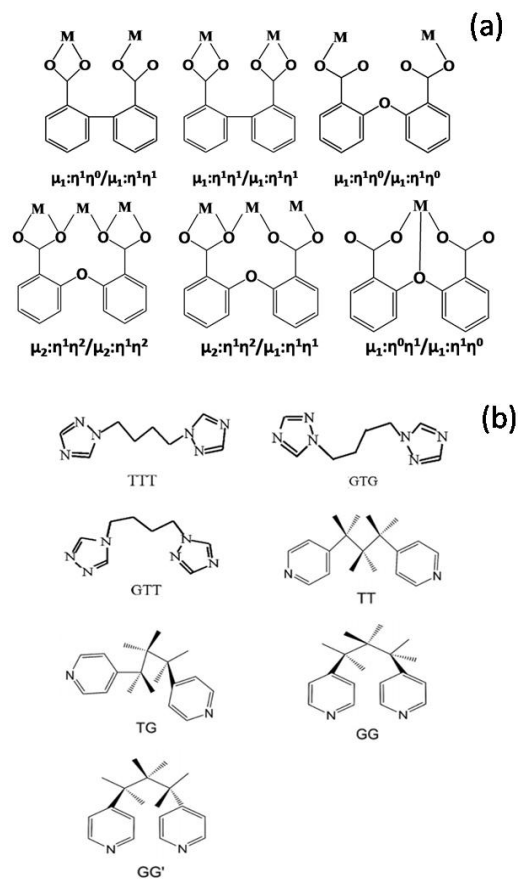


Supporting Information

Table of Contents

1. **The solvent sensing experiment.** Well-ground **4** powder (3 mg) was immersed in different organic solvents (3 ml), treated by ultrasonication for approximately 30 min, and then aged for three days.
2. **The Ln(III) ion sensitizing experiment.** Well-ground **4** powder (3 mg) was immersed in Ln(III) (Sm(III), Eu(III), Tb(III), Dy(III) 10^{-2} mol/L) aqueous solutions (3 ml), treated by ultrasonication for approximately 30 min, and then aged for three days.
3. The coordination modes of O-OBA and DPDC (a) and the configurations of BTB and BPP (b) (Scheme S1).
4. PXRD patterns of complexes **1-7** (Fig. S1).
5. 3D supramolecular arrangement of complexes **1-7** (Fig. S2-8).
6. The TGA curves of complexes **1-7** (Fig. S9)
7. The solid state emission spectra of complexes and the free ligands (Fig. S10).
8. The PXRD patterns for **4** after immersing in different solvents (Fig. S11).
9. The luminescence intensity of four recyclable experiments of sensing for nitrobenzene(NB) in DMF(a) and sensitizing Tb(III) in water (b) (Fig. S12)
10. PXRD patterns of complex **4** after two and four recycles of sensing for nitrobenzene(NB) in DMF(a) and sensitizing Tb(III) in water (b) (Fig. S13)
11. Emission decay profiles of 5D_4 Tb(III) in complex **4@Tb(III)/water** (Fig. S14).
12. The crystal data and structure refinement for complexes **1-7** (Table S1), Selected bond lengths [Å] and angles [°] for complexes **1-7** (Table S2).



Scheme S1 The coordination modes of O-OBA and DPDC (a) and the configurations of BTB and BPP (b).

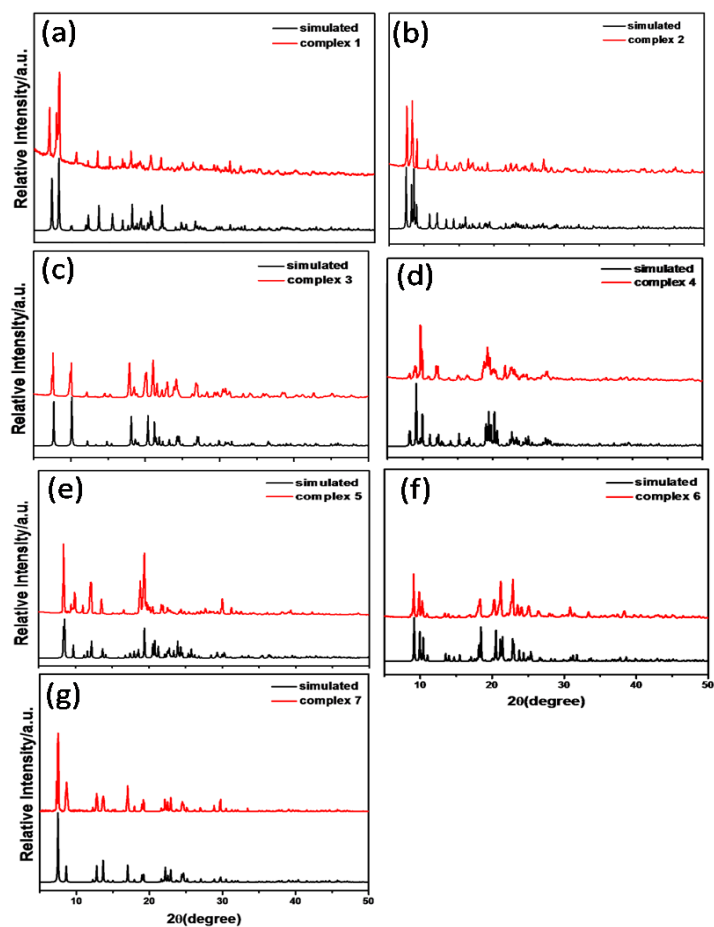


Fig. S1 PXRD patterns of complexes 1-7.

