Electronic Supplementary Information

Five complexes based on a new racemic tetraoxaspiro ligand: correlation of potential coordination preferences with structure, magnetic properties and luminescent properties

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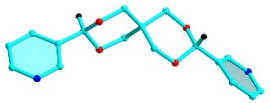
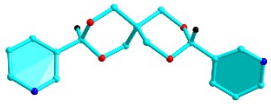
Table S1. The coordination configuration, dihedral angle(°) and N-to-N distances(Å) of the (*R,S*)-bptu ligand in **1**−**5**.

cis			*trans*		
1			**4**		
Dihedral angle(°)	13.505	13.505	Dihedral angle(°)	45.990	45.990
N···N(Å)	10.938	10.938	N···N(Å)	11.227	11.227
2			**5**		
Dihedral angle(°)	14.895	14.896	Dihedral angle(°)	52.162	52.162
N···N(Å)	10.406	10.406	N···N(Å)	11.475	11.475

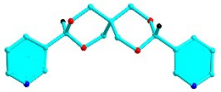
3					
Dihedral angle(°)	12.827	5.040			
N···N(Å)	9.897	9.999			

Table S2. Selected bond lengths (Å) and angles (°) for **1–5** and (*R,S*)-bptu ligand.

		1	
Cl(1)–Cu(1)	2.287(6)	Cl(2)–Cu(1)	2.305(5)
Cu(1)–N(1)#2	2.001(1)	Cu(1)–N(1)	2.001(1)
N(1)#2–Cu(1)–N(1)	170.4(5)	N(1)#2–Cu(1)–Cl(1)	88.8(3)
N(1)–Cu(1)–Cl(1)	88.8(3)	N(1)#2–Cu(1)–Cl(2)	90.2(3)
N(1)–Cu(1)–Cl(2)	90.2(3)	Cl(1)–Cu(1)–Cl(2)	169.0(3)
		2	
Zn(1)–N(1)	2.041(4)	Zn(1)-N(2)	2.086(4)
Zn(1)–Cl(3)	2.2154(1)	Zn(1)-Cl(2)	2.2194(1)
N(1)–Zn(1)–N(2)	105.68(1)	N(1)–Zn(1)–Cl(3)	110.81(1)
N(2)–Zn(1)–Cl(3)	104.49(1)	N(1)–Zn(1)–Cl(2)	107.13(1)
N(2)–Zn(1)–Cl(2)	105.53(1)	Cl(3)–Zn(1)–Cl(2)	121.96(7)
		3	
Cd(1)–N(1)	2.318(6)	Cd(1)–N(4)	2.338(7)
Cd(1)–O(9)	2.358(8)	Cd(1)–O(10)	2.391(7)
Cd(1)–Cl(2)	2.495(3)	Cd(1)–Cl(1)	2.656(3)
Cd(2)–N(2)	2.362(8)	Cd(2)–N(3)	2.370(7)
Cd(2)–Cl(3)	2.455(3)	Cd(2)–Cl(4)	2.481(4)
Cd(2)–Cl(1)	2.619(3)		
N(1)–Cd(1)–N(4)	175.9(4)	N(1)–Cd(1)–O(9)	94.8(3)
N(4)–Cd(1)–O(9)	81.8(3)	N(1)–Cd(1)–O(10)	83.4(2)
N(4)–Cd(1)–O(10)	98.2(2)	O(9)–Cd(1)–O(10)	76.8(3)
N(1)–Cd(1)–Cl(2)	92.2(3)	N(4)–Cd(1)–Cl(2)	91.7(2)
O(9)–Cd(1)–Cl(2)	162.5(2)	O(10)–Cd(1)–Cl(2)	88.1(2)
N(1)–Cd(1)–Cl(1)	89.35(1)	N(4)–Cd(1)–Cl(1)	88.23(1)

O(9)–Cd(1)–Cl(1)	90.7(2)	O(10)–Cd(1)–Cl(1)	164.9(2)
Cl(2)–Cd(1)–Cl(1)	105.43(1)	N(2)–Cd(2)–N(3)	171.8(3)
N(2)–Cd(2)–Cl(3)	94.5(2)	N(3)–Cd(2)–Cl(3)	92.03(19)
N(2)–Cd(2)–Cl(4)	89.9(3)	N(3)–Cd(2)–Cl(4)	90.6(3)
Cl(3)–Cd(2)–Cl(4)	123.56(1)	N(2)–Cd(2)–Cl(1)	89.5(3)
N(3)–Cd(2)–Cl(1)	83.8(2)	Cl(3)–Cd(2)–Cl(1)	107.96(1)
Cl(4)–Cd(2)–Cl(1)	128.35(1)	Cd(2)–Cl(1)–Cd(1)	149.82(1)

