Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Formation and conversion of six temperature-dependent fluorescent Zn^{II}-complexes containing two *in situ* formed N-rich heterocyclic ligands

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Contents

Table S1. Crystallographic data and structure refinement summary for **1** to **3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{18}H_{14}Cl_2N_4Zn$	$C_{18}H_{14}N_{10}Zn$	$C_{36}H_{28}Cl_4N_8OZn_2$
Formula weight	422.60	435.76	1246.63
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$	$P2_1/c$
a (Å)	7.229(3)	18.130(3)	15.388(6)
b (Å)	14.023(6)	18.615(3)	12.271(5)
c (Å)	19.027(7)	13.827(2)	19.046(6)
α (°)	90	90	90
β (°)	95.403(5)	128.341(2)	122.12(2)
γ (°)	90	90	90
V (Å^3)	1920.3(13)	3660.1(10)	3046.0(2)
Z	4	8	2
ρ (cald.) (mg m^{-3})	1.462	1.582	1.359
T(K)	298(2)	293(2)	298(2)
μ (mm^{-1})	1.564	1.371	0.688
R_{int}	0.0355	0.0395	0.0543
GOF	1.027	1.021	1.040
R_1 [$I > 2\sigma(I)$]^a	0.0320	0.0455	0.0491
wR_2 (all data)^b	0.0748	0.1137	0.1328

^{a} $R_1=\sum||F_o|-|F_c||/\sum|F_o|$. ^{b} $wR_2=\{\sum[w(F_o^2-F_c^2)^2]/\sum(F_o^2)^2\}^{1/2}$, where w = $1/(\sigma^2(F_o^2)+(aP)^2+bP)$, $P=(F_o^2+2F_c^2)/3$

(to be continued) **Table S1.** Crystallographic data and structure refinement summary for **4** to **6**.

Complex	**4**	**5**	**6**
Empirical formula	$C_{36}H_{26}Cl_4N_8Zn_2$	$C_{36}H_{26}N_2OZn_2$	$C_{36}H_{26}N_{20}Zn_2$
Formula weight	843.19	869.51	869.51
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	P-1
a (Å)	8.730(2)	8.884(2)	8.0218(8)
b (Å)	13.047(4)	19.730(5)	10.0798(10)
c (Å)	15.560(4)	21.404(6)	11.6154(12)
α (°)	90	90	83.9840(10)
β (°)	96.344(3)	93.623(4)	83.1740(10)
γ (°)	90	90	76.6970(10)
V (Å^3)	1761.5(8)	3744.1(18)	904.60(16)
Z	2	4	1
ρ (cald.) (mg m^{-3})	1.590	1.543	1.596
T(K)	296(2)	296(2)	296(2)
μ (mm^{-1})	1.705	1.340	1.386
R_{int}	0.0298	0.0672	0.0168
GOF	1.052	1.050	1.032
R_1 [$I > 2\sigma(I)$]^a	0.0395	0.0600	0.0483
wR_2 (all data)^b	0.1007	0.1514	0.1387

^{a} $R_1=\sum||F_o|-|F_c||/\sum|F_o|$. ^{b} $_wR_2=\{\sum[w(F_o^2-F_c^2)^2]/\sum(F_o^2)^2\}^{1/2}$, where w = $1/(\sigma^2(F_o^2)+(aP)^2+bP)$, $P=(F_o^2+2F_c^2)/3$

Table S2. Selected bond lengths (Å) and bond angles (º) for compounds **1**-**6**.

		1	
N(2)-Zn(1)-Cl(2)	102.98(10)	Cl(1)-Zn(1)-N(3)	89.91(10)
N(2)-Zn(1)-Cl(1)	148.81(10)	N(1)-Zn(1)-N(3)	139.66(13)
Cl(2)-Zn(1)-Cl(1)	106.89(6)	Zn(1)-N(2)	2.030(4)
N(2)-Zn(1)-N(1)	83.55(14)	Zn(1)-Cl(2)	2.2602(14)
Cl(2)-Zn(1)-N(1)	107.21(10)	Zn(1)-Cl(1)	2.2626(16)
Cl(1)-Zn(1)-N(1)	95.87(11)	Zn(1)-N(1)	2.275(3)
N(1)-Zn(2)-N(3)	71.82(14)	Zn(1)-N(3)	2.385(4)
Cl(2)-Zn(1)-N(3)	109.13(9)		
		2	
N(8)-Zn(1)-N(5)	113.4(2)	N(2)-Zn(1)-N(4)	74.61(12)
N(8)-Zn(1)-N(2)	128.08(18)	N(1)-Zn(1)-N(4)	160.18(12)
N(5)-Zn(1)-N(2)	118.04(15)	Zn(1)-N(8)	1.950(4)
N(8)-Zn(1)-N(1)	96.03(16)	Zn(1)-N(5)	2.007(5)
N(5)-Zn(1)-N(1)	95.31(15)	Zn(1)-N(2)	2.026(3)
N(2)-Zn(1)-N(1)	86.39(12)	Zn(1)-N(1)	2.212(3)
N(8)-Zn(1)-N(4)	100.08(15)	Zn(1)-N(4)	2.283(3)
N(5)-Zn(1)-N(4)	88.86(15)		
		3	
N(2)-Zn(1)-Cl(1)	118.98(18)	Cl(1)-Zn(1)-Cl(2)	118.66(13)
N(2)-Zn(1)-N(1)	85.2(3)	N(1)-Zn(1)-Cl(2)	93.44(18)
Cl(1)-Zn(1)-N(1)	97.40(18)	N(2)-Zn(1)-N(4)	73.5(3)
N(2)-Zn(1)-Cl(2)	122.01(17)	Zn(1)-N(2)	2.027(6)
Cl(1)-Zn(1)-N(4)	99.2(2)	Zn(1)-Cl(1)	2.219(3)
N(1)-Zn(1)-N(4)	157.5(3)	Zn(1)-N(1)	2.279(6)
Cl(2)-Zn(1)-N(4)	91.87(18)	Zn(1)-Cl(2)	2.279(4)
		4	
N(2)-Zn(1)-Cl(2)	117.00(13)	Cl(1)-Zn(1)-N(3)	90.13(13)
N(2)-Zn(1)-Cl(1)	121.41(12)	N(1)-Zn(1)-N(3)	155.69(19)
Cl(2)-Zn(1)-Cl(1)	121.29(7)	Zn(1)-N(2)	2.019(4)
N(2)-Zn(1)-N(1)	83.99(17)	Zn(1)-Cl(2)	2.2359(17)
Cl(2)-Zn(1)-N(1)	98.33(11)	Zn(1)-Cl(1)	2.2570(16)
Cl(1)-Zn(1)-N(1)	93.05(11)	Zn(1)-N(1)	2.308(4)
N(2)-Zn(1)-N(3)	73.9(2)	Zn(1)-N(3)	2.308(5)