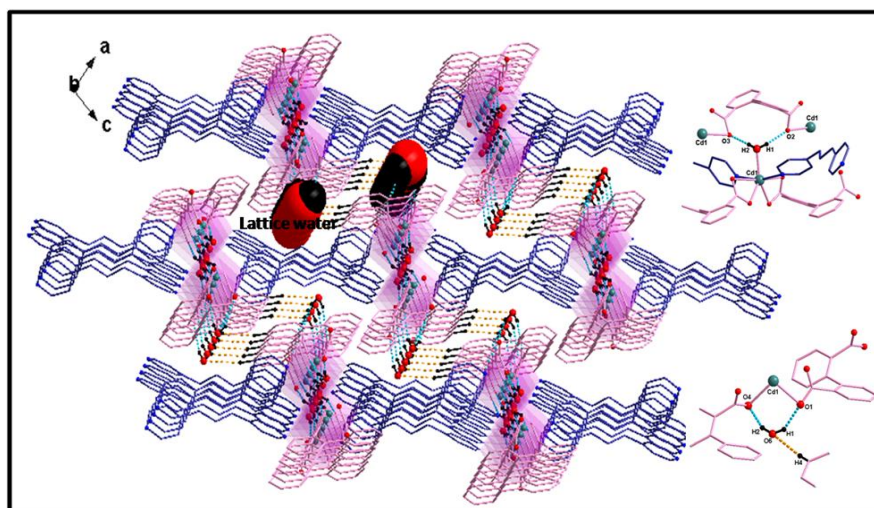


Fig. S2 3D supramolecular arrangement of complex 1.

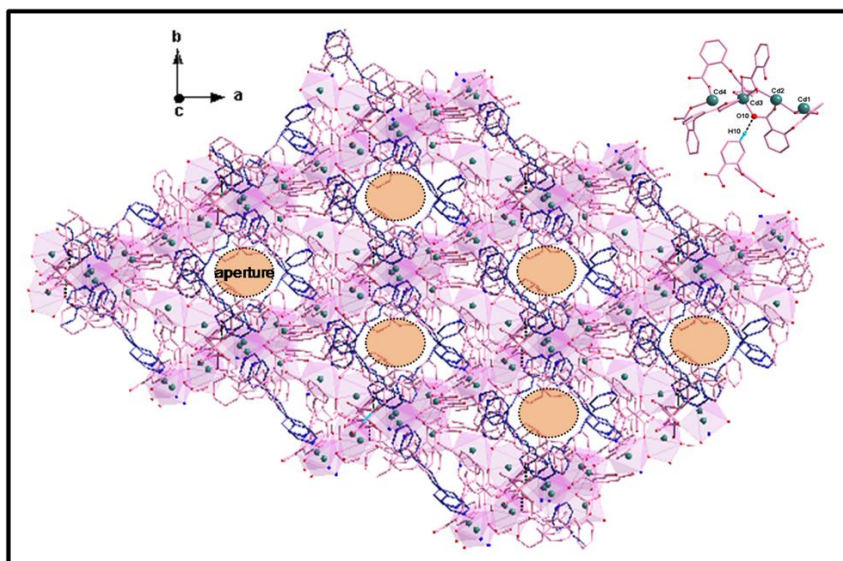


Fig S3 3D supramolecular arrangement of complex 2.

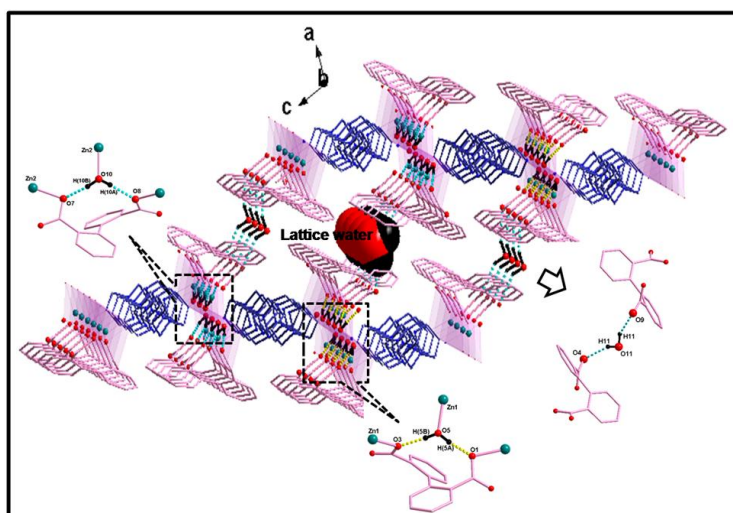


Fig S4 3D supramolecular arrangement of complex 3.