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Cd(1)–N(1)#3	2.390(4)	Cd(1)–N(1)	2.390(4)
Cd(1)–N(2)#3	2.414(4)	Cd(1)–N(2)	2.414(4)
Cd(1)–Cl(1)#3	2.6092(1)	Cd(1)–Cl(1)	2.6092(1)
N(1)#3–Cd(1)–N(1)	180	N(1)#3–Cd(1)–N(2)#3	87.43(1)
N(1)–Cd(1)–N(2)#3	92.57(1)	N(1)#3–Cd(1)–N(2)	92.57(1)
N(1)–Cd(1)–N(2)	87.43(1)	N(2)#3–Cd(1)–N(2)	180
N(1)#3–Cd(1)–Cl(1)#3	89.08(1)	N(1)–Cd(1)–Cl(1)#3	90.92(1)
N(2)#3–Cd(1)–Cl(1)#3	89.89(1)	N(2)–Cd(1)–Cl(1)#3	90.11(1)
N(1)#3–Cd(1)–Cl(1)	90.92(1)	N(1)–Cd(1)–Cl(1)	89.08(1)
N(2)#3–Cd(1)–Cl(1)	90.11(1)	N(2)–Cd(1)–Cl(1)	89.89(1)
Cl(1)#3–Cd(1)–Cl(1)	180		

5

Cd(1)–N(2)#1	2.370(6)	Cd(1)–N(1)	2.468(6)
Cd(1)–Cl(3)	2.603(2)	Cd(1)–Cl(2)	2.625(2)
Cd(1)–Cl(1)	2.645(2)	Cd(1)–Cl(3)#2	2.692(2)
Cd(2)–O(5)	2.289(5)	Cd(2)–O(5)#3	2.290(5)
Cd(2)–Cl(1)#3	2.6113(1)	Cd(2)–Cl(1)	2.6113(1)
Cd(2)–Cl(2)#3	2.657(2)	Cd(2)–Cl(2)	2.657(2)
N(2)#1–Cd(1)–N(1)	79.4(2)	N(2)#1–Cd(1)–Cl(3)	93.72(1)

N(1)–Cd(1)–Cl(3)	93.87(1)	N(2)#1–Cd(1)–Cl(2)	162.78(1)
N(1)–Cd(1)–Cl(2)	86.78(1)	Cl(3)–Cd(1)–Cl(2)	97.39(7)
N(2)#1–Cd(1)–Cl(1)	87.16(1)	N(1)–Cd(1)–Cl(1)	93.11(1)
Cl(3)–Cd(1)–Cl(1)	173.01(7)	Cl(2)–Cd(1)–Cl(1)	83.42(6)
N(2)#1–Cd(1)–Cl(3)#2	89.63(1)	N(1)–Cd(1)–Cl(3)#2	167.59(1)
Cl(3)–Cd(1)–Cl(3)#2	81.05(7)	Cl(2)–Cd(1)–Cl(3)#2	105.04(7)
Cl(1)–Cd(1)–Cl(3)#2	92.03(6)	O(5)–Cd(2)–O(5)#3	180
O(5)–Cd(2)–Cl(1)#3	86.92(1)	O(5)#3–Cd(2)–Cl(1)#3	93.08(1)
O(5)–Cd(2)–Cl(1)	93.08(1)	O(5)#3–Cd(2)–Cl(1)	86.92(1)
Cl(1)#3–Cd(2)–Cl(1)	180	O(5)–Cd(2)–Cl(2)#3	94.22(1)
O(5)#3–Cd(2)–Cl(2)#3	85.79(1)	Cl(1)#3–Cd(2)–Cl(2)#3	83.44(6)
Cl(1)–Cd(2)–Cl(2)#3	96.56(6)	O(5)–Cd(2)–Cl(2)	85.78(1)
O(5)#3–Cd(2)–Cl(2)	94.22(1)	Cl(1)#3–Cd(2)–Cl(2)	96.56(6)
Cl(1)–Cd(2)–Cl(2)	83.44(6)	Cl(2)#3–Cd(2)–Cl(2)	180.00(1)
		(*R*,*S*)-bptu	
C(1)–N(1)	1.327(3)	C(1)–C(2)	1.373(3)
C(1)–H(1)	0.93	C(2)–C(3)	1.376(3)
C(2)–H(2)	0.93	C(3)–C(4)	1.387(2)
C(3)–H(3)	0.93	C(4)–C(5)	1.389(2)
C(4)–C(6)	1.508(2)	C(5)–N(1)	1.338(2)
C(5)–H(5)	0.93	C(6)–O(2)	1.4078(1)
C(6)–O(1)	1.4122(1)	C(6)–H(6)	0.98
C(7)–O(1)	1.439(2)	C(7)–C(8)	1.527(2)
C(7)–H(7A)	0.97	C(7)–H(7B)	0.97
C(8)–C(9)#1	1.525(2)	C(8)–C(9)	1.525(2)
C(8)–C(7)#1	1.527(2)	C(9)–O(2)	1.438(2)
C(9)–H(9A)	0.97	C(9)–H(9B)	0.97