Cl(2)-Zn(1)-N(3)	100.55(14)		
		5	
N(4)-Zn(1)-N(5)	113.1(2)	Zn(1)-N(4)	1.954(5)
N(4)-Zn(1)-N(2)	136.3(2)	Zn(1)-N(5)	1.972(6)
N(5)-Zn(1)-N(2)	110.3(2)	Zn(1)-N(2)	2.029(4)
N(4)-Zn(1)-N(3)	92.5(2)	Zn(1)-N(3)	2.268(5)
N(5)-Zn(1)-N(3)	100.4(2)	Zn(1)-N(1)	2.342(5)
N(2)-Zn(1)-N(3)	84.50(18)	Zn(2)-N(14)	1.994(6)
N(4)-Zn(1)-N(1)	94.4(2)	Zn(2)-N(15)	2.000(6)
N(5)-Zn(1)-N(1)	99.6(2)	Zn(2)-N(12)	2.038(5)
N(2)-Zn(1)-N(1)	73.42(17)	Zn(2)-N(13)	2.284(5)
N(3)-Zn(1)-N(1)	154.26(18)	Zn(2)-N(11)	2.282(5)
N(14)-Zn(2)-N(15)	109.0(3)	N(12)-Zn(2)-N(13)	83.58(18)
N(14)-Zn(2)-N(12)	103.9(2)	N(14)-Zn(2)-N(11)	106.6(2)
N(15)-Zn(2)-N(12)	146.2(2)	N(15)-Zn(2)-N(11)	89.6(2)
N(14)-Zn(2)-N(13)	101.7(2)	N(12)-Zn(2)-N(11)	73.43(19)
N(15)-Zn(2)-N(13)	97.1(2)	N(13)-Zn(2)-N(11)	146.93(19)
		6	
N(10)-Zn(1)-N(2)	130.94(16)	N(9)-Zn(1)-N(1)	98.38(15)
N(10)-Zn(1)-N(9)	113.91(18)	N(3)-Zn(1)-N(1)	155.43(14)
N(2)-Zn(1)-N(9)	113.42(16)	Zn(1)-N(2)	2.029(3)
N(10)-Zn(1)N(3)	96.21(14)	Zn(1)-N(3)	2.216(3)
N(2)-Zn(1)-N(3)	86.71(12)	Zn(1)-N(10)	1.979(4)
N(9)-Zn(1)-N(3)	101.25(14)	Zn(1)-N(9)	1.988(4)
N(10)-Zn(1)-N(1)	89.15(15)	Zn(1)-N(1)	2.388(3)
N(2)-Zn(1)-N(1)	71.93(13)		

Table S3. Hydrogen bond parameters of compounds **1-6**.