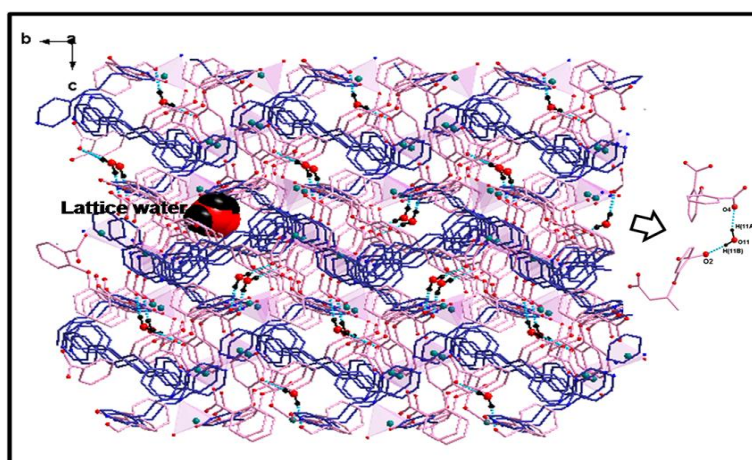


Fig S5 3D supramolecular arrangement of complex 4.

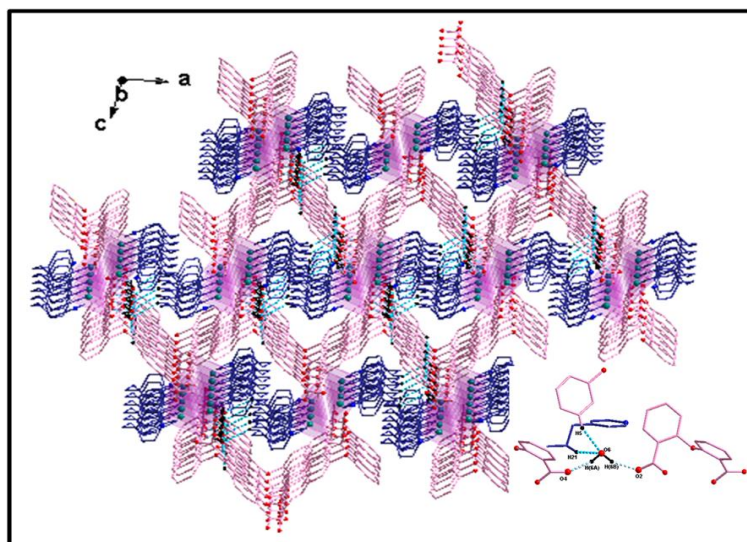


Fig S6 3D supramolecular arrangement of complex **5**.

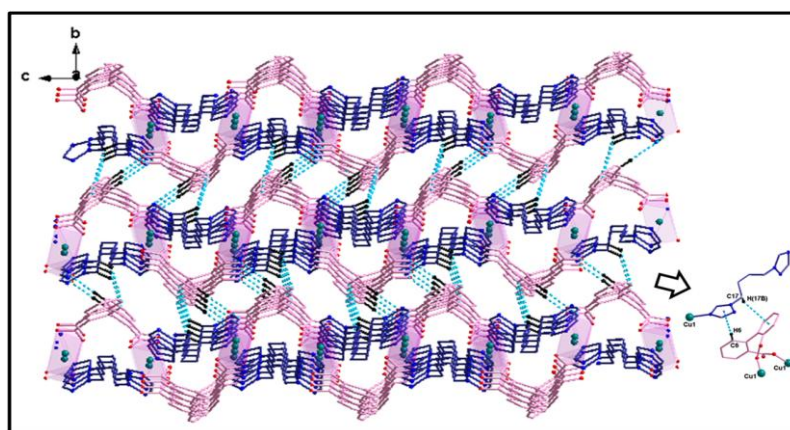


Fig S7 3D supramolecular arrangement of complex **6**.

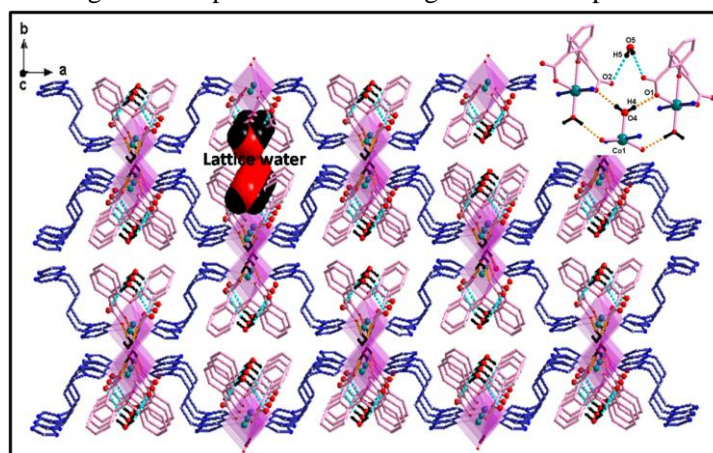


Fig S8 3D supramolecular arrangement of complex **7**.