N(1)–C(1)–C(2)	123.51(1)	N(1)–C(1)–H(1)	118.2
C(2)–C(1)–H(1)	118.2	C(1)–C(2)–C(3)	119.11(1)
C(1)–C(2)–H(2)	120.4	C(3)–C(2)–H(2)	120.4
C(2)–C(3)–C(4)	118.99(1)	C(2)–C(3)–H(3)	120.5
C(4)–C(3)–H(3)	120.5	C(3)–C(4)–C(5)	117.37(1)
C(3)–C(4)–C(6)	121.36(1)	C(5)–C(4)–C(6)	121.24(1)
N(1)–C(5)–C(4)	123.99(1)	N(1)–C(5)–H(5)	118
C(4)–C(5)–H(5)	118	O(2)–C(6)–O(1)	111.10(1)
O(2)–C(6)–C(4)	109.39(1)	O(1)–C(6)–C(4)	108.05(1)
O(2)–C(6)–H(6)	109.4	O(1)–C(6)–H(6)	109.4
C(4)–C(6)–H(6)	109.4	O(1)–C(7)–C(8)	111.29(1)
O(1)–C(7)–H(7A)	109.4	C(8)–C(7)–H(7A)	109.4
O(1)–C(7)–H(7B)	109.4	C(8)–C(7)–H(7B)	109.4
H(7A)–C(7)–H(7B)	108	C(9)#1–C(8)–C(9)	110.32(1)
C(9)#1–C(8)–C(7)#1	108.20(1)	C(9)–C(8)–C(7)#1	109.81(1)
C(9)#1–C(8)–C(7)	109.81(1)	C(9)–C(8)–C(7)	108.19(1)
C(7)#1–C(8)–C(7)	110.52(1)	O(2)–C(9)–C(8)	110.67(1)
O(2)–C(9)–H(9A)	109.5	C(8)–C(9)–H(9A)	109.5
O(2)–C(9)–H(9B)	109.5	C(8)–C(9)–H(9B)	109.5
H(9A)–C(9)–H(9B)	108.1	C(1)–N(1)–C(5)	117.01(1)
C(6)–O(1)–C(7)	110.36(1)	C(6)–O(2)–C(9)	109.94(1)

Symmetry codes: For **1**, #1 $-x+1$, y, $-z+1$, #2 x, $-y+1$, z, For **4**, #3 $-x+1$, $-y$, $-z$, For **5**, #1 $-x+2$, $-y+1$, $-z+2$, #2 $-x+1$, $-y+1$, $-z+1$, #3 $-x+1$, $-y+2$, $-z+1$. For bptu, #1 $-x+1$, $-y+2$, z

Table S3. Hydrogen bond geometries in the crystal structure of **1**−**5** and (*R,S*)-bptu**.**

D–H···A	D–H	H···A	D···A(Å)	D–H···A(°)
		1		
C(7)–H(7A)···Cl1#1	0.97	2.88	3.710(1)	158
		2		
C(13)–H(13)···Cl2#1	0.98	2.70	3.637(6)	160
C(20)–H(20)···Cl2#2	0.93	2.75	3.601(6)	152
C(10)–H(10)···O4	0.93	2.87	3.134	98
		3		
C(10)–H(10A)···Cl2#1	0.97	2.77	3.681(1)	156
C(18)–H(18)···O8#2	0.93	2.49	3.188(1)	132
		4		
C(10)–H(10B)···N3#1	0.97	2.50	3.420(1)	157
C(18)–H(18B)···Cl1#2	0.96	2.55	3.064(9)	114
C(18)–H(18C)···O3#3	0.96	2.34	2.919(1)	118
		5		
C(3)–H(3)···Cl1	0.93	2.90	3.623(4)	132
		(*R,S*)-bptu		
C(3)–H(3)···N1	0.93	2.59	3.471(3)	158
C(6)–H(6)···N1	0.98	2.59	3.542(2)	165
C(9)–H(9A)···O1	0.97	2.69	3.547	146

Symmetry codes: For **1**, – 1/2 + *x*, 1/2 + *y*, *z*; For **2**, #1 1/2 + *x*, 1/2 – *y*, 1/2 + *z*; #2 1/2 – *x*, 1/2 + *y*, 1/2 – *z*; For **3**, #1 – 1 + *x*, *y*, *z*; #2 1 – *x*, 1/2 + *y*, 2 – *z*; For **4**, #1 –1 + *x*, *y*,– 1 – *z*; #2 1 – *x*, – *y*, 1 – *z*; #3 *x*, *y*, 1 + *z*.

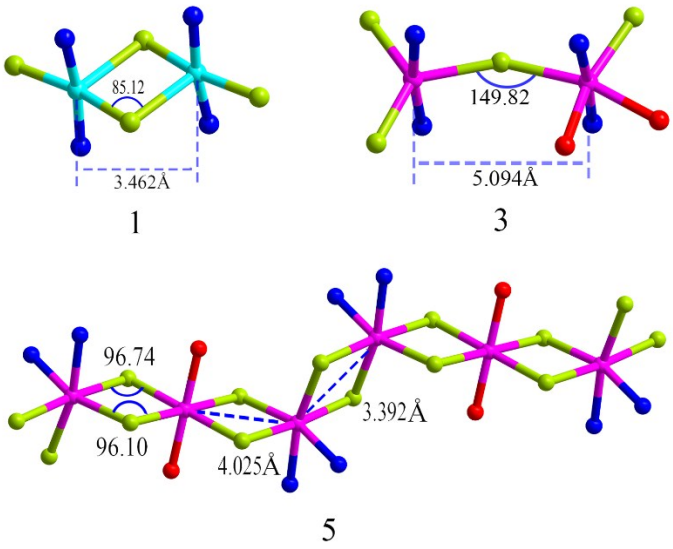

Fig. S1 M···M separation and the angle Cl–M–Cl in the M_2 unit of **1**, **3** and **5**.