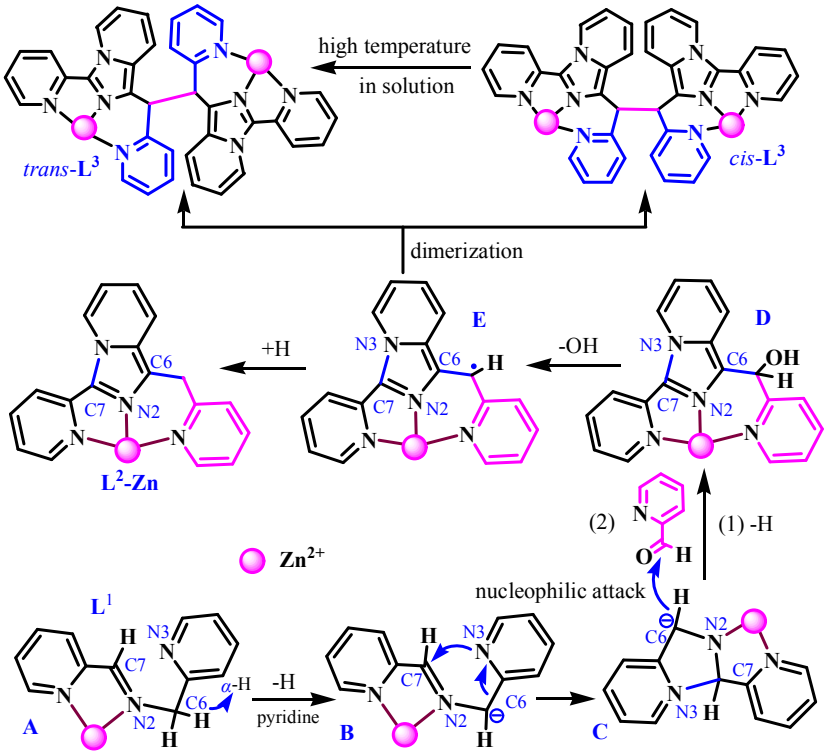
D-H···A	d (D-H) (Å)	d (H···A) (Å)	d (D···A) (Å)	∠ DHA (°)
		1		
C1-H1···Cl_1	0.93	2.64	3.310	129.7
C_{12}-H_{12}···Cl_2#1	0.93	2.87	3.681	146.2
C_{15}-H_{15}···Cl_2#1	0.93	2.86	3.700	150.8
C_9-H_9···Cl_2#2	0.93	2.89	3.721	149.3
π^a···π^b			3.760	
		2		
C_6-H_{6A}···N_7#7	0.97	2.61	3.461	145.8
C_6-H_{6B}···N_{10}#8	0.97	2.54	3.504	171.8
C_{12}-H_{12}···N_6#9	0.92	2.58	3.415	148.5
C_{16}-H_{16}···N_5#10	0.93	2.73	3.617	158.9
C_{17}-H_{17}···N_7#11	0.93	2.70	3.386	131.0
π^a···π^b			3.752	
		3		
C_{12}-H_{12}···Cl_2#12	0.93	2.76	3.588	147.6
C_{12}-H_{12}···Cl_2#13	0.93	2.76	3.588	147.6
π^a···π^b			3.873	
		4		
C_{10}-H_{10}···Cl_1#14	0.93	2.84	3.662	147.2
C_{10}-H_{10}···Cl_1#15	0.93	2.84	3.662	147.2
C_{18}-H_{18}···Cl_2#5	0.93	2.93	3.779	152.2
C_{18}-H_{18}···Cl_2#16	0.93	2.93	3.779	152.2
C_3-H_3···Cl_1#17	0.93	2.93	3.550	124.7
C_3-H_3···Cl_1#18	0.93	2.93	3.550	124.7
		5		
C_2-H_2···N_6#19	0.93	2.728	3.403	130.2
C_8-H_8···N_{17}#20	0.93	2.554	3.373	147.1
C_{10}-H_{10}···N_{10}#21	0.93	2.660	3.524	154.7
C_{25}-H_{25}···N_{20}#22	0.93	2.395	3.200	144.7
C_{34}-H_{34}···N_5#23	0.93	2.720	3.452	136.2
		6		
C_2-H_2···N_{10}#24	0.93	2.520	3.312	143.2
C_2-H_2···N_{10}#25	0.93	2.520	3.312	143.2
C_3-H_3···N_7#26	0.93	2.370	3.152	141.5
C_3-H_3···N_7#27	0.93	2.370	3.152	141.5
C_{10}-H_{10}···N_7#28	0.93	2.706	3.596	160.4
C_{10}-H_{10}···N_7#29	0.93	2.706	3.596	160.4
π^a···π^b			3.921	

*Symmetry transformations used to generate equivalent atoms: #**1** 1-x, 2-y, 2-z; #**2** 0.5-x, 0.5+y,1.5-z; #3 2-x,0.5+y,1.5-z; #4 2-x,2-y,2-z;#5 2-x,1-y,2-z;#6 2-x,-0.5+y,1.5-z; #**7** x, -y, 0.5+z, #**8** 0.5-x, -0.5+y, 0.5-z, #**9** 1-x, y, 0.5-z, #**10**

0.5+x, 0.5-y, 0.5+z, #**11** 0.5-x, 0.5-y, -z, #**12** 0.5+x, 0.5-y, 0.5+z, #**13** 1.5-x, 0.5-y, -z, #**14** 1+x, y, z, #**15** 1-x, -y, 2-z, #**16** x, -1+y, z, #**17** 2-x, -0.5+y, 1.5-z, #**18** x, 0.5-y, 0.5+z, #**19** 1+x, 1.5-y, 0.5+z, #**20** 1-x, 0.5+y, 0.5-z, #**21** -1+x, 1.5-y, -0.5+z, #**22** –x, 0.5+y, 0.5-z, #**23** 2-x, 1-y, 1-z, #**24** 1-x, 1-y, 1-z, #**25** 1+x, -1+y, -1+z, #**26** 1-x, -y, 1-z, #**27** 1+x, y, -1+z, #**28** 1+x, -1+y, z, #**29** 1-x, 1-y, -z.

$\pi^a \cdots \pi^b$ shows the distance between centroids of pyridyl/imidazol ring and pyridyl/imidazol ring.

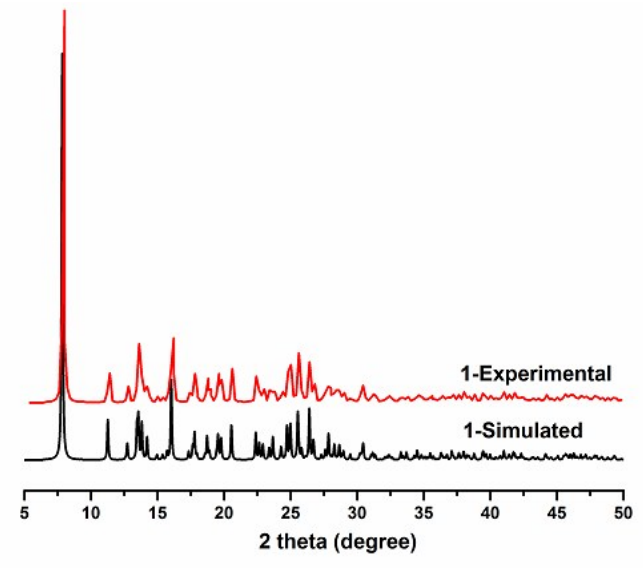
Scheme S1.



