

*Supporting information for:*

## **Four 2D Metal–Organic Networks Incorporating Cd–Cluster SUBs: Hydrothermal Synthesis, Structures and Photoluminescent Properties**

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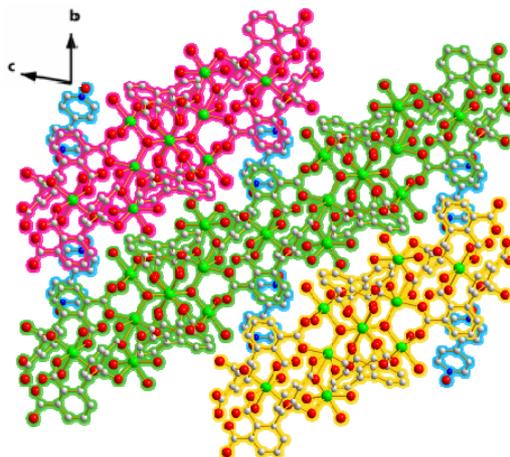
Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were obtained as KBr pellets on a VECTOR 22 spectrometer. Thermal analyses were performed on a TGA V5.1A Dupont 2100 instrument from room temperature to 750°C with a heating rate of 10°C/min in a nitrogen atmosphere. Luminescence spectra for the solid samples were recorded with a Hitachi 850 fluorescence spectrophotometer.

**Table S1.** Hydrogen bond distances (Å) and angles (°) for **2**, **3**, **4** and **5**. (D, donor atom; A, acceptor atom).

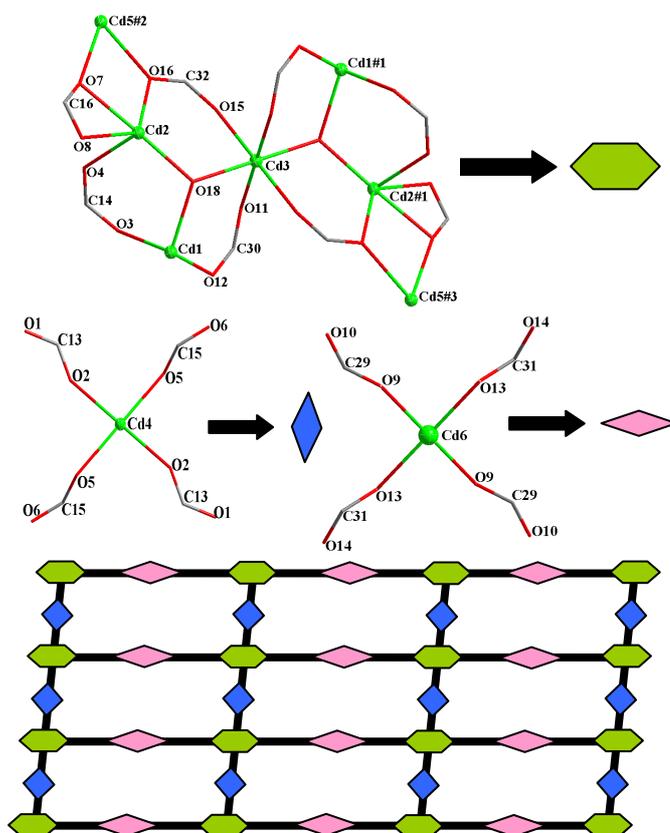
D-H	d(D-H)	d(H...A)	<DHA	d(D...A)	A
compound <b>2</b> <sup>#1</sup>					
O(18)-H(18A)	0.98	2.21	137	3.004	O(9)
O(21)-H(21C)	0.85	2.06	159	2.868	O(4)
O(26)-H(26D)	0.85	2.36	112	2.793	O(1)
O(18)-H(18A)	0.98	2.19	138	2.999	O(13) <sup>a</sup>
O(19)-H(19C)	0.85	2.27	138	2.957	O(13) <sup>a</sup>
O(25)-H(25C)	0.96	1.98	150	2.850	O(11) <sup>a</sup>
O(22)-H(22B)	0.96	1.77	158	2.682	O(2) <sup>b</sup>
O(23)-H(23C)	0.96	1.75	151	2.636	O(10) <sup>b</sup>
O(20)-H(20B)	0.85	2.39	112	2.823	O(17) <sup>c</sup>
O(21)-H(21A)	0.85	1.93	173	2.772	O(17) <sup>d</sup>
O(22)-H(22C)	0.96	2.40	156	3.297	O(17) <sup>d</sup>
O(24)-H(24A)	0.96	2.06	133	2.812	O(12) <sup>d</sup>
O(24)-H(24B)	0.96	1.85	156	2.757	O(14) <sup>e</sup>
O(25)-H(25B)	0.96	1.97	128	2.671	O(26) <sup>f</sup>
O(26)-H(26E)	0.85	2.27	138	2.964	O(8) <sup>g</sup>
compound <b>3</b> <sup>#2</sup>					
O(9)-H(9B)	0.85	1.94	165.6	2.772	O(3) <sup>a</sup>
O(10)-H(10B)	0.85	1.96	141.9	2.677	O(1) <sup>b</sup>
O(10)-H(10A)	0.85	1.78	166.9	2.617	O(5) <sup>b</sup>
O(9)-H(9A)	0.85	2.14	146.2	2.889	O(10) <sup>c</sup>
compound <b>4</b> <sup>#3</sup>					
O(18)-H(18A)	0.85	2.25	171	3.090	O(15)
O(20)-H(20B)	0.85	2.21	150	2.978	O(10)
O(17)-H(17B)	0.85	2.34	134	2.998	O(12) <sup>a</sup>
O(17)-H(17B)	0.85	2.42	170	3.258	O(11) <sup>a</sup>
O(17)-H(17A)	0.85	2.46	147	3.205	O(3) <sup>a</sup>
O(19)-H(19C)	0.85	2.48	157	3.276	O(17) <sup>a</sup>
O(18)-H(18B)	0.85	2.27	142	2.986	O(9) <sup>b</sup>
N(2)-H2	0.86	1.70	173.7	2.553	O(16) <sup>c</sup>
compound <b>5</b> <sup>#4</sup>					
O(9)-H(9B)	0.85	2.18	149.4	2.947	O(3) <sup>a</sup>
O(9)-H(9B)	0.85	2.45	126.1	3.026	O(3)
O(9)-H(9C)	0.85	2.19	156.3	2.991	O(8) <sup>b</sup>