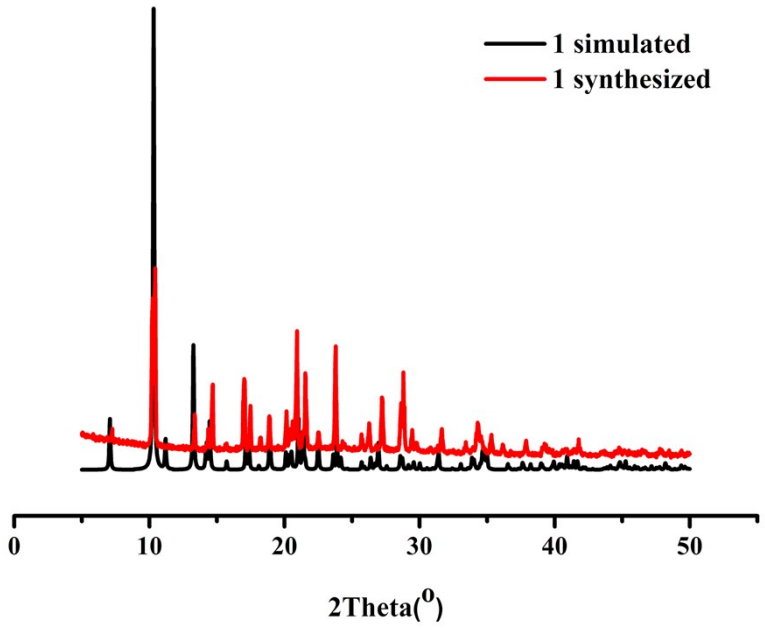

Fig. S2 PXRD patterns for **1**

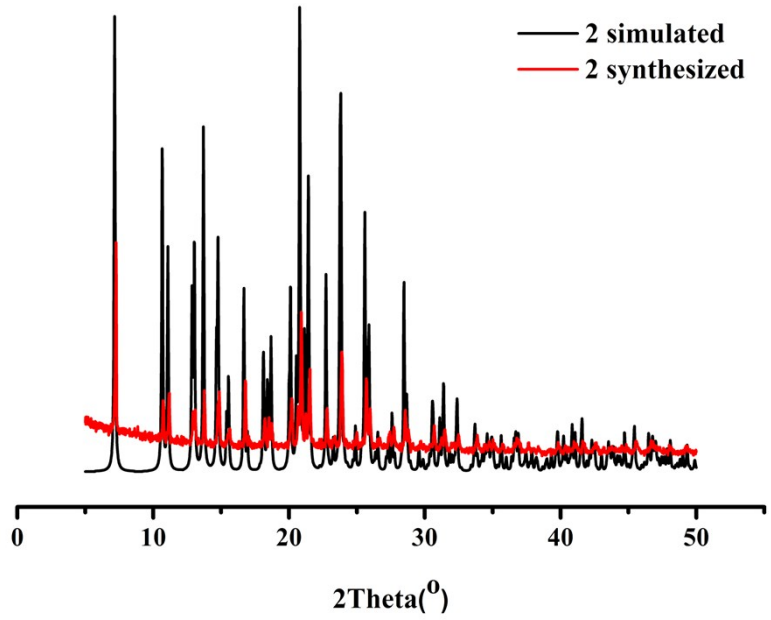

Fig. S3 PXRD patterns for **2**.

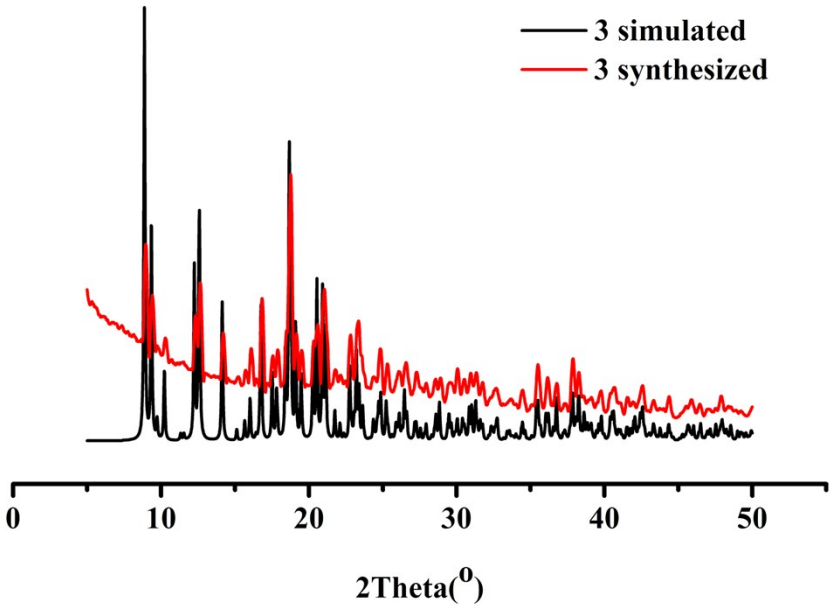

Fig. S4 PXRD patterns for **3**.