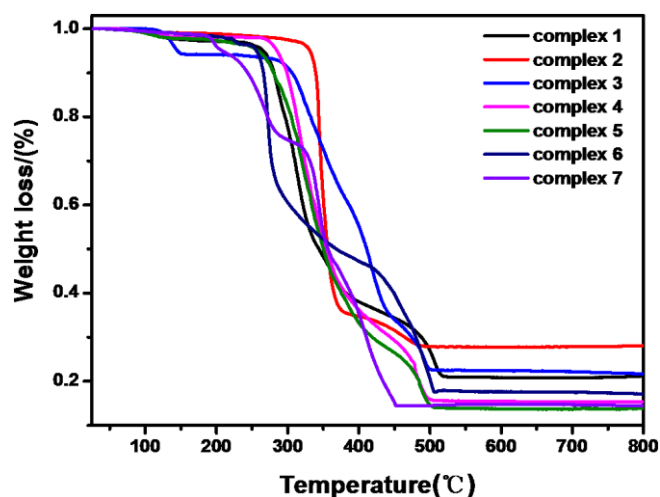


Fig. S9 The TGA curves of complexes 1-7.

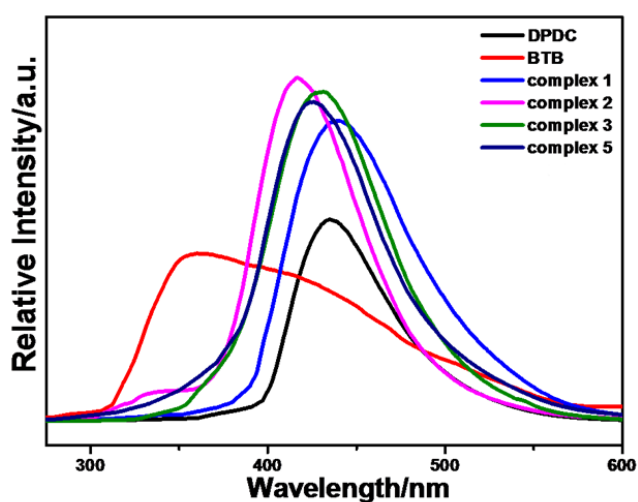


Fig. S10 The solid state emission spectra of complexes and the free ligands.

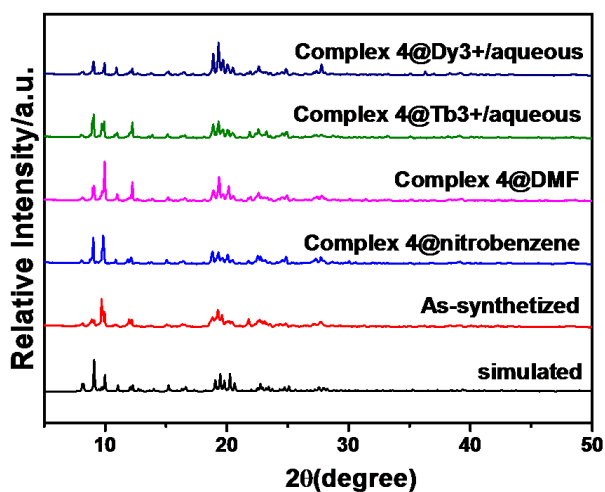


Fig. S11 PXRD patterns of complex 4 after immersing in different solvents.

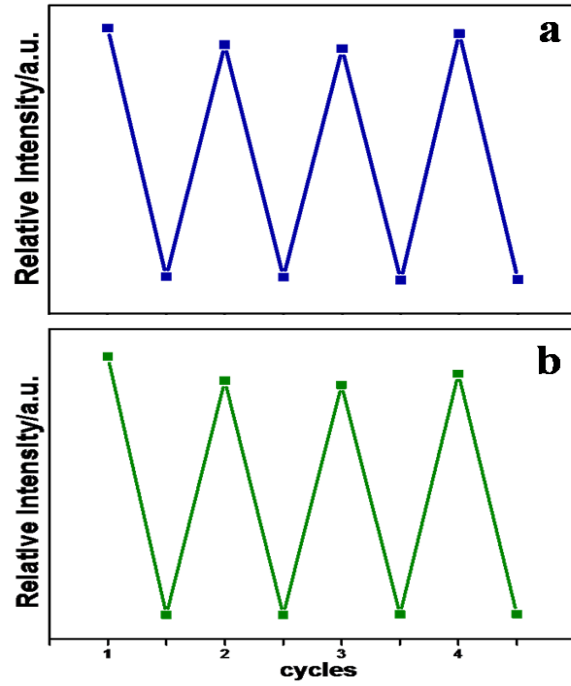


Fig. S12 The luminescence intensity of four recyclable experiments of sensing for nitrobenzene(NB) in DMF (a) and sensitizing Tb(III) in water (b).