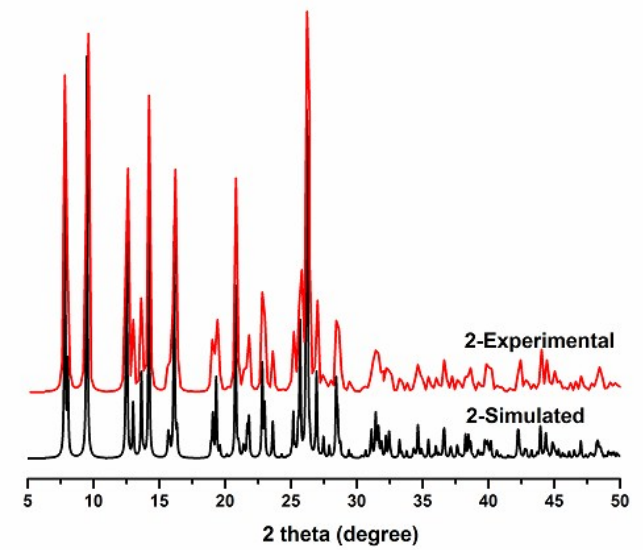
For ligands L^{2-3}, the possible formation mechanism is outlined in Scheme **S1**. Initially, the carbanion formed at C6 atom from the intermediate **B** increases the nucleophility at the heterocyclic nitrogen atom N3, which facilitates a nucleophilic attack at the imino carbon C7 to form C-N bond, resulting in the formation of intermediate **C**. And then coordination of the nitrogen atom of picolinaldehyde to Cd^{2+} enhances the electrophilicity of the carbon atom of the aldehyde, triggering the formation of an alcoholic intermediate **D** via the nucleophilic attack of **C** to the carbonyl electrophile. Finally, cleavage of the C–O bond in **D** gives a radical intermediate **E**, next two competitive reactions may occur for **E**, which subsequently either obtaining proton from intermediate **A** to furnish the formation of ligand L^2, or undergoing dimerization to give L^3. Because of the free rotation of C-C single bond and the steric hindrance from its four connecting groups, ligand L^3 shows two conformations of *cis*-/*trans*-form in formed compounds referring to C-C single bond such as complexes **3** and **5** (*cis*-form, dynamic stability) and **4** and **6** (*trans*-form, thermodynamic stability). Moreover, by increasing reaction temperature or prolonging reaction time, complexes **3** and **5** may be irreversibly transformed into **4** and **6**.

Figure S1.