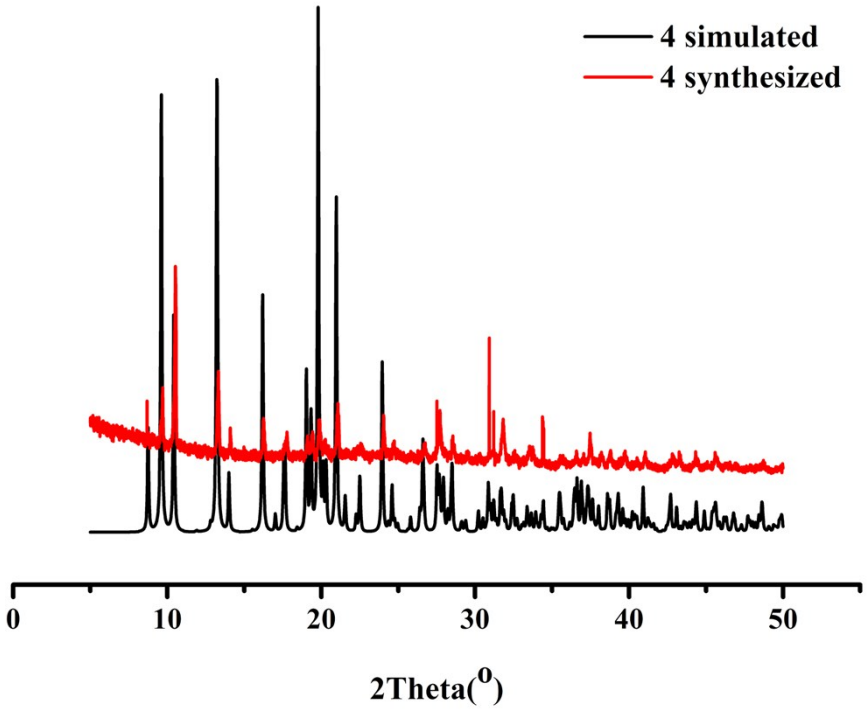

Fig. S5 PXRD patterns for **4**.

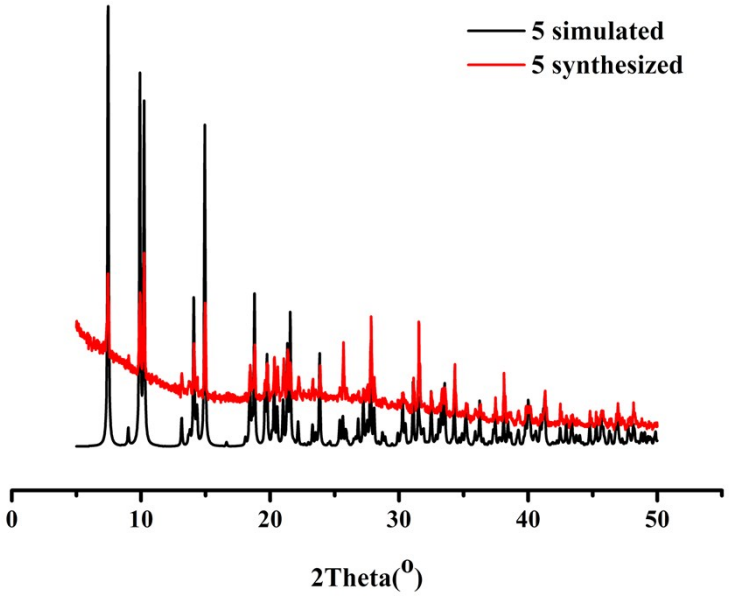

Fig. S6 PXRD patterns for **5**.