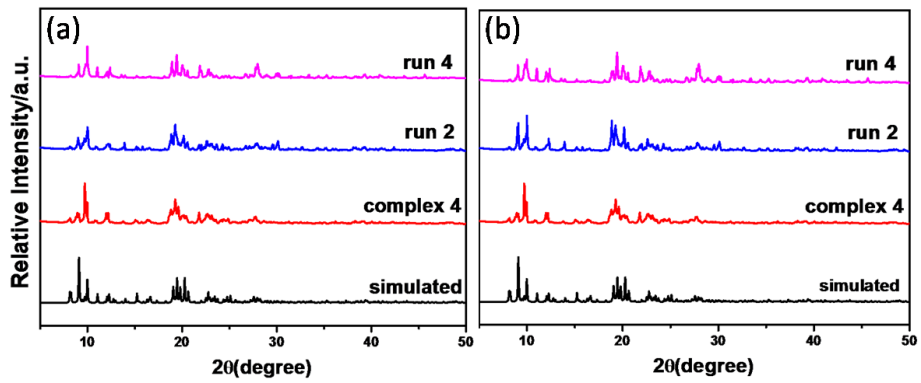


Fig. S13 PXRD patterns of complex 4 after two and four recycles of sensing for nitrobenzene(NB) in DMF (a) and sensitizing Tb(III) in water (b).

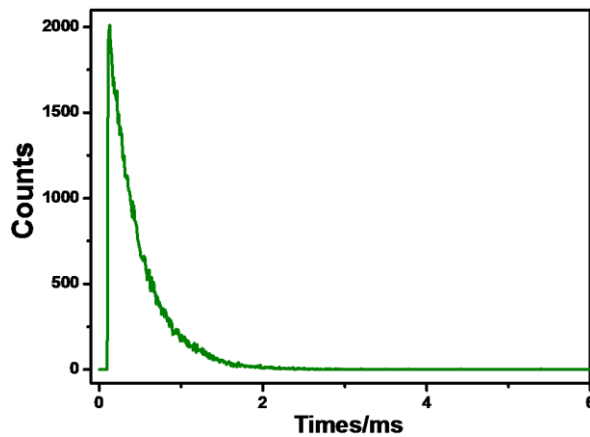


Fig. S14 Emission decay profiles of 5D_4 Tb(III) in complex 4@Tb(III)/water.

Table S1 The crystal data and structure refinement for complexes **1-7**.

Complex	1	2	3	4	5	6	7
Empirical formula	C ₂₇ H ₂₅ CdN ₂ O ₆	C ₈₂ H ₆₀ Cd ₄ N ₄ O ₂₀	C ₃₆ H ₃₄ N ₆ O ₁₁ Zn ₂	C ₃₄ H ₄₆ N ₄ O ₁₁ Zn ₂	C ₂₇ H ₂₄ N ₂ O ₆ Zn	C ₂₂ H ₂₀ CuN ₆ O ₄	C ₄₄ H ₄₆ Co ₂ N ₁₂ O ₁₃
Formula weight	585.89	1870.94	857.43	1057.69	537.85	495.98	1068.79
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P2₁/c</i>	<i>Cc</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>C2/c</i>
<i>a</i> / Å	10.915(7)	28.491(19)	12.429(4)	19.615(3)	9.2720(16)	10.2363(14)	20.666(9)
<i>b</i> / Å	9.528(6)	13.162(9)	7.950(2)	13.1022(19)	12.259(2)	17.779(3)	14.423(6)
<i>c</i> / Å	24.559(15)	21.213(14)	18.881(4)	18.765(3)	21.112(4)	12.1196(17)	8.174(5)
β / (°)	101.895(11)	102.974(11)	112.685(6)	97.504(3)	101.067(3)	109.452(2)	97.093(8)
Volume / Å ³	2499(3)	7752(9)	1721.3(8)	4781.3(12)	2355.0(7)	2079.7(5)	2418(2)
<i>Z</i>	4	4	4	4	4	4	2
Calculated density / mg · m ⁻³	1.5573(19)	1.603	1.647	1.469	1.517	1.584	1.468
Absorption coefficient / mm ⁻¹	0.919	1.157	1.468	1.071	1.09	1.095	0.762
<i>F</i> (000)	1188	3728	880	2184	1112	1020	1104
Crystal size / mm	0.08 × 0.10 × 0.10	0.21 × 0.18 × 0.10	0.45 × 0.25 × 0.18	0.25 × 0.18 × 0.13	0.18 × 0.15 × 0.10	0.12 × 0.08 × 0.06	0.350 × 0.200 × 0.200
θ Range for data collection / (°)	1.69-27.61	1.71-25.25	1.71-25.24	1.87-25.25	1.93-25.25	2.11-27.50	1.726-27.717
Limiting indices	-14 ≤ <i>h</i> ≤ 13; -12 ≤ <i>k</i> ≤ 12; -23 ≤ <i>l</i> ≤ 31	-34 ≤ <i>h</i> ≤ 34 -7 ≤ <i>k</i> ≤ 15 -25 ≤ <i>l</i> ≤ 25	-13 ≤ <i>h</i> ≤ 14 -9 ≤ <i>k</i> ≤ 9 -22 ≤ <i>l</i> ≤ 22	-19 ≤ <i>h</i> ≤ 23 -15 ≤ <i>k</i> ≤ 15 -22 ≤ <i>l</i> ≤ 21	-9 ≤ <i>h</i> ≤ 11 -14 ≤ <i>k</i> ≤ 14 -24 ≤ <i>l</i> ≤ 25	-13 ≤ <i>h</i> ≤ 13 -23 ≤ <i>k</i> ≤ 13 -15 ≤ <i>l</i> ≤ 15	-25 ≤ <i>h</i> ≤ 26 -18 ≤ <i>k</i> ≤ 18 -10 ≤ <i>l</i> ≤ 7
Reflections collected / unique	5758/5758	21064/13360	9911 / 5916	26725 / 8662	13127/4268	13945 / 4757	8254 / 2844
[<i>R</i> (int)=]	0.0000]	[<i>R</i> (int) =	[<i>R</i> (int) =	[<i>R</i> (int) =	[<i>R</i> (int) =	[<i>R</i> (int) =	[<i>R</i> (int) =
		0.0454]	0.0412]	0.0876]	0.0672]	0.0810]	0.0421]
Data / restraints / parameters	5758/18/338	13360/497/99 1	5916 /10 /514	8662 / 2 / 648	4268 / 0 / 333	4757 / 0 / 298	2844 / 0 / 165
Goodness-of-fit on <i>F</i> ²	1.044	0.97	1.02	0.948	1.037	0.959	1.061
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0663	0.0605	0.1073	0.0466	0.0484	0.0480	0.0312

