

## Supplementary Materials

**Fig. S1.** The coordination environment of the Zn(II) ion in **1**.

**Fig. S2.** Coordination environment of Cd(II) in **2**.

**Fig. S3.** The right-handed  $[Cd_2(L2)(bimh)]_n$  single helix viewed perpendicular to the *c* axis(a) and viewed from the *c* axis (b). (L2 ligands, bimh ligands and screw axis are shown as blue line, yellow line and green rods, respectively).

**Fig. S4.** Comparison of the interconnection of the helices in complex **2** (a) and document **5c** (b) viewed along the *c* axis (R represents right-handed and L represents left-handed).

**Fig. S5.** Comparison of the asymmetric unit of the complex **2** (a) and document **5c** (b)

**Fig. S5.** Comparison of PXRD pattern of the simulated pattern from the single-crystal structure determination, the as-synthesized product in compounds **2**.

**Fig. S6.** Comparison of PXRD pattern of the simulated pattern from the single-crystal structure determination, the as-synthesized product in complexes **1**(a), **2** (b)

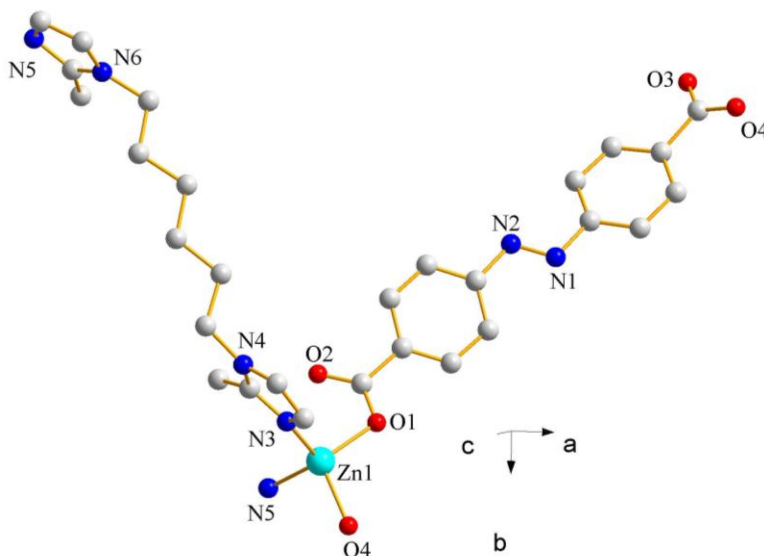
**Fig. S7.** TGA curve of **1**, **2** under  $N_2$  atmosphere.

**Fig. S8.** Emission spectra of **1**, **2**.

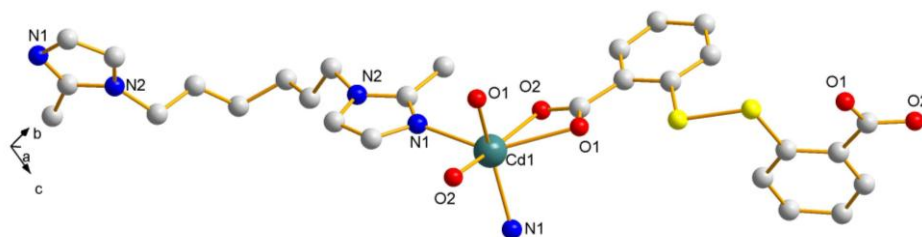
**Table S1.** Selected Bond Lengths (Å) and Angles (°) for Complexes **1-2**

**Table S2.** Crystal Data and Structure Refinements for Complexes **1-2**

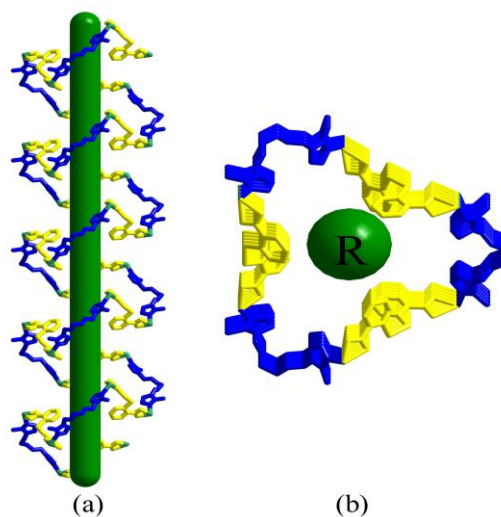
**Table S3.** Photoluminescent lifetime data for complex **2** at room temperature