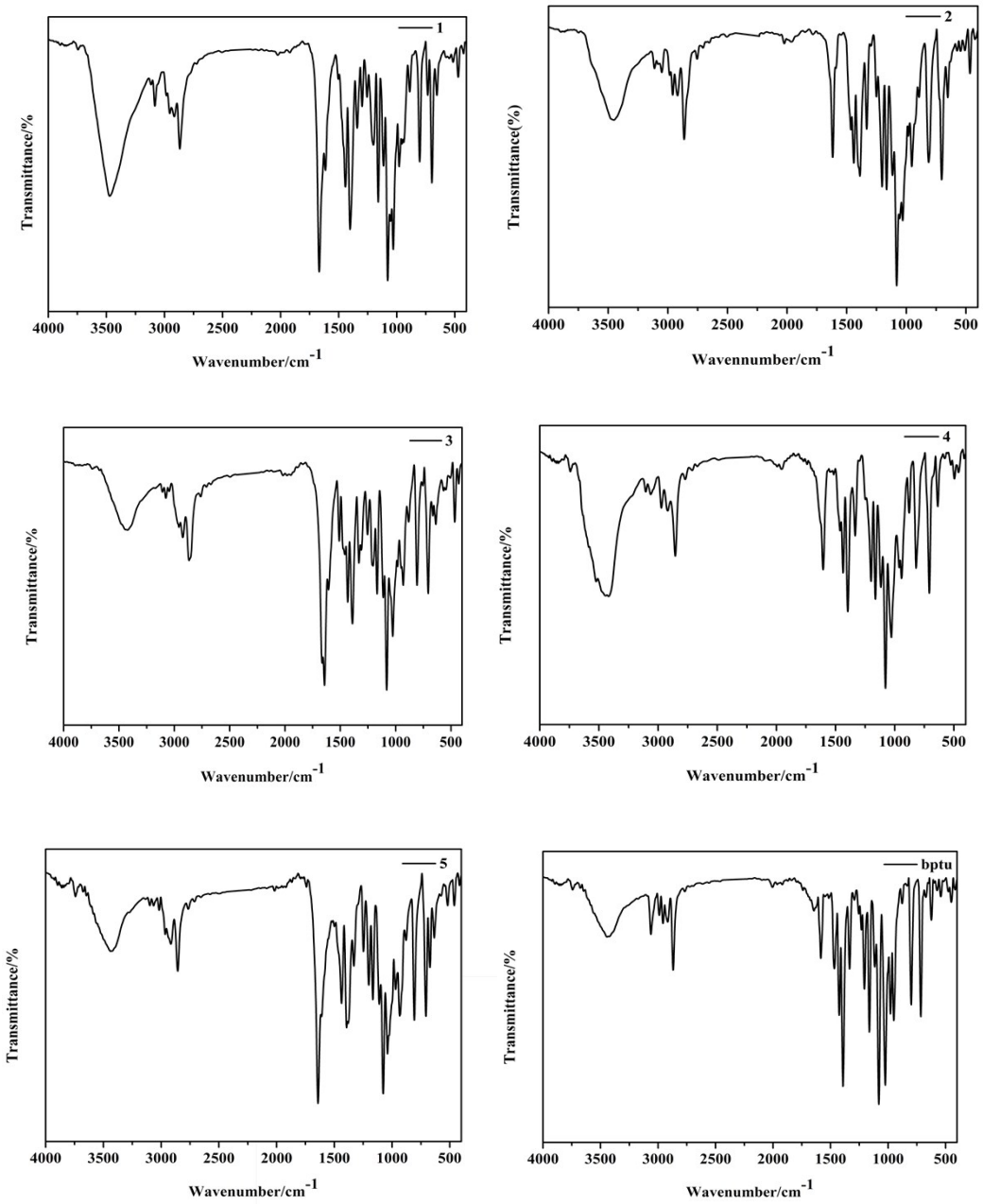

Fig. S7 IR for the free (*R,S*)-bptu ligand and complexes **1**–**5**.

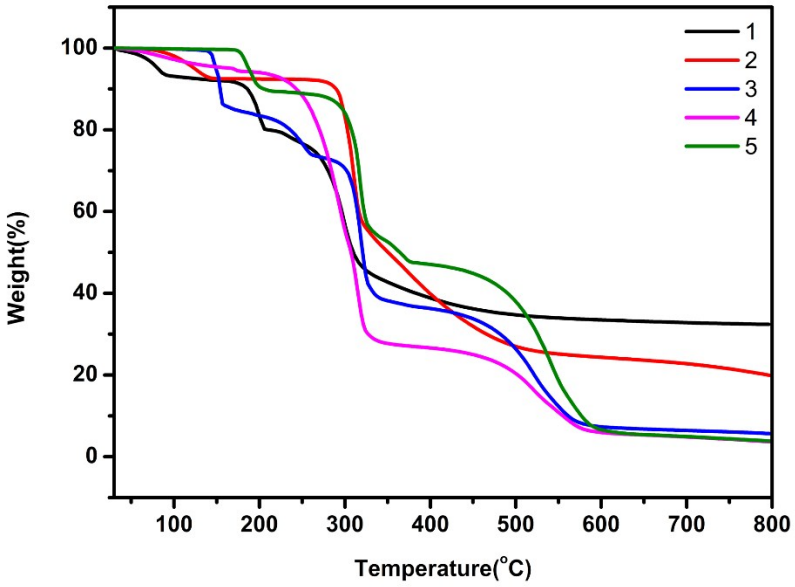

Fig. S8 TGA curves for **1**–**5** over the temperature 30–800 °C under a N_2 atmosphere.