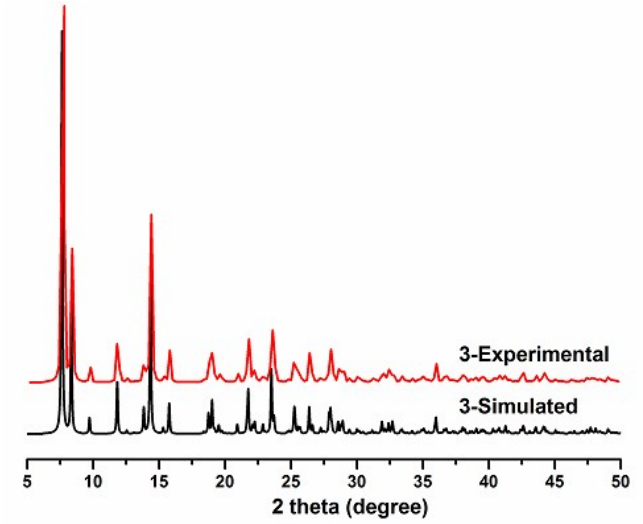
(a) For **1**



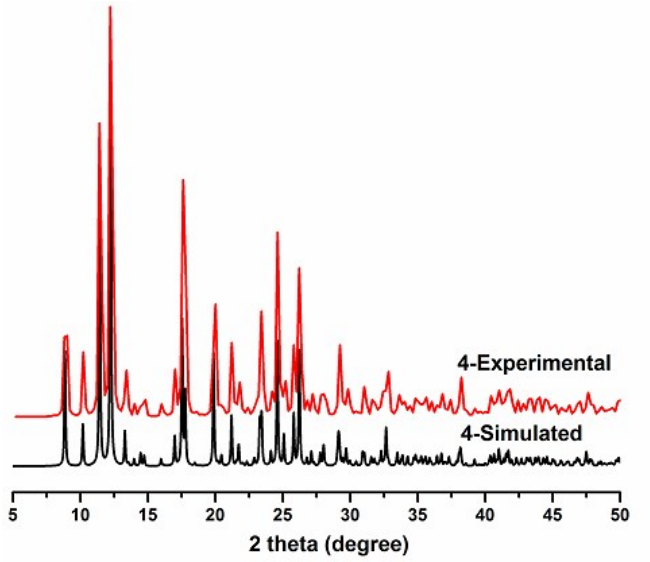
(b) For **2**



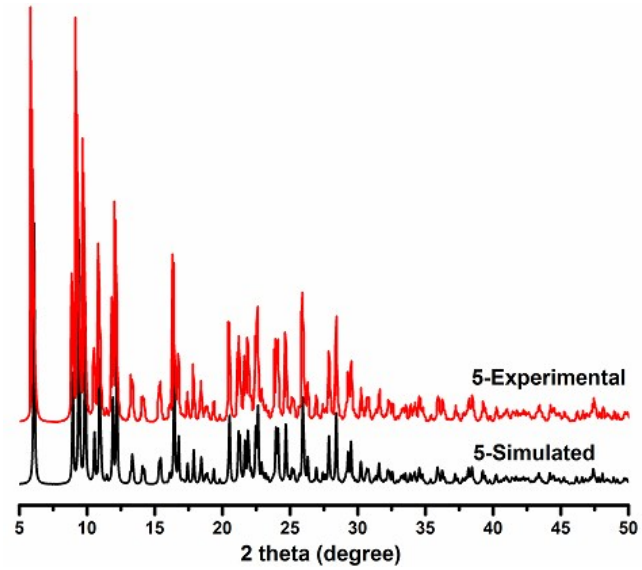
(c) For **3**



(d) For **4**



(e) For **5**



(f) For **6**

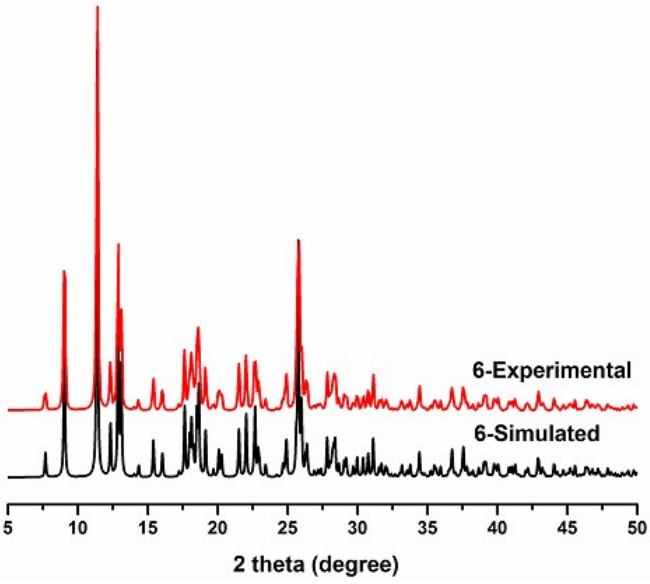
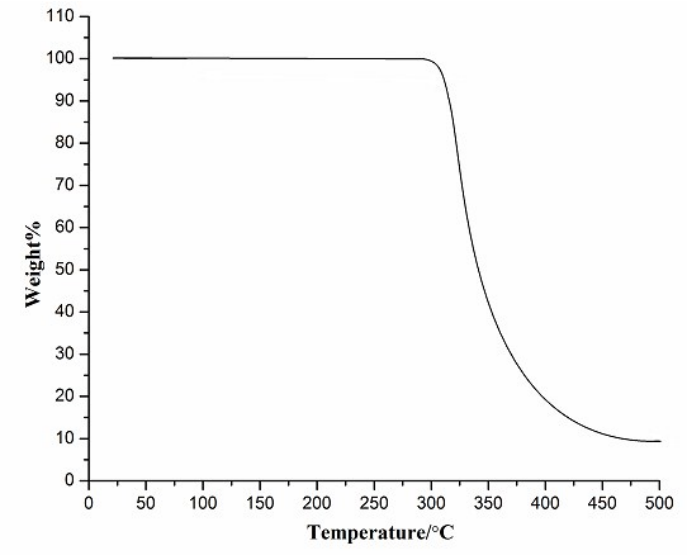
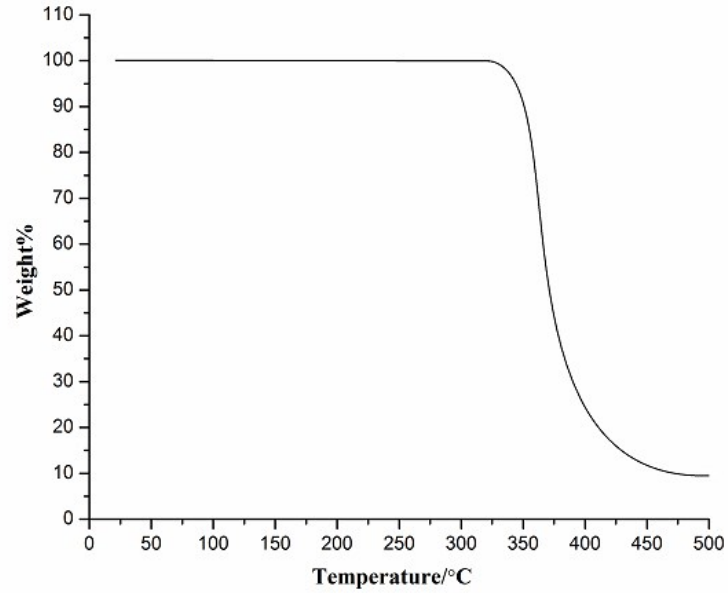


Figure S2.