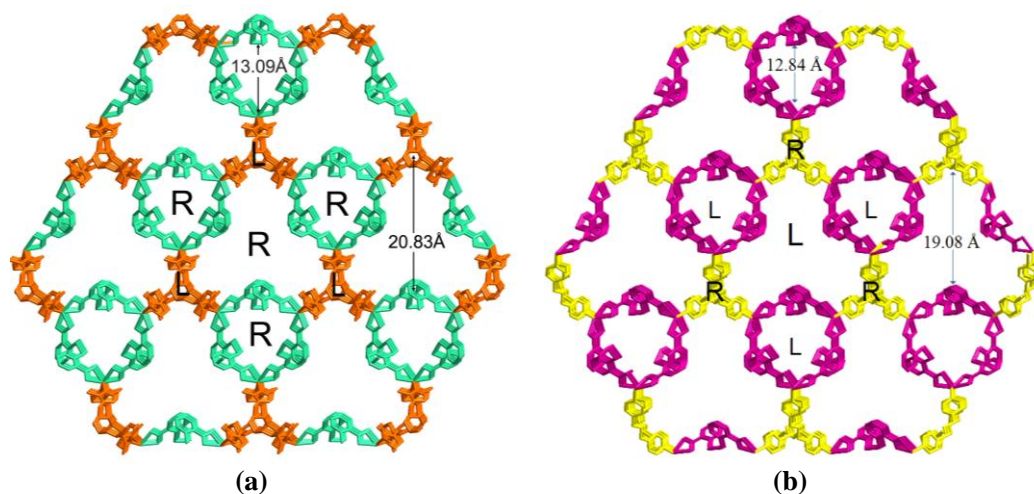
**Fig. S1.** The coordination environment of the Zn(II) ion in **1**.



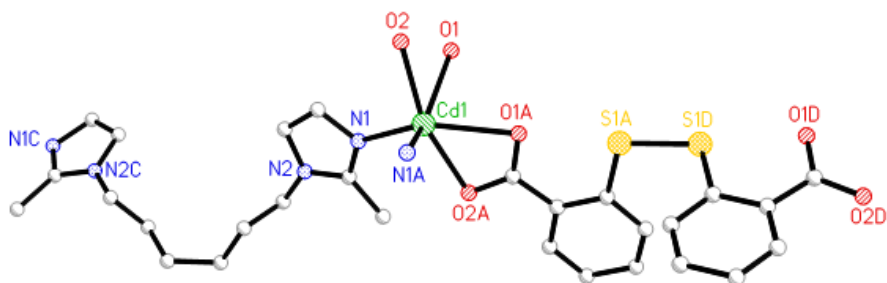
**Fig. S2.** The coordination environment of Cd(II) in **2**.



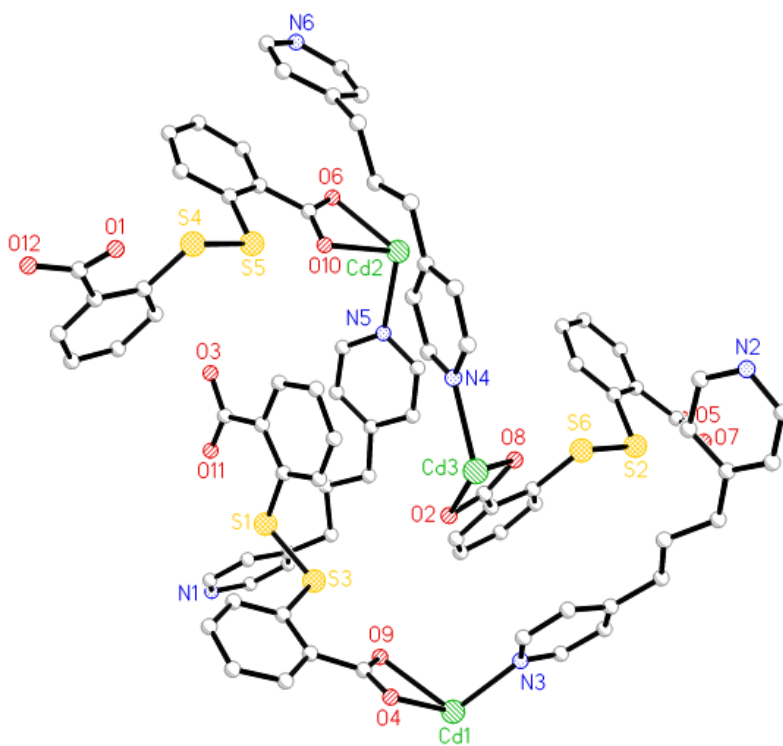
**Fig. S3.** The right-handed  $[Cd_2(dtba)(bimh)]_n$  single helix viewed perpendicular to the  $c$  axis (a) and viewed from the  $c$  axis (b) in **2**. (dtba ligands, bimh ligands and screw axis are shown as blue line, yellow line and green rods, respectively)



