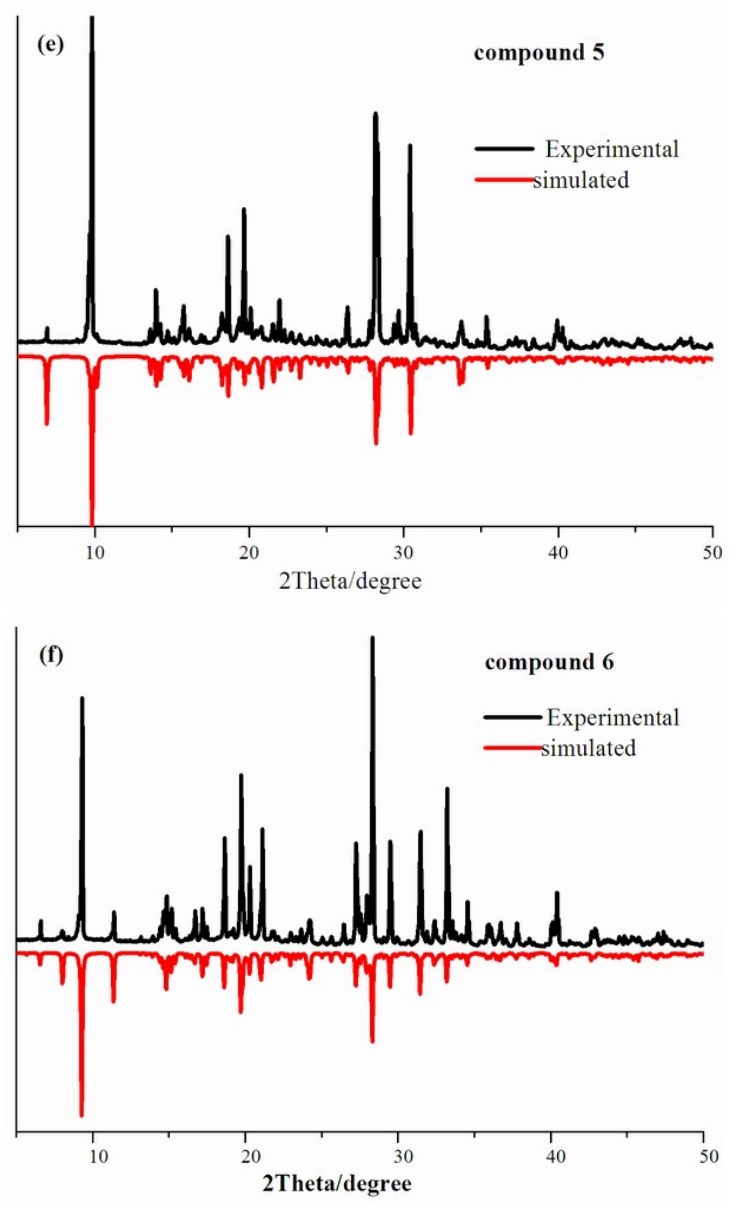


Fig. S4 Powder X-ray diffraction (PXRD) patterns for compounds 1-6