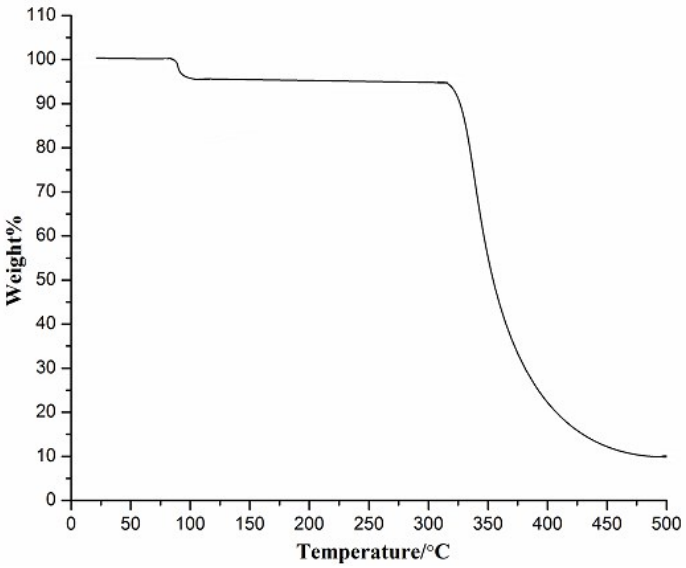
(a) For **1**



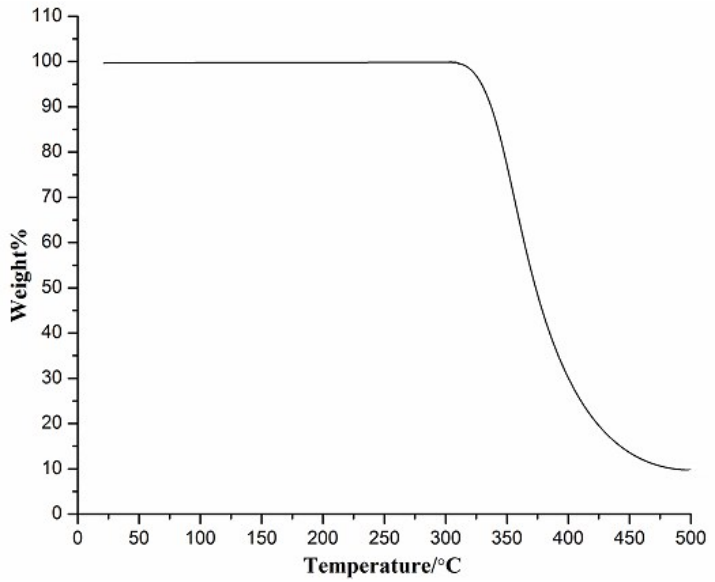
(b) For **2**



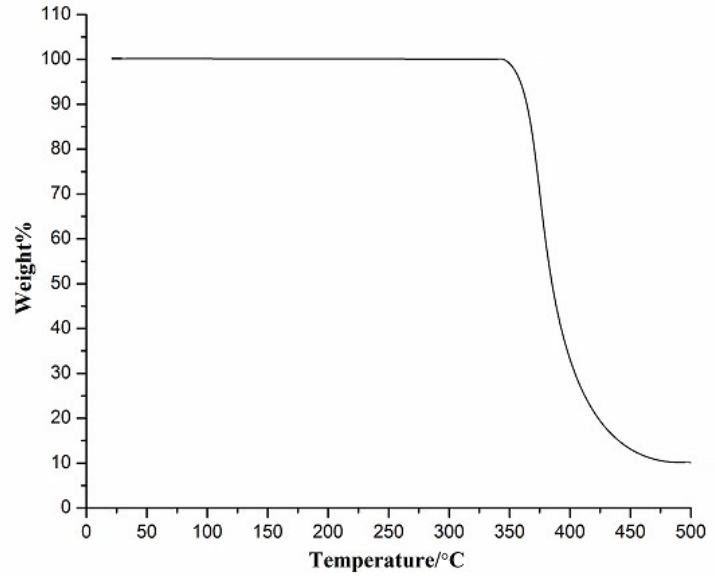
(c) For **3**



(d) For **4**



(e) For **5**



(f) For **6**

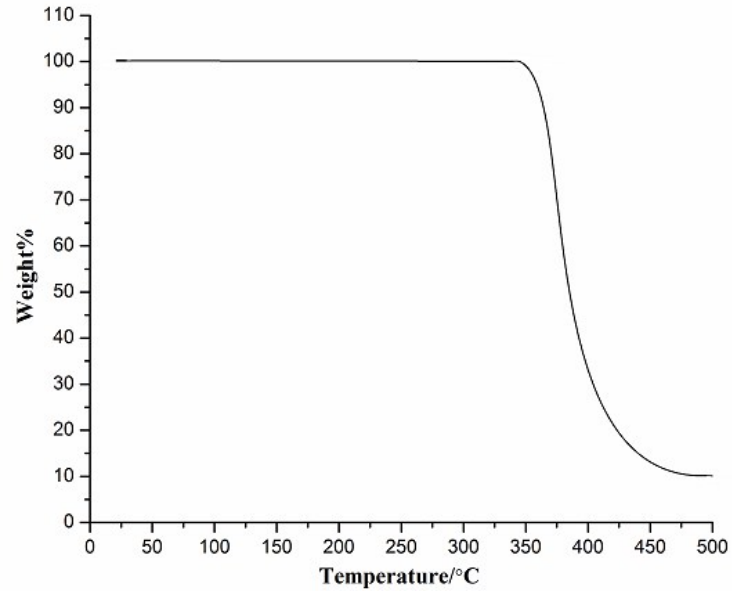


Figure S3.

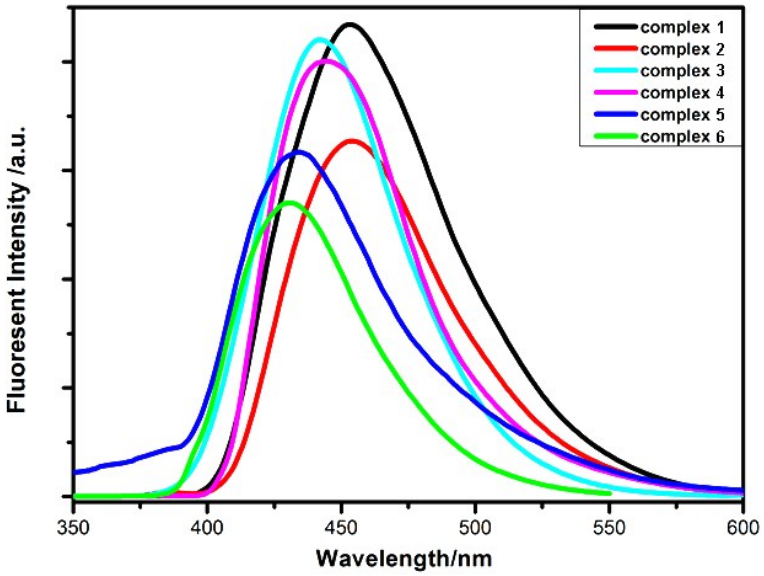


Figure S4.