**Fig. S4.** Comparison of the interconnection of the helices in complex **2** (a) and the document **5c** (b) viewed along the  $c$  axis (R represents right-handed and L represents left-handed).

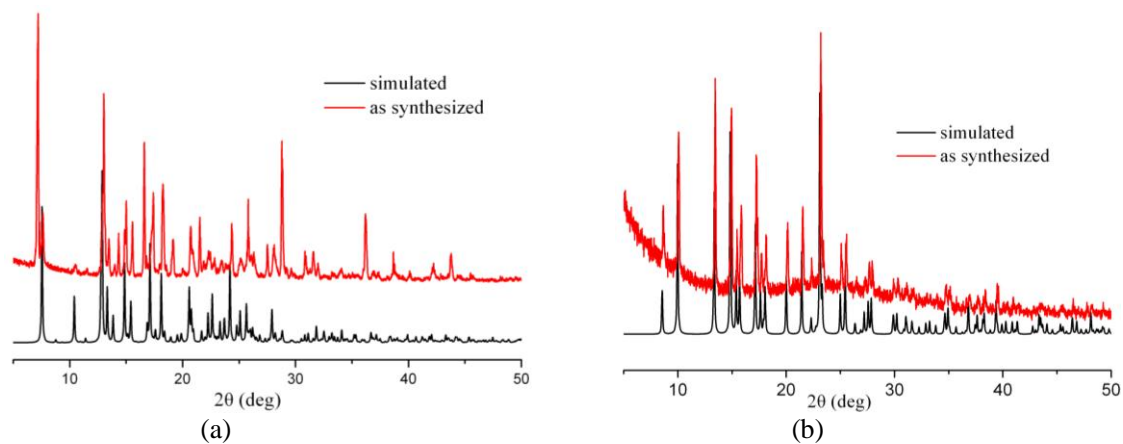


(a)