wR ₂ [I > 2sigma(I)]	0.1744	0.1484	0.2637	0.0821	0.1027	0.0746	0.0809
R ₁ [all data]	0.097	0.1232	0.0443	0.0855	0.0726	0.0879	0.0345
wR ₂ [all data]	0.1765	0.158	0.0875	0.096	0.1027	0.0978	0.0809
Largest diff. peak and hole / e · Å ⁻³	2.807 and -1.960	0.772 and -0.347	0.360 and -0.498	0.470 and -0.679	0.445 and -0.609	0.520 and -0.538	0.392 and -0.418

Table S2 Selected bond lengths [Å] and angles [°] for complex **1-7**

1			
Cd(1)-O(1)	2.475(5)	Cd(1)-O(2)	2.377(5)
Cd(1)-O(3)#1	2.630(5)	Cd(1)-O(4)#1	2.311(5)
Cd(1)-O(5)	2.287(5)	Cd(1)-N(2)#2	2.331(5)
Cd(1)-N(1)	2.379(6)		
O(1)-Cd(1)-O(3)#1	131.02(15)	O(2)-Cd(1)-O(1)	53.99(15)
O(2)-Cd(1)-O(3)#1	171.62(16)	O(4)#1-Cd(1)-O(3)#1	52.99(16)
O(4)#1-Cd(1)-O(1)	88.48(17)	O(4)#1-Cd(1)-O(2)	135.23(17)
O(5)-Cd(1)-O(1)	143.68(16)	O(5)-Cd(1)-O(2)	93.50(17)
O(5)-Cd(1)-O(3)#1	79.51(16)	O(5)-Cd(1)-O(4)#1	127.72(17)
O(4)#1-Cd(1)-N(2)#2	103.72(18)	O(5)-Cd(1)-N(1)	78.84(19)
O(2)-Cd(1)-N(1)	83.84(17)	O(4)#1-Cd(1)-N(1)	87.65(19)
N(1)-Cd(1)-O(1)	109.20(18)	N(1)-Cd(1)-O(3)#1	99.18(17)
N(2)#2-Cd(1)-O(1)	82.76(18)	N(2)#2-Cd(1)-O(2)	95.45(17)
N(2)#2-Cd(1)-O(3)#1	79.48(17)	O(5)-Cd(1)-N(2)#2	85.21(19)
N(2)#2-Cd(1)-N(1)	163.95(19)		

Symmetry transformations used to generate equivalent atoms: #1 x,y-1,z; #2 x-1,-y+1/2,z-1/2.

2			
Cd(1)-O(1)	2.428(12)	Cd(1)-O(2)	2.411(10)
Cd(1)-O(6)	2.336(11)	Cd(1)-O(7)	2.435(9)
Cd(1)-O(15)#2	2.221(9)	Cd(1)-O(19)#2	2.324(7)
Cd(1)-O(20)#2	2.420(8)	Cd(2)-O(9)	2.315(10)
Cd(2)-O(4)	2.340(7)	Cd(2)-O(2)	2.346(10)
Cd(2)-O(7)	2.361(7)	Cd(3)-O(10)	2.174(9)
Cd(3)-O(11)	2.272(8)	Cd(3)-O(16)	2.329(12)
Cd(3)-O(4)	2.349(8)	Cd(3)-O(5)	2.379(9)
Cd(3)-O(12)	2.491(12)	Cd(4)-O(14)	2.275(8)
Cd(4)-O(19)	2.337(8)	Cd(4)-O(11)	2.353(9)
Cd(4)-O(17)	2.357(10)	Cd(2)-N(1)	2.256(11)
Cd(2)-N(4)#3	2.272(11)	Cd(4)-N(3)	2.267(9)
Cd(4)-N(2)#4	2.268(10)		