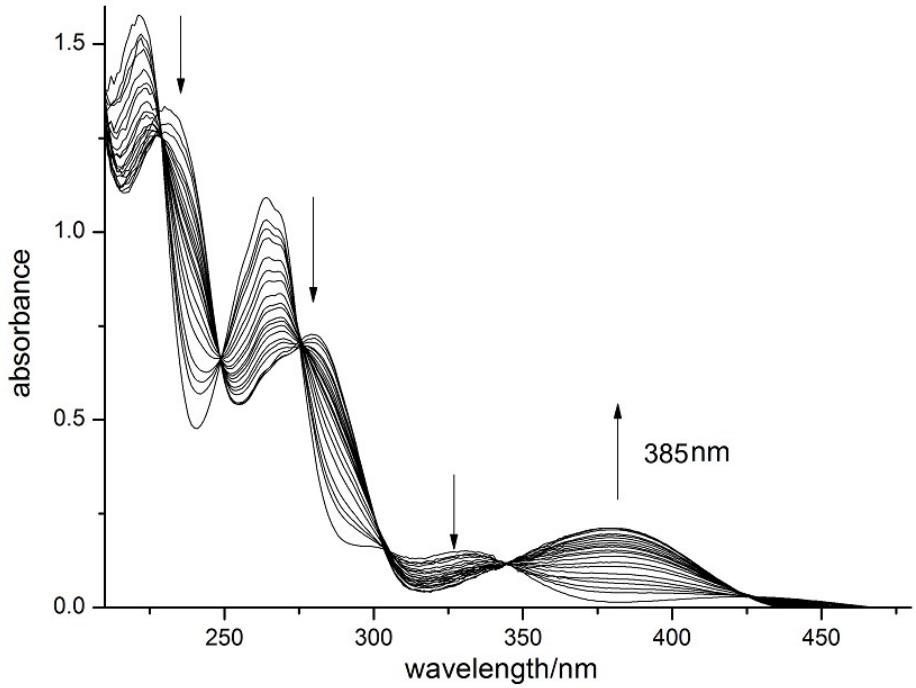


Figure S5.