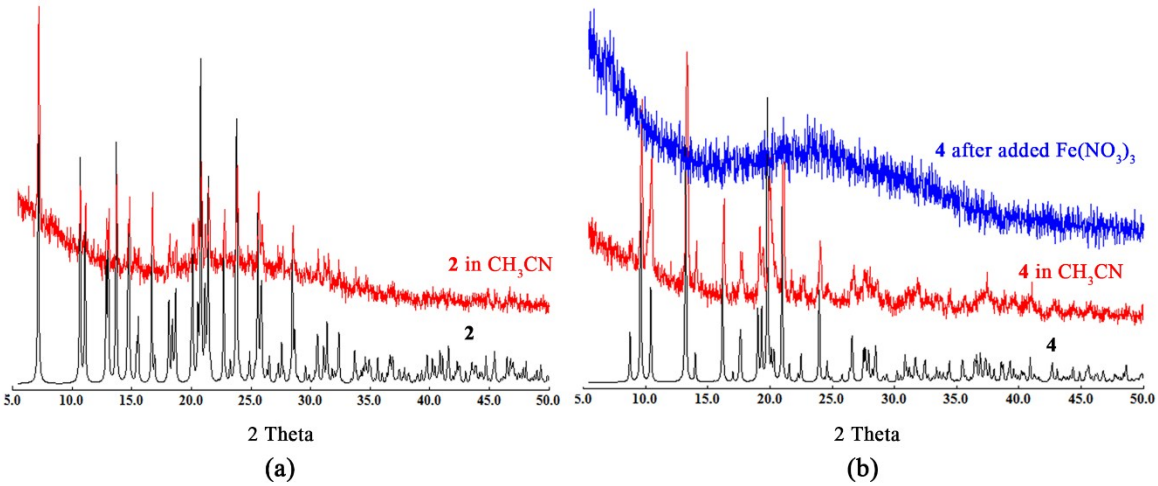

Fig. S9 The PXRD pattern of **2** and **4** after soaking in CH_3CN for 24 h, and pattern of **4** after fluorescence quenching of Fe^{3+}.

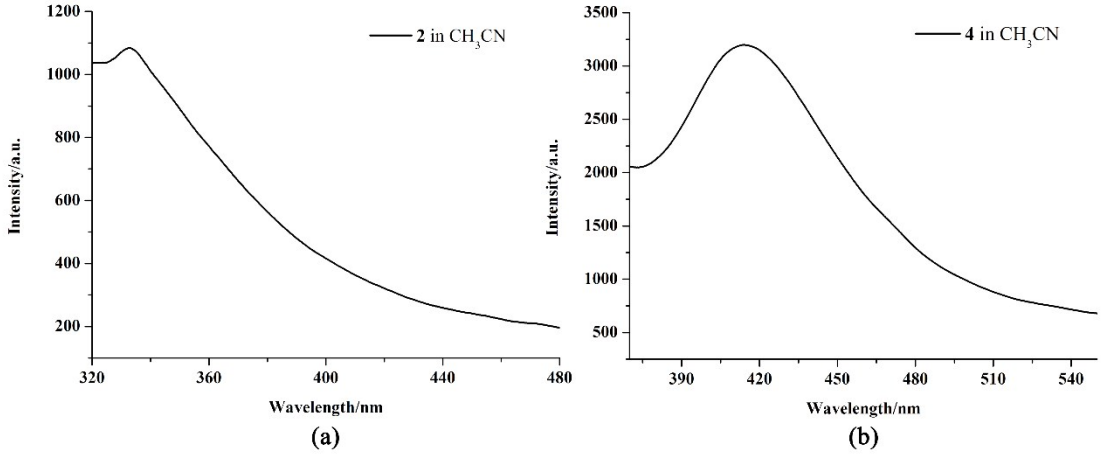

Fig. 10 Luminescent spectra of **2** and **4** in CH_3CN.

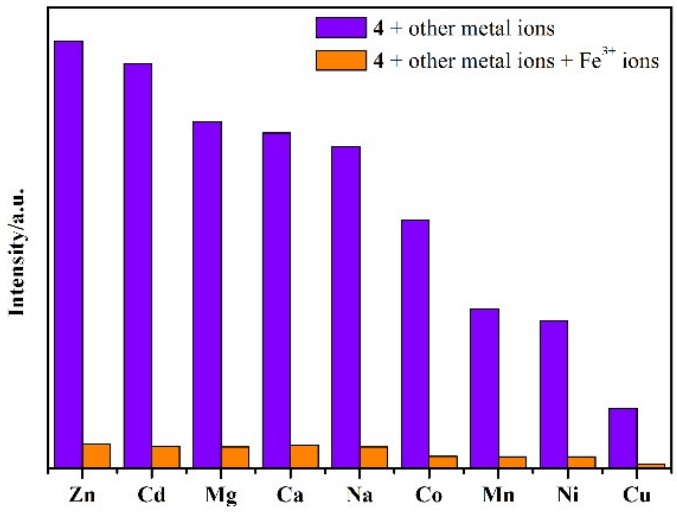

Fig. S11 The luminescence intensities of **4** upon the addition of different metal ions followed by Fe^{3+} ions.