<sup>#1</sup> Symmetry codes: <sup>a</sup>-x, -y+1, -z+1; <sup>b</sup>-x+1, -y+2, -z; <sup>c</sup>-x+1, -y+1, -z+1; <sup>d</sup>x, y, z-1; <sup>e</sup>x+1, y, z-1; <sup>f</sup>x-1, y, z; <sup>g</sup>-x+2, -y+2, -z. <sup>#2</sup> Symmetry codes: <sup>a</sup>-x+1, -y+1, -z+1; <sup>b</sup>-x+2, -y+1, -z+1; <sup>c</sup>x-1, y,

$z$ ;  $a-x+1, -y+1, -z$ . #3 Symmetry codes:  $a-x+1, -y, -z+1$ ;  $b-x+1, y, z$ ;  $b-x+1, -y+1, -z+2$ . #4  
Symmetry codes:  $a-x, -y+1, -z$ ;  $b-x+1, -y+1, -z$ .



**Fig. S1.** 3D supramolecular structure of **2**. Three adjacent metal-organic layers are marked as red, green and yellow, whereas the “template” bpydo molecules are highlighted as blue color.



**Fig. S2.** Topology structure of **2**.  $Cd_7$  cluster can be simplified as four connected net, whereas Cd4 and Cd6 atoms can be regarded as two connected nets.

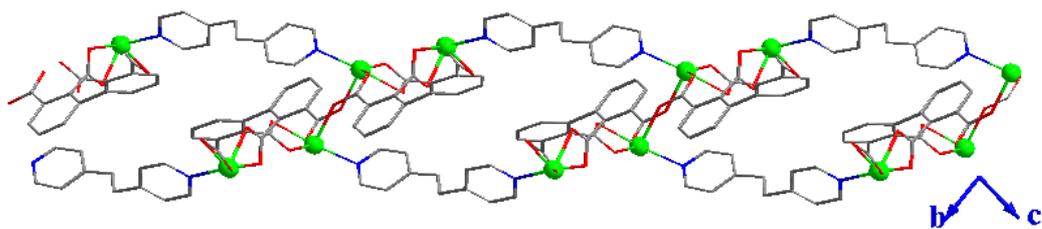


Fig. S3. 2D metal-organic double layer structure of **3**. Hydrogen atoms are omitted for clarity.

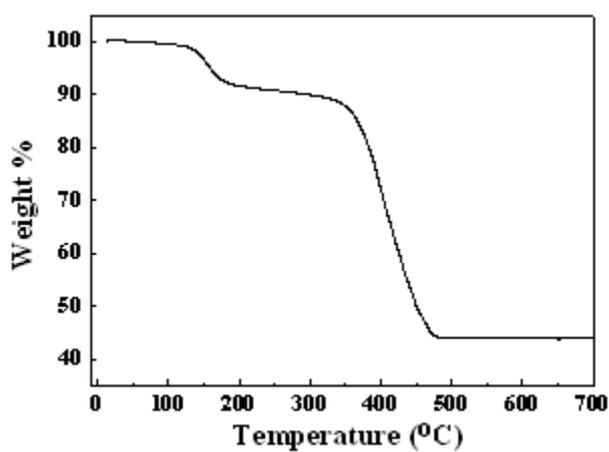


Fig. S4. TG curve of **2**.