O(15)#2-Cd(1)-O(19)#2	99.6(3)	O(15)#2-Cd(1)-O(6)	90.7(4)
O(19)#2-Cd(1)-O(6)	101.3(3)	O(15)#2-Cd(1)-O(2)	82.1(3)
O(19)#2-Cd(1)-O(2)	145.0(3)	O(6)-Cd(1)-O(2)	113.7(4)
O(15)#2-Cd(1)-O(20)#2	154.4(4)	O(19)#2-Cd(1)-O(20)#2	54.8(3)
O(6)-Cd(1)-O(20)#2	95.2(3)	O(2)-Cd(1)-O(20)#2	117.6(3)
O(15)#2-Cd(1)-O(1)	88.9(4)	O(19)#2-Cd(1)-O(1)	92.6(3)
O(6)-Cd(1)-O(1)	166.0(4)	O(2)-Cd(1)-O(1)	52.4(4)
O(20)#2-Cd(1)-O(1)	91.2(3)	O(15)#2-Cd(1)-O(7)	113.5(4)
O(19)#2-Cd(1)-O(7)	136.8(3)	O(6)-Cd(1)-O(7)	53.5(3)
O(2)-Cd(1)-O(7)	69.8(3)	O(20)#2-Cd(1)-O(7)	89.7(3)
O(1)-Cd(1)-O(7)	114.2(4)	O(9)-Cd(2)-O(4)	82.3(3)
O(9)-Cd(2)-O(2)	159.7(3)	O(4)-Cd(2)-O(2)	118.0(3)
O(9)-Cd(2)-O(7)	87.6(3)	O(4)-Cd(2)-O(7)	169.6(3)
O(2)-Cd(2)-O(7)	72.1(3)	O(10)-Cd(3)-O(11)	109.4(4)
O(10)-Cd(3)-O(16)	104.2(4)	O(11)-Cd(3)-O(16)	111.1(4)
O(10)-Cd(3)-O(4)	100.0(3)	O(11)-Cd(3)-O(4)	136.3(3)
O(16)-Cd(3)-O(4)	91.4(4)	O(10)-Cd(3)-O(5)	152.2(4)
O(11)-Cd(3)-O(5)	87.8(3)	O(16)-Cd(3)-O(5)	88.7(4)
O(4)-Cd(3)-O(5)	54.5(3)	O(10)-Cd(3)-O(12)	84.1(4)
O(11)-Cd(3)-O(12)	54.2(3)	O(16)-Cd(3)-O(12)	165.2(4)
O(4)-Cd(3)-O(12)	99.4(4)	O(5)-Cd(3)-O(12)	89.3(4)
O(14)-Cd(4)-O(19)	82.9(3)	O(14)-Cd(4)-O(11)	91.9(3)
O(19)-Cd(4)-O(11)	173.9(3)	O(14)-Cd(4)-O(17)	165.4(3)
O(19)-Cd(4)-O(17)	111.0(3)	O(11)-Cd(4)-O(17)	74.4(3)
N(1)-Cd(2)-N(4)#3	174.7(4)	N(1)-Cd(2)-O(9)	88.1(4)
N(4)#3-Cd(2)-O(9)	96.6(4)	N(1)-Cd(2)-O(4)	91.4(3)
N(4)#3-Cd(2)-O(4)	86.8(3)	N(1)-Cd(2)-O(2)	91.8(4)
N(4)#3-Cd(2)-O(2)	84.6(4)	N(1)-Cd(2)-O(7)	90.8(3)
N(4)#3-Cd(2)-O(7)	91.9(3)	N(3)-Cd(4)-N(2)#4	179.5(4)
N(3)-Cd(4)-O(14)	93.9(3)	N(2)#4-Cd(4)-O(14)	86.3(4)
N(3)-Cd(4)-O(19)	87.9(3)	N(2)#4-Cd(4)-O(19)	91.6(3)
N(3)-Cd(4)-O(11)	89.2(3)	N(2)#4-Cd(4)-O(11)	91.2(4)
N(3)-Cd(4)-O(17)	91.1(4)	N(2)#4-Cd(4)-O(17)	88.9(4)

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

3

O(1)-Zn(1)	1.988(4)	O(2)-Zn(1)	2.490(4)
O(5)-Zn(1)	2.015(4)	O(6)-Zn(2)	2.471(4)
O(7)-Zn(2)	1.988(4)	O(10)-Zn(2)	2.009(3)
Zn(1)-O(3)#2	1.959(4)	Zn(2)-O(8)#1	1.954(4)
N(1)-Zn(1)	2.029(4)	N(6)-Zn(2)	2.023(4)