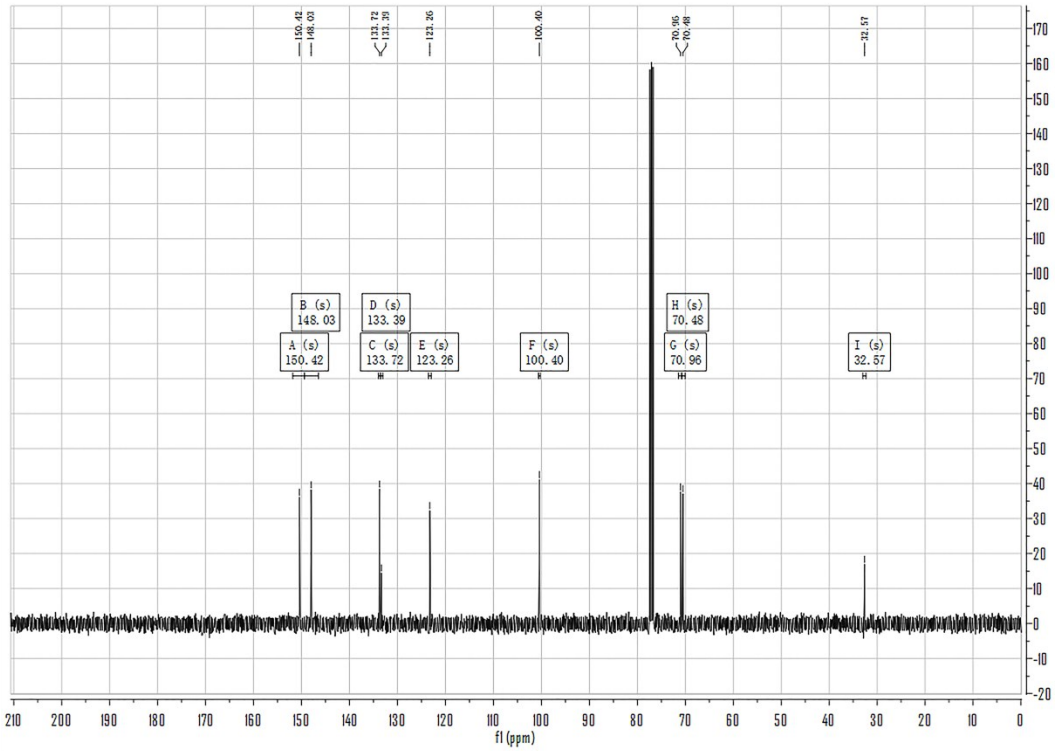

Fig. S12 ^{13}C NMR spectra of the (*R,S*)-bptu ligand

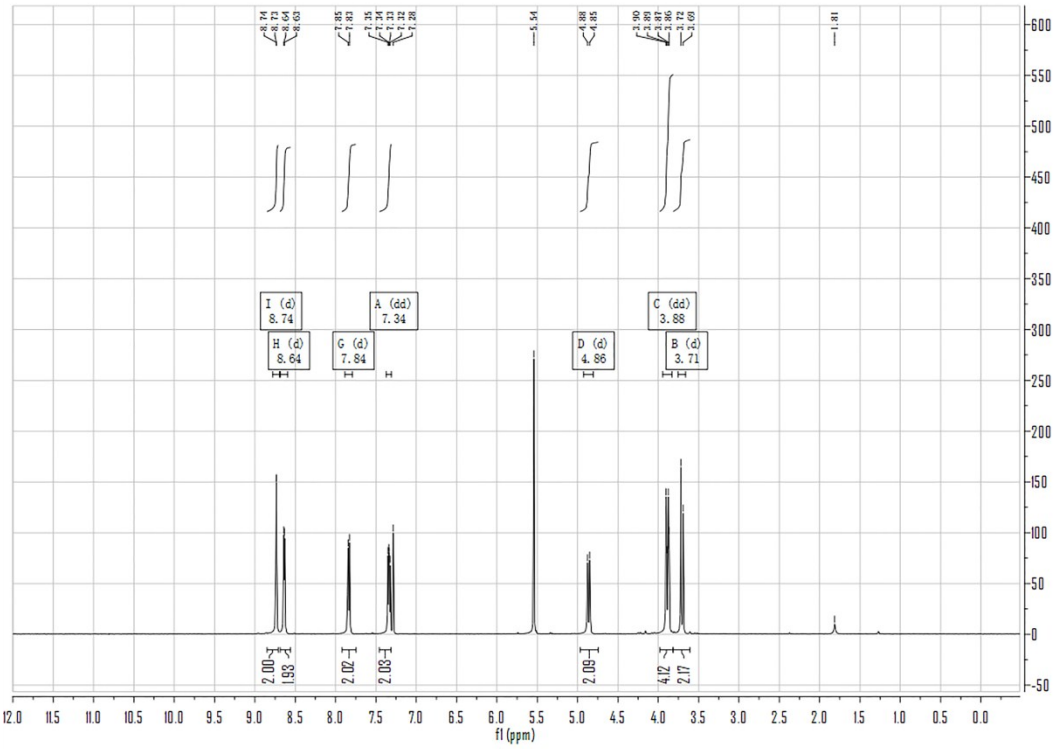

Fig. S13 ^{1}H NMR spectra of the e (*R,S*)-bptu ligand.