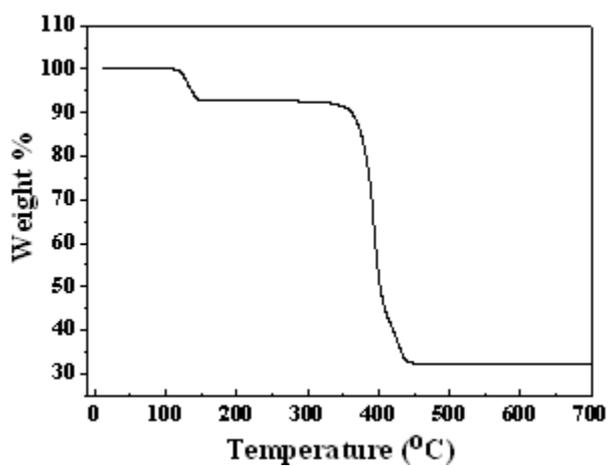


Fig. S5. TG curve of **3**.

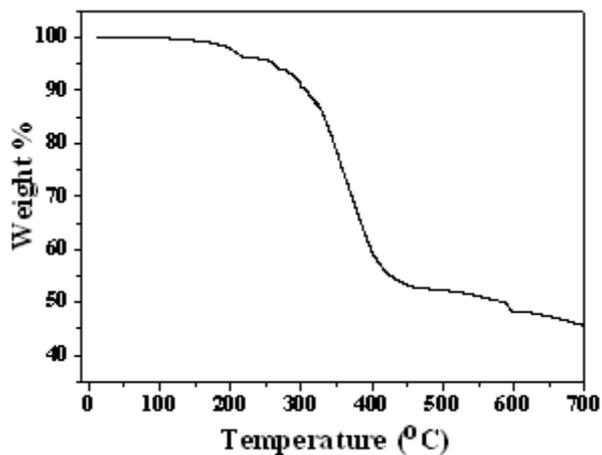


Fig. S6. TG curve of 4.

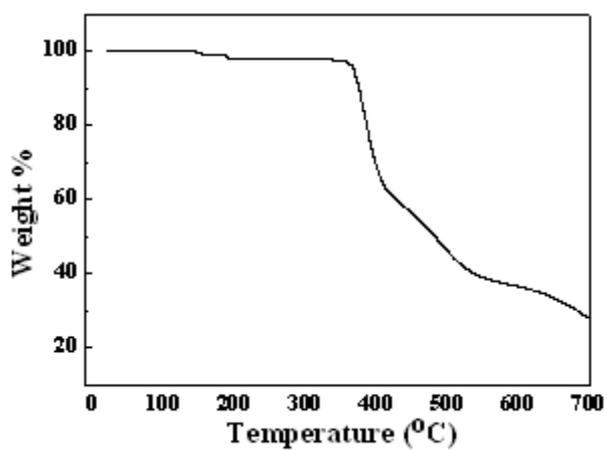


Fig. S7. TG curve of 5.

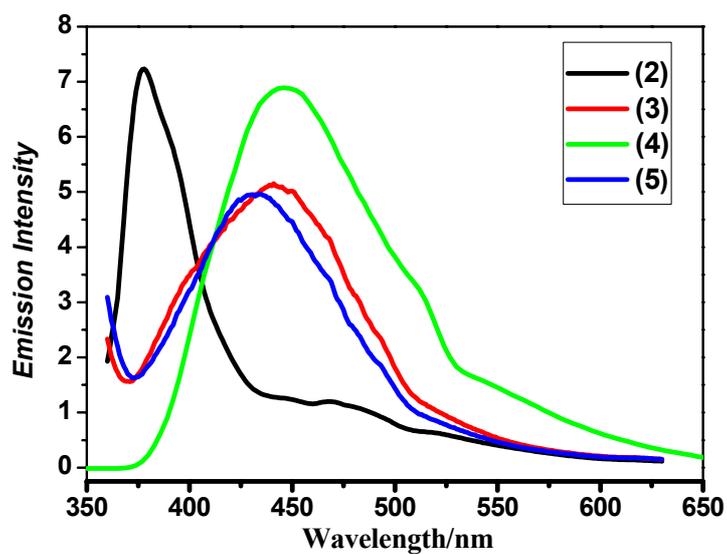


Fig. S8. Fluorescent emission spectra of 2, 3, 4 and 5 in solid state at room temperature.