O(3)#2-Zn(1)-O(1)	139.17(14)	O(3)#2-Zn(1)-O(5)	100.16(15)
O(1)-Zn(1)-O(5)	98.54(15)	O(3)#2-Zn(1)-O(2)	100.54(13)
O(1)-Zn(1)-O(2)	57.72(14)	O(5)-Zn(1)-O(2)	156.11(15)
O(8)#1-Zn(2)-O(7)	137.01(14)	O(8)#1-Zn(2)-O(10)	100.86(16)
O(7)-Zn(2)-O(10)	99.58(15)	O(8)#1-Zn(2)-O(6)	98.70(14)
O(7)-Zn(2)-O(6)	57.85(13)	O(10)-Zn(2)-O(6)	157.24(15)
O(3)#2-Zn(1)-N(1)	99.06(18)	O(1)-Zn(1)-N(1)	112.24(17)
O(5)-Zn(1)-N(1)	101.60(15)	N(1)-Zn(1)-O(2)	86.77(14)
O(8)#1-Zn(2)-N(6)	95.47(17)	O(7)-Zn(2)-N(6)	116.70(16)
O(10)-Zn(2)-N(6)	101.77(14)	N(6)-Zn(2)-O(6)	87.76(14)

Symmetry transformations used to generate equivalent atoms: #1 x,y-1,z; #2 x,y+1,z.

4

O(1)-Zn(1)	1.937(2)	Zn(1)-O(5)#2	1.957(2)
O(6)-Zn(2)	1.935(2)	Zn(2)-O(9)#5	1.964(2)
N(1)-Zn(1)	2.022(3)	N(2)-Zn(2)	2.050(3)
N(3)-Zn(2)	2.045(3)		
O(1)-Zn(1)-O(5)#2	104.36(10)	O(1)-Zn(1)-N(4)#4	117.01(12)
O(5)#2-Zn(1)-N(4)#4	110.07(10)	O(1)-Zn(1)-N(1)	97.29(11)
O(5)#2-Zn(1)-N(1)	116.94(12)	N(4)#4-Zn(1)-N(1)	110.80(11)
O(6)-Zn(2)-O(9)#5	143.67(12)	O(6)-Zn(2)-N(3)	95.61(11)
O(9)#5-Zn(2)-N(3)	106.03(11)	O(6)-Zn(2)-N(2)	104.08(11)
O(9)#5-Zn(2)-N(2)	97.05(11)	N(3)-Zn(2)-N(2)	107.17(12)

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

5

O(1)-Zn(1)	1.929(3)	Zn(1)-O(5)#2	1.923(3)
N(1)-Zn(1)	2.035(3)	Zn(1)-N(2)#3	2.047(3)
O(5)#2-Zn(1)-O(1)	121.38(11)	O(5)#2-Zn(1)-N(1)	117.96(11)
O(1)-Zn(1)-N(1)	107.84(12)	O(5)#2-Zn(1)-N(2)#3	97.63(11)
O(1)-Zn(1)-N(2)#3	98.16(11)	N(1)-Zn(1)-N(2)#3	110.95(12)

Symmetry transformations used to generate equivalent atoms: #1 x,y-1,z; #2 -x+1,-y+2,-z+1; #3 x,y+1,z.

6

Cu(1)-O(1)	1.976(2)	Cu(1)-O(3)#1	1.944(2)
Cu(1)-N(1)	1.982(2)	Cu(1)-N(6)#2	1.988(2)
O(3)#1-Cu(1)-O(1)	179.62(9)	O(3)#1-Cu(1)-N(1)	91.09(10)
O(1)-Cu(1)-N(1)	89.15(9)	O(3)#1-Cu(1)-N(6)#2	87.82(9)
O(1)-Cu(1)-N(6)#2	91.94(9)	N(1)-Cu(1)-N(6)#2	178.78(11)

Symmetry transformations used to generate equivalent atoms: #1 $x, -y+1/2, z+1/2$; #2 $x-1, -y+1/2, z+1/2$.

7			
Co(1)-O(1)	2.0519(15)	Co(1)-O(3)	2.2236(17)
Co(1)-O(4)	2.0468(17)	Co(1)-O(1)#1	2.0519(15)
Co(1)-N(1)	2.1045(15)	Co(1)-N(1)#1	2.1045(15)
O(4)-Co(1)-O(1)#1	101.42(3)	O(4)-Co(1)-O(1)	101.42(3)
O(1)#1-Co(1)-O(1)	157.16(6)	O(4)-Co(1)-N(1)#1	88.35(3)
O(1)#1-Co(1)-N(1)#1	89.79(5)	O(1)-Co(1)-N(1)#1	90.87(5)
O(4)-Co(1)-N(1)	88.35(3)	O(1)#1-Co(1)-N(1)	90.87(5)
O(1)-Co(1)-N(1)	89.79(5)	N(1)#1-Co(1)-N(1)	176.70(7)
O(4)-Co(1)-O(3)	180.0	O(1)#1-Co(1)-O(3)	78.58(3)
O(1)-Co(1)-O(3)	78.58(3)	N(1)#1-Co(1)-O(3)	91.65(3)
N(1)-Co(1)-O(3)	91.65(3)		

Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+3/2$.