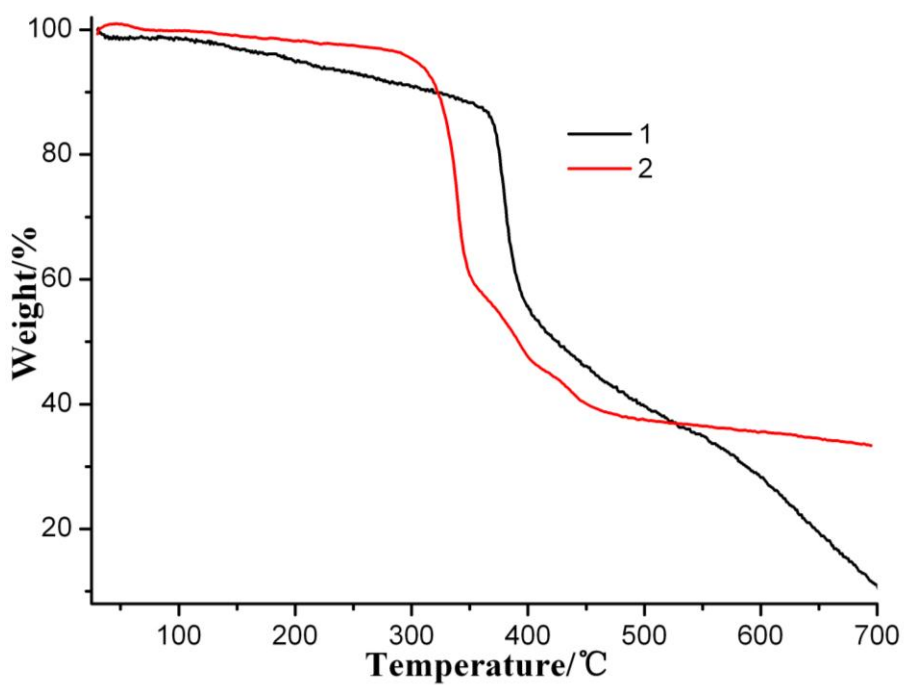


(b)

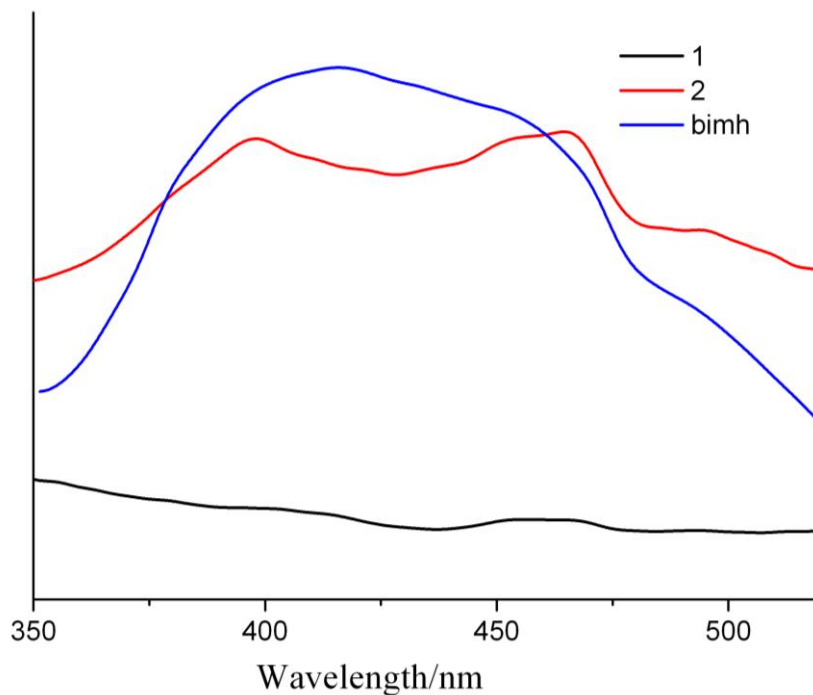
**Fig. S5.** Comparison of the asymmetric unit of the complex **2** (a) and document **5c** (b)



**Fig. S6.** Comparison of PXRD pattern of the simulated pattern from the single-crystal structure determination, the as-synthesized product in complexes **1**(a), **2** (b)



**Figure S7.** TGA curve of **1**, **2** under N<sub>2</sub> atmosphere.



**Figure S8.** Emission spectra of **1**, **2**.

**Table S1.** Selected Bond Lengths (Å) and Angles (°) for Compounds **1-2**

<b>1<sup>a</sup></b>			
N(5)-Zn(1)#1	2.009(3)	O(1)-Zn(1)#2	1.962(2)
Zn(1)-O(1)#3	1.962(2)	Zn(1)-N(5)#4	2.009(3)
Zn(1)-O(4)	1.969(2)	Zn(1)-N(3)	2.001(3)
C(22)-N(5)-Zn(1)#1	125.1(2)	C(28)-N(5)-Zn(1)#1	128.3(2)
C(19)-O(1)-Zn(1)#2	112.1(2)	O(1)#3-Zn(1)-O(4)	106.85(10)
O(1)#3-Zn(1)-N(3)	109.76(10)	O(4)-Zn(1)-N(3)	114.59(11)
O(1)#3-Zn(1)-N(5)#4	118.78(11)	O(4)-Zn(1)-N(5)#4	97.96(10)
N(3)-Zn(1)-N(5)#4	108.67(11)		
<b>2<sup>b</sup></b>			
Cd(1)-O(2)#1	2.249(4)	Cd(1)-O(2)	2.249(4)
Cd(1)-N(1)	2.286(4)	Cd(1)-N(1)#1	2.286(4)
Cd(1)-O(1)	2.494(4)	Cd(1)-O(1)#1	2.494(4)
S(1)-S(1)#2	2.047(3)	O(2)#1-Cd(1)-O(2)	161.8(2)
O(2)#1-Cd(1)-N(1)	95.10(15)	O(2)-Cd(1)-N(1)	95.11(16)
O(2)#1-Cd(1)-N(1)#1	95.11(16)	O(2)-Cd(1)-N(1)#1	95.10(15)