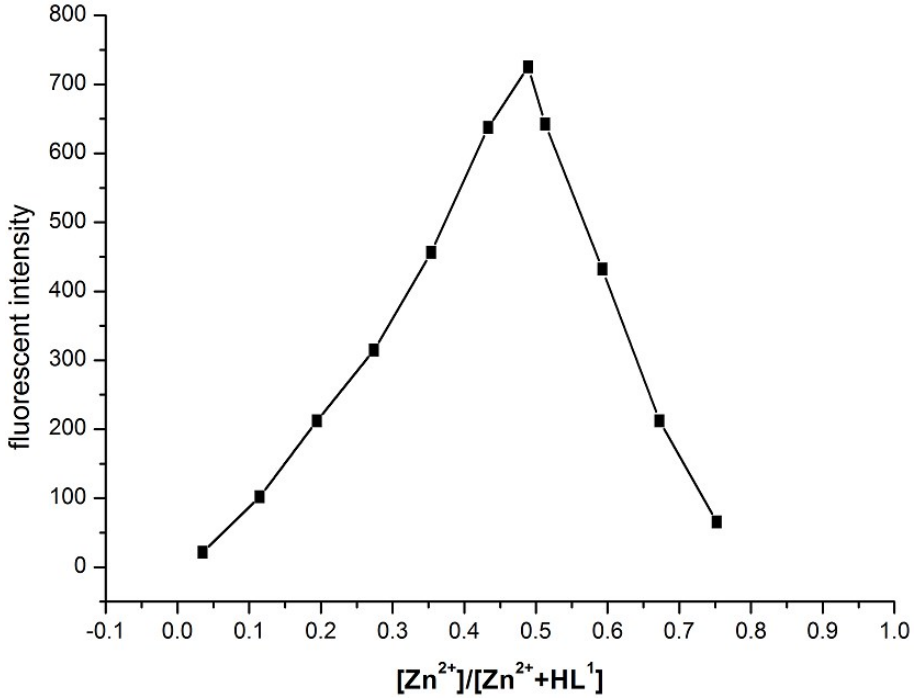


Figure S6

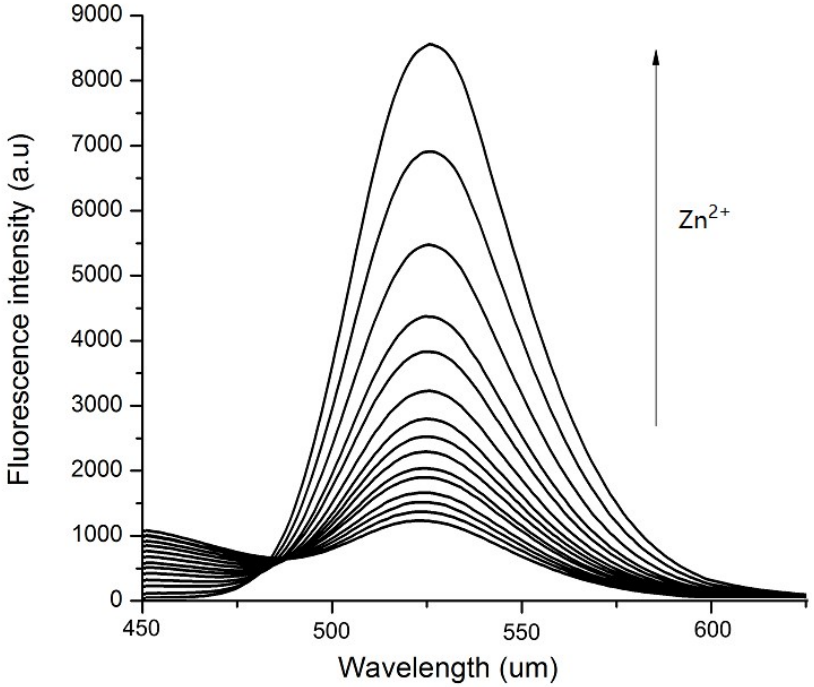


Figure S7

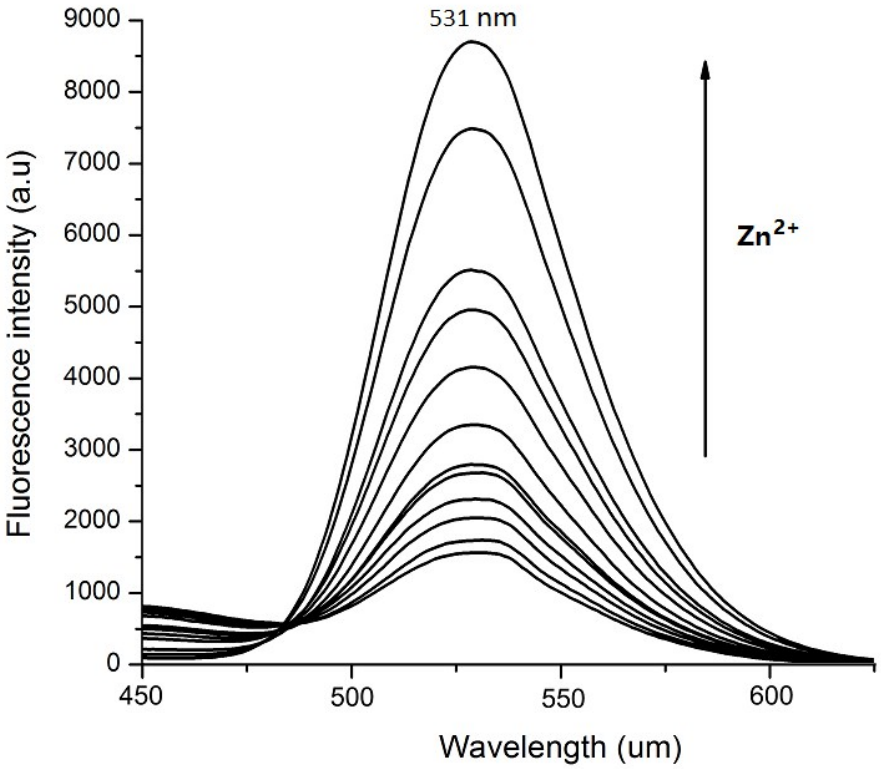


Figure S8.

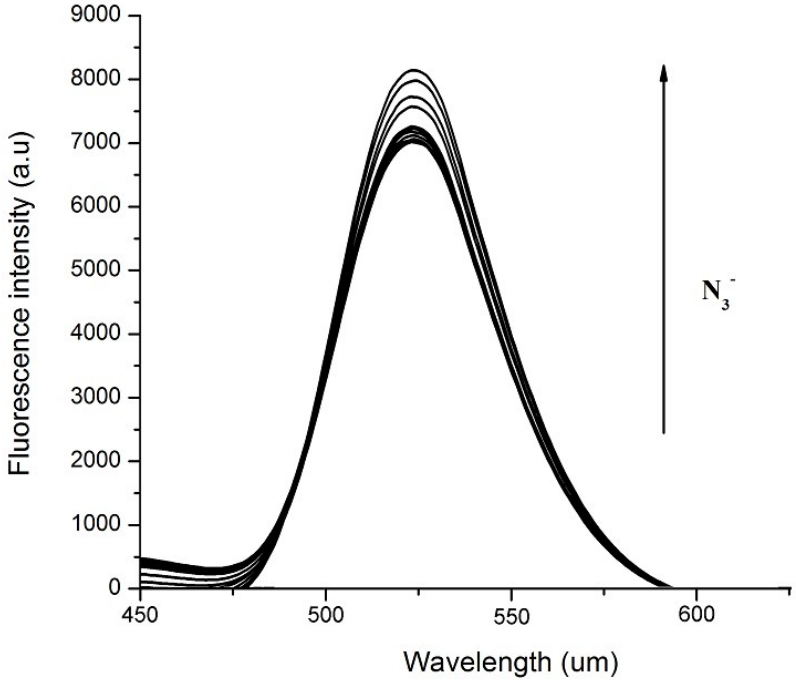
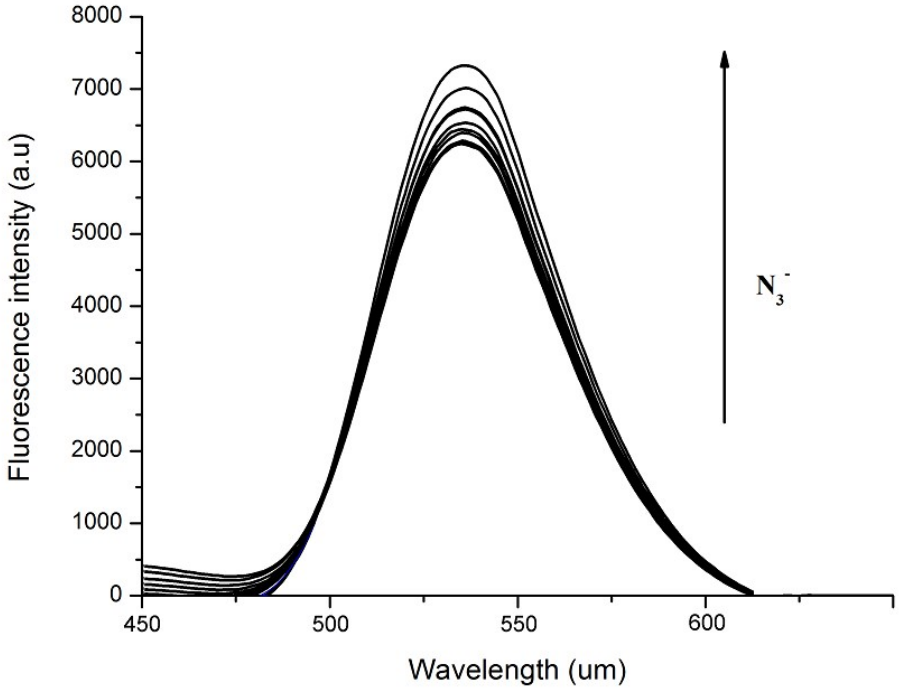


Figure S9.


Fluorescence intensity (a.u)
Wavelength (um)
N_3^-
8000
7000
6000
5000
4000
3000
2000
1000
0
450
500
550
600