N(1)-Cd(1)-N(1)#1	111.5(2)	O(2)#1-Cd(1)-O(1)	109.80(15)
O(2)-Cd(1)-O(1)	54.59(14)	N(1)-Cd(1)-O(1)	93.12(15)
N(1)#1-Cd(1)-O(1)	143.35(16)	O(2)#1-Cd(1)-O(1)#1	54.59(14)
O(2)-Cd(1)-O(1)#1	109.80(15)	N(1)-Cd(1)-O(1)#1	143.35(16)
N(1)#1-Cd(1)-O(1)#1	93.12(15)	O(1)-Cd(1)-O(1)#1	80.9(2)
O(2)#1-Cd(1)-C(39)#1	27.54(15)	O(2)-Cd(1)-C(39)#1	136.09(18)
N(1)-Cd(1)-C(39)#1	120.05(17)	N(1)#1-Cd(1)-C(39)#1	95.22(15)
O(1)-Cd(1)-C(39)#1	95.19(17)	O(1)#1-Cd(1)-C(39)#1	27.06(15)
C(26)-S(1)-S(1)#2	104.32(18)	C(39)-O(1)-Cd(1)	86.9(3)
C(39)-O(2)-Cd(1)	97.5(4)	C(57)-N(1)-Cd(1)	134.2(4)

Symmetry transformations used to generate equivalent atoms:

a #1 $-x+1/2, y-1/2, -z+1/2$	#2 $-x+5/2, y+1/2, -z+1/2$
#3 $-x+5/2, y-1/2, -z+1/2$	#4 $-x+1/2, y+1/2, -z+1/2$
b #1 $-x, -x+y, -z+1/3$	#2 $x-y+1, -y+2, -z+2/3$

**Table S2.** Crystal Data and Structure Refinements for Complexes **1-2**

	<b>1</b>	<b>2</b>
Molecular formula	C <sub>28</sub> H <sub>30</sub> N <sub>6</sub> O <sub>4</sub> Zn	C <sub>84</sub> H <sub>90</sub> N <sub>12</sub> O <sub>12</sub> S <sub>6</sub> Cd <sub>3</sub>
M	579.95	1989.24
T, K	296(2)	296(2)
Crystal system	monoclinic	trigonal
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 3 <sub>1</sub> 2 1
<i>a</i> (Å)	10.5666(16)	11.9375(13)
<i>b</i> (Å)	23.405(3)	11.9375(13)
<i>c</i> (Å)	11.4006(15)	17.2686(18)
$\beta$ (°)	101.661(2)	90
$\gamma$ (°)	90	120
<i>V</i> (Å <sup>3</sup> )	2761.3(7)	2131.2(4)
<i>Z</i>	4	1
$\rho$ (g cm <sup>-3</sup> )	1.395	1.550
<i>F</i> (000)	1208	1014
Reflections collected /unique	11309 / 4827	10764 / 2522

$[R_{\text{int}}]$	[0.0361]	[0.0439]
Goodness-of-fit on $F^2$	1.030	0.905
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0416$ , $wR_2 = 0.0988$	$R_1 = 0.0379$ , $wR_2 = 0.0971$
$R$ indices (all data)	$R_1 = 0.0714$ , $wR_2 = 0.1126$	$R_1 = 0.0527$ , $wR_2 = 0.1110$

**Table S3.** Photoluminescent lifetime data for complex **2** at room temperature

complex	Lifetime(ns)		
	$\tau_1$	$\tau_2$	$\tau_3$
<b>2</b>	1.2881 (15.33 %)	4.9936 (60.56 %)	10.1345 (24.11 %)